4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.1 GAS CHROMATOGRAPHIC METHODS

The following methods are included in this section:

Method 8000A:	Gas Chromatography
Method 8010B:	Halogenated Volatile Organics by Gas Chromatography
Method 8011:	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
Method 8015A:	Nonhalogenated Volatile Organics by Gas Chromatography
Method 8020A:	Aromatic Volatile Organics by Gas Chromatography
Method 8021A:	Halogenated Volatiles by Gas Chromatography Using Photoionization and Electrolytic Conductivity Detectors in Series: Capillary Column Technique
Method 8030A:	Acrolein and Acrylonitrile by Gas Chromatography
Method 8031:	Acrylonitrile by Gas Chromatography
Method 8032:	Acrylamide by Gas Chromatography
Method 8040A:	Phenols by Gas Chromatography
Method 8060:	Phthalate Esters
Method 8061:	Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)
Method 8070:	Nitrosamines by Gas Chromatography
Method 8080A:	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography
Method 8081:	Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique
Method 8090:	Nitroaromatics and Cyclic Ketones
Method 8100:	Polynuclear Aromatic Hydrocarbons
Method 8110:	Haloethers by Gas Chromatography
Method 8120A:	Chlorinated Hydrocarbons by Gas Chromatography
Method 8121:	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
Method 8140:	Organophosphorus Pesticides
Method 8141A:	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique
Method 8150B:	Chlorinated Herbicides by Gas Chromatography
Method 8151:	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization: Capillary Column Technique

METHOD 8000A

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative technique useful for the analysis of organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide concentrations, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

4.2 Gas chromatographic columns - See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements

of Section 8.6 are met.

5.0 REAGENTS

5.1 See the specific determinative method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Extraction - Adhere to those procedures specified in the referring determinative method.

7.2 Cleanup and separation - Adhere to those procedures specified in the referring determinative method.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.0 of the determinative method of interest. Prepare calibration standards using the procedures indicated in Section 5.0 of the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

7.4.2 External standard calibration procedure

7.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g. 2-5 μL injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the

percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^{*}}{\text{Mass injected (in nanograms)}}$$

* For multiresponse pesticides/PCBs, use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than $\pm$ 15%, a new calibration curve must be prepared for that analyte. For methods 8010, 8020, and 8030, see Table 3 in each method for calibration and quality control acceptance criteria.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 Internal standard calibration procedure

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentrations for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.3.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g. 2 to 5 µL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, µg/L.

C_s = Concentration of the analyte to be measured, µg/L.

If the RF value over the working range is constant (< 20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

7.4.3.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ± 15%, a new calibration curve must be prepared for that compound. For methods 8010, 8020, and 8030, see Table 3 in each method for calibration and quality control acceptance criteria.

7.5 Retention time windows

7.5.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

7.5.2 Calculate the standard deviation of the three retention times (use any function of retention time; including absolute retention time, or relative retention time) for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse analytes (i.e. PCBs), the analyst should use the retention time window, but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications (in Method 5030) where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multi-concentration calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 Direct Injection - Inject 2-5 μL of the sample extract using the solvent flush technique, if the extract is manually injected. Smaller volumes (1.0 μL) can be injected, and the solvent flush technique is not required, if automatic devices are employed. Record the volume injected to the nearest 0.05 μL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required.

7.6.7 Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method.

7.6.8 Calibrate the system immediately prior to conducting any analyses (see Section 7.4). A mid-concentration standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15% difference when compared to the initial standard of the analysis sequence. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary (see Section 7.7) before recalibrating and proceeding with sample analysis. All samples that were injected after the standard exceeding the criterion must be reinjected to avoid errors in quantitation, if the initial analysis indicated the presence of the specific target analytes that exceeded the criterion.

7.6.9 Establish daily retention time windows for each analyte. Use the retention time for each analyte from Section 7.6.8 as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 7.5.

7.6.9.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

7.6.9.2 Validation of GC system qualitative performance: Use the mid-concentration standards interspersed throughout the analysis sequence (Section 7.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Section 7.7). All samples that were injected after the standard exceeding the criteria must be reinjected to avoid false negatives and possibly false positives.

7.7 Suggested chromatography system maintenance - Corrective measures may require any one or more of the following remedial actions.

7.7.1 Packed columns - For instruments with injection port traps, replace the demister trap, clean, and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of the packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in Section 7.7.3) and/or repack/replace the column.

7.7.2 Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.7.3 Metal injector body - Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

7.7.3.2 Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.8 Calculations

7.8.1 External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Section 7.4.2. The concentration of a specific analyte is calculated as follows:

<u>Aqueous samples</u>

$$\text{Concentration } (\mu g/L) = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(V_s)]$$

where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of extract injected, μL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, μL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_s = Volume of sample extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(W)]$$

where:

W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples when a solid sample is purged (e.g., low concentration soil) for volatile organic analysis or for semivolatile organic and pesticide extracts. When the nonaqueous sample is extracted for purge and trap analysis, V_i = volume of methanol extract added to reagent water for purge and trap analysis.

7.8.2 Internal standard calibration - For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples

$$\text{Concentration } (\mu g/L) = [(A_x)(C_{is})(D)]/[(A_{is})(RF)(V_s)]$$

where:

A_x = Response of the analyte being measured, units may be in area counts or peak height.

C_{is} = Amount of internal standard added to extract or volume purged, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for analyte, as determined in Section 7.4.3.3.

V_s = Volume of water extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = [(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$$

where:

W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory should maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard should be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, an organic-free reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike, and duplicate or matrix spike duplicate should be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples should be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system should take place.

8.5 Required instrument QC

8.5.1 Step 7.4 requires that the %RSD vary by < 20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Section 7.4 sets a limit of ± 15% difference when comparing daily response of a given analyte versus the initial response. For Methods 8010, 8020, and 8030, follow the guidance on limits specified in Section 7.4.3.4. If the limit is exceeded, a new standard curve should be prepared unless instrument maintenance corrects the problem for that particular analyte.

8.5.3 Step 7.5 requires the establishment of retention time windows.

8.5.4 Section 7.6.8 sets a limit of ± 15% difference when comparing the response from the continuing calibration standard of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Step 7.6.9.2 requires that all succeeding standards in an analysis sequence should fall within the daily retention time window established by the first standard of the sequence.

8.6 To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations.

8.6.1 A quality control (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate should be made using stock standards prepared independently from those used for calibration.

8.6.1.1 The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the QC check sample concentrate.

8.6.2 Preparation of QC check samples

8.6.2.1 Volatile organic analytes (Methods 8010, 8020, and 8030) - The QC check sample is prepared by adding 200 µL of the QC check sample concentrate (Step 8.6.1) to 100 mL of water.

8.6.2.2 Semivolatile organic analytes (Methods 8040, 8060, 8070, 8080, 8090, 8100, 8110, and 8120) - The QC check sample is prepared by adding 1.0 mL of the QC check sample concentrate (Step 8.6.1) to each of four 1-L aliquots of water.

8.6.3 Four aliquots of the well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (Section 7.0 of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples should undergo solvent extraction (see Method 3500) prior to chromatographic analysis.

8.6.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte of interest using the four results.

8.6.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC Acceptance Criteria Table at the end of each of the determinative methods. If s and $\bar{x}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst should proceed according to Step 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Step 8.6.2.

8.6.6.2 Beginning with Step 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Step 8.6.2.

8.7 The laboratory should, on an ongoing basis, analyze a reagent blank and a matrix spiked duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked duplicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit, or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC reference sample (Step 8.6.2) or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger. For other matrices, the recommended spiking concentration is 20 times the EQL.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g. maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC reference sample concentration (Step 8.6.2). For other matrices, the recommended spiking concentration is 20 times the EQL.

8.7.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

8.7.2.1 Volatile organics - Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 μL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.2.2 Semivolatile organics - Analyze one sample aliquot (extract of 1-L sample) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1) appropriate for the background concentration in the sample. Spike a second 1-L sample aliquot with 1.0 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC reference sample concentration (Step 8.6.2), the analyst should use either the QC acceptance criteria presented in the Tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall_precision (S') using the equation in the same Table, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.7.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria should be

analyzed as described in Step 8.8.

8.8 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.7, a QC reference standard containing each analyte that failed should be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method should be measured in the sample in Step 8.7, the probability that the analysis of a QC check standard will be required is high. In this case, the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 Preparation of the QC check sample - For volatile organics, add 10 µL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 5 mL of water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 1 L of water. The QC check sample needs only to contain the analytes that failed criteria in the test in Step 8.7. Prepare the QC check sample for analysis following the guidelines given in Method 3500 (e.g. purge-and-trap, extraction, etc.).

8.8.2 Analyze the QC check sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Step 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem should be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied should be assessed and records should be maintained. After the analysis of five spiked samples (of the same matrix type) as in Step 8.7, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 Calculate surrogate control limits as follows:

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates when

surrogate data from 25 to 30 samples for each matrix is available.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.10.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits in Tables A and B of Methods 8240 and 8270, respectively. The limits given in these methods are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.10.3 should fall within those given in Tables A and B for these matrices.

8.10.5 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.10.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.11 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer should be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

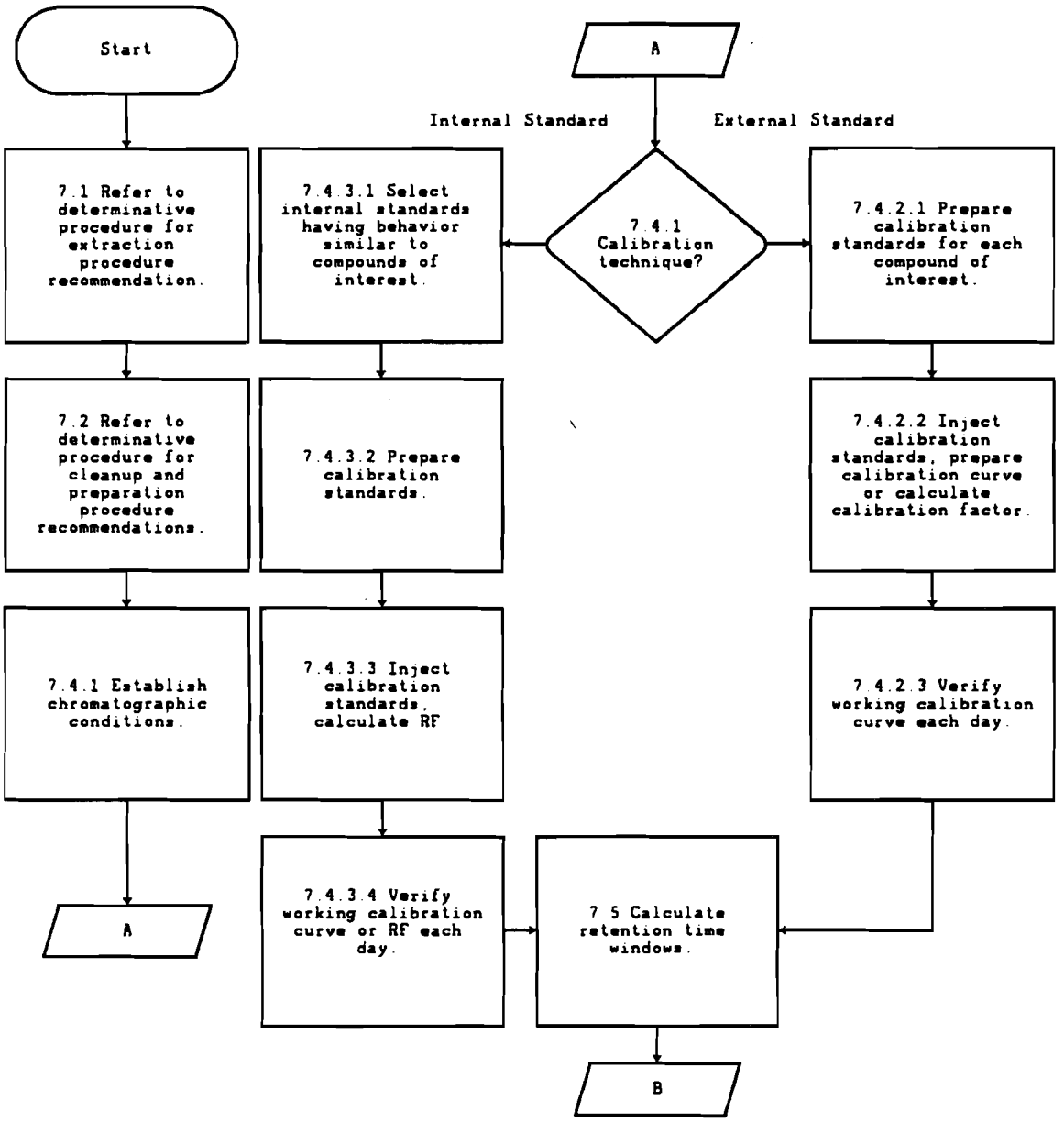
9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the referring analytical methods were obtained using water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

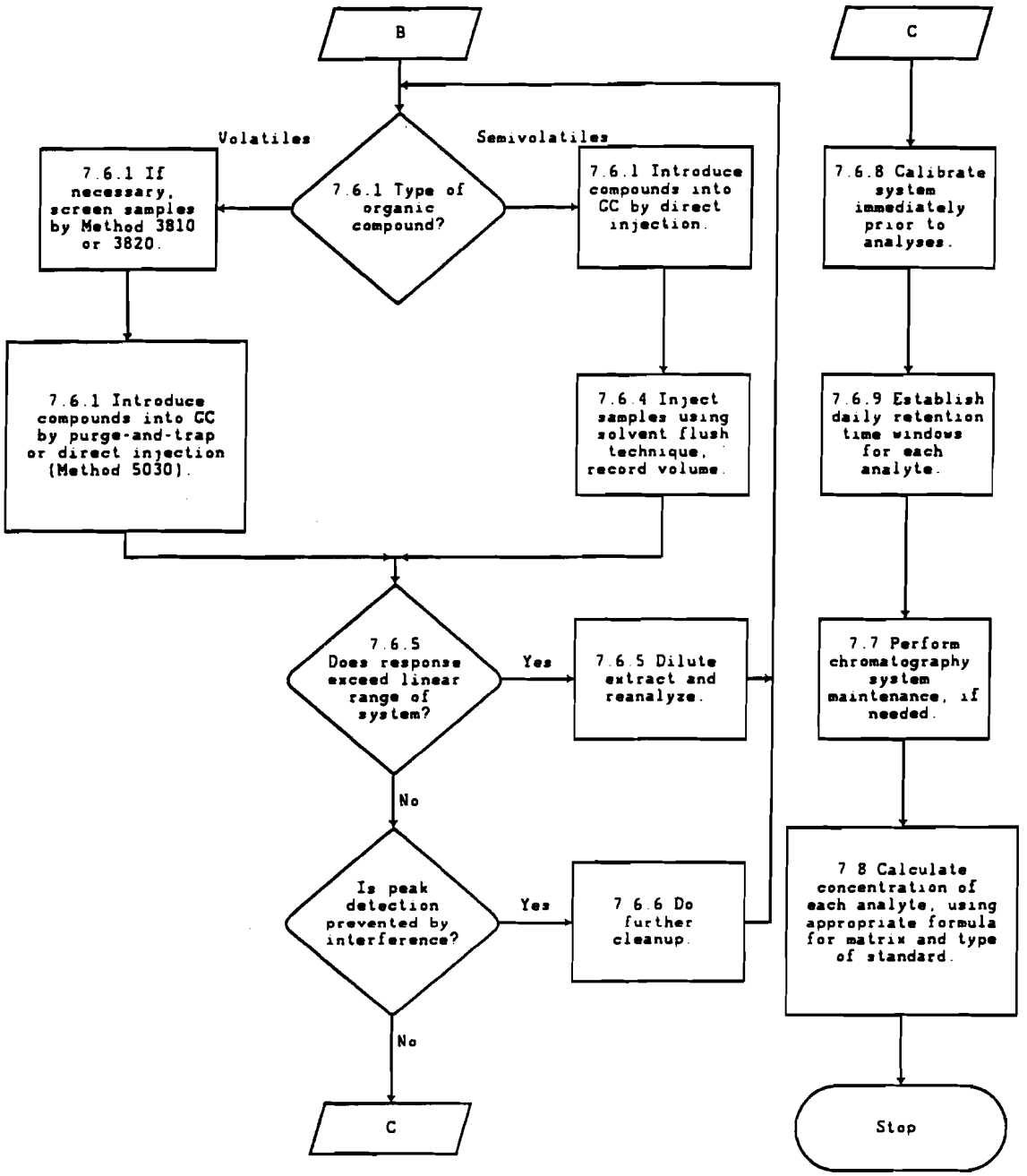
9.2 Refer to the determinative method for specific method performance information.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.


Start
A
Internal Standard
External Standard
7.1 Refer to determinative procedure for extraction procedure recommendation.
7.4.3.1 Select internal standards having behavior similar to compounds of interest.
7.4.1 Calibration technique?
7.4.2.1 Prepare calibration standards for each compound of interest.
7.2 Refer to determinative procedure for cleanup and preparation procedure recommendations.
7.4.3.2 Prepare calibration standards.
7.4.2.2 Inject calibration standards, prepare calibration curve or calculate calibration factor.
7.4.1 Establish chromatographic conditions.
7.4.3.3 Inject calibration standards, calculate RF
7.4.2.3 Verify working calibration curve each day.
A
7.4.3.4 Verify working calibration curve or RF each day.
7.5 Calculate retention time windows.
B


B
C
Volatiles
Semivolatiles
7.6.1 Type of organic compound?
7.6.1 If necessary, screen samples by Method 3810 or 3820.
7.6.1 Introduce compounds into GC by direct injection.
7.6.1 Introduce compounds into GC by purge-and-trap or direct injection (Method 5030).
7.6.4 Inject samples using solvent flush technique, record volume.
7.6.5 Does response exceed linear range of system?
Yes
7.6.5 Dilute extract and reanalyze.
No
Is peak detection prevented by interference?
Yes
7.6.6 Do further cleanup.
No
C
7.6.8 Calibrate system immediately prior to analyses.
7.6.9 Establish daily retention time windows for each analyte.
7.7 Perform chromatography system maintenance, if needed.
7.8 Calculate concentration of each analyte, using appropriate formula for matrix and type of standard.
Stop

METHOD 8010B

HALOGENATED VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Allyl chloride	107-05-1	b	b
Benzyl chloride	100-44-7	pp	b
Bis(2-chloroethoxy)methane	111-91-1	pp	pc
Bis(2-chloroisopropyl) ether	39638-32-9	b	b
Bromoacetone	598-31-2	pp	b
Bromobenzene	108-86-1	b	b
Bromodichloromethane	75-27-4	b	b
Bromoform	75-25-2	b	b
Bromomethane	74-83-9	b	b
Carbon tetrachloride	56-23-5	b	b
Chlorobenzene	108-90-7	b	b
Chloroethane	75-00-3	b	b
2-Chloroethanol	107-07-03	pp	b
2-Chloroethyl vinyl ether	110-75-8	b	b
Chloroform	67-66-3	b	b
1-Chlorohexane	544-10-5	pc	pc
Chloromethane	74-87-3	b	b
Chloromethyl methyl ether	107-30-2	pp	pc
Chloroprene	126-99-8	b	b
4-Chlorotoluene	106-43-4	b	b
Dibromochloromethane	124-48-1	b	b
1,2-Dibromo-3-chloropropane	96-12-8	b	b
Dibromomethane	74-95-3	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
1,4-Dichloro-2-butene	764-41-0	b	b
Dichlorodifluoromethane	75-71-8	b	b
1,1-Dichloroethane	75-34-3	b	b
1,2-Dichloroethane	107-06-2	b	b
1,1-Dichloroethene	75-35-4	b	b
trans-1,2-Dichloroethene	156-60-5	b	b
Dichloromethane	75-09-2	b	b
1,2-Dichloropropane	78-87-5	b	b
1,3-Dichloro-2-propanol	96-23-1	pp	b
cis-1,3-Dichloropropene	10061-01-5	b	b
trans-1,3-Dichloropropene	10061-02-6	b	b
Epichlorhydrin	106-89-8	pp	b

Compound Name	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Ethylene dibromide	106-93-4	b	b
Methyl iodide	74-88-4	pp	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	b
Tetrachloroethene	127-18-4	b	b
1,1,1-Trichloroethane	71-55-6	b	b
1,1,2-Trichloroethane	79-00-5	b	b
Trichloroethene	79-01-6	b	b
Trichlorofluoromethane	75-69-4	b	b
1,2,3-Trichloropropane	96-18-4	b	b
Vinyl Chloride	75-01-4	b	b

a Chemical Abstract Services Registry Number
b Adequate response using this technique
pp Poor purging efficiency, resulting in high EQLs
pc Poor chromatographic performance.

1.2 Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8010 provides gas chromatographic conditions for the detection of halogenated volatile organic compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a electrolytic conductivity detector (HECD).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in. ID stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass column packed with chemically bonded n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 Detector - Electrolytic conductivity (HECD).

4.2 Sample introduction apparatus, refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes, 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A, Appropriate sizes with ground glass stoppers.

4.5 Microsyringe, 10 and 25 μL with a 0.006 in. ID needle (Hamilton 702N or equivalent) and a 100 μL.

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH. Pesticide quality or equivalent. Store away from other solvents.

5.4 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.4.2 Add the assayed reference material, as described below.

5.4.2.1 Liquids. Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases. To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.4.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.4.5 Prepare fresh stock standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 20% drift.

5.4.6 Optionally calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte

mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.5 Secondary dilution standards. Using stock standard solutions, prepare secondary dilution standards in methanol, as needed, containing the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.6 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Calibration standards. Prepare calibration standards in organic-free reagent water from the secondary dilution of the stock standards, at a minimum of five concentrations. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of the concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.6.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.6.2 Use a 25 µL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.6.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.6.4 Mix aqueous standards by inverting the flask three times only.

5.6.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.6.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.6.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.7 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no

internal standard can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes (Sec. 5.8) have been used successfully as internal standards, because of their generally unique retention times.

5.7.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Sec. 5.6.

5.7.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Secs. 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ng/µL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

5.7.3 Analyze each calibration standard according to Sec. 7.0, adding 10 µL of internal standard spiking solution directly to the syringe.

5.8 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate halocarbons. A combination of bromochloromethane, bromochlorobenzene and bromofluorobenzene is recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Sec. 5.4, add a volume to give 750 µg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Sec. 5.7.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph using either direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1:

Helium flow rate = 40 mL/min

Temperature program:

Initial temperature =	45°C, hold for 3 minutes
Program =	45°C to 220°C at 8°C/min
Final temperature =	220°C, hold for 15 minutes.

7.2.2 Column 2:

Helium flow rate = 40 mL/min
Temperature program:

Initial temperature =	50°C, hold for 3 minutes
Program =	50°C to 170°C at 6°C/min
Final temperature =	170°C, hold for 4 minutes.

7.3 Calibration. The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 and Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Sec. 7.4.1).

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap) or the direct injection method (see Sec. 7.4.1.1). If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 In very limited applications (e.g. aqueous process wastes) direct injection of the sample onto the GC column with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L) therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two columns for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Refer to Method 8000 for guidance on calculation of concentration.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each analyte of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria, for water samples, for this method. Table 4 gives method accuracy and precision as functions of concentration, for water samples, for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required:

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Recalculate the data and/or re-analyze the sample if any of the above checks reveal a problem.

- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 8.0-500 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte, and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

9.3 The method detection limits reported in Table 1 were generated under optimum analytical conditions by an Agency contractor (Ref. 6) as guidance, and may not be readily achievable by all laboratories at all times.

10.0 REFERENCES

1. Bellar, T.A.; Lichtenberg, J.J. J. Amer. Water Works Assoc. 1974, 66(12), pp. 739-744.

2. Bellar, T.A.; Lichtenberg, J.J., Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, Measurement of Organic Pollutants in Water and Wastewater; Van Hall, Ed.; ASTM STP 686, pp 108-129, 1979.

3. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane"; report for EPA Contract 68-03-2635.

4. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule", October 26, 1984.

5. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)"; report for EPA Contract 68-03-2856.

6. Gebhart, J.E., S.V. Lucas, S.J. Naber, A.M. Berry, T.H. Danison and H.M. Burkholder, "Validation of SW-846 Methods 8010, 8015, and 8020"; Report for EPA Contract 68-03-1760, Work Assignment 2-15; US EPA, EMSL-Cincinnati, 1987.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR HALOGENATED VOLATILE ORGANICS

Compound	CAS Registry Number	Retention Time (minutes) Column 1	Column 2	Method Detection Limit[a] (µg/L)
Allyl chloride*	107-05-1	10.17	(b)	(b)
Benzyl chloride*,[c]	100-44-7	30.29	(b)	(b)
Bis(2-chloroethoxy)methane*	111-91-1	38.60	(b)	(b)
Bis(2-chloroisopropyl) ether*	39638-32-9	34.79	(b)	(b)
Bromobenzene	108-86-1	29.05	(b)	(b)
Bromodichloromethane	75-27-4	15.44	14.62	0.002
Bromoform*	75-25-2	21.12	19.17	0.020
Bromomethane*	74-83-9	2.90	7.05	0.030
Carbon tetrachloride*	56-23-5	14.58	11.07	0.003
Chloroacetaldehyde*	107-20-0	(b)	(b)	(b)
Chlorobenzene*	108-90-7	25.49	18.83	0.001
Chloroethane	75-00-3	5.18	8.68	0.008
Chloroform*	67-66-3	12.62	12.08	0.002
1-Chlorohexane	544-10-5	26.26	(b)	(b)
2-Chloroethyl vinyl ether*	110-75-8	19.23	(b)	0.130
Chloromethane*	74-87-3	1.40	5.28	0.010
Chloromethyl methyl ether*	107-30-2	8.88	(b)	(b)
4-Chlorotoluene	106-43-4	34.46	(b)	(b)
Dibromochloromethane	124-48-1	18.22	16.62	(b)
1,2-Dibromo-3-chloropropane*	96-12-8	28.09	(b)	0.030
Dibromomethane*	74-95-3	13.83	14.92	(b)
1,2-Dichlorobenzene*	95-50-1	37.96	23.52	(b)
1,3-Dichlorobenzene*	541-73-1	36.88	22.43	(b)
1,4-Dichlorobenzene*	106-46-7	38.64	22.33	(b)
1,4-Dichloro-2-butene*	764-41-0	23.45	(b)	(b)
Dichlorodifluoromethane*,[d]	75-71-8	3.68	(b)	(b)
1,1-Dichloroethane*	75-34-3	11.21	12.57	0.002
1,2-Dichloroethane*	107-06-2	13.14	15.35	0.002
1,1-Dichloroethene*	75-35-4	10.04	7.72	0.003
trans-1,2-Dichloroethene*	156-60-5	11.97	9.38	0.002
Dichloromethane*	75-09-2	7.56	10.12	(b)
1,2-Dichloropropane*	78-87-5	16.69	16.62	(b)
trans-1,3-Dichloropropene*	10061-02-5	16.97[e]	16.60	0.340
Ethylene dibromide*	106-93-4	19.59	(b)	(b)
1,1,2,2-Tetrachloroethane*	79-34-5	23.12	(b)	0.010
1,1,1,2-Tetrachloroethane*	630-20-6	21.10	21.70	(b)
Tetrachloroethene*	127-18-4	23.05	14.97	0.001
1,1,1-Trichloroethane	71-55-6	14.48	13.10	0.003
1,1,2-Trichloroethane*	79-00-5	18.27	18.07	0.007

TABLE 1.
Continued

Compound	CAS Registry Number	Retention Time (minutes) Column 1	Column 2	Method Detection Limit[a] (μg/L)
Trichloroethene*	79-01-6	17.40	13.12	0.001
Trichlorofluoromethane*	75-69-4	9.26	(b)	(b)
1,2,3-Trichloropropane*	96-18-4	22.95	(b)	(b)
Vinyl Chloride*	75-01-4	3.25	5.28	0.006

a = Using purge-and-trap method (Method 5030). See Sec. 9.3.
b = Not determined
* = Appendix VIII compounds
c = Demonstrated very erratic results when tested by purge-and-trap
d = See Sec. 4.10.2 of Method 5030 for guidance on selection of trapping material
e = Estimated retention time

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

[a] EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

TABLE 3.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Analyte	Range for Q (µg/L)	Limit for S (µg/L)	Range for $\bar{x}$ (µg/L)	Range P, P_s (%)
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.6	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.6	11.8-25.3	43-143
Chlorobenzene	14.4-25.6	5.0	10.2-27.4	38-150
Chloroethane	15.4-24.6	4.4	11.3-25.2	46-137
2-Chloroethylvinyl ether	12.0-28.0	8.3	4.5-35.5	14-186
Chloroform	15.0-25.0	4.5	12.4-24.0	49-133
Chloromethane	11.9-28.1	7.4	D-34.9	D-193
Dibromochloromethane	13.1-26.9	6.3	7.9-35.1	24-191
1,2-Dichlorobenzene	14.0-26.0	5.5	1.7-38.9	D-208
1,3-Dichlorobenzene	9.9-30.1	9.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.6	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
Dichloromethane	15.5-24.5	4.0	7.0-27.6	25-162
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	5.7	8.2-29.9	28-163

Q = Concentration measured in QC check sample, in µg/L.

S = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a] Criteria from 40 CFR Part 136 for Method 601 and were calculated assuming a QC check sample concentration of 20 µg/L.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Analyte	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Bromodichloromethane	1.12C-1.02	0.11X+0.04	0.20X+1.00
Bromoform	0.96C-2.05	0.12X+0.58	0.21X+2.41
Bromomethane	0.76C-1.27	0.28X+0.27	0.36X+0.94
Carbon tetrachloride	0.98C-1.04	0.15X+0.38	0.20X+0.39
Chlorobenzene	1.00C-1.23	0.15X-0.02	0.18X+1.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X+0.63
2-Chloroethyl vinyl ether[b]	1.00C	0.20X	0.35X
Chloroform	0.93C-0.39	0.13X+0.15	0.19X-0.02
Chloromethane	0.77C+0.18	0.28X-0.31	0.52X+1.31
Dibromochloromethane	0.94C+2.72	0.11X+1.10	0.24X+1.68
1,2-Dichlorobenzene	0.93C+1.70	0.20X+0.97	0.13X+6.13
1,3-Dichlorobenzene	0.95C+0.43	0.14X+2.33	0.26X+2.34
1,4-Dichlorobenzene	0.93C-0.09	0.15X+0.29	0.20X+0.41
1,1-Dichloroethane	0.95C-1.08	0.08X+0.17	0.14X+0.94
1,2-Dichloroethane	1.04C-1.06	0.11X+0.70	0.15X+0.94
1,1-Dichloroethene	0.98C-0.87	0.21X-0.23	0.29X-0.04
trans-1,2-Dichloroethene	0.97C-0.16	0.11X+1.46	0.17X+1.46
Dichloromethane	0.91C-0.93	0.11X+0.33	0.21X+1.43
1,2-Dichloropropane[b]	1.00C	0.13X	0.23X
cis-1,3-Dichloropropene[b]	1.00C	0.18X	0.32X
trans-1,3-Dichloropropene[b]	1.00C	0.18X	0.32X
1,1,2,2-Tetrachloroethane	0.95C+0.19	0.14X+2.41	0.23X+2.79
Tetrachloroethene	0.94C+0.06	0.14X+0.38	0.18X+2.21
1,1,1-Trichloroethane	0.90C-0.16	0.15X+0.04	0.20X+0.37
1,1,2-Trichloroethane	0.86C+0.30	0.13X-0.14	0.19X+0.67
Trichloroethene	0.87C+0.48	0.13X-0.03	0.23X+0.30
Trichlorofluoromethane	0.89C-0.07	0.15X+0.67	0.26X+0.91
Vinyl chloride	0.97C-0.36	0.13X+0.65	0.27X+0.40

x′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of x, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in μg/L.

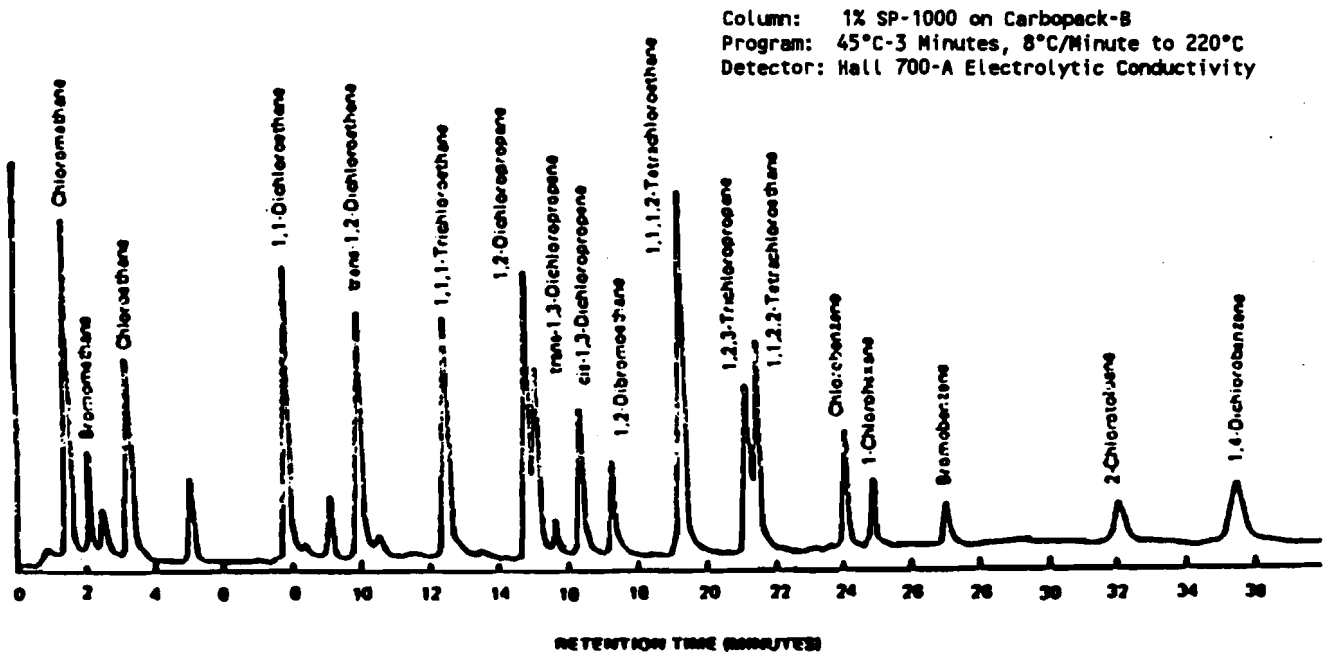
C = True value for the concentration, in μg/L.

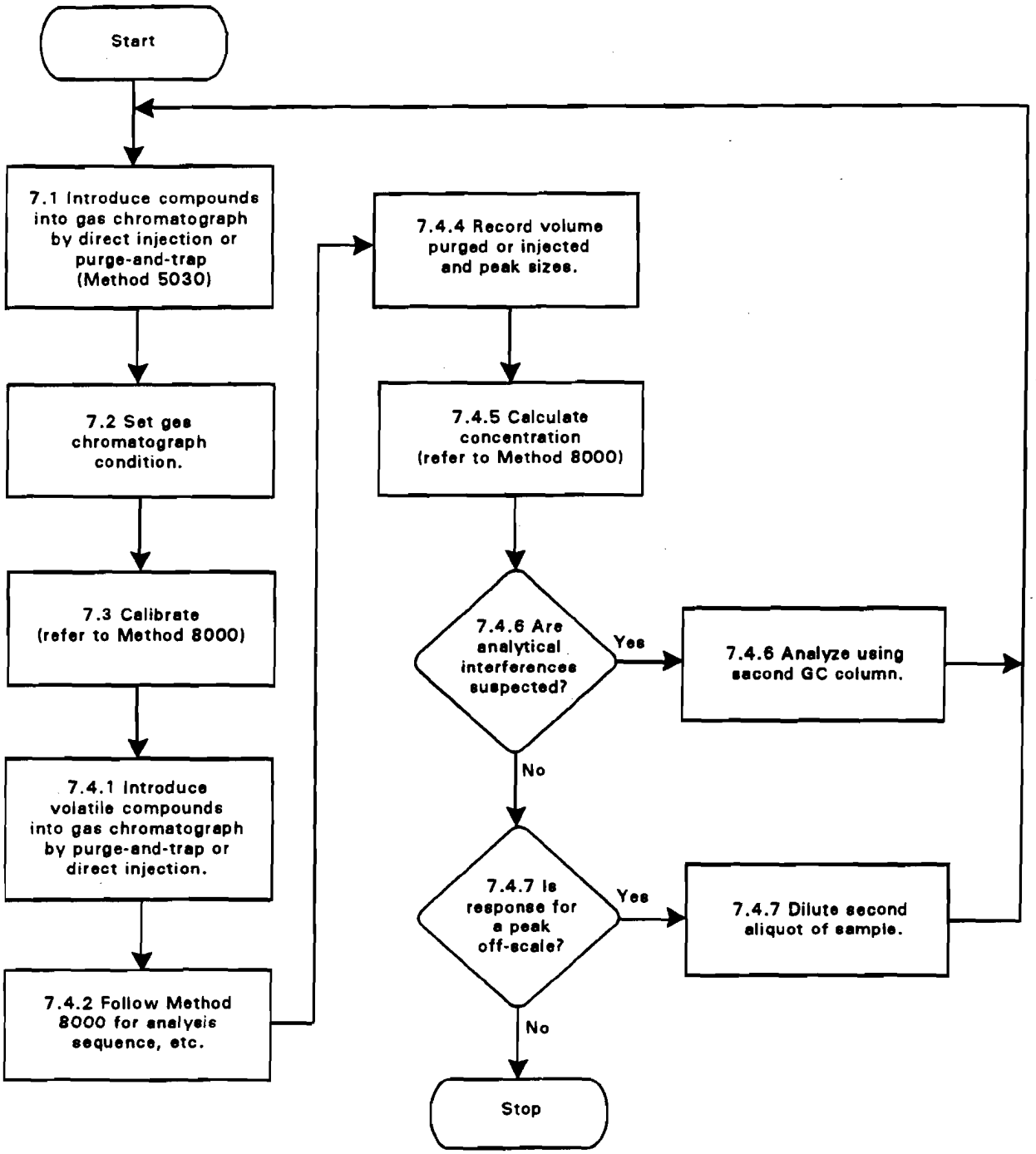
X = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

[a] From 40 CFR Part 136 for Method 601.

[b] Estimates based upon the performance in a single laboratory.

FIGURE 1.
GAS CHROMATOGRAM OF HALOGENATED VOLATILE ORGANICS




Start
7.1 Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
7.2 Set gas chromatograph condition.
7.3 Calibrate (refer to Method 8000)
7.4.1 Introduce volatile compounds into gas chromatograph by purge-and-trap or direct injection.
7.4.2 Follow Method 8000 for analysis sequence, etc.
7.4.4 Record volume purged or injected and peak sizes.
7.4.5 Calculate concentration (refer to Method 8000)
7.4.6 Are analytical interferences suspected?
Yes
7.4.6 Analyze using second GC column.
No
7.4.7 Is response for a peak off-scale?
Yes
7.4.7 Dilute second aliquot of sample.
No
Stop

METHOD 8011

1,2-DIBROMOETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the following compounds in drinking water and ground water:

Compound Name	CAS No.[a]
1,2-Dibromoethane (EDB)	106-93-4
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8

[a] Chemical Abstract Services Registry Number.

1.2 For compounds and matrices other than those listed in Section 1.1, the laboratory must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS).

1.3 The experimentally determined method detection limits (MDL) for EDB and DBCP were calculated to be 0.01 µg/L. The method has been shown to be useful for these analytes over a concentration range of approximately 0.03 to 200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system, sample matrix, and calibration.

1.4 This method is restricted to use by or under the Supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.5 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

2.0 SUMMARY OF METHOD

2.1 Thirty five mL of sample are extracted with 2 mL of hexane. Two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous matrix spikes are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

2.2 The extraction and analysis time is 30 to 50 minutes per sample

depending upon the analytical conditions chosen. See Table 1 and Figure 1.

2.3 Confirmatory evidence is obtained using a different column (Table 1).

3.0 INTERFERENCES

3.1 Impurities contained in the extracting solvent (hexane) usually account for the majority of the analytical problems. Reagent blanks should be analyzed for each new bottle of hexane before use. Indirect daily checks on the hexane are obtained by monitoring the reagent blanks. Whenever an interference is noted in the method or instrument blank, the laboratory should reanalyze the hexane. Low level interferences generally can be removed by distillation or column chromatography, however, it is generally more economical to obtain a new source of hexane solvent. Interference-free hexane is defined as containing less than 0.01 µg/L of the analytes. Protect interference-free hexane by storing it in an area known to be free of organochlorine solvents.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. Trip blanks must be used to monitor for this problem.

3.3 This liquid/liquid extraction technique extracts a wide boiling range of non-polar organic compounds and, in addition, extracts some polar organic compounds.

3.4 EDB at low concentrations may be masked by very high concentrations of dibromochloromethane (DBCM), a common chlorinated drinking water contaminant, when using the confirmation column.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringe - 10, 25, and 100 µL with a 2 in. x 0.006 in. needle (Hamilton 702N or equivalent).

4.2 Gas Chromatograph

4.2.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector.

4.2.2 Columns

4.2.2.1 Column A - 0.32 mm ID x 30 m fused silica capillary with dimethyl silicone mixed phase (Durawax-DX 3, 0.25 µm film, or equivalent).

4.2.2.2 Column B (confirmation column) - 0.32 mm ID x 30 m fused silica capillary with methyl polysiloxane phase (DB-1, 0.25 µm film, or equivalent).

4.3 Volumetric flasks, Class A - 10 mL.

4.4 Glass bottles - 15 mL, with Teflon lined screw caps or crimp tops.

4.5 Analytical balance - 0.0001 g.

4.6 Graduated cylinder - 50 mL.

4.7 Transfer pipet.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Hexane, C_6H_{14} - UV grade (Burdick and Jackson #216 or equivalent).

5.4 Methyl alcohol, CH_3OH - Demonstrated to be free of analytes.

5.5 Sodium chloride, NaCl - Pulverize a batch of NaCl and place it in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 minutes. Store in a capped bottle.

5.6 1,2-Dibromoethane (99%), $C_2H_4Br_2$, (Aldrich Chemical Company, or equivalent).

5.7 1,2-Dibromo-3-chloropropane (99.4%), $C_3H_5Br_2Cl$, (AMVAC Chemical Corporation, Los Angeles, California, or equivalent).

5.8 Stock standards - These solutions may be purchased as certified solutions or prepared from pure standards using the following procedures:

5.8.1 Place about 9.8 mL of methanol into a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes and weigh to the nearest 0.0001 g.

5.8.2 Use a 25 µL syringe and immediately add two or more drops (≈ 10 µL) of standard to the flask. Be sure that the standard falls directly into the alcohol without contacting the neck of the flask.

5.8.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.8.4 Store stock standards in 15 mL bottles equipped with Teflon lined screw-caps or crimp tops. Stock standards are stable for at least

four weeks when stored at 4°C and away from light.

5.9 Intermediate standard - Use stock standards to prepare an intermediate standard that contains both analytes in methanol. The intermediate standard should be prepared at a concentration that can be easily diluted to prepare aqueous calibration standards that will bracket the working concentration range. Store the intermediate standard with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standards also applies to the intermediate standard.

5.10 Quality control (QC) reference sample - Prepare a QC reference sample concentrate at 0.25 mg/L of both analytes from standards from a different source than the standards used for the stock standard.

5.11 Check standard - Add an appropriate volume of the intermediate standard to an aliquot of organic-free reagent water in a volumetric flask. Do not add more than 20 µL of an alcoholic intermediate standard to the water or poor precision will result. Use a 25 µL microsyringe and rapidly inject the alcoholic intermediate standard into the expanded area of the almost filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask several times. Discard the contents contained in the neck of the flask. Aqueous calibration standards should be prepared every 8 hours.

6.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Recommended Chromatographic Conditions

Two gas chromatography columns are recommended. Column A is a highly efficient column that provides separations for EDB and DBCP without interferences from trihalomethanes. Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for EDB and DBCP on these columns are presented in Table 1.

Column A:

Injector temperature:	200°C.
Detector temperature:	290°C.
Carrier gas (Helium) Linear velocity:	25 cm/sec.
Temperature program:	
Initial temperature:	40°C, hold for 4 min.
Program:	40°C to 190°C at 8°C/min.
Final temperature:	190°C, hold for 25 min., or until all expected analytes have eluted.

See Figure 1 for a sample chromatogram and Table 1 for retention data.

Column B:

Injector temperature:	200°C.
Detector temperature:	290°C.
Carrier gas (Helium) Linear velocity:	25 cm/sec.
Temperature program:	
Initial temperature:	40°C, hold for 4 min.
Program:	40°C to 270°C at 10°C/min.
Final temperature:	270°C, hold for 10 min., or until all expected analytes have eluted.

See Table 1 for retention data.

7.2 Calibration

7.2.1 Prepare at least five calibration standards. One should contain EDB and DBCP at a concentration near, but greater than, the method detection limit (Table 1) for each compound. The others should be at concentrations that bracket the range expected in the samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous calibration standards should be prepared at concentrations of 0.03 µg/L, 0.05 µg/L, 0.10 µg/L, 0.15 µg/L, and 0.20 µg/L.

7.2.2 Analyze each calibration standard and tabulate peak height or area response versus the concentration in the standard. Prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation), linearity can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Sample preparation

7.3.1 Remove samples and standards from storage and allow them to reach room temperature.

7.3.2 For samples and field blanks contained in 40 mL bottles, remove the container cap. Discard a 5 mL volume using a 5 mL transfer pipet. Replace the container cap and weigh the container with contents to the nearest 0.1 g and record this weight for subsequent sample volume determination.

7.3.3 For calibration standards, check standards, QC reference samples, and blanks, measure a 35 mL volume using a 50 mL graduated cylinder and transfer it to a 40 mL sample container.

7.4 Extraction

7.4.1 Remove the container cap and add 7 g of NaCl to all samples.

7.4.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 seconds.

7.4.3 Remove the cap and using a transfer pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 minute. Allow the water and hexane phases to separate. If stored at this stage, keep the container upside down.

7.4.4 Remove the cap and carefully transfer a sufficient amount (0.5-1.0 mL) of the hexane layer into a vial using a disposable glass pipet.

7.4.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second vial. Reserve this second vial at 4°C for reanalysis if necessary.

7.5 Analysis

7.5.1 Transfer the first sample vial to an autosampler set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternately, 2 µL portions of samples, blanks and standards may be manually injected, using the solvent flush technique, although an auto sampler is strongly recommended.

7.6 Determination of sample volume

7.6.1 For samples and field blanks, remove the cap from the sample container. Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements. Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight is equivalent to the volume of water extracted.

7.7 Calculations

7.7.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the check standard.

7.7.2 Use the calibration curve or calibration factor to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g. calibration factor x response).

7.7.3 Calculate the sample volume (V_s) as equal to the net sample weight:

V_s (mL) = gross weight (grams) - bottle tare (grams)

7.7.4 Calculate the corrected sample concentration as:

$$\text{Concentration } (\mu g/L) = \frac{C_i \times 35}{V_s}$$

7.7.5 Report the results for the unknown samples in µg/L. Round the

results to the nearest 0.01 μg/L or two significant figures.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program.

8.1.1 The laboratory must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable accuracy and precision with this method. This is established as described in Section 8.2.

8.1.2 In recognition of laboratory advances that are occurring in chromatography, the laboratory is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 7.1 and 8.2.

8.1.3 The laboratory must analyze a reagent and calibration blank to demonstrate that interferences from the analytical system are under control every twenty samples or per analytical batch, whichever is more frequent.

8.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of QC reference samples and check standards that the operation of the measurement system is in control. The frequency of the check standard analyses is equivalent to 5% of all samples or every analytical batch, whichever is more frequent. On a weekly basis, the QC reference sample must be run.

8.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst must perform the following operations:

8.2.1 Prepare seven samples each at a concentration of 0.03 μg/L.

8.2.2 Analyze the samples according to the method beginning in Section 7.0.

8.2.3 Calculate the average concentration ($\bar{X}$) in μg/L and the standard deviation of the concentrations (s) in μg/L, for each analyte using the seven results. Then calculate the MDL at 99% confidence level for seven replicates as 3.143s.

8.2.4 For each analyte in an aqueous matrix sample, $\bar{X}$ must be between 60% and 140% of the true value. Additionally, the MDL may not exceed the 0.03 μg/L spiked concentration. If both analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to meet a criterion, repeat the test. It is recommended that the laboratory repeat the MDL determination on a regular basis.

8.3 The laboratory must demonstrate on a frequency equivalent to 5% of

the sample load or once per analytical batch, whichever is more frequent, that the measurement system is in control by analyzing a check standard of both analytes at 0.25 µg/L.

8.3.1 Prepare a check standard (0.25 µg/L) by diluting the intermediate standard with water to 0.25 µg/L.

8.3.2 Analyze the sample according to Section 7.0 and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value for aqueous matrices. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second calibration verification standard containing each analyte that failed must be analyzed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test.

8.4 On a weekly basis, the laboratory must demonstrate the ability to analyze a QC reference sample.

8.4.1 Prepare a QC reference sample at 0.10 µg/L by diluting the QC reference sample concentrate (Section 5.9).

8.4.2 For each analyte in an aqueous matrix, the recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst must repeat the test only for that analyte which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.5 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.5.1 Peak tailing significantly in excess of that shown in the chromatogram (Figure 1) must be corrected. Tailing problems are generally traceable to active sites on the GC column or to the detector operation.

8.5.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

9.0 METHOD PERFORMANCE

9.1 Method detection limits are presented in Table 1. Single laboratory accuracy and precision at several concentrations in tap water are presented in Table 2.

9.2 In a preservation study extending over a 4 week period, the average percent recoveries and relative standard deviations presented in Table 3 were observed for organic-free reagent water (acidified), tap water and ground water. The results for acidified and non-acidified samples were not significantly different.

10.0 REFERENCES

1. Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water, EPA-600/S4-83-052, 1984.

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3. Richard J.J.; Junk, G.A. Journal AWWA 1977, 69, 62.

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TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS (MDL) FOR 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Minutes		MDL (µg/L)
	Column A	Column B	
EDB	9.5	8.9	0.01
DBCP	17.3	15.0	0.01

Column A: Durawax-DX 3

Column B: DB-1

TABLE 2.
SINGLE LABORATORY ACCURACY AND PRECISION FOR EDB AND DBCP IN TAP WATER

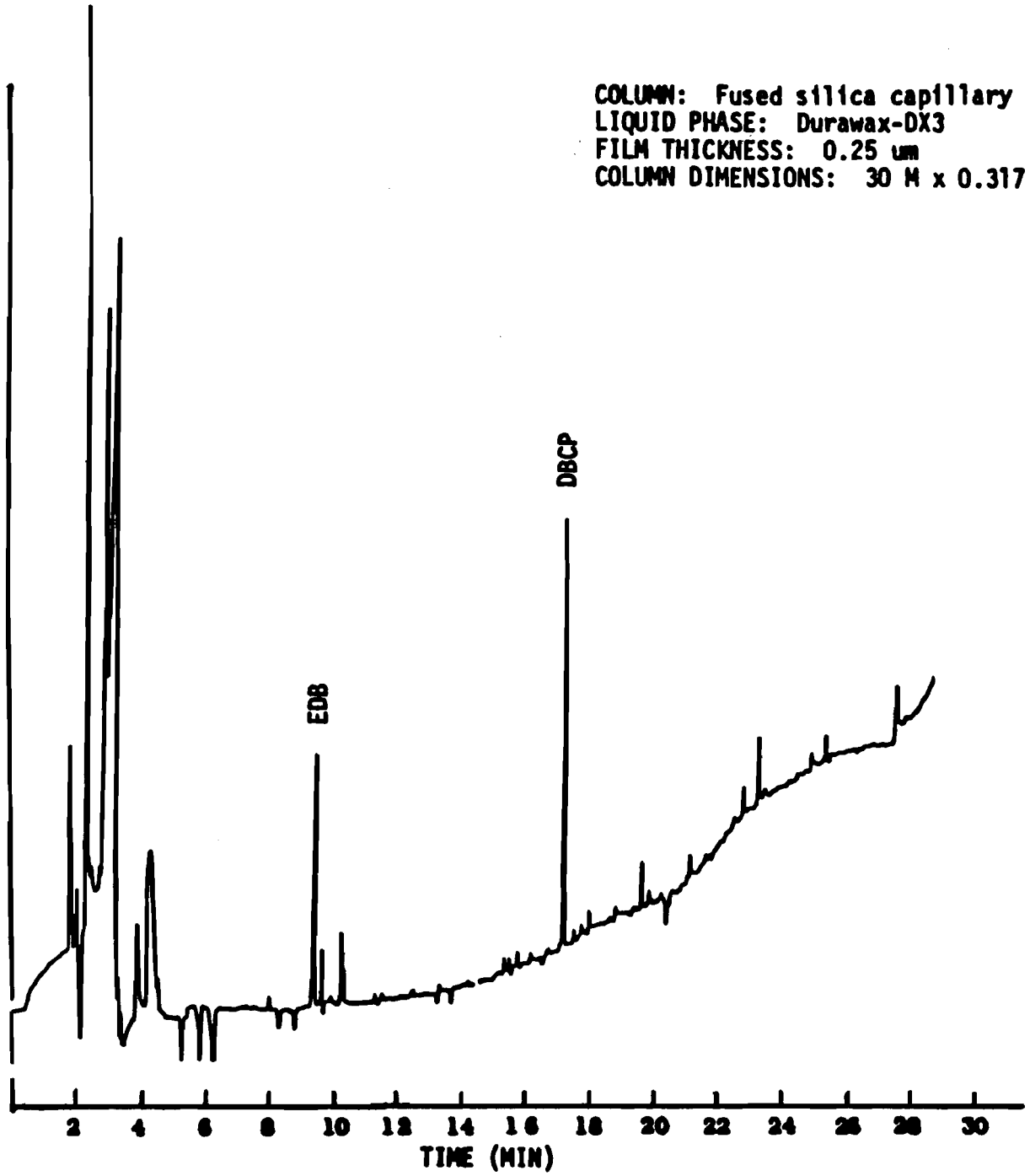
Analyte	Number of Samples	Spike Concentration (µg/L)	Average Recovery (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

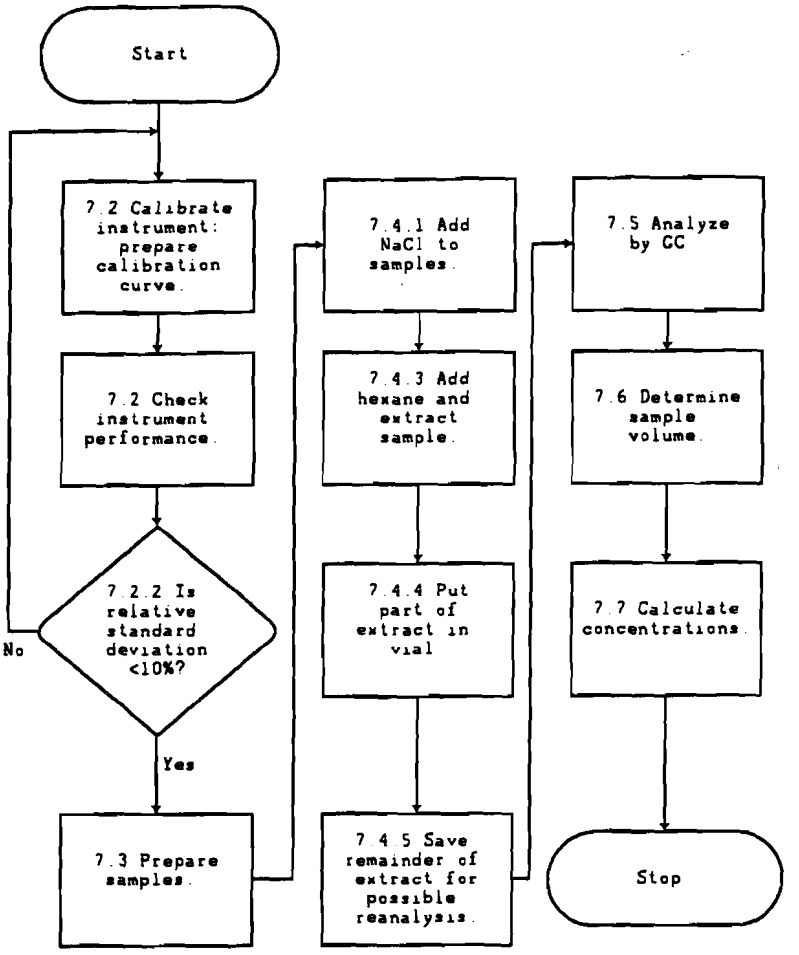
TABLE 3.
ACCURACY AND PRECISION AT 2.0 µg/L
OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix[1]	Number of Samples	Average Accuracy (% Recovery)	Relative Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

[1] RW-A = Organic-free reagent water at pH 2
GW = Ground water, ambient pH
GW-A = Ground water at pH 2
TW = Tap water, ambient pH
TW-A = Tap water at pH 2

FIGURE 1.
SAMPLE CHROMATOGRAM FOR EXTRACT OF WATER SPIKED
AT 0.114 μg/L WITH EDB AND DBCP




Start
7.2 Calibrate instrument: prepare calibration curve.
7.2 Check instrument performance.
7.2.2 Is relative standard deviation <10%?
No
Yes
7.3 Prepare samples.
7.4.1 Add NaCl to samples.
7.4.3 Add hexane and extract sample.
7.4.4 Put part of extract in vial
7.4.5 Save remainder of extract for possible reanalysis.
7.5 Analyze by GC
7.6 Determine sample volume.
7.7 Calculate concentrations.
Stop

METHOD 8015A

NONHALOGENATED VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8015 is used to determine the concentration of various nonhalogenated volatile organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Diethyl ether	60-29-7	b	b
Ethanol	64-17-5	i	b
Methyl ethyl ketone (MEK)	78-93-3	pp	b
Methyl isobutyl ketone (MIBK)	108-10-1	pp	b

a Chemical Abstract Services Registry Number.
b Adequate response using this technique
i Inappropriate technique for this analyte
pp Poor purging efficiency, resulting in high EQLs

2.0 SUMMARY OF METHOD

2.1 Method 8015 provides gas chromatographic conditions for the detection of certain nonhalogenated volatile organic compounds. Samples may be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed by Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in. ID stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass column packed with n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 Detector - Flame ionization (FID).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

4.5 Microsyringes - 10 and 25 μL with a 0.006 in. ID needle (Hamilton 702N or equivalent) and a 100 μL.

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH. Pesticide quality or equivalent. Store away from other solvents.

5.4 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in

methanol using assayed liquids.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared, ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.4.2 Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.4.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards - Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.5 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Calibration standards - Calibration standards at a minimum of five concentrations are prepared in water from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Section 1.1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

5.6.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.6.2 Use a 25 µL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.6.3 Rapidly inject the alcoholic standard into the filled

volumetric flask. Remove the needle as fast as possible after injection.

5.6.4 Mix aqueous standards by inverting the flask three times only.

5.6.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.6.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.6.7 Aqueous standards are not stable and should be discarded after 1 hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.7 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.7.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.6.

5.7.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ng/µL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

5.7.3 Analyze each calibration standard according to Section 7.0, adding 10 µL of internal standard spiking solution directly to the syringe.

5.8 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and water blank with one or two surrogate compounds recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Section 5.4, add a volume to give 750 µg of each surrogate to 45 mL of water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.7.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For high-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis. Method 5030 also provides guidance on the analysis of aqueous miscible and non-aqueous miscible liquid wastes (see Section 7.4.1.1).

7.2 Chromatographic conditions (Recommended)

7.2.1 Column 1

Carrier gas (Helium) flow rate:	40 mL/min
Temperature program:	
Initial temperature:	45°C, hold for 3 minutes
Program:	45°C to 220°C at 8°C/min
Final temperature:	220°C, hold for 15 minutes.

7.2.2 Column 2

Carrier gas (Helium) flow rate:	40 mL/min
Temperature program:	
Initial temperature:	50°C, hold for 3 minutes
Program:	50°C to 170°C at 6°C/min
Final temperature:	170°C, hold for 4 minutes.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

Non-aqueous miscible wastes may also be analyzed by direct injection if the concentration of target analytes in the sample falls within the calibration range. If dilution of the sample is necessary, follow the guidance for High Concentration samples in Method 5030, Section 7.3.3.2.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Calculation of concentration is covered in Method 8000.

7.4.5 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.6 If the response for a peak is off-scale, prepare a dilution of the sample with water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000, Section 8.6.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required:

- Check to be sure that there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.

  Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and calibration procedures used.

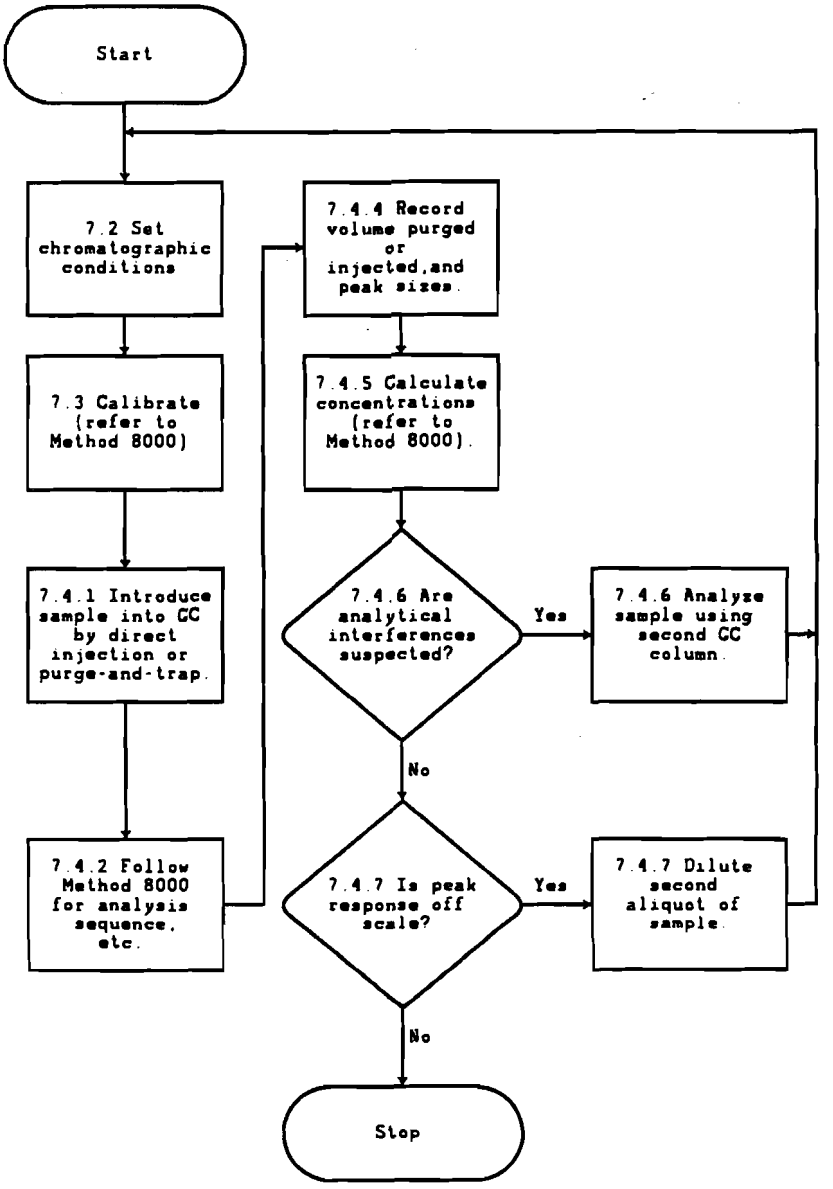
9.2 Specific method performance information will be provided as it becomes available.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography, J. Amer. Water Works Assoc., 66(12), pp. 739-744 (1974).

2. Bellar, T.A., and J.J. Lichtenberg, Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

3. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635 (in preparation).


Start
7.2 Set chromatographic conditions
7.3 Calibrate (refer to Method 8000)
7.4.1 Introduce sample into GC by direct injection or purge-and-trap.
7.4.2 Follow Method 8000 for analysis sequence, etc.
7.4.4 Record volume purged or injected, and peak sizes.
7.4.5 Calculate concentrations (refer to Method 8000).
7.4.6 Are analytical interferences suspected?
Yes
7.4.6 Analyze sample using second GC column.
No
7.4.7 Is peak response off scale?
Yes
7.4.7 Dilute second aliquot of sample.
No
Stop

METHOD 8020A

AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Chlorobenzene	108-90-7	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Ethylbenzene	100-41-4	b	b
Toluene	108-88-3	b	b
Xylenes		b	b

a Chemical Abstract Services Registry Number.
b adequate response by this technique.

1.2 Table 1 lists the method detection limit for each target analyte in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1: 6 ft x 0.082 in ID #304 stainless steel or glass column packed with 5% SP-1200 and 1.75% Bentone-34 on 100/120 mesh Supelcoport, or equivalent.

4.1.2.2 Column 2: 8 ft x 0.1 in ID stainless steel or glass column packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW, or equivalent.

4.1.3 Detector - Photoionization (PID) (h-Nu Systems, Inc. Model PI-51-02 or equivalent).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A - Appropriate sizes with ground glass stoppers.

4.5 Microsyringe - 10 and 25 μL with a 0.006 in ID needle (Hamilton 702N or equivalent) and a 100 μL.

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol (CH_3OH) - pesticide quality or equivalent. Store away from other solvents.

5.3 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.3.5 All standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.5 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in the target analyte list may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 μL of alcoholic standards into 100 mL of organic-free reagent water.

5.5.2 Use a 25 μL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. Alpha,alpha,alpha-trifluorotoluene has been used successfully as an internal standard.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.5.

5.6.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4. It is recommended that the secondary dilution standard be prepared at a concentration of 15 mg/L of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μg/L.

5.6.3 Analyze each calibration standard according to Section 7.0, adding 10 μL of internal standard spiking solution directly to the syringe.

5.7 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate compounds (bromochlorobenzene, bromofluorobenzene, 1,1,1-trifluorotoluene, fluorobenzene, and difluorobenzene are recommended) which encompass the range of the temperature program used in this method. From stock

standard solutions prepared as in Section 5.3, add a volume to give 750 μg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/μL. Add 10 μL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.6.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis. Method 5030 also provides guidance on the analysis of aqueous miscible and non-aqueous miscible liquid wastes (see Section 7.4.1.1 below).

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (He) flow rate:	36 mL/min
For lower boiling compounds:	
Initial temperature:	50°C, hold for 2 min;
Temperature program:	50°C to 90°C at 6°C/min, hold until all compounds have eluted.
For higher boiling range of compounds:	
Initial temperature:	50°C, hold for 2 min;
Temperature program:	50°C to 110°C at 3°C/min, hold until all compounds have eluted.

Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 Column 2:

Carrier gas (He) flow rate:	30 mL/min
Initial temperature:	40°C, hold for 2 min;
Temperature program:	40°C to 100°C at 2°C/min, hold until all compounds have eluted.

Column 2, an extremely high polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, because resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

Non-aqueous miscible wastes may also be analyzed by direct injection if the concentration of target analytes in the sample falls within the calibration range. If dilution of the sample is necessary, follow the guidance for High Concentration samples in Method 5030, Section 7.3.3.2.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. Figure 2 shows an example of the separation achieved using Column 2.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1 - 500 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

9.3 The method detection limits reported in Table 1 were generated under optimum analytical conditions by an Agency contractor (Ref. 7) as guidance, and may not be readily achievable by all laboratories at all times.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.

2. Bellar, T.A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", in Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

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TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Col. 2	Method detection limit[a] (µg/L)
Benzene	3.33	2.75	0.2
Chlorobenzene[b]	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

a Using purge-and-trap method (Method 5030). See Sec. 9.3.
b Chlorobenzene and m-xylene may co-elute on some columns.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs)
FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

a EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs determined herein are provided for guidance and may not always be achievable.

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (μg/L)	Limit for s (μg/L)	Range for $\bar{x}$ (μg/L)	Range P, P_s (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in μg/L.

s = Standard deviation of four recovery measurements, in μg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in μg/L.

P, P_s = Percent recovery measured.

a Criteria from 40 CFR Part 136 for Method 602, using packed columns, and were calculated assuming a check sample concentration of 20 μg/L. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 1. When capillary columns are used, see Method 8021 for performance data.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Benzene	0.92C+0.57	$0.09\bar{x}+0.59$	$0.21\bar{x}+0.56$
Chlorobenzene	0.95C+0.02	$0.09\bar{x}+0.23$	$0.17\bar{x}+0.10$
1,2-Dichlorobenzene	0.93C+0.52	$0.17\bar{x}-0.04$	$0.22\bar{x}+0.53$
1,3-Dichlorobenzene	0.96C-0.04	$0.15\bar{x}-0.10$	$0.19\bar{x}+0.09$
1,4-Dichlorobenzene	0.93C-0.09	$0.15\bar{x}+0.28$	$0.20\bar{x}+0.41$
Ethylbenzene	0.94C+0.31	$0.17\bar{x}+0.46$	$0.26\bar{x}+0.23$
Toluene	0.94C+0.65	$0.09\bar{x}+0.48$	$0.18\bar{x}+0.71$

x′ = Expected recovery for one or more measurements of a sample containing concentration C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

Figure 1
Chromatogram of Aromatic Volatile Organics
(column 1 conditions)

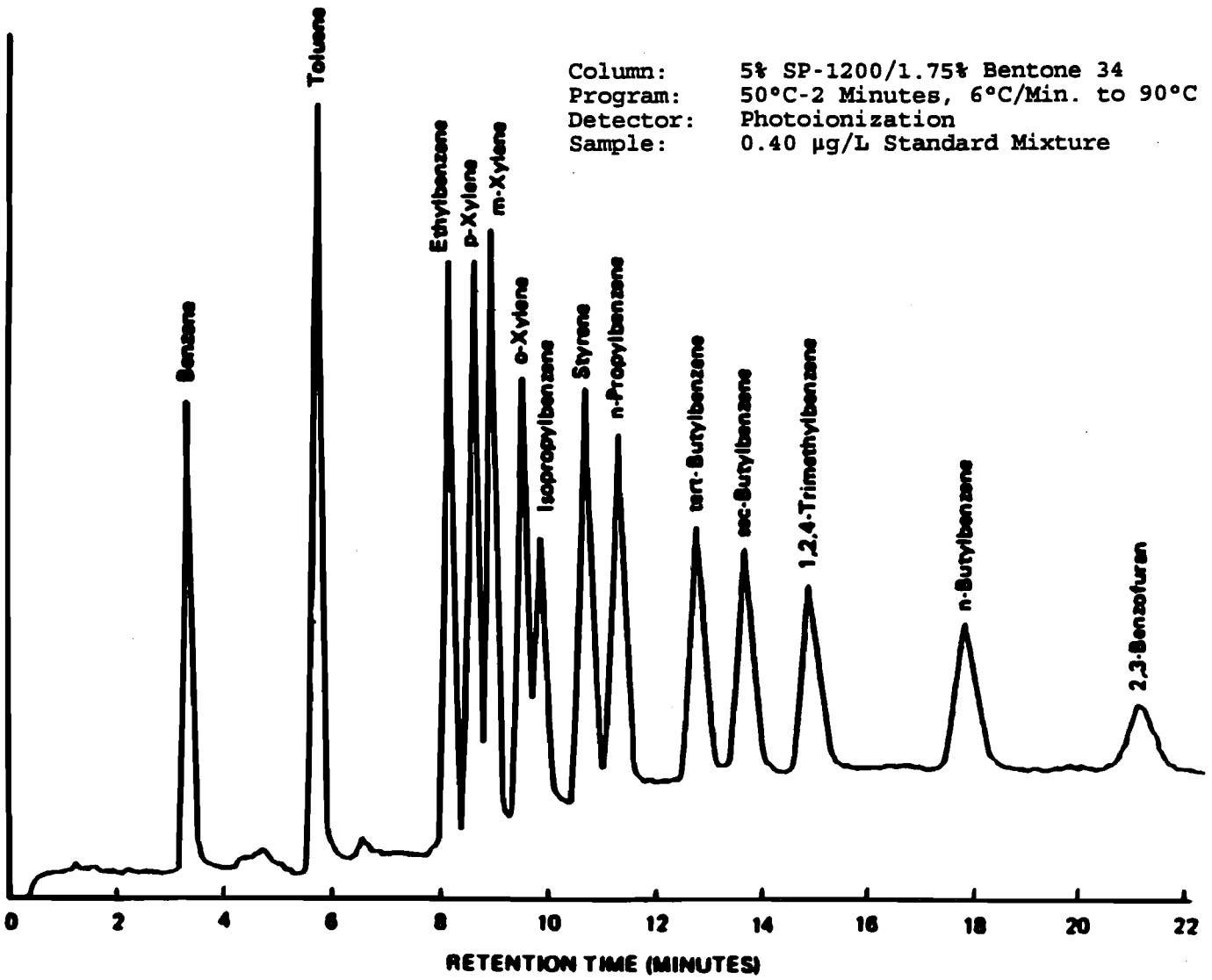
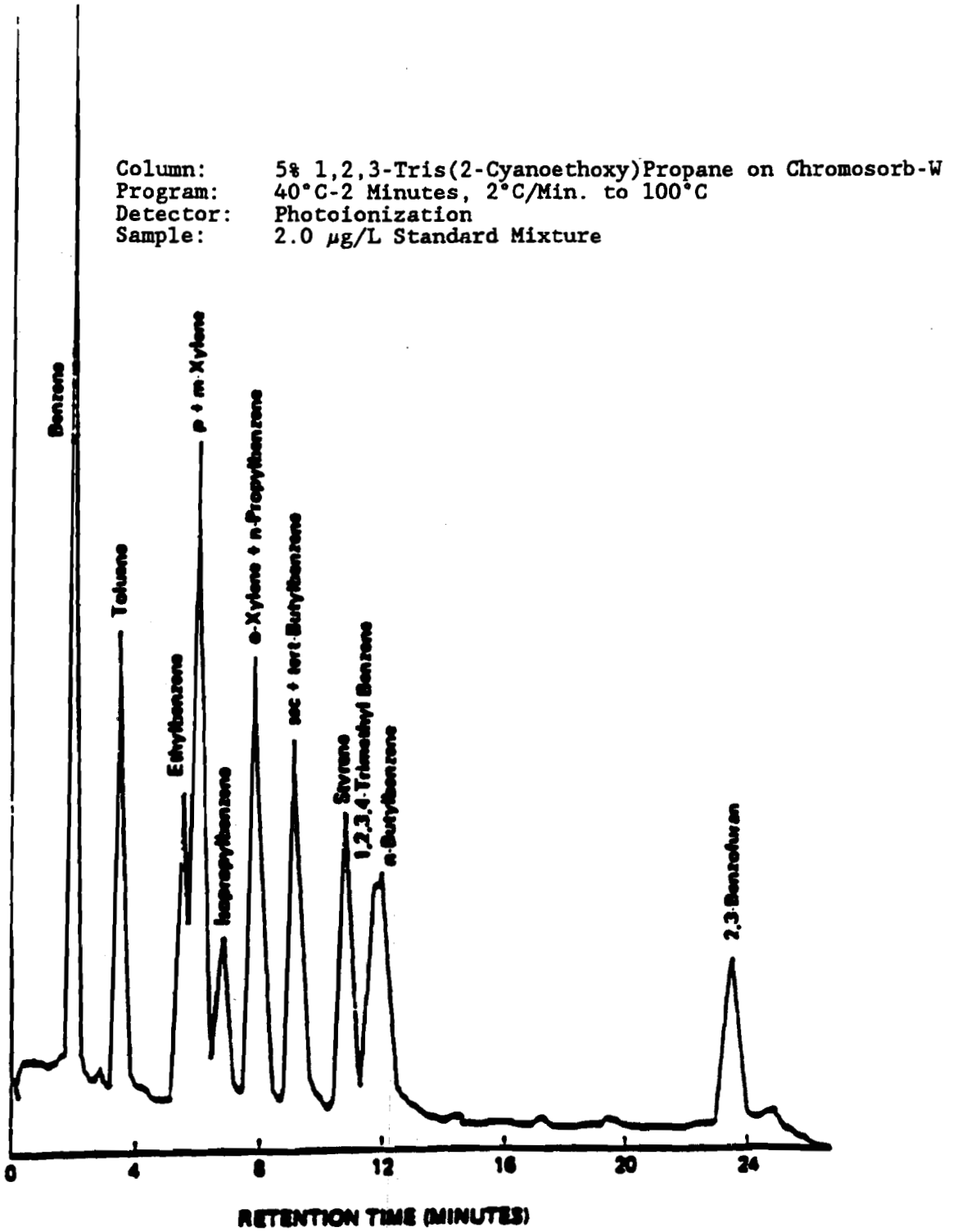
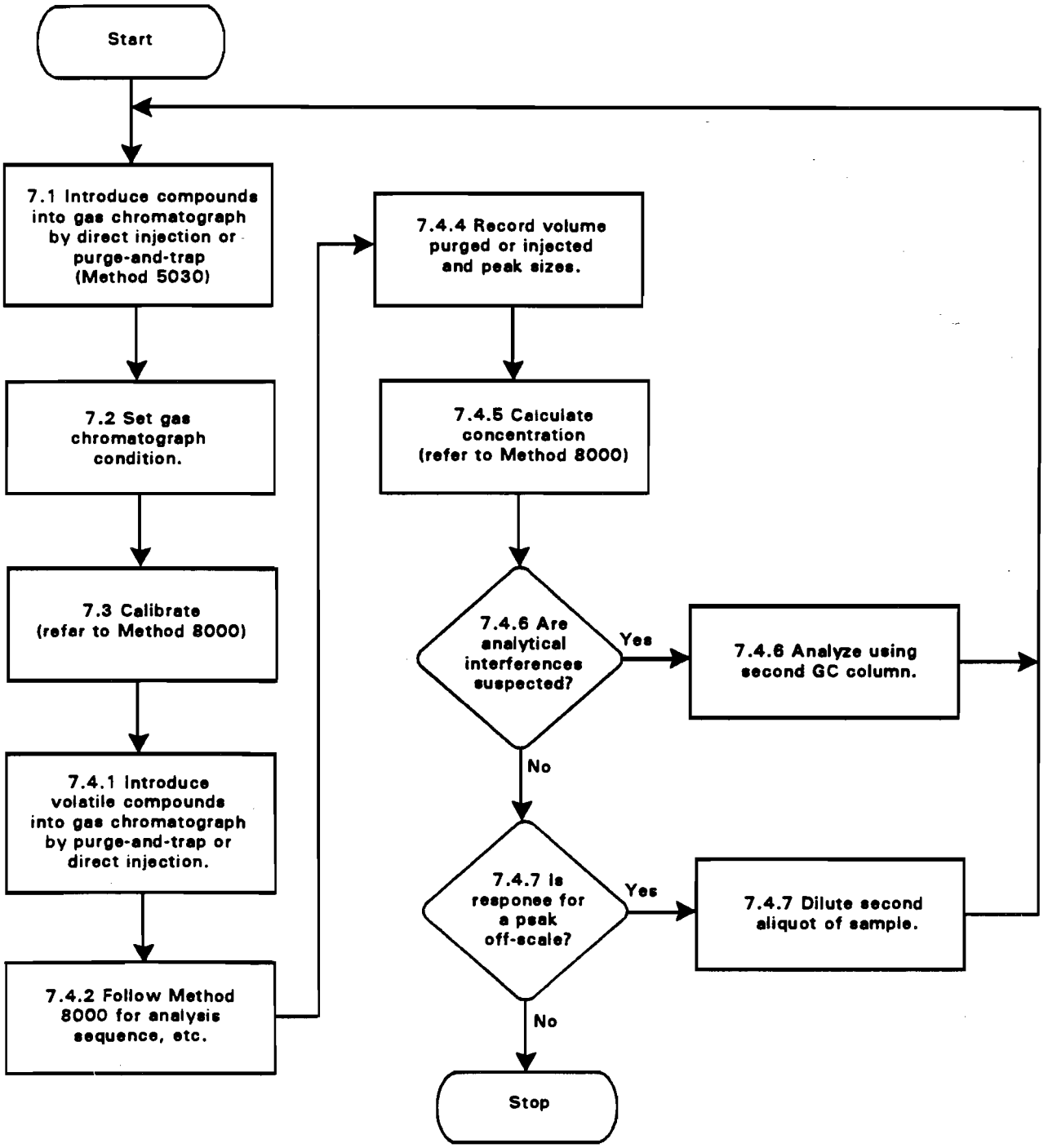


Figure 2
Chromatogram of Aromatic Volatile Organics
(column 2 conditions)




Start
7.1 Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
7.2 Set gas chromatograph condition.
7.3 Calibrate (refer to Method 8000)
7.4.1 Introduce volatile compounds into gas chromatograph by purge-and-trap or direct injection.
7.4.2 Follow Method 8000 for analysis sequence, etc.
7.4.4 Record volume purged or injected and peak sizes.
7.4.5 Calculate concentration (refer to Method 8000)
7.4.6 Are analytical interferences suspected?
Yes
7.4.6 Analyze using second GC column.
No
7.4.7 Is response for a peak off-scale?
Yes
7.4.7 Dilute second aliquot of sample.
No
Stop

METHOD 8021A

HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8021 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Technique	
Analyte	CAS No.[a]	Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Bromobenzene	108-86-1	b	b
Bromochloromethane	74-97-5	b	b
Bromodichloromethane	75-27-4	b	b
Bromoform	75-25-2	b	b
Bromomethane	74-83-9	b	b
n-Butylbenzene	104-51-8	b	b
sec-Butylbenzene	135-98-8	b	b
tert-Butylbenzene	98-06-6	b	b
Carbon tetrachloride	56-23-5	b	b
Chlorobenzene	108-90-7	b	b
Chlorodibromomethane	124-48-1	b	b
Chloroethane	75-00-3	b	b
Chloroform	67-66-3	b	b
Chloromethane	74-87-3	b	b
2-Chlorotoluene	95-49-8	b	b
4-Chlorotoluene	106-43-4	b	b
1,2-Dibromo-3-chloropropane	96-12-8	pp	b
1,2-Dibromoethane	106-93-4	b	b
Dibromomethane	74-95-3	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Dichlorodifluoromethane	75-71-8	b	b
1,1-Dichloroethane	75-34-3	b	b
1,2-Dichloroethane	107-06-2	b	b
1,1-Dichloroethene	75-35-4	b	b
cis-1,2-Dichloroethene	156-59-4	b	b
trans-1,2-Dichloroethene	156-60-5	b	b

Analyte	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
1,2-Dichloropropane	78-87-5	b	b
1,3-Dichloropropane	142-28-9	b	b
2,2-Dichloropropane	590-20-7	b	b
1,1-Dichloropropene	563-58-6	b	b
cis-1,3-dichloropropene	10061-01-5	b	b
trans-1,3-dichloropropene	10061-02-6	b	b
Ethylbenzene	100-41-4	b	b
Hexachlorobutadiene	87-68-3	b	b
Isopropylbenzene	98-82-8	b	b
p-Isopropyltoluene	99-87-6	b	b
Methylene chloride	75-09-2	b	b
Naphthalene	91-20-3	b	b
n-Propylbenzene	103-65-1	b	b
Styrene	100-42-5	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b
Tetrachloroethene	127-18-4	b	b
Toluene	108-88-3	b	b
1,2,3-Trichlorobenzene	87-61-6	b	b
1,2,4-Trichlorobenzene	120-82-1	b	b
1,1,1-Trichloroethane	71-55-6	b	b
1,1,2-Trichloroethane	79-00-5	b	b
Trichloroethene	79-01-6	b	b
Trichlorofluoromethane	75-69-4	b	b
1,2,3-Trichloropropane	96-18-4	b	b
1,2,4-Trimethylbenzene	95-63-6	b	b
1,3,5-Trimethylbenzene	108-67-8	b	b
Vinyl chloride	75-01-4	b	b
o-Xylene	95-47-6	b	b
m-Xylene	108-38-3	b	b
p-Xylene	106-42-3	b	b

a Chemical Abstract Services Registry Number.
b Adequate response by this technique.
pp Poor purging efficiency resulting in high EQLs.

1.2 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e. xylenes) may be hampered by coelution.

1.3 The estimated quantitation limit (EQL) of Method 8021A for an individual compound is approximately 1 µg/kg (wet weight) for soil/sediment samples, 0.1 mg/kg (wet weight) for wastes, and 1 µg/L for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low µg/L level or by experienced technicians under the close supervision of a qualified analyst.

1.5 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst (references 4 and 6).

1.6 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachloro-butadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8021 provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030 (where applicable). A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series.

2.2 Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from

organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.3 Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

4.0 APPARATUS AND MATERIALS

4.1 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.2 Gas Chromatograph - capable of temperature programming; equipped with variable-constant differential flow controllers, subambient oven controller, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing, 0.32-0.5 mm ID, and data system.

4.2.1 Column - 60 m x 0.75 mm ID VOCOL wide-bore capillary column with 1.5 μm film thickness (Supelco Inc., or equivalent).

4.2.2 Photoionization detector (PID) (Tracor Model 703, or equivalent).

4.2.3 Electrolytic conductivity detector (HECD) (Tracor Hall Model 700-A, or equivalent).

4.3 Syringes - 5 mL glass hypodermic with Luer-Lok tips.

4.4 Syringe valves - 2-way with Luer ends (Teflon or Kel-F).

4.5 Microsyringe - 25 μL with a 2 in. x 0.006 in. ID, 22° bevel needle (Hamilton #702N or equivalent).

4.6 Microsyringes - 10, 100 μL.

4.7 Syringes - 0.5, 1.0, and 5 mL, gas-tight with shut-off valve.

4.8 Bottles - 15 mL, Teflon lined with screw-cap or crimp top.

4.9 Analytical balance - 0.0001 g.

4.10 Refrigerator.

4.11 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades

may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store away from other solvents.

5.4 Vinyl chloride, (99.9% pure), CH_2=CHCl. Vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey, as well as from other sources. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

5.5 Stock standards - Stock solutions may either be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity should be prepared in a hood.

NOTE: If direct injection is used, the solvent system of standards must match that of the sample. It is not necessary to prepare high concentration aqueous mixed standards when using direct injection.

5.5.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material, as described below.

5.5.2.1 Liquids: Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.5.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed

to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap or crimp top. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.5.5 Prepare fresh stock standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 20% drift.

5.6 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.7 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.7 Calibration standards, at a minimum of five concentration levels are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of the concentrations found in real samples or should define the working range of the GC. Standards (one or more) should contain each analyte for detection by this method. In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

NOTE: Prepare calibration solutions for use with direct injection analyses in water at the concentrations required.

5.7.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.7.2 Use a 25 µL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.7.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.7.4 Mix aqueous standards by inverting the flask three times.

5.7.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.7.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.7.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 12 hours, if held in sealed vials with zero headspace.

5.7.8 Optionally calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.8 Internal standards - Prepare a spiking solution containing fluorobenzene and 2-bromo-1-chloropropane in methanol, using the procedures described in Secs. 5.5 and 5.6. It is recommended that the secondary dilution standard be prepared at a concentration of 5 mg/L of each internal standard compound. The addition of 10 μL of such a standard to 5.0 mL of sample or calibration standard would be equivalent to 10 μg/L.

5.9 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with two or more surrogate compounds. A combination of 1,4-dichlorobutane and bromochlorobenzene is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Sec. 5.5, add a volume to give 750 μg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/μL. Add 10 μL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Sec. 5.8).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Set up the gas chromatograph system so that the photoionization detector (PID) is in series with the electrolytic conductivity detector (HECD).

7.2.2 Oven settings:

Carrier gas (Helium) Flow rate: 6 mL/min.
Temperature program

Initial temperature:	10°C, hold for 8 minutes at
Program:	10°C to 180°C at 4°C/min
Final temperature:	180°C, hold until all expected compounds have eluted.

7.2.3 The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

7.2.4 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data presented in Table 2. The operating conditions used to collect these data are:

Reactor tube:	Nickel, 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-Propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

7.2.5 A sample chromatogram obtained with this column is presented in Figure 5. This column was used to develop the method performance statements in Sec. 9.0. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Sec. 8.0 are met.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Sec. 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method (see Sec. 7.4.1.1). If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes) direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L), therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Sec. 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two detectors for a number of organic compounds analyzable using this method.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using a second GC column is recommended.

7.4.7 If the response for a peak is off-scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control reference sample (Method 8000) should contain each parameter of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 2 gives method accuracy and precision as functions of concentration for the analytes of interest.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 Method detection limits for these analytes have been calculated from data collected by spiking organic-free reagent water at 0.1 µg/L. These data are presented in Table 1.

9.2 This method was tested in a single laboratory using organic-free reagent water spiked at 10 µg/L. Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

10.0 REFERENCES

1. Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series, Method 502.2, Rev. 2.0 (1989); Methods for the Determination of Organic Compounds in Drinking Water", Environmental Monitoring Systems Laboratory, Cincinnati, OH, EPA/600/4-88/039, December, 1988

2. The Determination of Halogenated Chemicals in Water by the Purge and Trap Method, Method 502.1; Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio 45268, September, 1986.

3. Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography, Method 503.1; Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio, September, 1986.

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TABLE 1.

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time[a] minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
Dichlorodifluoromethane	-[b]	8.47		0.05
Chloromethane	-	9.47		0.03
Vinyl Chloride	9.88	9.93	0.02	0.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	ND[c]	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	28.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		ND
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethylbenzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropylbenzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

TABLE 1.
(Continued)

Analyte	PID Ret. Time[a] minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
n-Propylbenzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethylbenzene	41.41	-	0.004	
2-Chlorotoluene	41.41	41.45	ND	0.01
4-Chlorotoluene	41.60	41.63	0.02	0.01
tert-Butylbenzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3-Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	ND	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

[a] Retention times determined on 60 m x 0.75 mm ID VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

[b] Dash (-) indicates detector does not respond.

[c] ND = Not determined.

TABLE 2.
SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery,[a] %	Standard Deviation of Recovery	Recovery,[a] %	Standard Deviation of Recovery
Benzene	99	1.2	-[b]	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
sec-Butylbenzene	97	2.6	-	-
tert-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
2-Chlorotoluene	ND[c]	ND	97	2.6
4-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Dibromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Dibromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	ND	ND	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
2,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
Ethylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

TABLE 2.
(Continued)

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery,[a] %	Standard Deviation of Recovery	Recovery,[a] %	Standard Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

[a] Recoveries and standard deviations were determined from seven samples and spiked at 10 µg/L of each analyte. Recoveries were determined by internal standard method. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

[b] Detector does not respond.

[c] ND = Not determined.

[d] This method was tested in a single laboratory using water spiked at 10 µg/L (see reference 5).

TABLE 3.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

a EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

FIGURE 1.
PURGING DEVICE

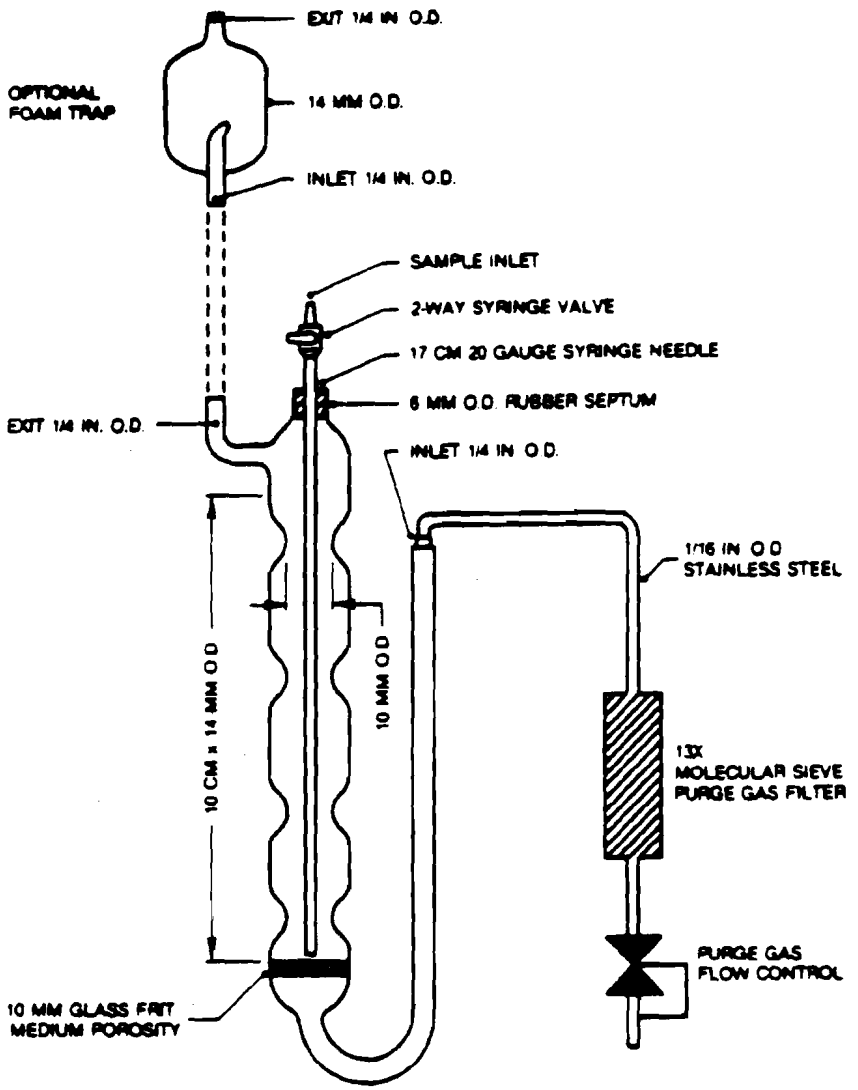


FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

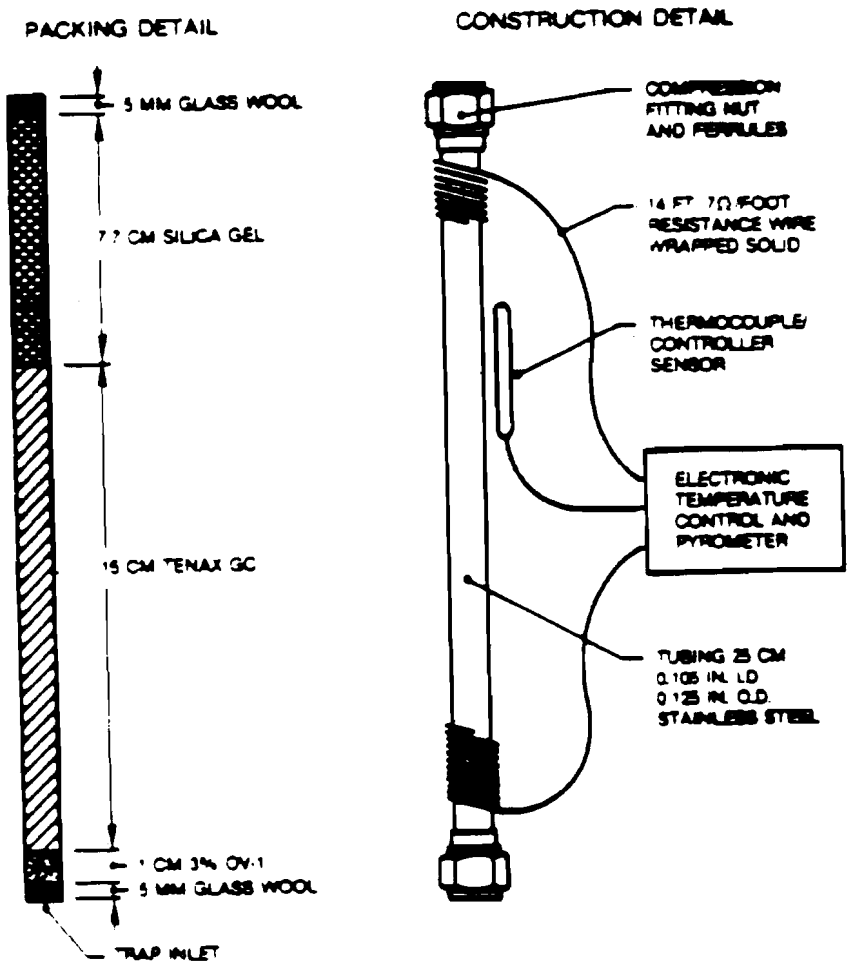


FIGURE 3.
PURGE-AND-TRAP SYSTEM - PURGE MODE

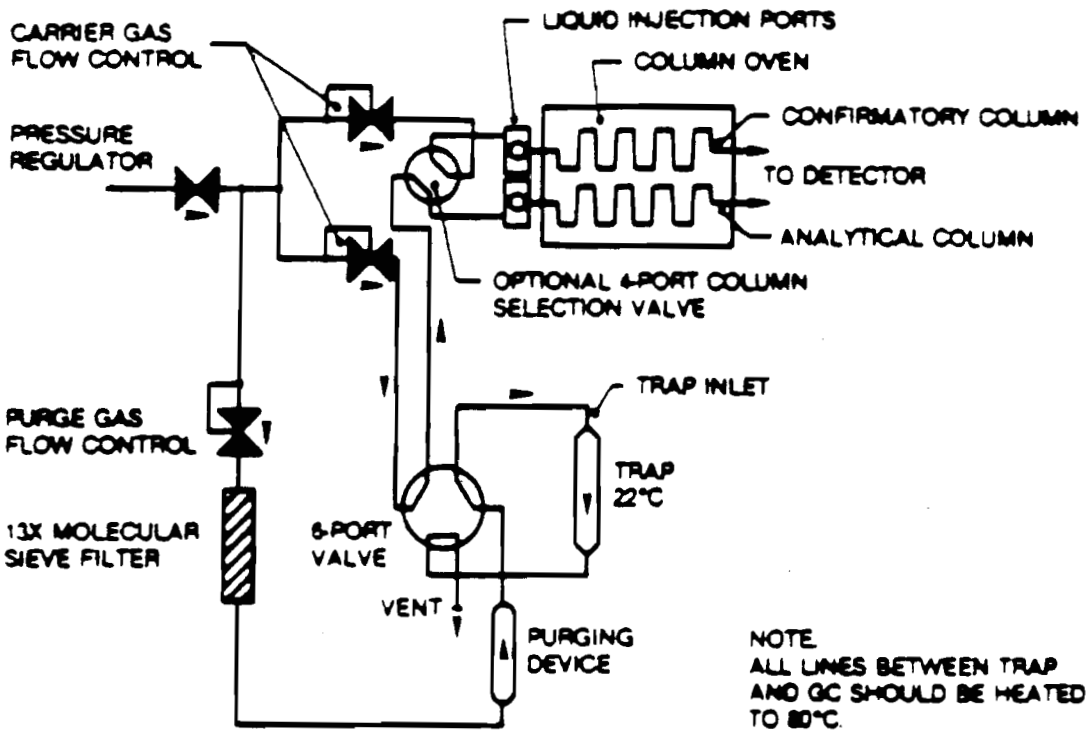


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

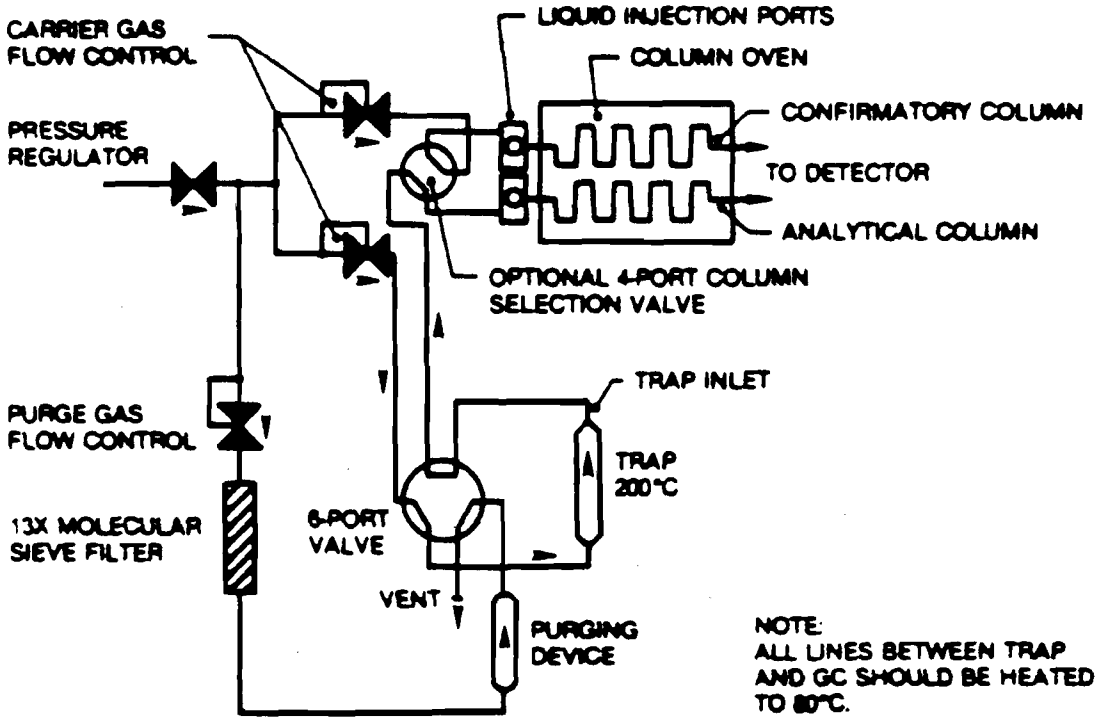
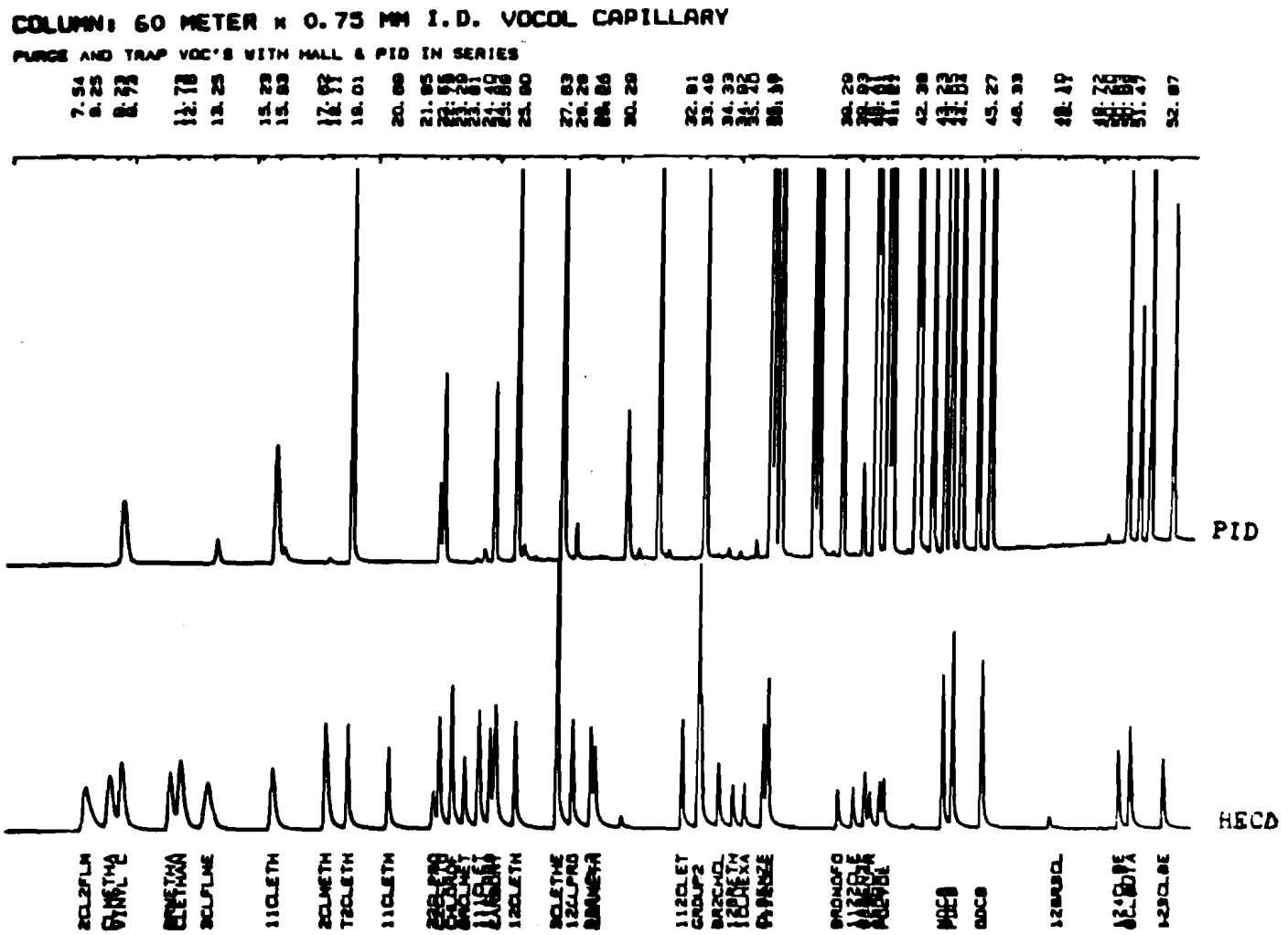
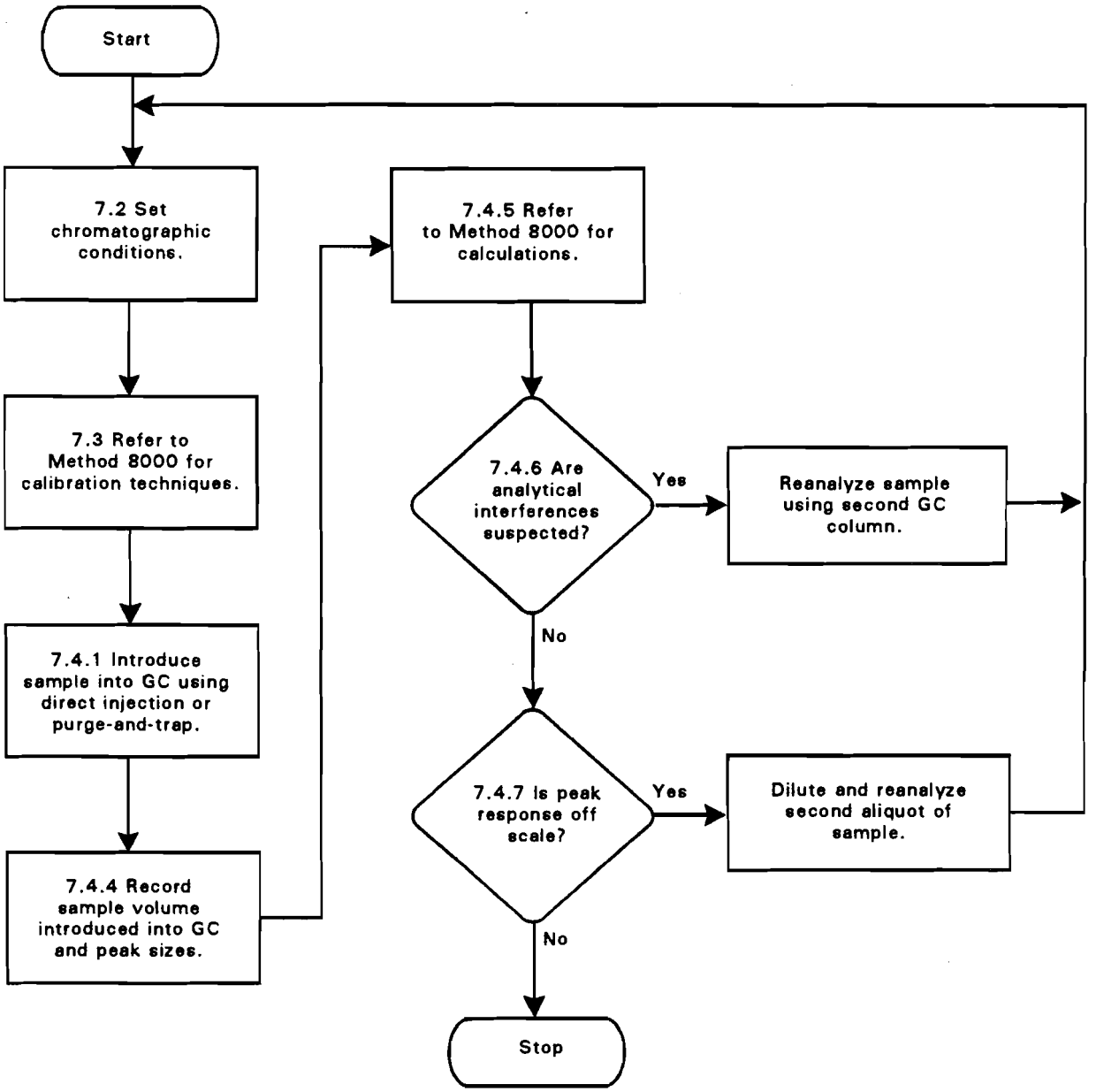


FIGURE 5.
GAS CHROMATOGRAM OF VOLATILE ORGANICS




Start
7.2 Set chromatographic conditions.
7.3 Refer to Method 8000 for calibration techniques.
7.4.1 Introduce sample into GC using direct injection or purge-and-trap.
7.4.4 Record sample volume introduced into GC and peak sizes.
7.4.5 Refer to Method 8000 for calculations.
7.4.6 Are analytical interferences suspected?
Yes
Reanalyze sample using second GC column.
No
7.4.7 Is peak response off scale?
Yes
Dilute and reanalyze second aliquot of sample.
No
Stop

METHOD 8030A

ACROLEIN AND ACRYLONITRILE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8030 is used to determine the concentration of the following volatile organic compounds:

Compound Name	CAS No.[a]
Acrolein (Propenal)	107-02-8
Acrylonitrile	107-13-1

[a] Chemical Abstract Services Registry Number.

1.2 Table 1 lists chromatographic conditions and method detection limits for acrolein and acrylonitrile in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8030 provides gas chromatographic conditions for the detection of the target analytes. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Tenax should be used as the trap packing material. Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak area is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 10 ft x 2 mm ID stainless steel or glass packed with Porapak-QS (80/100 mesh) or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass packed with Chromosorb 101 (60/80 mesh) or equivalent.

4.1.3 Detector - Flame ionization (FID).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luer-lok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

4.5 Microsyringes - 10 and 25 µL with a 0.006 in. ID needle (Hamilton 702N, or equivalent) and a 100 µL.

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water: All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Hydrochloric acid, HCl - 1:1 (v/v).

5.4 Sodium hydroxide, NaOH - 10N solution. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.5 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in

organic-free reagent water using assayed liquids. Because acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood.

5.5.1 Place about 9.8 mL of organic-free reagent water in a 10 mL tared ground-glass stoppered volumetric flask. For acrolein standards the water must be adjusted to pH 4-5 using hydrochloric acid (1:1 v/v) or sodium hydroxide (10N), if necessary. Weigh the flask to the nearest 0.0001 g.

5.5.2 Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the water without contacting the neck of the flask.

5.5.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration, if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at 4°C and protect from light.

5.5.5 Prepare fresh standards daily.

5.6 Secondary dilution standards - Prepare secondary dilution standards as needed, in organic-free reagent water, from the stock standard solutions. The secondary dilution standards must contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.7 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace, and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.7 Calibration standards - Prepare calibration standards in organic-free reagent water from the secondary dilution standards at a minimum of five concentrations. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC. Each standard should contain each analyte for detection by this method. In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.7.1 Use a 25 μL Hamilton 702N microsyringe, or equivalent, (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of standards into water).

5.7.2 Never use pipets to dilute or transfer samples or aqueous standards.

5.7.3 Standards must be prepared daily.

5.8 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.8.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest, as described in Section 5.7.

5.8.2 Prepare a spiking solution containing each of the internal standards, using the procedures described in Sections 5.5 and 5.6. It is recommended that the secondary dilution standard be prepared at a concentration of 15 mg/L of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

5.8.3 Analyze each calibration standard according to Section 7.0, adding 10 µL of internal standard spiking solution directly to the syringe.

5.9 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two surrogate compounds (e.g. compounds similar in analytical behavior to the analytes of interest but which are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.5, add a volume to give 750 µg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.8.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or heated purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For high-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1:

Helium flow rate =	30 mL/min
Temperature program:	
Initial temperature =	110°C, hold for 1.5 minutes
Program =	110°C to 150°C, heating as rapidly as possible
Final temperature =	150°C, hold for 20 minutes.

7.2.2 Column 2:

Helium flow rate =	40 mL/min
Temperature program:	
Initial temperature =	80°C, hold for 4 minutes
Program =	80°C to 120°C at 50°C/min
Final temperature =	120°C, hold for 12 minutes.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (heated purge-and-trap method using Tenax as the trap packing material) or the direct injection method. If the internal standard calibration technique is used, add 10 µL of the internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this

method. Figure 1 illustrates the chromatographic separation of acrolein and of acrylonitrile using Column 1.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 25 mg/L in water.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives single laboratory accuracy and precision for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the average recoveries and standard deviations presented in Table 4 were obtained using Method 5030. Seven replicate samples were analyzed at each spike concentration.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

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7. "Evaluation of Method 603," Final Report for EPA Contract 68-03-1760 (in preparation).

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (µg/L)
Acrolein	10.6	8.2	0.7
Acrylonitrile	12.7	9.8	0.5

[a] Based on using purge-and-trap, Method 5030.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

[a] Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Analyte	Range for Q (µg/L)	Limit for S (µg/L)	Range for $\bar{x}$ (µg/L)	Range P, P_s (%)
Acrolein	45.9 - 54.1	4.6	42.9 - 60.1	88-118
Acrylonitrile	41.2 - 58.8	9.9	33.1 - 69.9	71-135

Q = Concentration measured in QC check sample, in µg/L.
S = Standard deviation of four recovery measurements, in µg/L.
$\bar{R}$ = Average recovery for four recovery measurements, in µg/L.
P, P_s = Percent recovery measured.

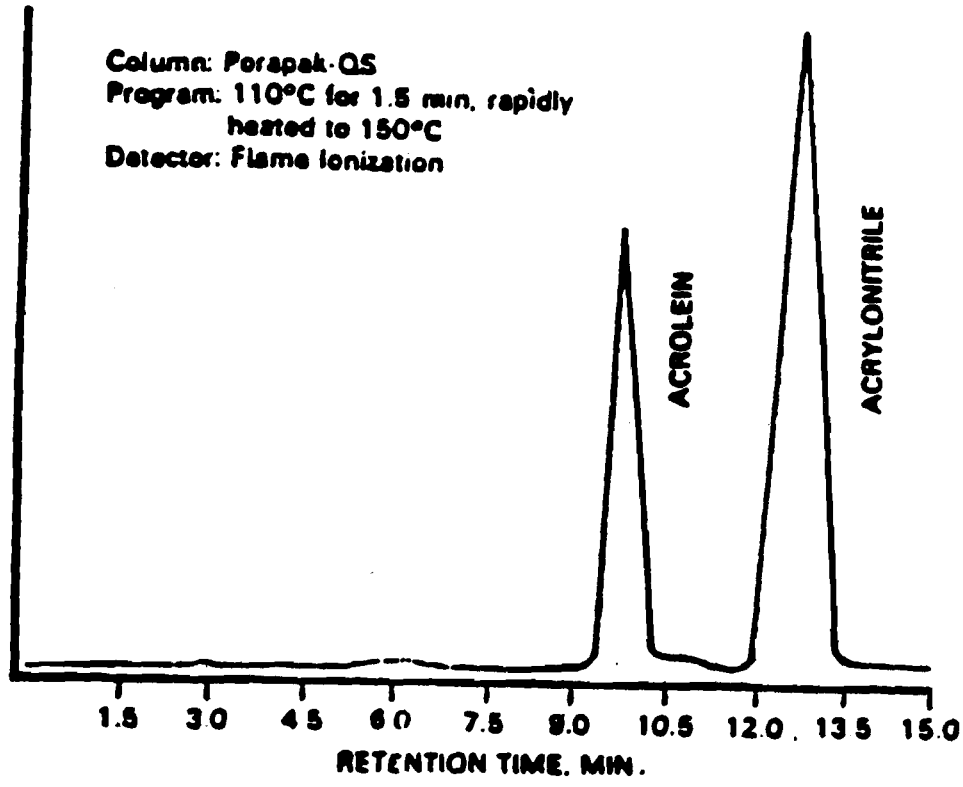
[a] Criteria from 40 CFR Part 136 for Method 603 and were calculated assuming a QC check sample concentration of 50 µg/L.

TABLE 4.
SINGLE LABORATORY ACCURACY AND PRECISION

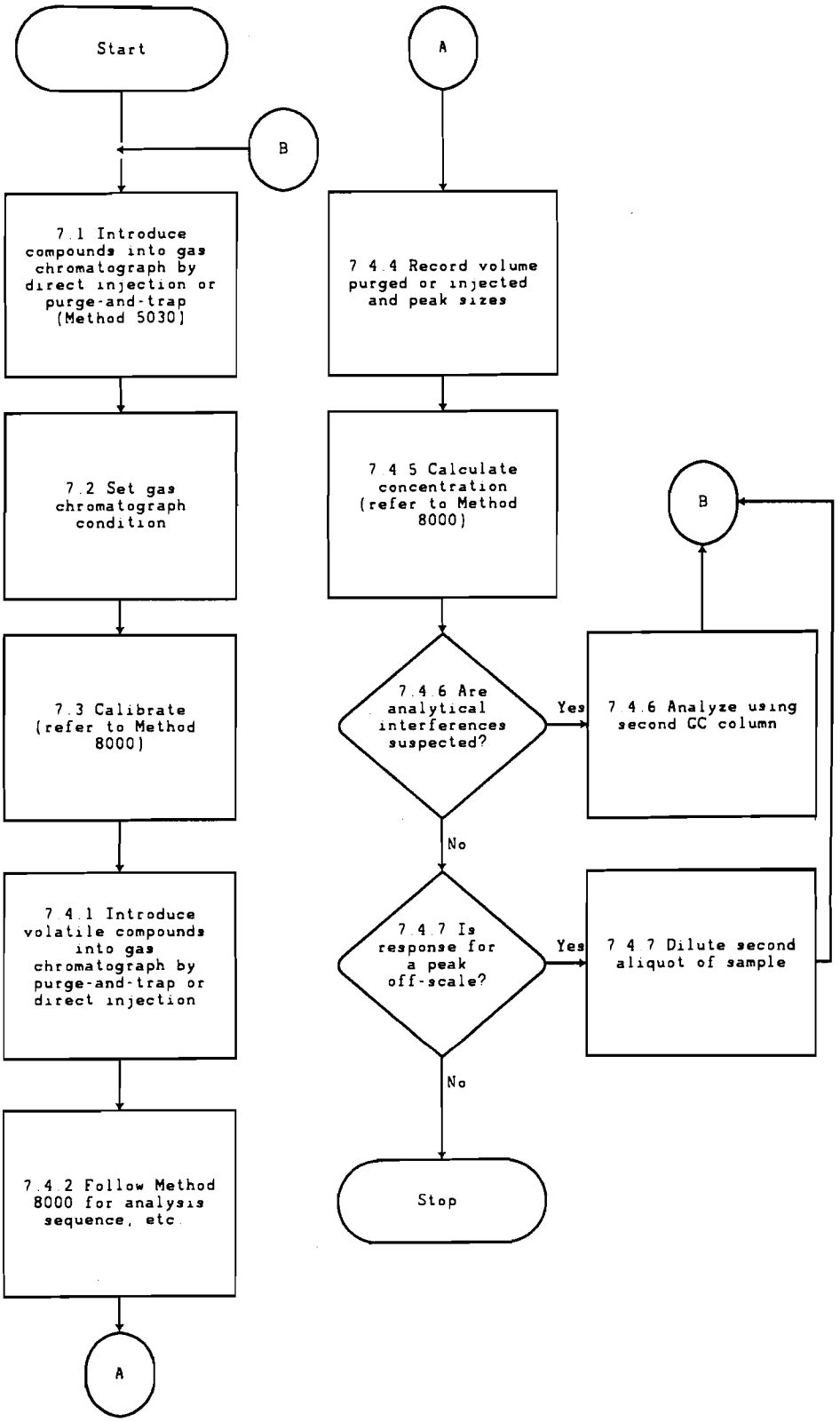
Parameter	Spike conc. (µg/L)	Average recovery (µg/L)	Standard deviation (µg/L)	Average percent recovery	Sample matrix
Acrolein	5.0	5.2	0.2	104	AW
	50.0	51.4	0.7	103	AW
	5.0	4.0	0.2	80	POTW
	50.0	44.4	0.8	89	POTW
	5.0	0.1	0.1	2	IW
	100.0	9.3	1.1	9	IW
Acrylonitrile	5.0	4.2	0.2	84	AW
	50.0	51.4	1.5	103	AW
	20.0	20.1	0.8	100	POTW
	100.0	101.3	1.5	101	POTW
	10.0	9.1	0.8	91	IW
	100.0	104.0	3.2	104	IW

AW = ASTM Type II water.
POTW = Prechlorination secondary effluent from a municipal sewage treatment plant.
IW = Industrial wastewater containing an unidentified acrolein reactant.

Figure 1
Gas Chromatogram of Acrolein and Acrylonitrile



METHOD 8030A
ACROLEIN AND ACRYLONITRILE BY GAS CHROMATOGRAPHY



METHOD 8031

ACRYLONITRILE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8031 is used to determine the concentration of acrylonitrile in water. This method may also be applicable to other matrices. The following compound can be determined by this method:

Compound Name	CAS No.[a]
Acrylonitrile	107-13-1

[a] Chemical Abstract Services Registry Number.

1.2 The estimated quantitation limit of Method 8031 for determining the concentration of acrylonitrile in water is approximately 10 µg/L.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured sample volume is micro-extracted with methyl tert-butyl ether. The extract is separated by gas chromatography and measured with a Nitrogen/Phosphorus detector.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that leads to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

3.2 Samples can be contaminated by diffusion of volatile organics around the septum seal into the sample during handling and storage. A field blank should be prepared from organic-free reagent water and carried through the sampling and sample handling protocol to serve as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the

sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph system

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Column: Porapak Q - 6 ft., 80/10 Mesh, glass column, or equivalent.

4.1.3 Nitrogen/Phosphorus detector.

4.2 Materials

4.2.1 Grab sample bottles - 40 mL VOA bottles.

4.2.2 Mixing bottles - 90 mL bottle with a Teflon lined cap.

4.2.3 Syringes - 10 μL and 50 μL.

4.2.4 Volumetric flask (Class A) - 100 mL.

4.2.5 Graduated cylinder - 50 mL.

4.2.6 Pipet (Class A) - 5, 15, and 50 mL.

4.2.7 Vials - 10 mL.

4.3 Preparation

4.3.1 Prepare all materials to be used as described in Chapter 4 for volatile organics.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 General

5.2.1 Methanol, CH_3OH - Pesticide quality, or equivalent.

5.2.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.3 Methyl tert-butyl ether, $CH_3Ot\text{-}C_4H_9$ - Pesticide quality, or equivalent.

5.2.4 Acrylonitrile, $H_2C{:}CHCN$, 98%.

5.3 Stock standard solution

5.3.1 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Prepare stock standards in organic-free reagent water using assayed liquids.

5.3.2 The stock standard solution may be prepared by volume or by weight. Stock solutions must be replaced after one year, or sooner if comparison with the check standards indicates a problem.

<u>CAUTION</u>: Acrylonitrile is toxic. Standard preparation should be performed in a laboratory fume hood.

5.3.2.1 To prepare the stock standard solution by volume: inject 10 µL of acrylonitrile (98%) into a 100 mL volumetric flask with a syringe. Make up to volume with methanol.

5.3.2.2 To prepare the stock standard solution by weight: Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.0001 g. Add two drops of pure acrylonitrile, using a 50 µL syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask. Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight.

5.4 Working standard solutions

5.4.1 Prepare a minimum of 5 working standard solutions that cover the range of analyte concentrations expected in the samples. Working standards of 20, 40, 60, 80, and 100 µg/L may be prepared by injecting 10, 20, 30, 40, and 50 µL of the stock standard solution prepared in Sec. 5.3.2.1 into 5 separate 90 mL mixing bottles containing 40 mL of organic-free reagent water.

5.4.2 Inject 15 mL of methyl tert-butyl ether into each mixing bottle, shake vigorously, and let stand 5 minutes, or until layers have separated.

5.4.3 Remove 5 mL of top layer by pipet, and place in a 10 mL vial.

5.4.4 Keep all standard solutions below 4°C until used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample Extraction

7.1.1 Pour 40 mL of the sample into a 90 mL mixing bottle. Pipet 15 mL of Methyl tert-butyl ether into the mixing bottle. Shake vigorously for about 2 min. and let stand for about 5 min. Remove about 5 mL of the top layer and store in a 10 mL vial.

7.2 Chromatographic Conditions (Recommended)

Carrier Gas (He) flow rate:	35 mL/min.
Column Temperature:	180° C, Isothermal
Injection port temperature:	250° C
Detector temperature:	250° C
Detector Current (DC):	18 volts
Gases:	Hydrogen, 3 mL/min; Air, 290 mL/min.

7.3 Calibration of GC

7.3.1 On a daily basis, inject 3 µL of methyl tert-butyl ether directly into the GC to flush the system. Also purge the system with methyl tert-butyl ether injections between injections of standards and samples.

7.3.2 Inject 3 µL of a sample blank (organic-free reagent water carried through the sample storage procedures and extracted with methyl tert-butyl ether).

7.3.3 Inject 3 µL of at least five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte. The range of standard solution concentrations used should not exceed the working range of the GC system.

7.3.4 Prepare a calibration curve using the peak areas of the standards (retention time of acrylonitrile under the conditions of Sec. 7.2 is approximately 2.3 minutes). If the calibration curve deviates significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Sec. 7.4.2, for additional guidance on calibration by the external standard method.

7.4 Sample Analysis

7.4.1 Inject 3 μL of the sample extract, using the same chromatographic conditions used to prepare the standard curve. Calculate the concentration of acrylonitrile in the extract, using the area of the peak, against the calibration curve prepared in Sec. 7.3.4.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol and methyl tert-butyl ether reagents should be analyzed gas chromatographically under the conditions described in Sec. 7.2, to determine possible interferences with the acrylonitrile peak. If the solvent blanks show contamination, a different batch of solvents should be used.

9.0 METHOD PERFORMANCE

9.1 Method 8031 was tested in a single laboratory over a period of days. Duplicate samples and one spiked sample were run for each calculation. The GC was calibrated daily. Results are presented in Table 1.

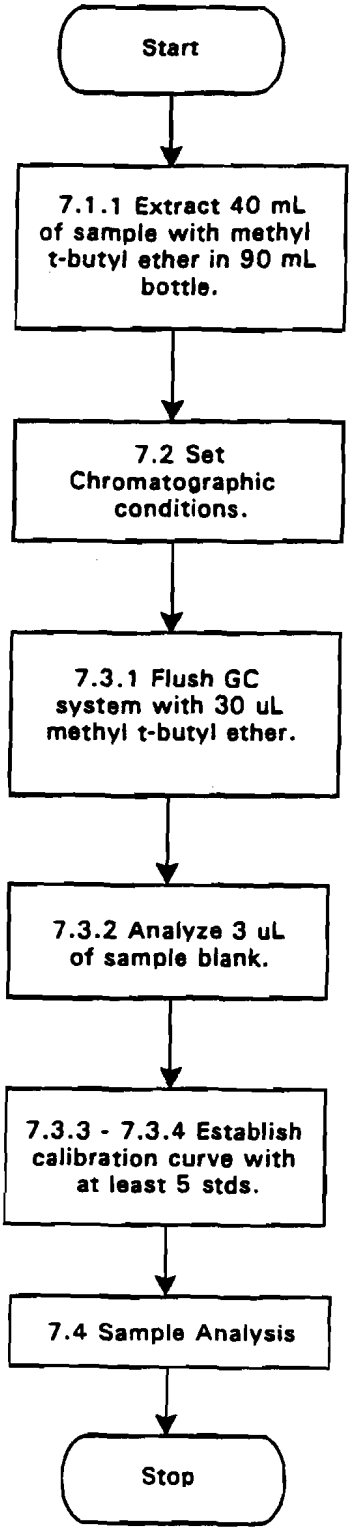
10.0 REFERENCES

1. K.L. Anderson, "The Determination of Trace Amounts of Acrylonitrile in Water by Specific Nitrogen Detector Gas Chromatograph", American Cynamid Report No. WI-88-13, 1988.

TABLE 1

SINGLE LABORATORY METHOD PERFORMANCE

SAMPLE	CONCENTRATION SPIKE (μg/L)	% RECOVERY
A	60	100
B	60	105
C	40	86
D	40	100
E	40	88
F	60	94
Average		96


Start
7.1.1 Extract 40 mL of sample with methyl t-butyl ether in 90 mL bottle.
7.2 Set Chromatographic conditions.
7.3.1 Flush GC system with 30 uL methyl t-butyl ether.
7.3.2 Analyze 3 uL of sample blank.
7.3.3 - 7.3.4 Establish calibration curve with at least 5 stds.
7.4 Sample Analysis
Stop

METHOD 8032

ACRYLAMIDE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8032 is used to determine trace amounts of acrylamide monomer in aqueous matrices. This method may be applicable to other matrices. The following compound can be determined by this method:

Compound Name	CAS No.[a]
Acrylamide	79-06-01

[a] Chemical Abstract Services Registry Number.

1.2 The method detection limit (MDL) in clean water is 0.032 µg/L.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Method 8032 is based on bromination of the acrylamide double bond. The reaction product (2,3-dibromopropionamide) is extracted from the reaction mixture with ethyl acetate, after salting out with sodium sulfate. The extract is cleaned up using a Florisil column, and analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 Compound identification should be supported by at least one additional qualitative technique. Analysis using a second gas chromatographic column or gas chromatography/mass spectrometry may be used for compound confirmation.

3.0 INTERFERENCES

3.1 No interference is observed from sea water or in the presence of 8.0% of ammonium ions derived from ammonium bromide. Impurities from potassium bromide are removed by the Florisil clean up procedure.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatographic System

4.1.1 Gas chromatograph suitable for on-column injections with all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Column: 2 m x 3 mm glass column, 5% FFAP (free fatty acid polyester) on 60-80 mesh acid washed Chromosorb W, or equivalent.

4.1.3 Detector: electron capture detector.

4.2 Kuderna-Danish (K-D) apparatus.

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Separatory funnel - 150 mL.

4.4 Volumetric flask (Class A) - 100 mL, with ground glass stopper; 25 mL, amber, with ground glass stopper.

4.5 Syringe - 5 mL.

4.6 Microsyringes - 5 μL, 100 μL.

4.7 Pipets (Class A).

4.8 Glass column (30 cm x 2 cm).

4.9 Mechanical shaker.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Ethyl acetate, $C_2H_5CO_2C_2H_5$. Pesticide quality, or equivalent.

5.3.2 Diethyl ether, $C_2H_5OC_2H_5$. Pesticide quality, or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.3.3 Methanol, CH_3OH. Pesticide quality, or equivalent.

5.3.4 Benzene, C_6H_6. Pesticide quality, or equivalent.

5.3.5 Acetone, CH_3COCH_3. Pesticide quality, or equivalent.

5.4 Saturated bromine water. Prepare by shaking organic-free reagent water with bromine and allowing to stand for 1 hour, in the dark, at 4°C. Use the aqueous phase.

5.5 Sodium sulfate (anhydrous, granular), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.6 Sodium thiosulfate, $Na_2S_2O_3$, 1 M aqueous solution.

5.7 Potassium bromide, KBr, prepared for infrared analysis.

5.8 Concentrated hydrobromic acid, HBr, specific gravity 1.48.

5.9 Acrylamide monomer, $H_2C{:}CHCONH_2$, electrophoresis reagent grade, minimum 95% purity.

5.10 Dimethyl phthalate, $C_6H_4(COOCH_3)_2$, 99.0% purity.

5.11 Florisil (60/100 mesh): Prepare Florisil by activating at 130°C for at least 16 hours. Alternatively, store Florisil in an oven at 130°C. Before use, cool the Florisil in a desiccator. Pack 5 g of the Florisil, suspended in benzene, in a glass column (Sec. 4.8).

5.12 Stock standard solutions

5.12.1 Prepare a stock standard solution of acrylamide monomer as specified in Sec. 5.12.1.1. When compound purity is assayed to be 96%

or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.12.1.1 Dissolve 105.3 mg of acrylamide monomer in organic-free reagent water in a 100 mL volumetric flask, and dilute to the mark with organic-free reagent water. Dilute the solution of acrylamide monomer so as to obtain standard solutions containing 0.1 - 10 mg/L of acrylamide monomer.

5.13 Calibration standards

5.13.1 Dilute the acrylamide stock solution with organic-free reagent water to produce standard solutions containing 0.1 - 5 mg/L of acrylamide. Prior to injection the calibration standards are reacted and extracted in the same manner as environmental samples (Sec. 7).

5.14 Internal standards

5.14.1 The suggested internal standard is dimethyl phthalate. Prepare a solution containing 100 mg/L of dimethyl phthalate in ethyl acetate. The concentration of dimethyl phthalate in the sample extracts and calibration standards should be 4 mg/L.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Bromination

7.1.1 Pipet 50 mL of sample into a 100 mL glass stoppered flask. Dissolve 7.5 g of potassium bromide into the sample, with stirring.

7.1.2 Adjust the pH of the solution with concentrated hydrobromic acid until the pH is between 1 and 3.

7.1.3 Wrap the flask with aluminum foil in order to exclude light. Add 2.5 mL of saturated bromine water, with stirring. Store the flask and contents in the dark, at 0°C, for at least 1 hour.

7.1.4 After reacting the solution for at least an hour, decompose the excess of bromine by adding 1 M sodium thiosulfate solution, dropwise, until the color of the solution is discharged.

7.1.5 Add 15 g of sodium sulfate, using a magnetic stirrer to effect vigorous stirring.

7.2 Extraction

7.2.1 Transfer the solution into a 150 mL separatory funnel. Rinse the reaction flask three times with 1 mL aliquots of organic-free reagent water. Transfer the rinsings into the separatory funnel.

7.2.2 Extract the aqueous solution with two 10 mL portions of ethyl acetate for 2 min each, using a mechanical shaker (240 strokes per min). Dry the organic phase with 1 g of sodium sulfate.

7.2.3 Transfer the organic phase into a 25 mL amber volumetric flask. Rinse the sodium sulfate with three 1.5 mL portions of ethyl acetate and combine the rinsings with the organic phase.

7.2.4 Add exactly 100 µg of dimethyl phthalate to the flask and make the solution up to the 25 mL mark with ethyl acetate. Inject 5 µL portions of this solution into the gas chromatograph.

7.3 Florisil cleanup: Whenever interferences are observed, the samples should be cleaned up as follows.

7.3.1 Transfer the dried extract into a Kuderna-Danish evaporator with 15 mL of benzene. Evaporate the solvent at 70°C under reduced pressure, and concentrate the solution to about 3 mL.

7.3.2 Add 50 mL of benzene and subject the solution to Florisil column chromatography at a flow rate of 3 mL/min. Elute the column first with 50 mL of diethyl ether/benzene (1:4) at a flow rate of 5 mL/min, and then with 25 mL of acetone/benzene (2:1) at a flow rate of 2 mL/min. Discard all of the first eluate and the initial 9 mL portion of the second eluate, and use the remainder for the determination, using dimethyl phthalate (4 mg/L) as an internal standard.

NOTE: Benzene is toxic, and should be only be used under a ventilated laboratory hood.

7.4 Gas chromatographic conditions:

Nitrogen carrier gas flow rate:	40 mL/min
Column temperature:	165°C.
Injector temperature:	180°C
Detector temperature:	185°C.
Injection volume:	5 µL

7.5 Calibration:

7.5.1 Inject 5 µL of a sample blank (organic-free reagent water carried through all sample storage, handling, bromination and extraction procedures).

7.5.2 Prepare standard solutions of acrylamide as described in Sec. 5.13.1. Brominate and extract each standard solution as described in Secs. 7.1 and 7.2.

7.5.2.1 Inject 5 μL of each of a minimum of five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte.

7.5.2.2 Prepare a calibration curve using the peak areas of the standards. If the calibration curve deviates significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Sec. 7.4.3, for additional guidance on calibration by the internal standard method.

7.5.2.3 Calculate the response factor for each standard according to Equation 1.

$$RF = \frac{(P_s)\ (M_{is})}{(P_{is})\ (M_A)} \qquad \text{Equation 1}$$

RF	=	Response factor
P_s	=	Peak height of acrylamide
M_{is}	=	Amount of internal standard injected (ng)
P_{is}	=	Peak height of internal standard
M_A	=	Amount of acrylamide injected (ng)

7.5.3 Calculate the mean response factor according to Equation 2.

$$\overline{RF} = \frac{\sum_{i=1}^{n} RF}{n} \qquad \text{Equation 2}$$

$\overline{RF}$	=	Mean response factor
RF	=	Response factors from standard analyses (calculated in Equation 1)
n	=	Number of analyses

7.6 Gas chromatographic analysis:

7.6.1 Inject 5 μL portions of each sample (containing 4 mg/L internal standard) into the gas chromatograph. An example GC/ECD chromatogram is shown in Figure 1.

7.6.2 The concentration of acrylamide monomer in the sample is given by Equation 3.

$$[A] = \frac{(P_A)\ (M_{is})}{(P_{is})\ (\overline{RF})\ (V_i)\ (V_s)} \qquad \text{Equation 3}$$

[A] = Concentration of acrylamide monomer in sample (mg/L)

P_A	=	Peak height of acrylamide monomer
M_{is}	=	Amount of internal standard injected (ng)
V_s	=	Total volume of sample (mL)
P_{is}	=	Peak height of internal standard
$\overline{RF}$	=	Mean response factor from Equation 2
V_i	=	Injection volume (μL)

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 The following performance data have been generated under the conditions described in this method:

9.1.1 The calibration curve for Method 8032 is linear over the range 0-5 μg/L of acrylamide monomer.

9.1.2 The limit of detection for an aqueous solution is 0.032 μg/L.

9.1.3 The yields of the brominated compound are 85.2 ± 3.3% and 83.3 ± 0.9%, at fortification concentrations of 1.0 and 5.0 μg/L, respectively.

9.2 Table 1 provides the recoveries of acrylamide monomer from river water, sewage effluent, and sea water.

9.3 The recovery of the bromination product as a function of the amount of potassium bromide and hydrobromic acid added to the sample is shown in Figure 2.

9.4 The effect of the reaction time on the recovery of the bromination product is shown in Figure 3. The yield was constant when the reaction time was more than 1 hour.

9.5 Figure 4 shows the recovery of the bromination product as a function of the initial pH from 1 to 7.35. The yield was constant within this pH range. The use of conventional buffer solutions, such as sodium acetate - acetic acid solution or phosphate solution, caused a significant decrease in yield.

10.0 REFERENCES

1. Hashimoto, A., "Improved Method for the Determination of Acrylamide Monomer in Water by Means of Gas-Liquid Chromatography with an Electron-capture Detector," Analyst, 101:932-938, 1976.

TABLE 1

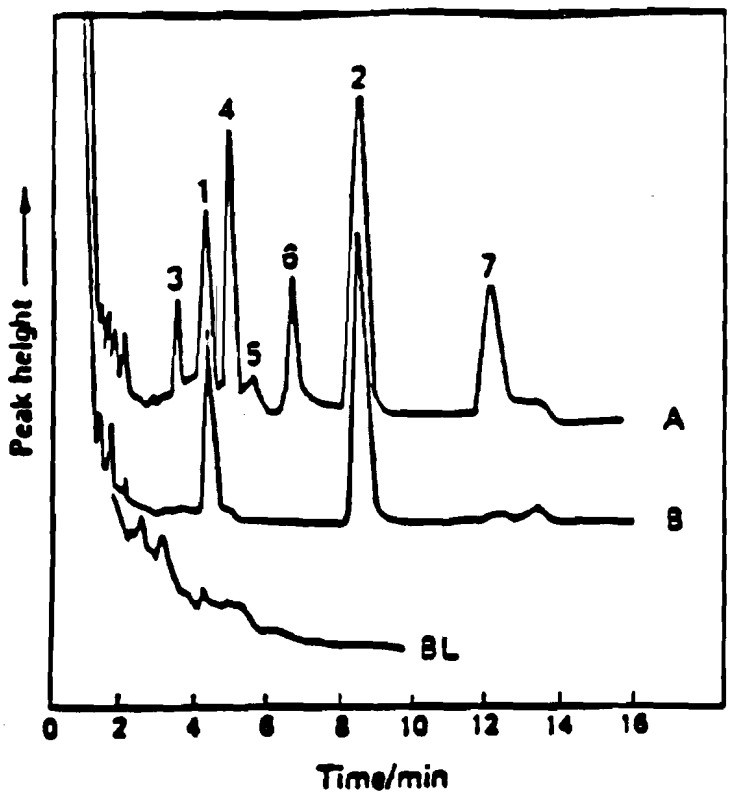
RECOVERY OF ACRYLAMIDE FROM WATER SAMPLES AS 2,3-DIBROMOPROPIONAMIDE

Sample Matrix	Acrylamide Monomer Spiked/μg	Amount of 2,3-DBPA[a]/μg		Overall Bromination Recovery %[b]	Recovery of Acrylamide Monomer, %[b]	Coefficient of Variation
		Calculated	Found[b]			
Standard	0.05	0.162	0.138	85.2	---	3.3
	0.20	0.649	0.535	82.4	---	1.0
	0.25	0.812	0.677	83.3	---	0.9
River Water	0.20	0.649	0.531	81.8	99.4	2.5
Sewage Effluent	0.20	0.649	0.542	83.5	101.3	3.0
Sea Water	0.20	0.649	0.524	80.7	98.8	3.5

[a] 2,3-Dibromopropionamide

[b] Mean of five replicate determinations

Figure 1



Typical gas chromatograms of the bromination product obtained from aqueous acrylamide monomer solution:

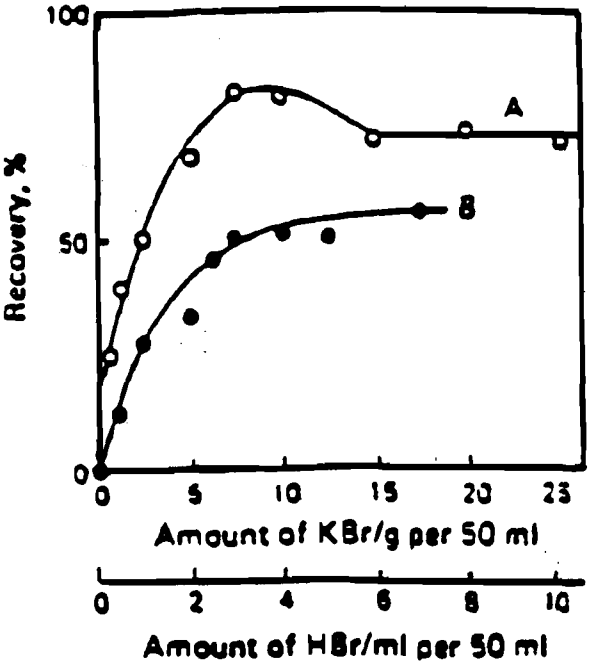
A. Untreated
B. With Florisil cleanup
BL. Chromatogram of blank, concentrated five-fold before gas chromatographic analysis.

Peaks:

1. 2,3-Dibromopropionamide
2. Dimethyl phthalate
4-7. Impurities from potassium bromide

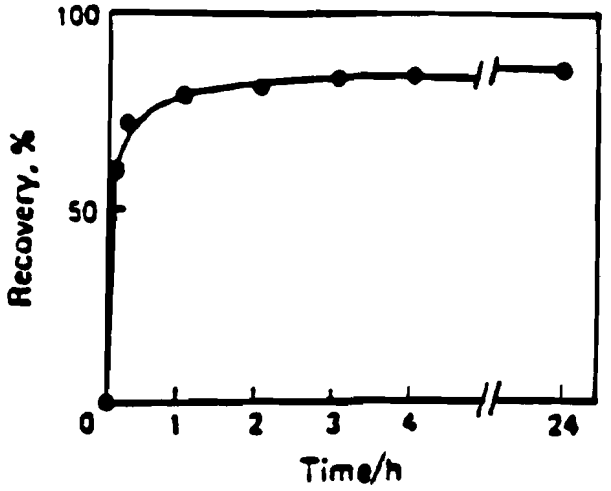
Sample size = 100 mL; acrylamide monomer = 0.1 μg

Figure 2



Effect of (A) potassium bromide and (B) hydrobromic acid on the yield of bromination. Sample size = 50 mL; acrylamide monomer = 0.25 μg

Figure 3



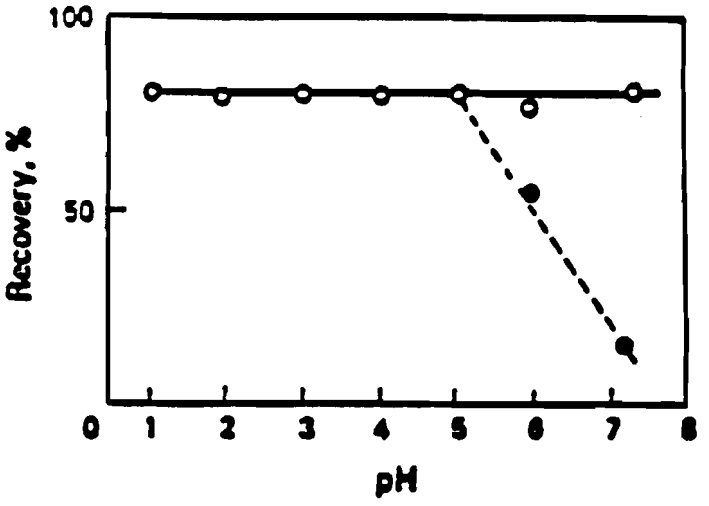
Effect of reaction time on the bromination. Reaction conditions:

50 mL of sample;
0.25 μg of acrylamide monomer;
7.5 g of potassium bromide;
2.5 mL of saturated bromine water

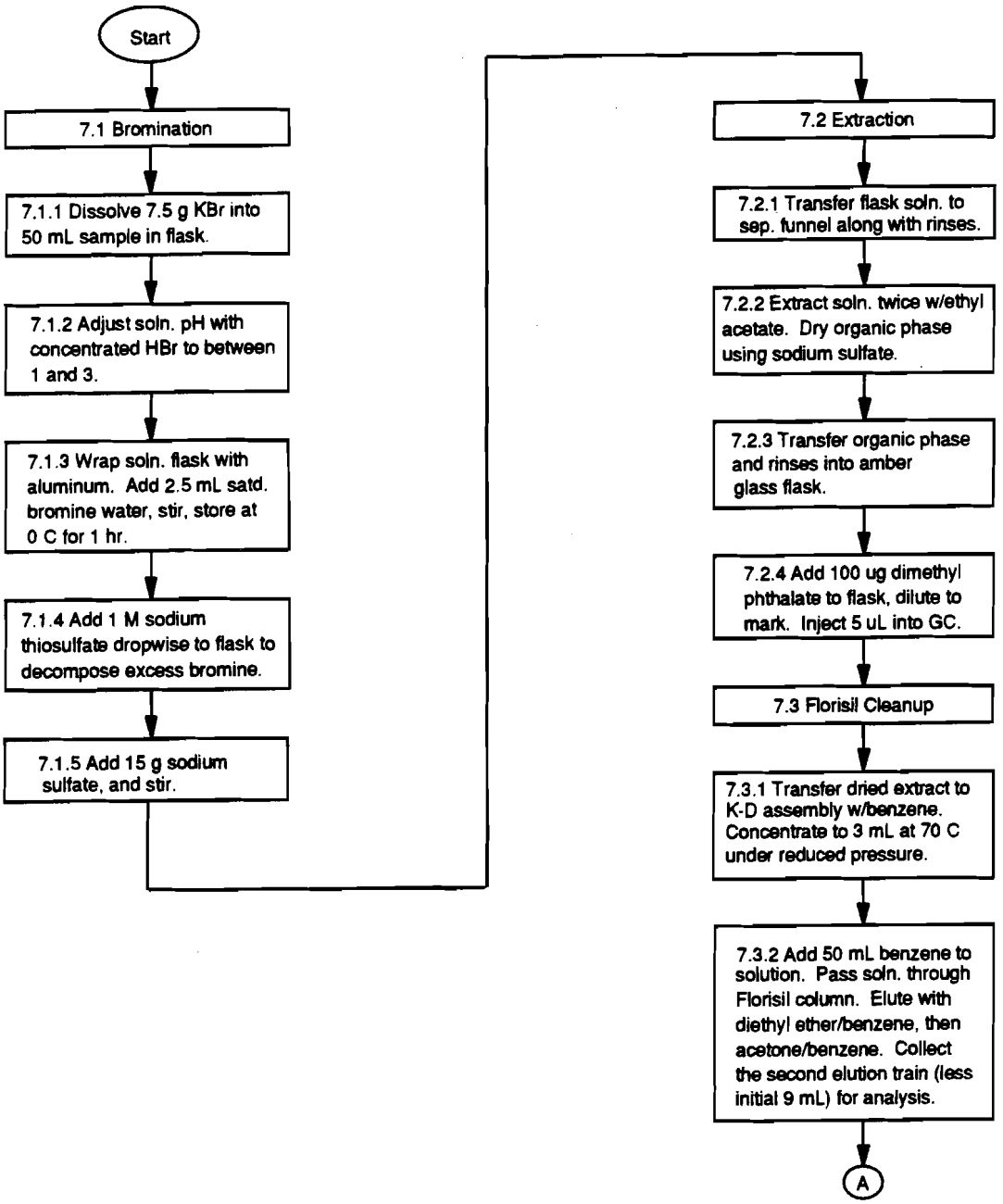
Extraction conditions:

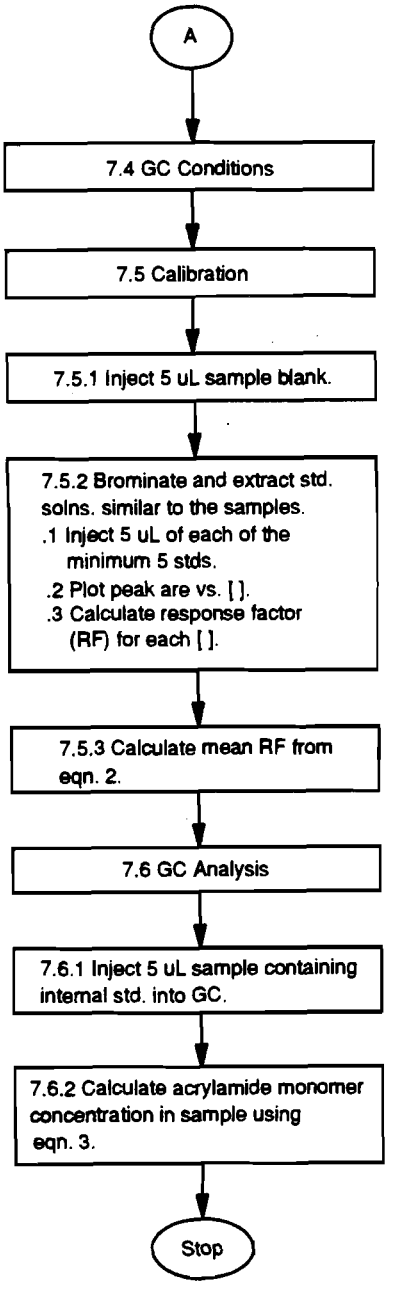
15 g of sodium sulfate;
extraction at pH 2;
solvent = 10 mL of ethyl acetate (X2)

Figure 4



Effect of initial pH on the bromination. Reaction and extraction conditions as in Figure 3. The pH was adjusted to below 3 with concentrated hydrobromic acid, and to 4-5 with dilute hydrobromic acid. Reaction at pH 6 was in distilled water. pH 7.35 was achieved by careful addition of dilute sodium hydroxide solution. The broken line shows the result obtained by the use of sodium acetate - acetic acid buffer solution.


Start
7.1 Bromination
7.1.1 Dissolve 7.5 g KBr into 50 mL sample in flask.
7.1.2 Adjust soln. pH with concentrated HBr to between 1 and 3.
7.1.3 Wrap soln. flask with aluminum. Add 2.5 mL satd. bromine water, stir, store at 0 C for 1 hr.
7.1.4 Add 1 M sodium thiosulfate dropwise to flask to decompose excess bromine.
7.1.5 Add 15 g sodium sulfate, and stir.
7.2 Extraction
7.2.1 Transfer flask soln. to sep. funnel along with rinses.
7.2.2 Extract soln. twice w/ethyl acetate. Dry organic phase using sodium sulfate.
7.2.3 Transfer organic phase and rinses into amber glass flask.
7.2.4 Add 100 ug dimethyl phthalate to flask, dilute to mark. Inject 5 uL into GC.
7.3 Florisil Cleanup
7.3.1 Transfer dried extract to K-D assembly w/benzene. Concentrate to 3 mL at 70 C under reduced pressure.
7.3.2 Add 50 mL benzene to solution. Pass soln. through Florisil column. Elute with diethyl ether/benzene, then acetone/benzene. Collect the second elution train (less initial 9 mL) for analysis.
A


A
7.4 GC Conditions
7.5 Calibration
7.5.1 Inject 5 uL sample blank.
7.5.2 Brominate and extract std. solns. similar to the samples.
.1 Inject 5 uL of each of the minimum 5 stds.
.2 Plot peak are vs. [ ].
.3 Calculate response factor (RF) for each [ ].
7.5.3 Calculate mean RF from eqn. 2.
7.6 GC Analysis
7.6.1 Inject 5 uL sample containing internal std. into GC.
7.6.2 Calculate acrylamide monomer concentration in sample using eqn. 3.
Stop

METHOD 8040A

PHENOLS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8040 is used to determine the concentration of various phenolic compounds. The following compounds can be determined by this method:

		Appropriate Technique				
Compound Name	CAS No.[a]	3510	3520	3540	3550	3580
2-sec-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	88-85-7	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
Cresols (methyl phenols)	1319-77-3	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitrophenol	131-89-5	X	ND	ND	ND	LR
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2-Methyl-4,6-dinitrophenol	534-52-1	X	X	X	X	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Phenol	108-95-2	DC(28)	X	X	X	X
Tetrachlorophenols	25167-83-3	X	ND	ND	ND	X
Trichlorophenols	25167-82-2	X	X	X	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

a Chemical Abstract Services Registry Number.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
LR = Low response.
ND = Not determined.
X = Greater than 70 percent recovery by this technique.

1.2 Table 1 lists the method detection limit for the target analytes in water. Table 2 lists the estimated quantitation limit (EQL) for all matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8040 provides gas chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques (see Chapter Two for guidance). Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct

injection. A 2 to 5 μL sample is injected into a gas chromatograph using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 Method 8040 also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives, with additional cleanup procedures for electron capture gas chromatography. This is to lower the detection limits of some phenols and to aid the analyst in the elimination of interferences.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

3.4 The decomposition of some analytes under basic extraction conditions has been demonstrated. Specifically, phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510.

3.5 The flame ionization detector (FID) is very susceptible to false positives caused by the presence of hydrocarbons commonly found in samples from waste sites. The problem may be minimized by applying acid-base cleanup (Method 3650) and/or alumina column chromatography (Method 3611) prior to GC/FID analysis or using the derivatization technique and analyzing by GC/electron capture detector. Initial site investigation should always be performed utilizing GC/MS analysis to characterize the site and determine the feasibility of utilizing Method 8040 with a GC/FID.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns

4.1.2.1 Column for underivatized phenols - 1.8 m x 2.0 mm

ID glass column packed with 1% SP-1240DA on Supelcoport 80/100 mesh, or equivalent.

4.1.2.2 Column for derivatized phenols - 1.8 m x 2 mm ID glass column packed with 5% OV-17 on Chromosorb W-AW-DMCS 80/100 mesh, or equivalent.

4.1.3 Detectors - Flame ionization (FID) and electron capture (ECD).

4.2 Reaction vial - 20 mL, with Teflon lined screw-cap or crimp top.

4.3 Volumetric flask, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Kuderna-Danish (K-D) apparatus

4.4.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.4.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.5 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Microsyringe - 10 µL.

4.8 Syringe - 5 mL.

4.9 Balance - analytical, 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Hexane, $CH_3(CH_2)_4CH_3$ - Pesticide quality or equivalent.

5.4 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.5 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.6 Derivatization reagent - Add 1 mL pentafluorobenzyl bromide and 1 g 18-crown-6-ether to a 50 mL volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly. This operation should be carried out in a hood. Store at 4°C and protect from light.

5.6.1 Pentafluorobenzyl bromide (alpha-Bromopentafluorotoluene), $C_6F_5CH_2Br$. 97% minimum purity.

NOTE: This chemical is a lachrymator.

5.6.2 18-crown-6-ether (1,4,7,10,13,16-Hexaoxacyclooctadecane) - 98% minimum purity.

NOTE: This chemical is highly toxic.

5.7 Potassium carbonate (Powdered), K_2CO_3.

5.8 Stock standard solutions

5.8.1 Prepare stock standard solution at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in 2-propanol and diluting to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.8.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.8.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.9 Calibration standards - Prepare calibration standards at a minimum of five concentrations through dilution of the stock standards with 2-propanol. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.10 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.10.1 Prepare calibration standards at a minimum of five concentrations for each analyte as described in Section 5.9.

5.10.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with 2-propanol.

5.10.3 Analyze each calibration standard according to Section 7.0.

5.11 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with phenolic surrogates (e.g. 2-fluorophenol and 2,4,6-tribromophenol) recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of acid surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of less than or equal to 2 with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550, and non-aqueous samples using Method 3580. Extracts obtained from application of either Method 3540 or 3550 should undergo Acid-Base Partition Cleanup, using Method 3650.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to 2-propanol. The exchange is performed as follows:

7.1.2.1 Following concentration of the extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw-cap or crimp top. If the extract requires no further derivatization or cleanup, proceed with gas chromatographic analysis.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column for underivatized phenols -

Carrier gas (N_2) flow rate:	30 mL/min
Initial temperature:	80°C
Temperature program:	80°C to 150°C at 8°C/min
Final Temperature:	150°C, hold until all compounds have eluted.

7.2.2 Column for derivatized phenols -

Carrier gas (5% methane/95% argon) flow rate:	30 mL/min
Initial temperature:	200°C
Temperature program:	isothermal, hold until all compounds have eluted.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used for the underivatized phenols. Refer to Method 8000 for a description of each of these procedures. If derivatization of the phenols is required, the method of external calibration should be used by injecting five or more concentrations of calibration standards that have also undergone derivatization and cleanup prior to instrument calibration.

7.4 Gas chromatographic analysis

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 μL of internal standard to the sample prior to injection.

7.4.2 Phenols are to be determined on a gas chromatograph equipped with a flame ionization detector according to the conditions listed for the 1% SP-1240DA column (Section 7.2.1). Table 1 summarizes estimated retention times and sensitivities that should be achieved by this method for clean water samples. Estimated quantitation limits for other matrices are list in Table 2.

7.4.3 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and

identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.4 An example of a GC/FID chromatogram for certain phenols is shown in Figure 1. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

7.4.5 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.6 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.4.7 If peak detection using the SP-1240DA column with the flame ionization detector is prevented by interferences, PFB derivatives of the phenols should be analyzed on a gas chromatograph equipped with an electron capture detector according to the conditions listed for the 5% OV-17 column (Section 7.2.2). The derivatization and cleanup procedure is outlined in Sections 7.5 through 7.6. Table 3 summarizes estimated retention times for derivatives of some phenols using the conditions of this method.

7.4.8 Figure 2 shows a GC/ECD chromatogram of PFB derivatives of certain phenols.

7.4.9 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.10 Determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. The method of external calibration should be used (see Method 8000 for guidance). The concentration of the individual compounds in the sample is calculated as follows:

$$\text{Concentration } (\mu g/L) = \frac{[(A)(V_t)(B)(D)]}{[(V_i)(X)(C)(E)]}$$

where:

A = Mass of underivatized phenol represented by area of peak in sample chromatogram, determined from calibration curve (see Method 8000), ng.

V_t = Total amount of column eluate or combined fractions from which V_i was taken, μL.

B = Total volume of hexane added in Section 7.5.5, mL.

D = Total volume of 2-propanol extract prior to derivatization, mL.

V_i = Volume injected, μL.

X = Volume of water extracted, mL, or weight of nonaqueous sample extracted, g, from Section 7.1. Either the dry or wet weight of the nonaqueous sample may be used, depending upon the specific application of the data.

C = Volume of hexane sample solution added to cleanup column (Method 3630), mL.

E = Volume of 2-propanol extract carried through derivatization in Section 7.5.1, mL.

7.5 Derivatization - If interferences prevent measurement of peak area during analysis of the extract by flame ionization gas chromatography, the phenols must be derivatized and analyzed by electron capture gas chromatography.

7.5.1 Pipet a 1.0 mL aliquot of the 2-propanol stock standard solution or of the sample extract into a glass reaction vial. Add 1.0 mL derivatization reagent (Section 5.3). This amount of reagent is sufficient to derivatize a solution whose total phenolic content does not exceed 300 mg/L.

7.5.2 Add approximately 0.003 g of potassium carbonate to the solution and shake gently.

7.5.3 Cap the mixture and heat it for 4 hours at 80°C in a hot water bath.

7.5.4 Remove the solution from the hot water bath and allow it to cool.

7.5.5 Add 10 mL hexane to the reaction vial and shake vigorously for 1 minute. Add 3.0 mL organic-free reagent water to the reaction vial and shake for 2 minutes.

7.5.6 Decant the organic layer into a concentrator tube and cap with a glass stopper. Proceed with cleanup procedure.

7.6 Cleanup

7.6.1 Cleanup of the derivatized extracts takes place using Method 3630 (Silica Gel Cleanup), in which specific instructions for cleanup of the derivatized phenols appear.

7.6.2 Following column cleanup, analyze the samples using GC/ECD, as described starting in Section 7.4.7.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in

the extraction method used. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at a concentration of 100 mg/L in 2-propanol.

8.2.2 Table 4 indicates the calibration and QC acceptance criteria for this method. Table 5 gives method accuracy and precision as functions of concentration for the analytes. The contents of both tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 12 to 450 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 5.

9.2 The accuracy and precision obtained will be affected by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons and Category 8 - Phenols. Report for EPA Contract 68-03-2625 (in preparation).

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. "Determination of Phenols in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

4. "EPA Method Validation Study Test Method 604 (Phenols)," Report for EPA Contract 68-03-2625 (in preparation).

5. Kawahara, F.K. "Microdetermination of Derivatives of Phenols and Mercaptans by Means of Electron Capture Gas Chromatography," Analytical Chemistry, 40, 1009, 1968.

6. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

TABLE 1.
FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS[a]

Analyte	Retention time (minutes)	Method Detection limit (μg/L)
2-sec-Butyl-4,6-dinitrophenol (DNBP)		
4-Chloro-3-methylphenol	7.50	0.36
2-Chlorophenol	1.70	0.31
Cresols (methyl phenols)		
2-Cyclohexyl-4,6-dinitrophenol		
2,4-Dichlorophenol	4.30	0.39
2,6-Dichlorophenol		
2,4-Dimethylphenol	4.03	0.32
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
2-Nitrophenol	2.00	0.45
4-Nitrophenol	24.25	2.8
Pentachlorophenol	12.42	7.4
Phenol	3.01	0.14
Tetrachlorophenols		
Trichlorophenols		
2,4,6-Trichlorophenol	6.05	0.64

[a] - 1% SP-1240DA on Supelcoport 80/100 mesh column.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES[a]

Parent compound	Retention time (min)	Method detection limit (μg/L)
4-Chloro-2-methylphenol	4.8	1.8
2-Chlorophenol	3.3	0.58
2,4-Dichlorophenol	5.8	0.68
2,4-Dimethylphenol	2.9	0.63
2,4-Dinitrophenol	46.9	
2-Methyl-4,6-dinitrophenol	36.6	
2-Nitrophenol	9.1	0.77
4-Nitrophenol	14.0	0.70
Pentachlorophenol	28.8	0.59
Phenol	1.8	2.2
2,4,6-Trichlorophenol	7.0	0.58

[a] - 5% OV-17 on Chromosorb W-AW-DMCS 80/100 mesh column.

TABLE 4.
QC ACCEPTANCE CRITERIA[a]

Analyte	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Recovery Range (%)
4-Chloro-3-methylphenol	100	16.6	56.7-113.4	99-122
2-Chlorophenol	100	27.0	54.1-110.2	38-126
2,4-Dichlorophenol	100	25.1	59.7-103.3	44-119
2,4-Dimethylphenol	100	33.3	50.4-100.0	24-118
4,6-Dinitro-2-methylphenol	100	25.0	42.4-123.6	30-136
2,4-Dinitrophenol	100	36.0	31.7-125.1	12-145
2-Nitrophenol	100	22.5	56.6-103.8	43-117
4-Nitrophenol	100	19.0	22.7-100.0	13-110
Pentachlorophenol	100	32.4	56.7-113.5	36-134
Phenol	100	14.1	32.4-100.0	23-108
2,4,6-Trichlorophenol	100	16.6	60.8-110.4	53-119

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

a Criteria from 40 CFR Part 136 for Method 604. These criteria are based directly upon the method performance data in Table 5. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 5.

TABLE 5.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Analyte	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
4-Chloro-3-methylphenol	0.87C-1.97	$0.11\bar{x}-0.21$	$0.16\bar{x}+1.41$
2-Chlorophenol	0.83C-0.84	$0.18\bar{x}+0.20$	$0.21\bar{x}+0.75$
2,4-Dichlorophenol	0.81C+0.48	$0.17\bar{x}-0.02$	$0.18\bar{x}+0.62$
2,4-Dimethylphenol	0.62C-1.64	$0.30\bar{x}-0.89$	$0.25\bar{x}+0.48$
4,6-Dinitro-2-methylphenol	0.84C-1.01	$0.15\bar{x}+1.25$	$0.19\bar{x}+5.85$
2,4-Dinitrophenol	0.80C-1.58	$0.27\bar{x}-1.15$	$0.29\bar{x}+4.51$
2-Nitrophenol	0.81C-0.76	$0.15\bar{x}+0.44$	$0.14\bar{x}+3.84$
4-Nitrophenol	0.46C+0.18	$0.17\bar{x}+2.43$	$0.19\bar{x}+4.79$
Pentachlorophenol	0.83C+2.07	$0.22\bar{x}-0.58$	$0.23\bar{x}+0.57$
Phenol	0.43C+0.11	$0.20\bar{x}-0.88$	$0.17\bar{x}+0.77$
2,4,6-Trichlorophenol	0.86C-0.40	$0.10\bar{x}+0.53$	$0.13\bar{x}+2.40$

x′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

[a]From 40 CFR Part 136 for Method 604.

Figure 1
Gas Chromatogram of Phenols

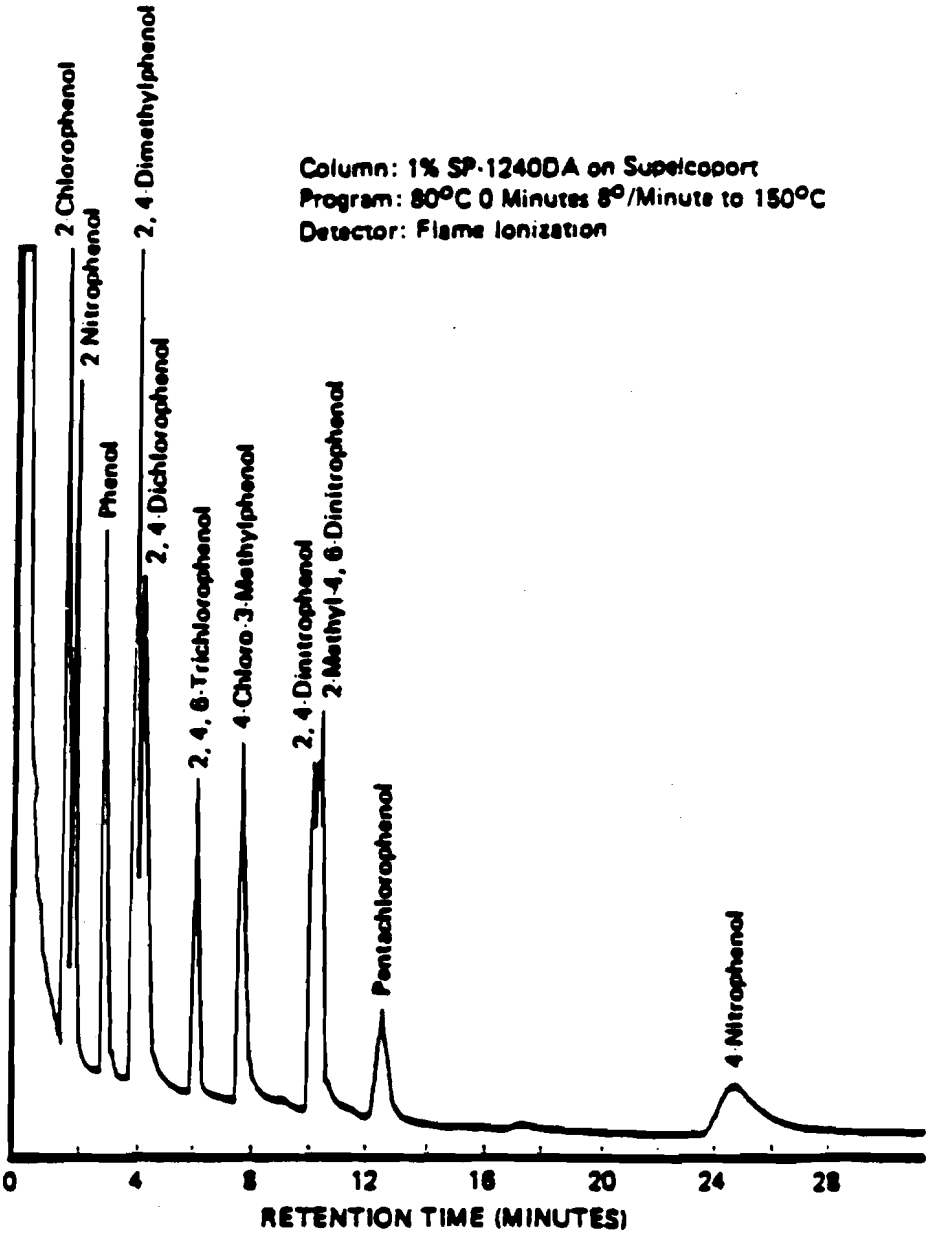
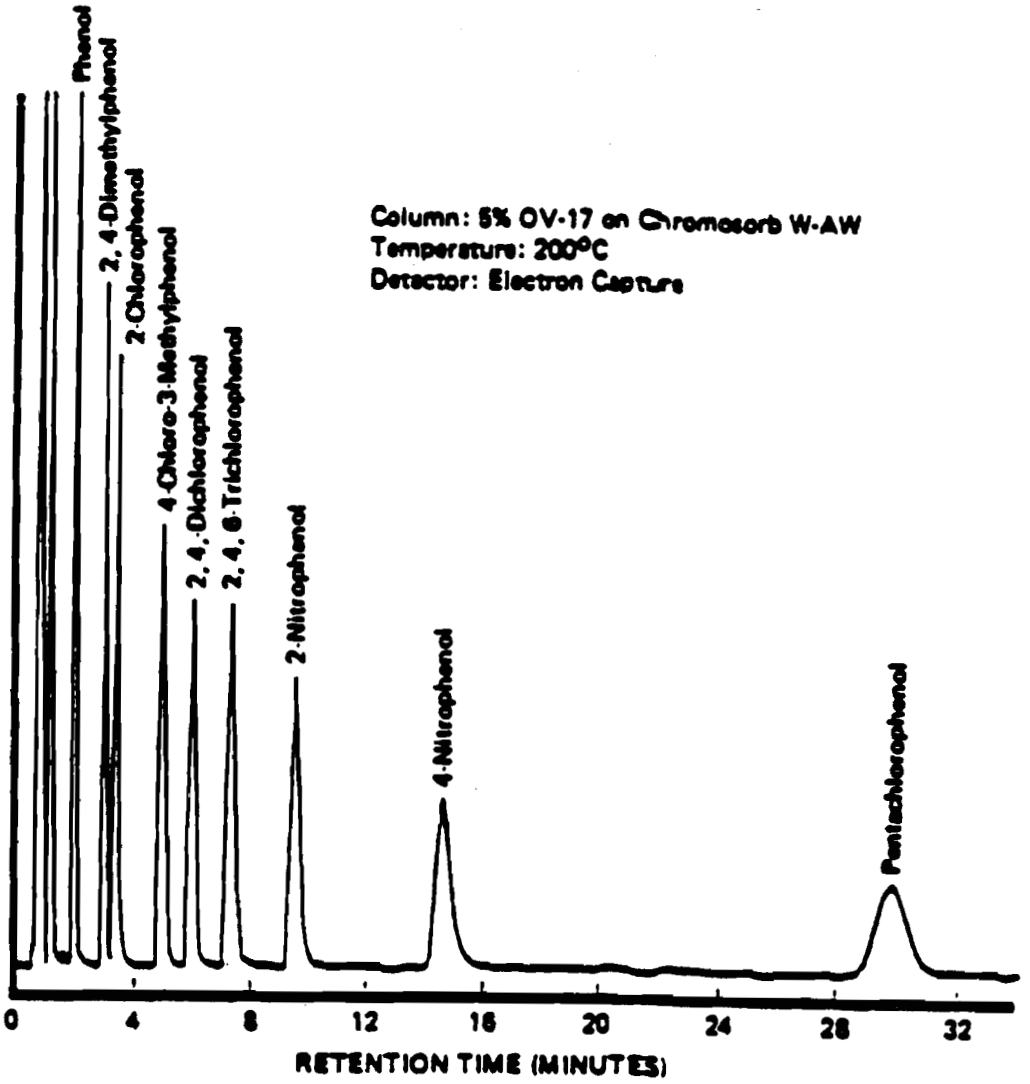
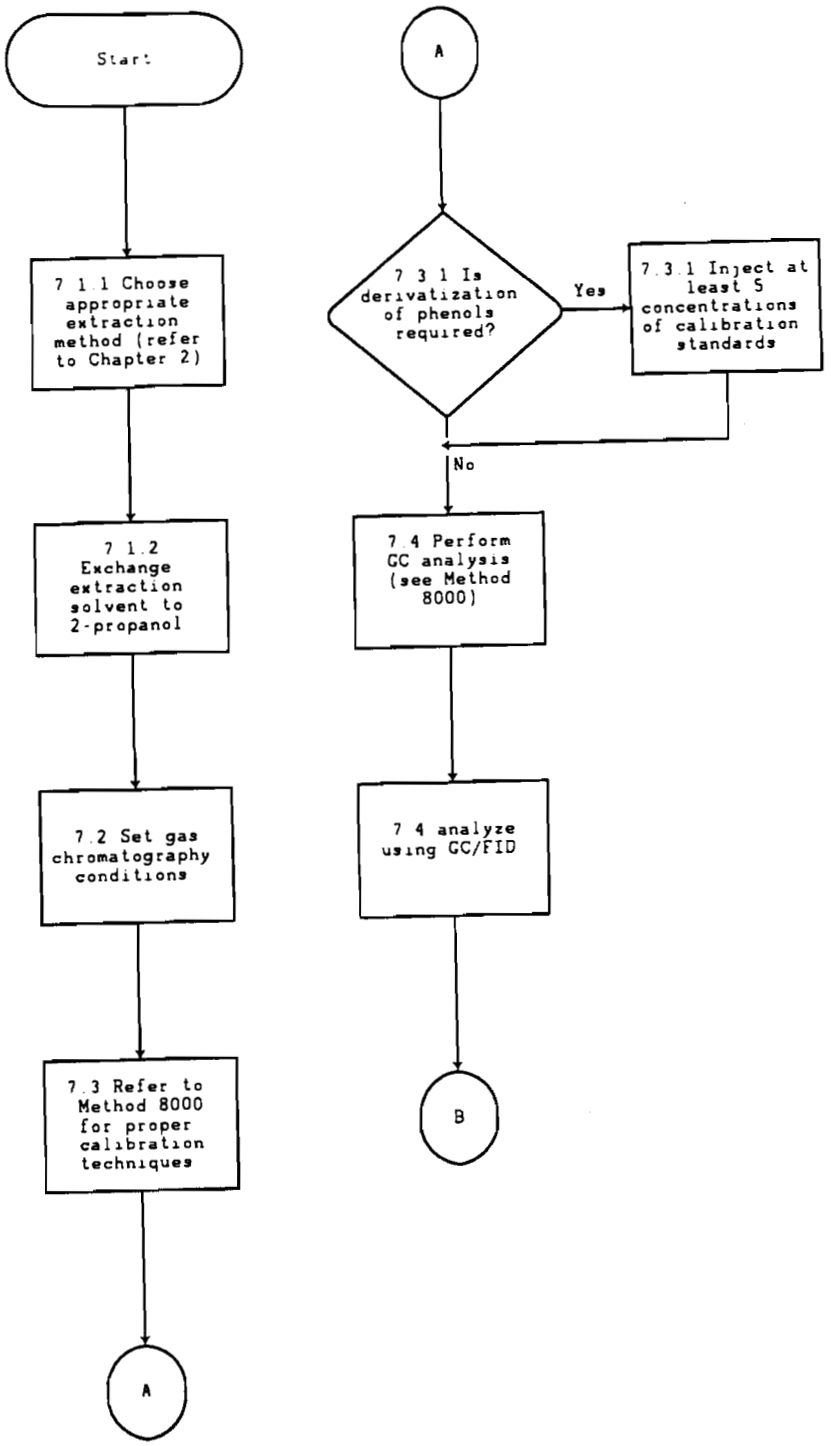
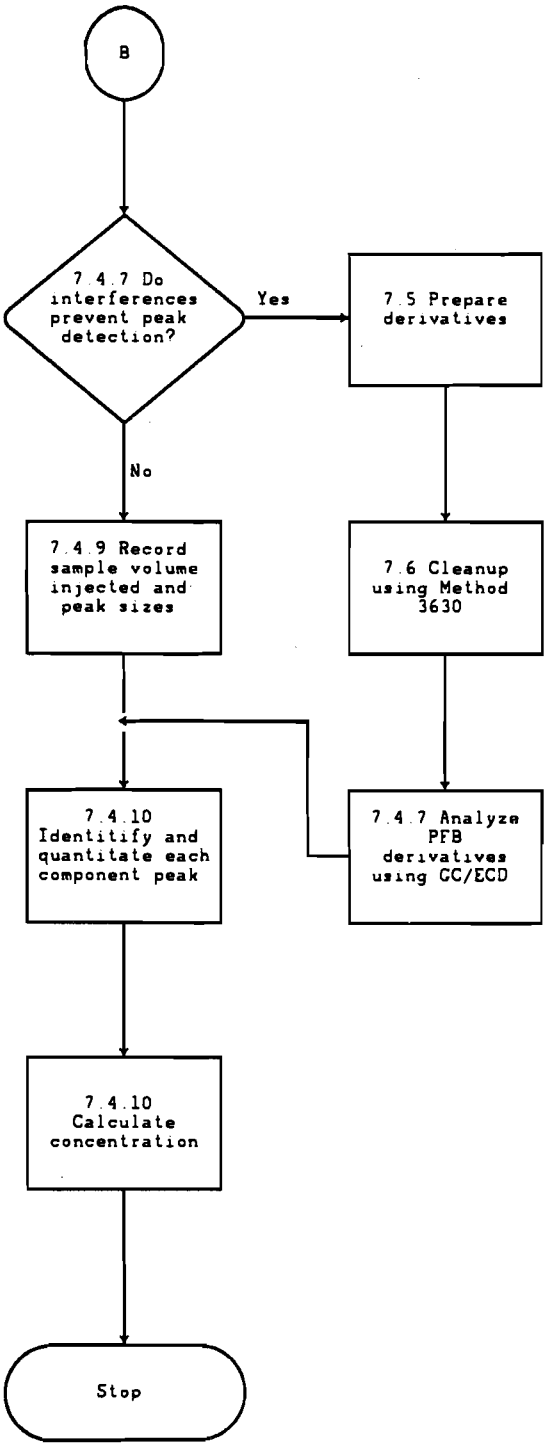


Figure 2
Gas Chromatogram of PFB Derivatives of Phenols




Start
7 1 1 Choose appropriate extraction method (refer to Chapter 2)
7 1.2 Exchange extraction solvent to 2-propanol
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
A
A
7 3 1 Is derivatization of phenols required?
Yes
7.3.1 Inject at least 5 concentrations of calibration standards
No
7 4 Perform GC analysis (see Method 8000)
7 4 analyze using GC/FID
B


B
7.4.7 Do interferences prevent peak detection?
Yes
7.5 Prepare derivatives
No
7.4.9 Record sample volume injected and peak sizes
7.6 Cleanup using Method 3630
7.4.10 Identitify and quantitate each component peak
7.4.7 Analyze PFB derivatives using GC/ECD
7.4.10 Calculate concentration
Stop

METHOD 8060

PHTHALATE ESTERS

1.0 SCOPE AND APPLICATION

1.1 Method 8060 is used to determine the concentration of various phthalate esters. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8060 provides gas chromatographic conditions for the detection of ppb levels of phthalate esters. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a flame ionization detector (FID). Ground water samples should be determined by ECD.

2.2 The method provides a second gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of analysis. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.3 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.4 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. RETENTION TIME AND DETECTION LIMIT INFORMATION FOR PHTHALATE ESTERS

Compound	Retention time (min)		Method detection limit (ug/L)	
	Col. 1[a]	Col. 2[b]	ECD	FID
Benzyl butyl phthalate	*6.94	**5.11	0.34	15
Bis(2-ethylhexyl)phthalate	*8.92	**10.5	2.0	20
Di-n-butyl phthalate	8.65	3.50	0.36	14
Diethyl phthalate	2.82	1.27	0.49	31
Dimethyl phthalate	2.03	0.95	0.29	19
Di-n-octyl phthalate	*16.2	**8.0	3.0	31

[a]Column 1: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 180°C, except where * indicates 220°C. Under these conditions the retention time of Aldrin is 5.49 min at 180°C and 1.84 min at 220°C.

[b]Column 2: Supelcoport 100/120 mesh with 3% OV-1 in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 200°C, except where ** indicates 220°C. Under these conditions the retention time of Aldrin is 3.18 min at 200°C and 1.46 min at 220°C.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 1.8-m x 4-mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport 100/120 mesh or equivalent.

4.1.2.2 Column 2: 1.8-m x 4-mm I.D. glass column packed with 3% OV-1 on Supelcoport 100/120 mesh or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) or electron capture (ECD).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2- and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each

sample, standard, and reagent water blank with one or two surrogates (e.g., phthalates that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.2.3. If cleanup is needed, proceed to Paragraph 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to

10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.2 Gas chromatography conditions (Recommended): The analysis for phthalate esters may be conducted using either a flame ionization or an electron capture detector. The ECD may, however, provide substantially better sensitivity.

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 180°C isothermal.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 200°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for phthalate esters are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

7.5 Cleanup:

7.5.1 Proceed with either Method 3610 or 3620, using the 2-mL hexane extracts obtained from Paragraph 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl) phthalate, 50 ug/mL; di-n-octyl phthalate, 50 ug/mL; and any other phthalate, 25 ug/mL.

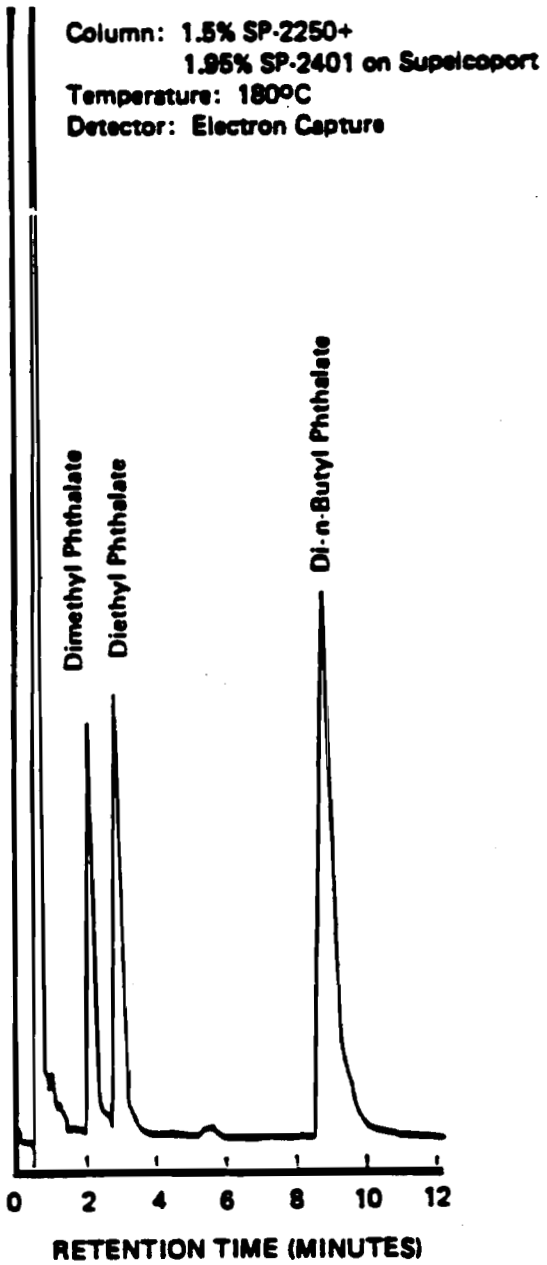


Figure 1. Gas chromatogram of phthalates (example 1).

Column: 1.5% SP-2250+
1.95% SP-2401 on Supelcoport
Temperature: 180°C
Detector: Electron Capture

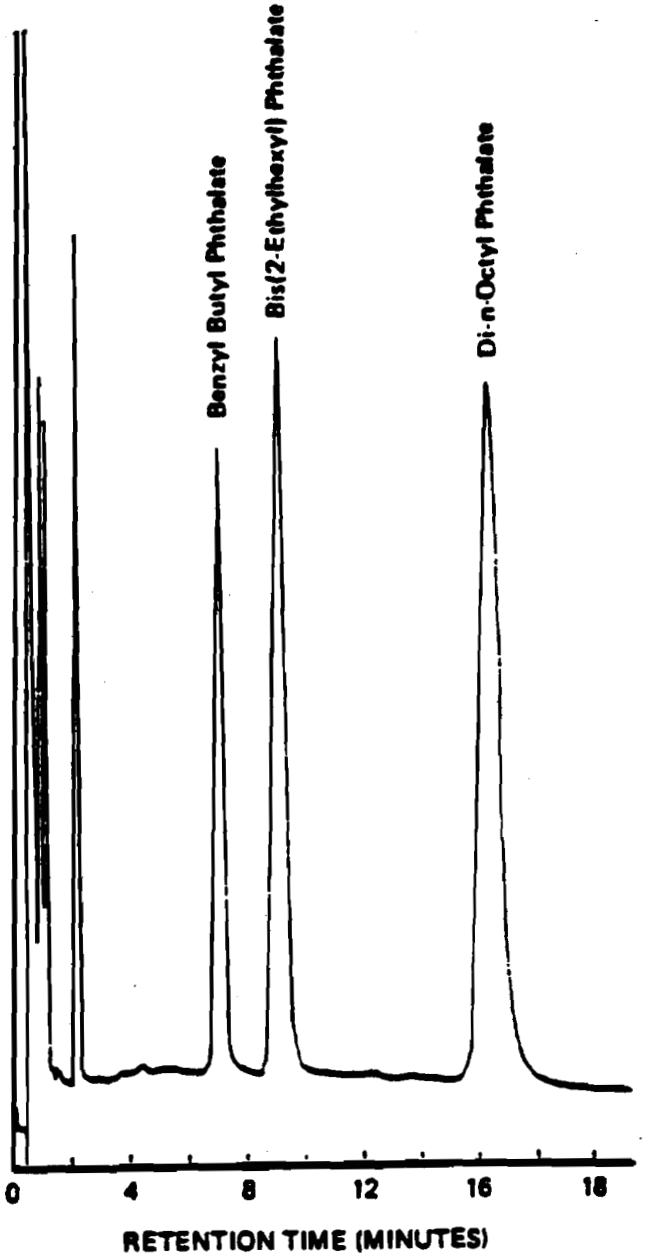


Figure 2. Gas chromatogram of phthalates (example 2).

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.7 to 106 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 1 - Phthalates. Report for EPA Contract 68-03-2606 (in preparation).

2. "Determination of Phthalates in Industrial and Municipal Wastewaters," EPA-600/4-81-063, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, October 1981.

3. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. "EPA Method Validation Study 16, Method 606 (Phthalate Esters)," Report for EPA Contract 68-03-2606 (in preparation).

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Bis(2-ethylhexyl)phthalate	50	38.4	1.2-55.9	D-158
Butyl benzyl phthalate	10	4.2	5.7-11.0	30-136
Di-n-butyl phthalate	25	8.9	10.3-29.6	23-136
Diethyl phthalate	25	9.0	1.9-33.4	D-149
Dimethyl phthalate	25	9.5	1.3-35.5	D-156
Di-n-octyl phthalate	50	13.4	D-50.0	D-114

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 606. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Bis(2-ethylhexyl) phthalate	0.53C+2.02	0.80$\bar{X}$-2.56	0.73$\bar{X}$-0.17
Butyl benzyl phthalate	0.82C+0.13	0.26$\bar{X}$+0.04	0.25$\bar{X}$+0.07
Di-n-butyl phthalate	0.79C+0.17	0.23$\bar{X}$+0.20	0.29$\bar{X}$+0.06
Diethyl phthalate	0.70C+0.13	0.27$\bar{X}$+0.05	0.45$\bar{X}$+0.11
Dimethyl phthalate	0.73C+0.17	0.26$\bar{X}$+0.14	0.44$\bar{X}$+0.31
Di-n-octyl phthalate	0.35C-0.71	0.38$\bar{X}$+0.71	0.62$\bar{X}$+0.34

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

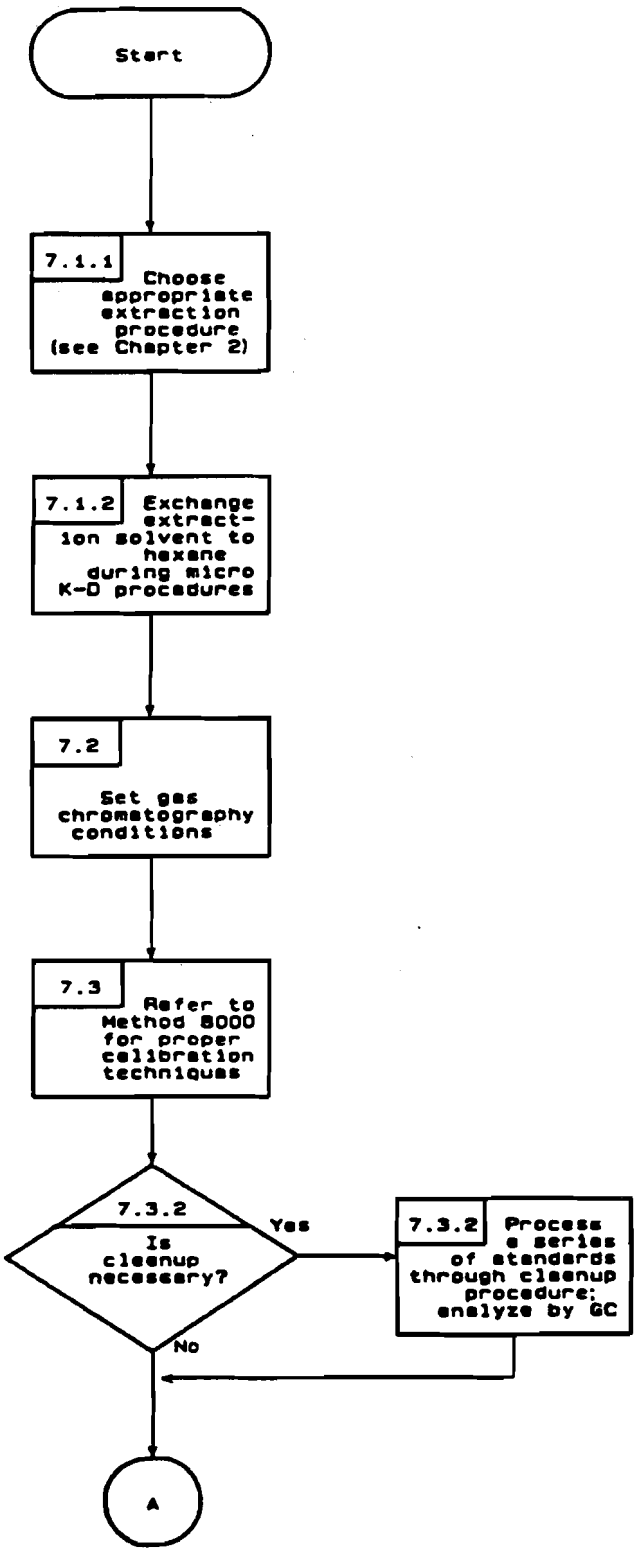
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

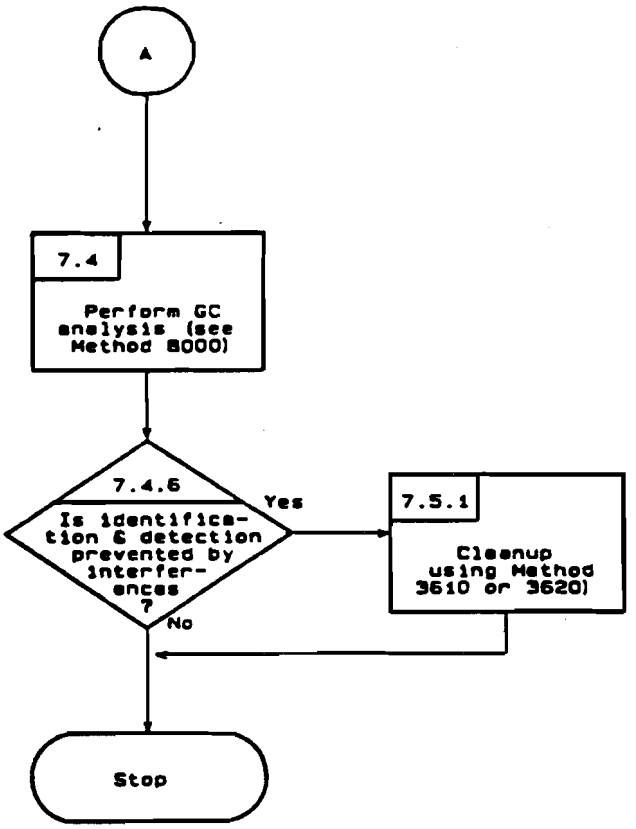
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]Criteria from 40 CFR Part 136 for Method 606.


Start
7.1.1
Choose appropriate extraction procedure (see Chapter 2)
7.1.2
Exchange extraction solvent to hexane during micro K-D procedures
7.2
Set gas chromatography conditions
7.3
Refer to Method 8000 for proper calibration techniques
7.3.2
Is cleanup necessary?
Yes
No
7.3.2
Process a series of standards through cleanup procedure; analyze by GC
A


A
7.4
Perform GC analysis (see Method 8000)
7.4.6
Is identification & detection prevented by interferences ?
Yes
No
7.5.1
Cleanup using Method 3610 or 3620)
Stop

METHOD 8061

PHTHALATE ESTERS BY CAPILLARY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION (GC/ECD)

1.0 SCOPE AND APPLICATION

1.1 Method 8061 is used to determine the identities and concentrations of various phthalate esters in liquid, solid and sludge matrices. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Benzyl benzoate (I.S.)	120-51-4
Bis(2-ethylhexyl) phthalate	117-81-7
Butyl benzyl phthalate	85-68-7
Di-n-butyl phthalate	84-74-2
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
Di-n-octyl phthalate	117-84-0

[a] Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limits (MDL) for the target analytes in a water matrix. The MDLs for the components of a specific sample may differ from those listed in Table 1 because MDLs depend on the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.3 When this method is used to analyze for any or all of the target analytes, compound identification should be supported by at least one additional qualitative technique. This method describes conditions for parallel column, dual electron capture detector analysis which fulfills the above requirement. Retention time information obtained on two megabore fused-silica open tubular columns is given in Table 1. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation.

1.4 The following compounds, bis(2-n-butoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, bis(2-methoxyethyl) phthalate, bis(4-methyl-2-pentyl) phthalate, diamyl phthalate, dicyclohexyl phthalate, dihexyl phthalate, diisobutyl phthalate, dinonyl phthalate, and hexyl 2-ethylhexyl phthalate can also be analyzed by this method and may be used as surrogates.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 liter for liquids, 10 to 30 grams for solids and sludges) is extracted by using the appropriate sample extraction technique specified in Methods 3510, 3540, 3541 and 3550. Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Aqueous samples are extracted at a pH of 5 to 7, with methylene chloride, in a separatory funnel (Method 3510). Alternatively, particulate-free aqueous samples could be filtered through membrane disks that contain C_{18}-bonded silica. The phthalate esters are retained by the silica and, later eluted with acetonitrile. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Methods 3540/3541) or with an ultrasonic extractor (Method 3550). After cleanup, the extract is analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 The sensitivity of Method 8061 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, cleanup of the sample extracts is necessary. Either Method 3610 or 3620 alone or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, Gel Permeation Cleanup, is applicable for samples that contain high amounts of lipids and waxes.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities for the target analytes.

3.3 Glassware must be scrupulously clean. All glassware require treatment in a muffle furnace at 400 °C for 2 to 4 hrs, or thorough rinsing with pesticide-grade solvent, prior to use. Refer to Chapter 4, Sec. 4.1.4, for further details regarding the cleaning of glassware. Volumetric glassware should not be heated in a muffle furnace.

If Soxhlet extractors are baked in the muffle furnace, care must be taken to ensure that they are dry (breakage may result if any water is left in the side-arm). Thorough rinsing with hot tap water, followed by deionized water and acetone is not an adequate decontamination procedure. Even after a Soxhlet extractor was refluxed with acetone for three days, with daily solvent changes, the concentrations of bis(2-ethylhexyl) phthalate were as high as 500 ng per washing. Storage of glassware in the laboratory introduces contamination, even if the glassware is wrapped in aluminum foil. Therefore, any glassware used in Method 8061 should be cleaned immediately prior to use.

3.4 Florisil and alumina may be contaminated with phthalate esters and, therefore, use of these materials in sample cleanup should be employed

cautiously. If these materials are used, they must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters). Washing of these materials prior to use with the solvent(s) used for elution during extract cleanup was found helpful, however, heating at 320 °C for Florisil and 210 °C for alumina is recommended. Phthalate esters were detected in Florisil cartridge method blanks at concentrations ranging from 10 to 460 ng, with 5 phthalate esters in the 105 to 460 ng range. Complete removal of the phthalate esters from Florisil cartridges does not seem possible, and it is therefore desirable to keep the steps involved in sample preparation to a minimum.

3.5 Paper thimbles and filter paper must be exhaustively washed with the solvent that will be used in the sample extraction. Soxhlet extraction of paper thimbles and filter paper for 12 hrs with fresh solvent should be repeated for a minimum of three times. Method blanks should be obtained before any of the precleaned thimbles or filter papers are used. Storage of precleaned thimbles and filter paper in precleaned glass jars covered with aluminum foil is recommended.

3.6 Glass wool used in any step of sample preparation should be a specially treated pyrex wool, pesticide grade, and must be baked at 400°C for 4 hrs. immediately prior to use.

3.7 Sodium sulfate must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters), and must be purified by heating at 400 °C for 4 hrs. in a shallow tray, or by precleaning with methylene chloride (Sec. 5.3). To avoid recontamination, the precleaned material must be stored in glass-stoppered glass bottles, or glass bottles covered with precleaned aluminum foil. The storage period should not exceed two weeks. To minimize contamination, extracts should be dried directly in the glassware in which they are collected by adding small amounts of precleaned sodium sulfate until an excess of free flowing material is noted.

3.8 The presence of elemental sulfur will result in large peaks which often mask the region of the compounds eluting before dicyclohexyl phthalate (Compound No. 14) in the gas chromatograms shown in Figure 1. Method 3660 is suggested for removal of sulfur.

3.9 Waxes and lipids can be removed by Gel Permeation Chromatography (Method 3640). Extracts containing high concentrations of lipids are viscous, and may even solidify at room temperature.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatography

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column and split/splitless injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.1.1 Eight inch injection tee (Supelco, Inc., Catalog No. 2-3665, or equivalent) or glass Y splitter for megabore columns (J&W Scientific, "press-fit", Catalog No. 705-0733, or equivalent).

4.1.2 Columns

4.1.2.1 Column 1, 30 m x 0.53 mm ID, 5% phenyl/95% methyl silicone fused-silica open tubular column (DB-5, J&W Scientific, or equivalent), 1.5 μm film thickness.

4.1.2.2 Column 2, 30 m x 0.53 mm ID, 14% cyanopropyl phenyl silicone fused-silica open tubular column (DB-1701, J&W Scientific, or equivalent), 1.0 μm film thickness.

4.1.3 Detector - Dual electron capture detector (ECD)

4.2 Glassware, see Methods 3510, 3540, 3541, 3550, 3610, 3620, 3640, and 3660 for specifications.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips, approximately 10/40 mesh. Heat to 400 °C for 30 min, or Soxhlet-extract with methylene chloride prior to use.

4.5 Water bath, heated, with concentric ring cover, capable of temperature control (± 2°C).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400 °C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Solvents:

5.4.1 Hexane, C_6H_{14} - Pesticide quality, or equivalent.

5.4.2 Methylene chloride, CH_2Cl_2 - Pesticide quality, or equivalent.

5.4.3 Acetone, CH_3COCH_3 - Pesticide quality, or equivalent.

5.4.4 Acetonitrile, CH_3CN - HPLC grade.

5.4.5 Methanol, CH_3OH - HPLC grade.

5.4.6 Diethyl Ether, $C_2H_5OC_2H_5$ - Pesticide quality, or equivalent. Must be free of peroxides, as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.5 Stock standard solutions:

5.5.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in hexane, and diluting to volume in a 10 mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at 4 °C and protect from light. Stock standard solutions should be checked periodically by gas chromatography for signs of degradation or evaporation, especially just prior to preparation of calibration standards.

5.5.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards: Calibration standards are prepared at a minimum of five concentrations for each parameter of interest through dilution of the stock standard solutions with hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC. Calibration

solutions must be replaced after 1 to 2 months, or sooner if comparison with calibration verification standards indicates a problem.

5.7 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Benzyl benzoate has been tested and found appropriate for Method 8061.

5.7.1 Prepare a spiking solution of benzyl benzoate in hexane at 5000 mg/L. Addition of 10 µL of this solution to 1 mL of sample extract is recommended. The spiking concentration of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solution at 4 °C in glass vials with Teflon lined screw-caps or crimp tops. Standard solutions should be replaced when ongoing QC (Sec. 8) indicates a problem.

5.8 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with surrogate compounds. Three surrogates may be used for Method 8061 in addition to those listed in Sec. 1.4: diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate. However, the compounds listed in Sec. 1.4 are recommended.

5.8.1 Prepare a surrogate standard spiking solution, in acetone, which contains 50 ng/µL of each compound. Addition of 500 µL of this solution to 1 L of water or 30 g solid sample is equivalent to 25 µg/L of water or 830 µg/kg of solid sample. The spiking concentration of the surrogate standards may be adjusted accordingly, if the final volume of extract is reduced below 2 mL for water samples or 10 mL for solid samples. Store the surrogate spiking solution at 4 °C in glass vials with Teflon lined screw-caps or crimp tops. The solution must be replaced after 6 months, or sooner if ongoing QC (Sec. 8) indicates problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of 5 to 7 with methylene chloride in a separatory funnel (Method 3510). Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to

the glassware and consequently, their extraction recoveries are <40 percent. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Methods 3540/3541) or with an ultrasonic extractor (Method 3550). Immediately prior to extraction, spike 500 μL of the surrogate standard spiking solution (concentration = 50 ng/μL) into 1 L aqueous sample or 30 g solid sample.

7.1.2 Extraction of particulate-free aqueous samples using C_{18}-extraction disks (optional):

7.1.2.1 Disk preconditioning: Place the C_{18}-extraction disk into the filtration apparatus and prewash the disk with 10 to 20 mL of acetonitrile. Apply vacuum to pull the solvent through the disk. Maintain vacuum to pull air through for 5 min. Follow with 10 mL of methanol. Apply vacuum and pull most of the methanol through the disk. Release vacuum before the disk gets dry. Follow with 10 mL organic-free reagent water. Apply vacuum and pull most of the water through the disk. Release the vacuum before the disk gets dry.

7.1.2.2 Sample preconcentration: Add 2.5 mL of methanol to the 500 mL aqueous sample in order to get reproducible results. Pour the sample into the filtration apparatus. Adjust vacuum so that it takes approximately 20 min to process the entire sample. After all of the sample has passed through the membrane disk, pull air through the disk for 5 to 10 min. to remove any residual water.

7.1.2.3 Sample elution: Break the vacuum and place the tip of the filter base into the test tube that is contained inside the suction flask. Add 10 mL of acetonitrile to the graduated funnel, making sure to rinse the walls of the graduated funnel with the solvent. Apply vacuum to pass the acetonitrile through the membrane disk.

7.1.2.4 Extract concentration (if necessary): Concentrate the extract to 2 mL or less, using either the micro Snyder column technique (Sec. 7.1.2.4.1) or nitrogen blowdown technique (Sec. 7.1.2.4.2).

7.1.2.4.1 Micro Snyder Column Technique

7.1.2.4.1.1 Add one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of acetonitrile to the top of the column. Place the K-D apparatus in a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively

chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL with solvent.

7.1.2.4.2 Nitrogen Blowdown Technique

7.1.2.4.2.1 Place the concentrator tube in a warm water bath (approximately 35 °C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

<u>CAUTION:</u> Do not use plasticized tubing between the carbon trap and the sample.

7.1.2.4.2.2 The internal wall of the tube must be rinsed down several times with acetonitrile during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.2 Solvent Exchange: Prior to Florisil cleanup or gas chromatographic analysis, the methylene chloride and methylene chloride/acetone extracts obtained in Sec. 7.1.1 must be exchanged to hexane, as described in Secs. 7.2.1 through 7.2.3. Exchange is not required for the acetonitrile extracts obtained in Sec. 7.1.2.4.

7.2.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Concentrate the extract as described in Sec. 7.1.2.4.1, using 1 mL of methylene chloride to prewet the column, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and attach the macro Snyder column. Concentrate the extract as described in Sec. 7.1.2.4.1, using 1 mL of hexane to prewet the Snyder column, raising the temperature of the water bath, if necessary, to maintain proper distillation, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 2 mL for water samples, using either the micro Snyder column technique (Sec.

7.1.2.4.1) or nitrogen blowdown technique (Sec. 7.1.2.4.2), or 10 mL for solid samples. Stopper the concentrator tube and store at 4 °C if further processing will be performed immediately. If the extract will be stored for two days or longer, it should be transferred to a glass vial with a Teflon lined screw-cap or crimp top. Proceed with the gas chromatographic analysis.

7.3 Cleanup/Fractionation:

7.3.1 Cleanup may not be necessary for extracts from a relatively clean sample matrix. If polychlorinated biphenyls (PCBs) and organochlorine pesticides are known to be present in the sample, use the procedure outlined in Methods 3610 or 3620. When using column cleanup, collect Fraction 1 by eluting with 140 mL (Method 3610) or 100 mL (Method 3620) of 20-percent diethyl ether in hexane. Note that, under these conditions, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are not recovered from the Florisil column. The elution patterns and compound recoveries are given in Table 3.

7.3.2 Methods 3610 and 3620 also describe procedures for sample cleanup using Alumina and Florisil Cartridges. With this method, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are recovered quantitatively.

7.4 Gas chromatographic conditions (recommended):

7.4.1 Column 1 and Column 2 (Sec. 4.1.2):

Carrier gas (He) =	6 mL/min.
Injector temperature =	250 °C.
Detector temperature =	320 °C.
Column temperature:	
Initial temperature =	150 °C, hold for 0.5 min.
Temperature program =	150 °C to 220 °C at 5 °C/min., followed by 220 °C to 275 °C at 3 °C/min.
Final temperature =	275 °C hold for 13 min.

7.4.2 Table 1 gives the retention times and MDLs that can be achieved by this method for the 16 phthalate esters. An example of the separations achieved with the DB-5 and DB-1701 fused-silica open tubular columns is shown in Figure 1.

7.5 Calibration:

7.5.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.5.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for the description of each of these procedures.

7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard solution at 5000 mg/L to the sample prior to injection.

7.6.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.6.3 Record the sample volume injected and the resulting peak areas.

7.6.4 Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.6.5 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.6.6 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements of actual retention time variations over the course of 10 consecutive injections. Three times the standard deviation of the retention time can be used to calculate a suggested window size.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC specified in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain the test compounds at 5 to 10 ng/µL.

8.3 Calculate the recoveries of the surrogate compounds for all samples, method blanks, and method spikes. Determine if the recoveries are within limits established by performing QC procedures outlined in Method 8000.

8.3.1 If the recoveries are not within limits, the following are required:

8.3.1.1 Make sure there are no errors in calculations, surrogate solutions and internal standards. Also check instrument performance.

8.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentration."

8.4 An internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 30 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.5 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

8.5.1 The GC/MS would normally require a minimum concentration of 10 ng/μL in the final extract for each single-component compound.

8.5.2 The sample extract and associated blank should be analyzed by GC/MS as per Sec. 7.0 of Method 8270. Normally, analysis of a blank is not required for confirmation analysis, however, analysis for phthalates is a special case because of the possibility for sample contamination through septum punctures, etc.

8.5.3 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a concentration that would demonstrate the ability to confirm the phthalate esters identified by GC/ECD.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within $\pm$ 15 percent of the average values for the multiconcentration calibration.

8.7 Demonstrate through the analyses of standards that the Florisil fractionation scheme is reproducible. When using the fractionation schemes given in Methods 3610 or 3620, batch-to-batch variations in the composition of the alumina or Florisil material may cause variations in the recoveries of the phthalate esters.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Table 1 were obtained using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDL actually achieved in a given analysis will vary, as it is dependent on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using different types of aqueous samples and solid samples which were fortified with the test

compounds at two concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compounds and the type of matrix. Results of the single-laboratory method evaluation are presented in Tables 4 and 5.

9.3 The accuracy and precision obtained is determined by the sample matrix, sample preparation technique, cleanup techniques, and calibration procedures used.

10.0 REFERENCES

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2. Lopez-Avila, V., Baldin, E., Benedicto, J., Milanes, J., and Beckert, W.F., "Application of Open-Tubular Columns to SW-846 GC Methods", EMSL-Las Vegas, 1990.

3. Beckert, W.F. and Lopez-Avila, V., "Evaluation of SW-846 Method 8060 for Phthalate Esters", Proceedings of Fifth Annual Testing and Quality Assurance Symposium, USEPA, 1989.

TABLE 1.
GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE PHTHALATE ESTERS[a]

Compound No.	Compound name	Chemical Abstract Registry No.	Retention time[a] (min)		MDL[b]
			Column 1	Column 2	Liquid (ng/L)
1	Dimethyl phthalate	131-11-3	7.06	6.37	640
2	Diethyl phthalate	84-66-2	9.30	8.45	250
3	Diisobutyl phthalate	84-69-5	14.44	12.91	120
4	Di-n-butyl phthalate	84-74-2	16.26	14.66	330
5	Bis(4-methyl-2-pentyl) phthalate	146-50-9	18.77	16.27	370
6	Bis(2-methoxyethyl) phthalate	117-82-8	17.02	16.41	510
7	Diamyl phthalate	131-18-0	20.25	18.08	110
8	Bis(2-ethoxyethyl) phthalate	605-54-9	19.43	18.21	270
9	Hexyl 2-ethylhexyl phthalate	75673-16-4	21.07	18.97	130
10	Dihexyl phthalate	84-75-3	24.57	21.85	68
11	Butyl benzyl phthalate	85-68-7	24.86	23.08	42
12	Bis(2-n-butoxyethyl) phthalate	117-83-9	27.56	25.24	84
13	Bis(2-ethylhexyl) phthalate	117-81-7	29.23	25.67	270
14	Dicyclohexyl phthalate	84-61-7	28.88	26.35	22
15	Di-n-octyl phthalate	117-84-0	33.33	29.83	49
16	Dinonyl phthalate	84-76-4	38.80	33.84	22
IS	Benzyl benzoate	120-51-4	12.71	11.07	[c]
SU-1	Diphenyl phthalate	84-62-8	29.46	28.32	[c]
SU-2	Diphenyl isophthalate	744-45-6	32.99	31.37	[c]
SU-3	Dibenzyl phthalate	523-31-9	34.40	32.65	[c]

Table 1. (continued)

[a] Column 1 is a 30 m x 0.53 mm ID DB-5 fused-silica open tubular column (1.5 μm film thickness). Column 2 is a 30 m 0.53 mm ID DB-1701 fused-silica open tubular column (1.0 μm film thickness). Temperature program is 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min. An 8-in Supelco injection tee or a J&W Scientific press fit glass inlet splitter is used to connect the two columns to the injection port of a gas chromatograph. Carrier gas helium at 6 mL/min; makeup gas nitrogen at 20 mL/min; injector temperature 250°C; detector temperature 320°C.

[b] MDL is the method detection limit. The MDL was determined from the analysis of seven replicate aliquots of organic-free reagent water processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis using the single column approach: DB-5 fused-silica capillary column). MDL = $t_{(n-1,\ 0.99)}$ x SD where $t_{(n-1,\ 0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements. Values measured were not corrected for method blanks.

[c] Not applicable.

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor
Groundwater	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

[a] EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs determined herein are provided for guidance and may not always be achievable.

TABLE 3.
AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING METHODS 3610 AND 3620

Compound	Alumina column[a]	Florisil column[a]	Alumina cartridge[b]	Florisil cartridge[d]
Dimethyl phthalate	64.5	40.0	101	89.4
Diethyl phthalate	62.5	57.0	103	97.3
Diisobutyl phthalate	77.0	80.0	104	91.8
Di-n-butyl phthalate	76.5	85.0	108	102
Bis(4-methyl-2-pentyl) phthalate	89.5	84.5	103	105
Bis(2-methoxyethyl) phthalate	70.5	0	64.1[c]	78.3[e]
Diamyl phthalate	75.0	81.5	103	94.5
Bis(2-ethoxyethyl) phthalate	67.0	0	111	93.6
Hexyl 2-ethylhexyl phthalate	90.5	105	101	96.0
Dihexyl phthalate	73.0	74.5	108	96.8
Benzyl butyl phthalate	87.0	90.0	103	98.6
Bis(2-n-butoxyethyl) phthalate	62.5	0	108	91.5
Bis(2-ethylhexyl) phthalate	91.0	82.0	97.6	97.5
Dicyclohexyl phthalate	84.5	83.5	97.5	90.5
Di-n-octyl phthalate	108	115	112	97.1
Dinonyl phthalate	71.0	72.5	97.3	105

[a] 2 determinations; alumina and Florisil chromatography performed according to Methods 3610 and 3620, respectively.

[b] 2 determinations, using 1 g alumina cartridges; Fraction 1 was eluted with 5 mL of 20-percent acetone in hexane. 40 μg of each component was spiked per cartridge.

[c] 36.8 percent was recovered by elution with an additional 5 mL of 20-percent acetone in hexane.

[d] 2 determinations, using 1 g Florisil cartridges; Fraction 1 was eluted with 5 mL of 10-percent acetone in hexane. 40 μg of each component was spiked per cartridge.

[e] 14.4 percent was recovered by elution with an additional 5 mL of 10-percent acetone in hexane.

TABLE 4.
ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8061[a]

Estuarine Compound	Spike Concentration (20 µg/L)			Spike Concentration (60 µg/L)		
	water	Leachate	Estuarine Groundwater	water	Leachate	Groundwater
Dimethyl phthalate	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
Diethyl phthalate	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
Diisobutyl phthalate	76.0 (6.5)	95.3 (16.9)	92.7 (17.1)	99.1 (19.0)	100 (9.6)	83.2 (3.3)
Di-n-butyl phthalate	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
Bis(4-methyl-2-pentyl) phthalate	78.6 (2.6)	87.3 (18.2)	92.6 (13.7)	97.4 (15.0)	107 (13.3)	87.6 (2.9)
Bis(2-methoxyethyl) phthalate	73.8 (1.0)	87.2 (21.7)	82.4 (4.4)	82.5 (5.5)	99.0 (13.7)	76.9 (6.6)
Diamyl phthalate	78.2 (7.3)	92.1 (21.5)	88.8 (7.5)	89.2 (2.8)	112 (14.2)	92.5 (1.8)
Bis(2-ethoxyethyl) phthalate	75.6 (3.3)	90.8 (22.4)	86.4 (5.8)	88.7 (4.9)	109 (14.6)	84.8 (5.9)
Hexyl 2-ethylhexyl phthalate	84.7 (5.3)	91.1 (27.5)	81.4 (17.6)	107 (16.8)	117 (11.4)	80.1 (4.1)
Dihexyl phthalate	79.8 (7.2)	102 (21.5)	90.9 (7.6)	90.1 (2.4)	109 (20.7)	88.9 (2.4)
Benzyl butyl phthalate	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.0)
Bis(2-n-butoxyethyl) phthalate	78.5 (3.5)	92.3 (16.1)	89.3 (3.6)	86.1 (6.2)	107 (15.3)	92.4 (0.6)
Bis(2-ethylhexyl) phthalate	81.4 (4.1)	93.0 (15.0)	90.5 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
Dicyclohexyl phthalate	77.4 (6.5)	88.2 (13.2)	91.7 (15.2)	87.7 (9.6)	102 (14.3)	71.9 (2.4)
Di-n-octyl phthalate	74.9 (4.9)	87.5 (18.7)	87.2 (3.7)	85.1 (8.3)	105 (17.7)	90.4 (2.0)
Dinonyl phthalate	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)
Surrogates:						
Diphenyl phthalate	98.5 (2.6)	113 (14.9)	110 (3.3)	110 (12.4)	95.1 (7.2)	107 (2.4)
Diphenyl isophthalate	95.8 (1.9)	112 (11.7)	109 (3.3)	104 (5.9)	97.1 (7.1)	106 (2.8)
Dibenzyl phthalate	93.9 (4.4)	112 (14.0)	106 (3.8)	111 (5.9)	93.3 (9.5)	105 (2.4)

[a] The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 5.
ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8061[a]

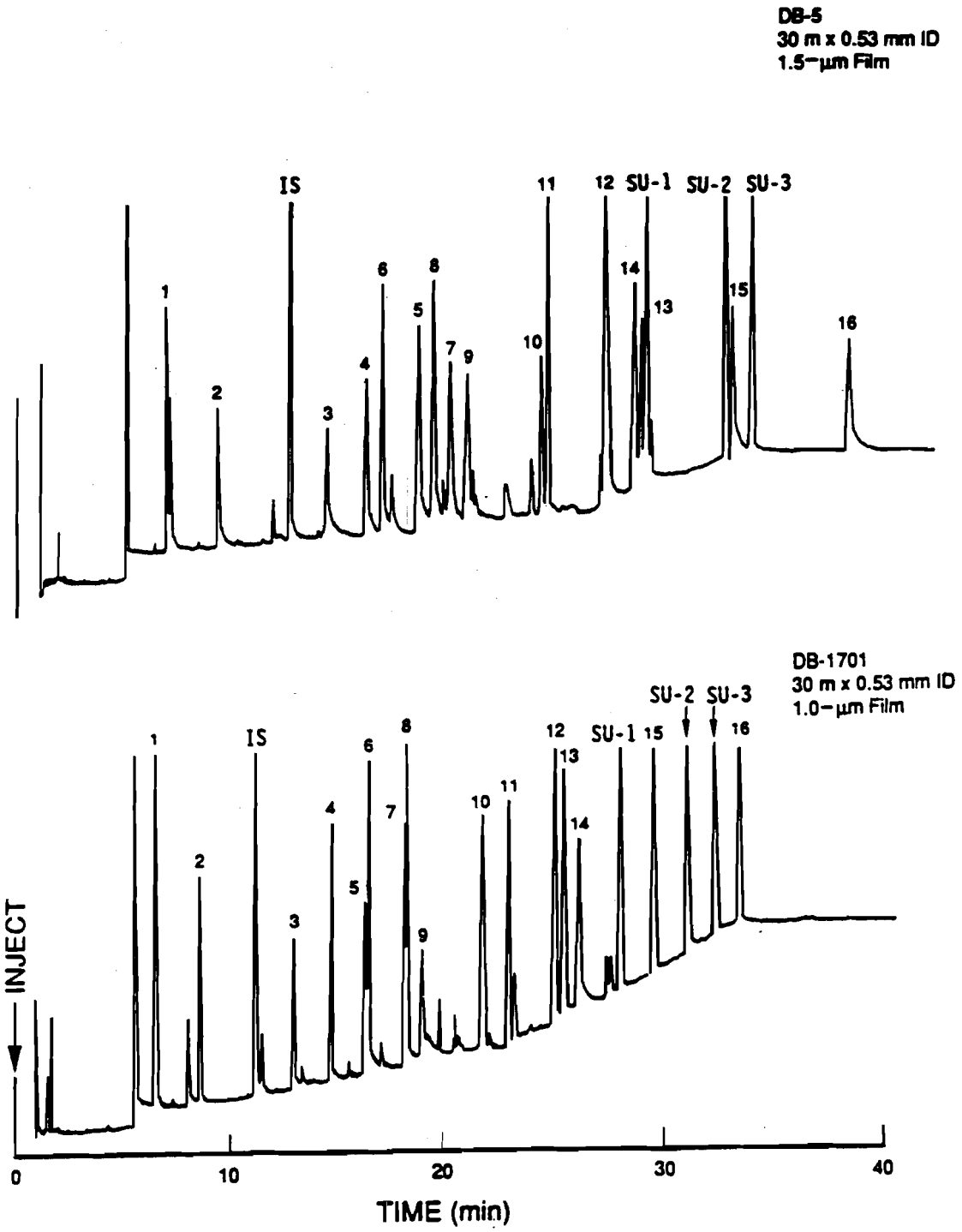
Compound	Spike Concentration (1 mg/kg)			Spike Concentration (3 µg/g)		
	Estuarine sediment	Municipal sludge	Sandy loam soil	Estuarine sediment	Municipal sludge	Sandy loam soil
Dimethyl phthalate	77.9 (42.8)	52.1 (35.5)	[c]	136 (9.6)	64.8 (11.5)	70.2 (2.0)
Diethyl phthalate	68.4 (1.7)	68.6 (9.1)	54.7 (6.2)	60.2 (12.5)	72.8 (10.0)	67.0 (15.1)
Diisobutyl phthalate	103 (3.1)	106 (5.3)	70.3 (3.7)	74.8 (6.0)	84.0 (4.6)	79.2 (0.1)
Di-n-butyl phthalate	121 (25.8)	86.3 (17.7)	72.6 (3.7)	74.6 (3.9)	113 (5.8)	70.9 (5.5)
Bis(4-methyl-2-pentyl) phthalate	108 (57.4)	97.3 (7.4)	[c]	104 (1.5)	150 (6.1)	83.9 (11.8)
Bis(2-methoxyethyl) phthalate	26.6 (26.8)	72.7 (8.3)	0	19.5 (14.8)	59.9 (5.4)	0
Diamyl phthalate	95.0 (10.2)	81.9 (7.1)	81.9 (15.9)	77.3 (4.0)	116 (3.7)	82.1 (15.5)
Bis(2-ethoxyethyl) phthalate	[c]	66.6 (4.9)	[c]	21.7 (22.8)	57.5 (9.2)	84.7 (8.5)
Hexyl 2-ethylhexyl phthalate	[c]	114 (10.5)	57.7 (2.8)	72.7 (11.3)	26.6 (47.6)	28.4 (4.3)
Dihexyl phthalate	103 (3.6)	96.4 (10.7)	77.9 (2.4)	75.5 (6.8)	80.3 (4.7)	79.5 (2.7)
Benzyl butyl phthalate	113 (12.8)	82.8 (7.8)	56.5 (5.1)	72.9 (3.4)	76.8 (10.3)	67.3 (3.8)
Bis(2-n-butoxyethyl) phthalate	114 (21.1)	74.0 (15.6)	[c]	38.3 (25.1)	98.0 (6.4)	62.0 (3.4)
Bis(2-ethylhexyl) phthalate	[c]	76.6 (10.6)	99.2 (25.3)	59.5 (18.3)	85.8 (6.4)	65.4 (2.8)
Dicyclohexyl phthalate	36.6 (48.8)	65.8 (15.7)	92.8 (35.9)	33.9 (66.1)	68.5 (9.6)	62.2 (19.1)
Di-n-octyl phthalate	[c]	93.3 (14.6)	84.7 (9.3)	36.8 (16.4)	88.4 (7.4)	115 (29.2)
Dinonyl phthalate	[c]	80.0 (41.1)	64.2 (17.2)	[c]	156 (8.6)	115 (13.2)

[a] The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries. All samples were subjected to Florisil cartridge cleanup.

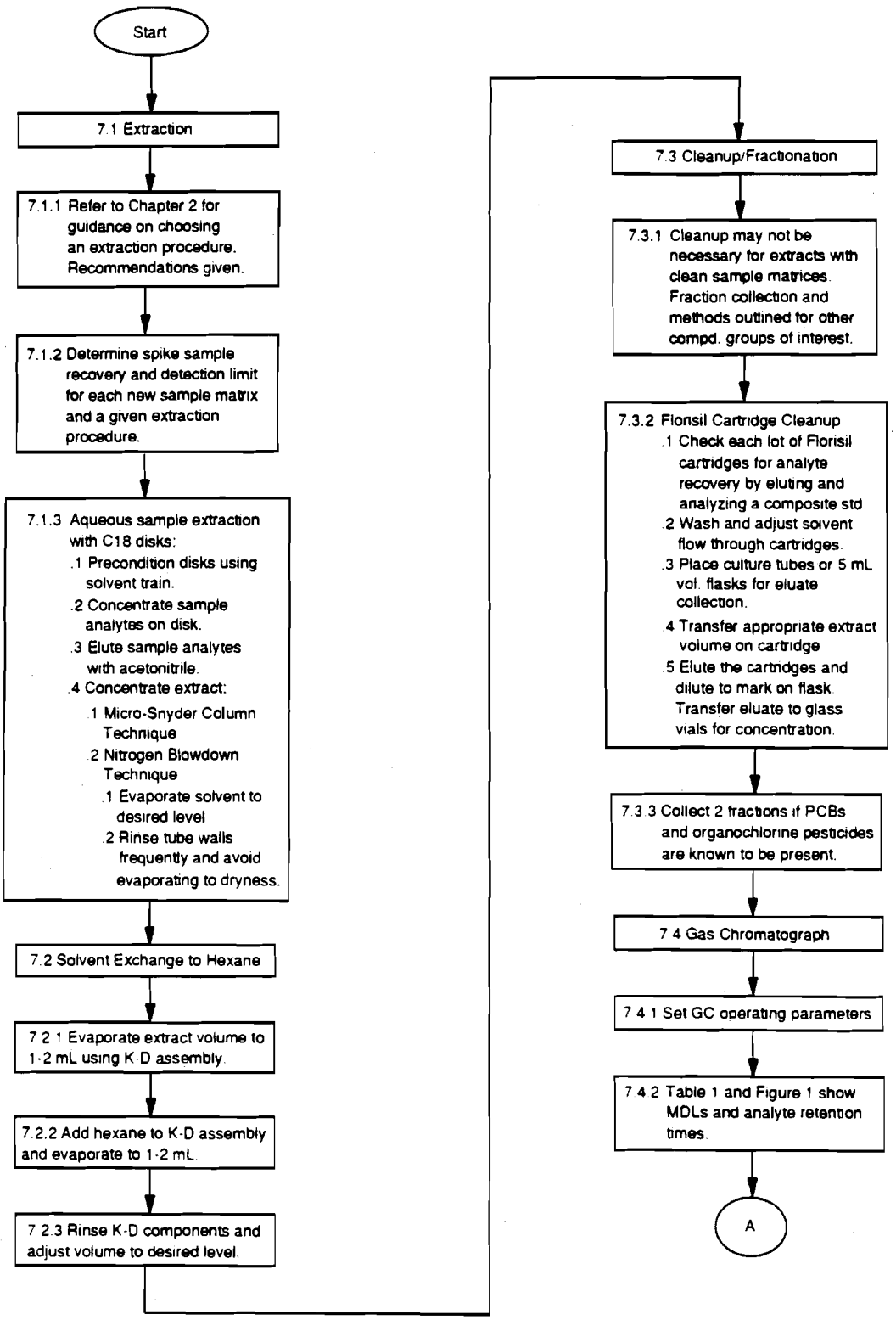
[b] The estuarine sediment extract (Florisil, Fraction 1) was subjected to sulfur cleanup (Method 3660 with tetrabutylammonium sulfite reagent).

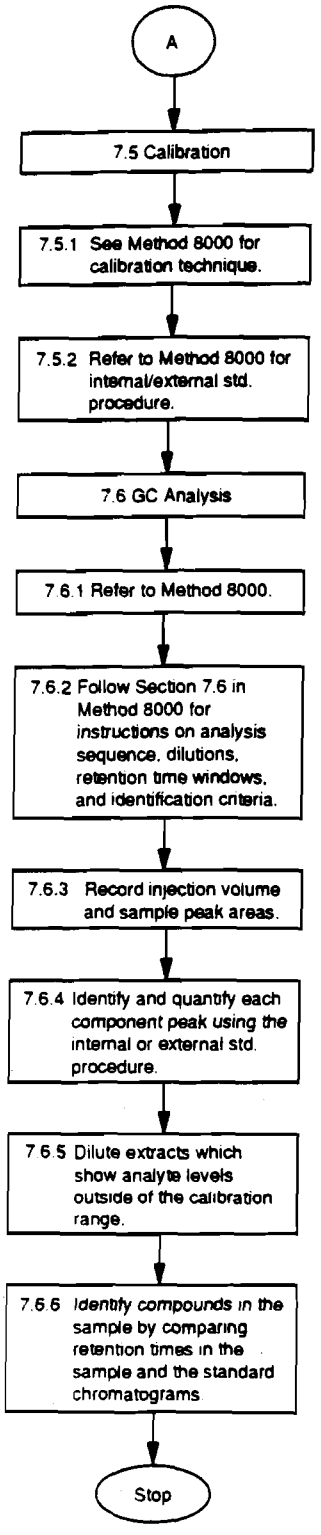
[c] Not able to determine because of matrix interferant.

Figure 1



GC/ECD chromatograms of a composite phthalate esters standard (concentration 10 ng/μL per compound) analyzed on a DB-5 and a DB-1701 fused-silica open tubular column. Temperature program: 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min.


Start
7.1 Extraction
7.1.1 Refer to Chapter 2 for guidance on choosing an extraction procedure. Recommendations given.
7.1.2 Determine spike sample recovery and detection limit for each new sample matrix and a given extraction procedure.
7.1.3 Aqueous sample extraction with C18 disks:
.1 Precondition disks using solvent train.
.2 Concentrate sample analytes on disk.
.3 Elute sample analytes with acetonitrile.
.4 Concentrate extract:
.1 Micro-Snyder Column Technique
.2 Nitrogen Blowdown Technique
.1 Evaporate solvent to desired level
.2 Rinse tube walls frequently and avoid evaporating to dryness.
7.2 Solvent Exchange to Hexane
7.2.1 Evaporate extract volume to 1-2 mL using K-D assembly.
7.2.2 Add hexane to K-D assembly and evaporate to 1-2 mL.
7.2.3 Rinse K-D components and adjust volume to desired level.
7.3 Cleanup/Fractionation
7.3.1 Cleanup may not be necessary for extracts with clean sample matrices. Fraction collection and methods outlined for other compd. groups of interest.
7.3.2 Florisil Cartridge Cleanup
.1 Check each lot of Florisil cartridges for analyte recovery by eluting and analyzing a composite std.
.2 Wash and adjust solvent flow through cartridges.
.3 Place culture tubes or 5 mL vol. flasks for eluate collection.
.4 Transfer appropriate extract volume on cartridge
.5 Elute the cartridges and dilute to mark on flask. Transfer eluate to glass vials for concentration.
7.3.3 Collect 2 fractions if PCBs and organochlorine pesticides are known to be present.
7.4 Gas Chromatograph
7.4.1 Set GC operating parameters
7.4.2 Table 1 and Figure 1 show MDLs and analyte retention times.
A


A
7.5 Calibration
7.5.1 See Method 8000 for calibration technique.
7.5.2 Refer to Method 8000 for internal/external std. procedure.
7.6 GC Analysis
7.6.1 Refer to Method 8000.
7.6.2 Follow Section 7.6 in Method 8000 for instructions on analysis sequence, dilutions, retention time windows, and identification criteria.
7.6.3 Record injection volume and sample peak areas.
7.6.4 Identify and quantify each component peak using the internal or external std. procedure.
7.6.5 Dilute extracts which show analyte levels outside of the calibration range.
7.6.6 Identify compounds in the sample by comparing retention times in the sample and the standard chromatograms
Stop

METHOD 8070

NITROSAMINES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of certain nitrosamines. The following compounds can be determined by this method:

		Appropriate Technique				
Compound Name	CAS No.[a]	3510	3520	3540	3550	3580
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X

a Chemical Abstract Services Registry Number.
X Greater than 70 percent recovery by this preparation technique.

1.2 This is a gas chromatographic (GC) method applicable to the determination of the parameters listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 8270 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for N-nitrosodi-n-propylamine. In order to confirm the presence of N-nitrosodiphenylamine, the cleanup procedure specified in Section 7.3.3 or 7.3.4 must be used. In order to confirm the presence of N-nitrosodimethylamine by GC/MS, chromatographic column 1 of this method must be substituted for the column recommended in Method 8270. Confirmation of these parameters using GC-high resolution mass spectrometry or a Thermal Energy Analyzer is also recommended practice.

1.3 The method detection limit (MDL) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix. Table 2 lists the Estimated Quantitation Limits (EQLs) for various matrices.

1.4 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible concentration by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also

be made available to all personnel involved in the chemical analysis.

1.5 These nitrosamines are known carcinogens. Therefore, utmost care must be exercised in the handling of these materials. Nitrosamine reference standards and standard solutions should be handled and prepared in a ventilated glove box within a properly ventilated room.

1.6 N-Nitrosodiphenylamine is reported to undergo transnitrosation reactions. Care must be exercised in the heating or concentrating of solutions containing this compound in the presence of reactive amines.

2.0 SUMMARY OF METHOD

2.1 A measured volume of aqueous sample, approximately one liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is washed with dilute HCl to remove free amines, dried, and concentrated to a volume of 10 mL or less. Gas chromatographic conditions are described which permit the separation and measurement of the compounds in the extract after it has been exchanged to methanol.

2.2 Method 8070 provides gas chromatographic conditions for the detection of ppb concentrations of nitrosamines. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 μL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a nitrogen-phosphorus detector (NPD) or a Thermal Energy Analyzer and the reductive Hall detector.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures (Methods 3610 or 3620) can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Nitrosamines contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no nitrosamine residues contaminate the sample or solvent extract under the conditions of analysis. Plastics, in particular, must be avoided because nitrosamines are commonly used as plasticizers and are easily extracted from plastic materials. Serious nitrosamine contamination may result at any time if consistent quality control is not practiced.

3.4 The sensitive and selective Thermal Energy Analyzer and the reductive Hall detector may be used in place of the nitrogen-phosphorus detector when

interferences are encountered. The Thermal Energy Analyzer offers the highest selectivity of the non-mass spectrometric detectors.

3.5 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.6 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

4.1.1 Column 1 - 1.8 m x 4 mm ID Pyrex glass, packed with Chromosorb W AW, (80/100 mesh) coated with 10% Carbowax 20 M/2% KOH or equivalent. This column was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate column packings are provided in Section 7.3.2.

4.1.2 Column 2 - 1.8 m x 4 mm ID Pyrex glass, packed with Supelcoport (100/120 mesh) coated with 10% SP-2250, or equivalent.

4.1.3 Detector - Nitrogen-Phosphorus, reductive Hall or Thermal Energy Analyzer. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope. A nitrogen-phosphorus detector was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate detectors are provided in Section 7.3.2.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or

equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.5 Balance - Analytical, 0.0001 g.

4.6 Vials - 10 to 15 mL, amber glass with Teflon lined screw-cap or crimp top.

4.7 Volumetric flasks, Class A, Appropriate sizes with ground glass stoppers.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent.

5.4 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6 Stock standard solutions (1000 mg/L) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.6.1 Prepare stock standard solutions by accurately weighing 0.1000 ± 0.0010 g of pure material. Dissolve the material in pesticide quality methanol and dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps or crimp tops. Store at 4°C and protect from light.

Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.7 Calibration standards - A minimum of five concentrations should be prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.8 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.8.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest, as described in Section 5.7.

5.8.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.8.3 Analyze each calibration standard according to Section 7.0.

5.9 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with one or two surrogates (e.g. nitrosamines that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored at 4°C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to methanol. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of methanol, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of methanol to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Section 7.1.2.3. If cleanup is needed, proceed to Section 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methanol. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw-cap or crimp top. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of methylene chloride. A 5 mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride to the top. Place the micro K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-

10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the extract volume to 2.0 mL and proceed with either Method 3610, 3620, or 3640.

7.1.3 If N-nitrosodiphenylamine is to be measured by gas chromatography, the analyst must first use a cleanup column to eliminate diphenylamine interference (Methods 3610 or 3620). If N-nitrosodiphenylamine is of no interest, the analyst may proceed directly with gas chromatographic analysis (Section 7.3).

7.2 Cleanup

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedure recommended in this method has been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%. Diphenylamine, if present in the original sample extract must be separate from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.2.2 Proceed with either Method 3610 or 3620, using the 2 mL methylene chloride extracts obtained from Section 7.1.2.5.

7.2.3 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.3 Gas Chromatography

7.3.1 N-nitrosodiphenylamine completely reacts to form diphenylamine at the normal operating temperatures of a GC injection port (200 to 250°C). Thus, N-nitrosodiphenylamine is chromatographed and detected as diphenylamine. Accurate determination depends on removal of diphenylamine that may be present in the original extract prior to GC (see Section 7.1.3).

7.3.2 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDLs that were obtained under these conditions. Examples of the parameter separations achieved by these columns are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

7.4 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.4.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.5 Gas chromatographic analysis

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.5.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration check standard after each group of 10 samples in the analysis sequence.

7.5.3 Examples of GC/NPD chromatograms for nitrosamines are shown in Figures 1 and 2.

7.5.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.5.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Method 8000 for calculation equations.

7.5.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control (QC) reference sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at 20 mg/L.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions

of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration.

9.0 METHOD PERFORMANCE

9.1 This method has been tested for linearity of recovery from spiked organic-free reagent water and has been demonstrated to be applicable for the concentration range from 4 x MDL to 1000 x MDL.

9.2 In a single laboratory (Southwest Research Institute), using spiked wastewater samples, the average recoveries presented in Table 2 were obtained. Each spiked sample was analyzed in triplicate on three separate occasions. The standard deviation of the percent recovery is also included in Table 2.

10.0 REFERENCES

1. Fed. Regist. 1984, 49, 43234; October 26.

2. "Determination of Nitrosamines in Industrial and Municipal Wastewaters"; Report for EPA Contract 68-03-2606, in preparation.

3. Burgess, E.M.; Lavanish, J.M. "Photochemical Decomposition of N-nitrosamines"; Tetrahedron Letters 1964, 1221.

4. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1979; EPA-600/4-79-020.

5. "Method Detection Limit and Analytical Curve Studies EPA Methods 606, 607, 608"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory, Cincinnati, OH, special letter report for EPA Contract 68-03-2606.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Analyte	Retention Time (minutes) Column 1	Column 2	Method Detection Limit (μg/L)
N-Nitrosodimethylamine	4.1	0.88	0.15
N-Nitrosodi-n-propylamine	12.1	4.2	0.46
N-Nitrosodiphenylamine[a]	12.8[b]	6.4[c]	0.81

Column 1 conditions:
Carrier gas (He) flow rate: 40 mL/min
Column temperature: Isothermal, at 110°C, except as otherwise indicated.

Column 2 conditions:
Carrier gas (He) flow rate: 40 mL/min
Column temperature: Isothermal, at 120°C, except as otherwise indicated.

a Measured as diphenylamine.
b Determined isothermally at 220°C.
c Determined isothermally at 210°C.

TABLE 2.
SINGLE OPERATOR ACCURACY AND PRECISION

Analyte Types	Average Percent Recovery	Standard Deviation %	Spike Range (μg/L)	Number of Analyses	Matrix
N-Nitrosodimethylamine	32	3.7	0.8	29	5
N-Nitrosodiphenylamine	79	7.1	1.2	29	5
N-Nitrosodi-n-propylamine	61	4.1	9.0	29	5

TABLE 3.
QC ACCEPTANCE CRITERIA

Analyte	Test Conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Recovery Range (%)
N-Nitrosodimethylamine	20	3.4	4.6-20.0	13-109
N-Nitrosodiphenylamine	20	6.1	2.1-24.5	D-139
N-Nitrosodi-n-propylamine	20	5.7	11.5-26.8	45-146

s = Standard deviation for four recovery measurements, in µg/L.

$\bar{X}$ = Average recovery for four recovery measurements, in µg/L.

D = Detected, result must be greater than zero.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Analyte	Accuracy, as recovery, X′ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S′ (µg/L)
N-Nitrosodimethylamine	0.37C+0.06	0.25$\bar{X}$-0.04	0.25$\bar{X}$+0.11
N-Nitrosodiphenylamine	0.64C+0.52	0.36$\bar{X}$-1.53	0.46$\bar{X}$-0.47
N-Nitroso-n-propylamine	0.96C-0.07	0.15$\bar{X}$+0.13	0.21$\bar{X}$+0.15

X′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

FIGURE 1.
GAS CHROMATOGRAM OF NITROSAMINES

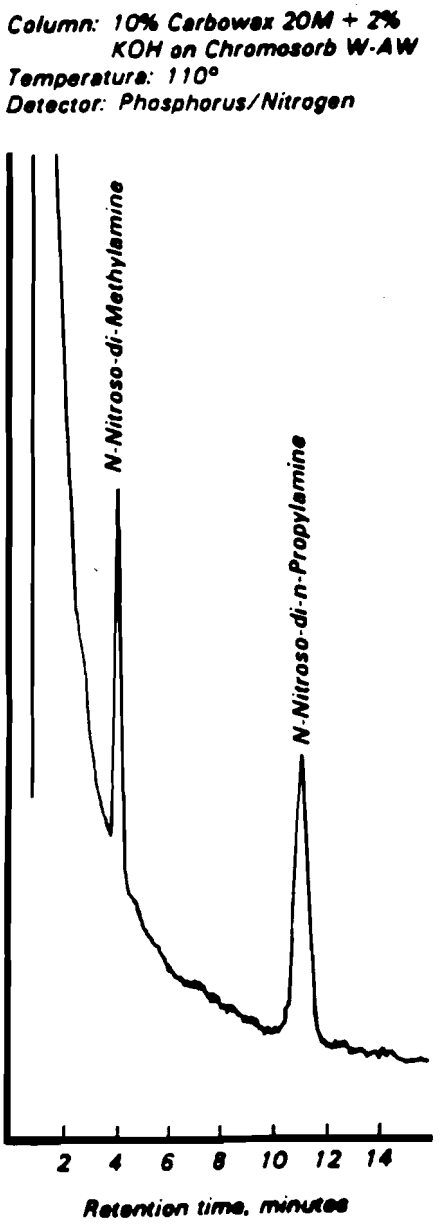
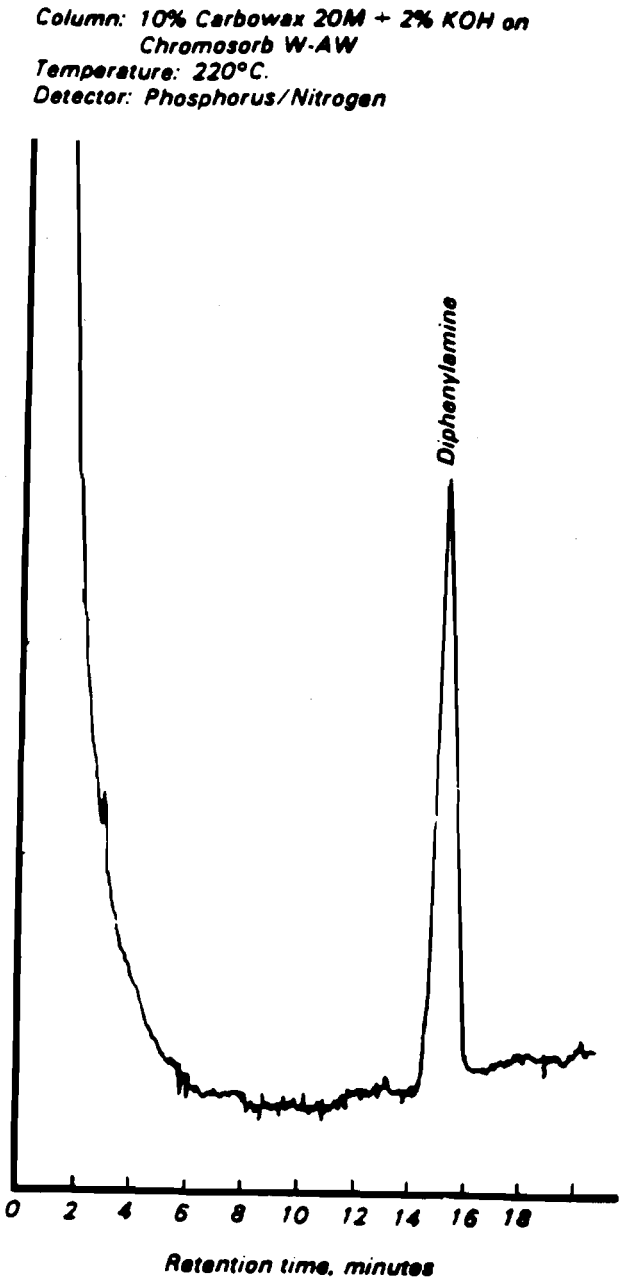
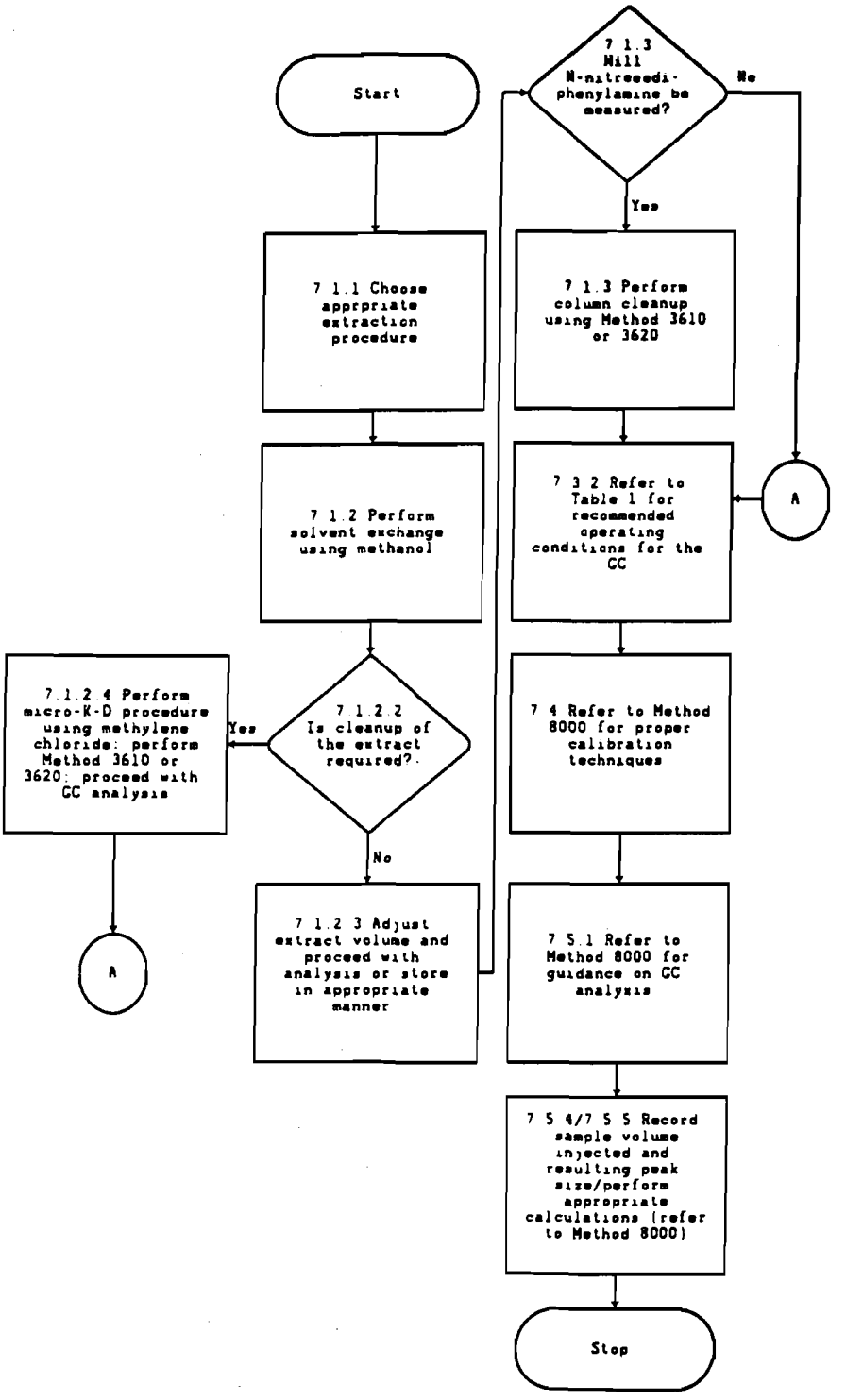


FIGURE 2.
GAS CHROMATOGRAM OF N-NITROSODIPHENYLAMINE AS DIPHENYLAMINE



METHOD 8070
NITROSAMINES BY GAS CHROMATOGRAPHY



METHOD 8080A

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
δ-BHC	319-86-8
γ-BHC (Lindane)	58-89-9
Chlordane (technical)	12789-03-6
4,4′-DDD	72-54-8
4,4′-DDE	72-55-9
4,4′-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4′-Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

a Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 µL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or an electrolytic conductivity detector (HECD).

2.2 The sensitivity of Method 8080 usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.3 Detectors: Electron capture (ECD) or electrolytic conductivity detector (HECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube: 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask: 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column: Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks, Class A: sizes as appropriate with ground-glass stoppers.

4.6 Microsyringe: 10 µL.

4.7 Syringe: 5 mL.

4.8 Vials: Glass, 2, 10, and 20 mL capacity with Teflon-lined screw caps or crimp tops.

4.9 Balances: Analytical, 0.0001 g and Top loading, 0.01 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.3.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.3.3 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.3.4 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.4 Stock standard solutions:

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10 mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into vials with Teflon-lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Sec. 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.6.3 Analyze each calibration standard according to Sec. 7.0.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Two surrogate standards (tetrachloro-m-xylene (TCMX) and decachlorobiphenyl) are added to each sample; however, only one need be calculated for recovery. Proceed with corrective action when both surrogates are out of limits for a sample (Sec. 8.3). Method 3500 indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using Method 3540, 3541, or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid

reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap or crimp top. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (5% methane/95% argon) flow rate:	60 mL/min
Column temperature:	200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 Column 2:

Carrier gas (5% methane/95% argon) flow rate:	60 mL/min
Column temperature:	200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow to provide sufficient resolution for accurate quantitation of the analytes. This will normally result in a retention time of 10 to 12 minutes for 4,4′-DDT, depending on the packed column used.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 μL of internal standard to the sample prior to injection.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

NOTE: A 72 hour sequence is not required with this method.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Sec. 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4′-DDT and endrin. Look for the degradation products of 4,4′-DDT (4,4′-DDE and 4,4′-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in of Method 8000. Calculate percent breakdown as follows:

$$\text{\% breakdown for 4,4′-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\text{\% breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

7.4.6 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10 mL hexane extracts obtained from Sec. 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous sections and in Method 8000.

7.5.3 If only PCBs are to be measured in a sample, the sulfuric acid/permanganate cleanup (Method 3665), followed by Silica Cleanup (Method 3630) or Florisil Cleanup (Method 3620), is recommended.

7.6 Calculations (excerpted from U.S. FDA, PAM):

7.6.1 Calculation of Certain Residues: Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. In the following sections suggestions are offered for handling toxaphene, chlordane, PCB, DDT, and BHC. A 10% DC-200 stationary phase column was used to obtain the chromatograms in Figures 6-9.

7.6.2 Toxaphene: Quantitative calculation of toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust sample size so that toxaphene major peaks are 10-30% full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ±10 ng of the sample; (c) construct the baseline of standard toxaphene between its extremities; and (d) construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide (Figures 7, 8, and 9). This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard. A toxaphene standard that has been passed through a Florisil column will show a shorter retention time for peak X and an enlargement of peak Y.

7.6.3 Toxaphene and DDT: If DDT is present, it will superimpose itself on toxaphene peak V. To determine the approximate baseline of the DDT, draw a line connecting the trough of peaks U and V with the trough of peaks W and X and construct another line parallel to this line which will just cut the top of peak W (Figure 61). This procedure was tested with ratios of standard toxaphene-DDT mixtures from 1:10 to 2:1 and the results of added and calculated DDT and toxaphene by the "parallel lines" method of baseline construction were within 10% of the actual values in all cases.

7.6.3.1 A series of toxaphene residues have been calculated using total peak area for comparison to the standard and also using area of the last four peaks only in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram is interfered with by other substances.

7.6.3.2 The baseline for methoxychlor superimposed on toxaphene (Figure 8b) was constructed by overlaying the samples on a toxaphene standard of approximately the same concentration (Figure 8a) and viewing the charts against a lighted background.

7.6.4 Chlordane is a technical mixture of at least 11 major components and 30 or more minor ones. Gas chromatography-mass spectrometry and nuclear magnetic resonance analytical techniques have been applied to the elucidation of the chemical structures of the many chlordane constituents. Figure 9a is a chromatogram of standard chlordane. Peaks E and F are responses to trans- and cis-chlordane, respectively. These are the two major components of technical chlordane, but the exact percentage of each in the technical material is not completely defined and is not consistent from batch to batch. Other labelled peaks in Figure 9a are thought to represent: A, monochlorinated adduct of pentachlorocyclopentadiene with cyclopentadiene; B, coelution of heptachlor and α-chlordene; C, coelution of β-chlordene and γ-chlordene; D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.4.5 To measure the total area of the chlordane chromatogram, proceed as in Sec. 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a chromatogram in which peaks E and F are approximately the same size as those in the sample chromatograms. Construct the baseline beneath the standard from the beginning of peak A to the end of peak F as shown in Figure 9a. Use the distance from the trough between peaks E and F to the baseline in the chromatogram of the standard to construct the baseline in the chromatogram of the sample. Figure 9b shows how the presence of toxaphene causes the baseline under chlordane to take an upward angle. When the size of peaks E and F in standard and sample chromatograms are the same, the distance from the trough of the peaks to the baselines should be the same. Measurement of chlordane area should be done by total peak area if possible.

NOTE: A comparison has been made of the total peak area integration method and the addition of peak heights method for several samples containing chlordane. The peak heights A, B, C, D, E, and F were measured in millimeters from peak maximum of each to the baseline constructed under the total chlordane area and were then added together. These results obtained by the two techniques are too close to ignore this method of "peak height addition" as a means of calculating chlordane. The technique has inherent difficulties because not all the peaks are symmetrical and not all are present in the same ratio in standard and in sample. This method does offer a means of calculating results if no means of measuring total area is practical.

7.6.5 Polychlorinated biphenyls (PCBs): Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, Strobane, and chlordane. In each case, the chemical is made up of numerous compounds. So the chromatograms are multi-peak. Also in each case, the chromatogram of the residue may not match that of the standard.

7.6.5.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the

tradename Aroclor (1200 series and 1016). Though these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

7.6.5.2 PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgment about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area of height of peaks from appropriate Aroclor(s) reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. Mixtures of Aroclors may be required to provide the best match of GC patterns of sample and reference.

7.6.6 DDT: DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and DDD are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α-, γ-, and δ-isomers and 14 weeks for the β-isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β-isomer.

7.6.7.2 Individual isomers (α, β, γ, and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α-, γ-, and δ-isomers show equal electron affinity. β-BHC shows a much weaker electron affinity compared to the other isomers.

7.6.7.3 Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each single-component parameter of interest at the following concentrations in acetone or other water miscible solvent: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; endrin, 10 mg/L; and any other single-component pesticide, 2 mg/L. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 mg/L in acetone.

8.2.2 Table 3 indicates the QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.4 <u>GC/MS confirmation</u>: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/μL in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Sec. 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for an electron capture detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. U.S. EPA, "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10: Pesticides and PCBs," Report for EPA Contract 68-03-2605.

2. U.S. EPA, "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, October 1980.

3. Pressley, T.A., and J.E. Longbottom, "The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater: Method 617," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-84-006, 1982.

4. "Determination of Pesticides and PCB's in Industrial and Municipal Wastewaters, U.S. Environmental Protection Agency," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, EPA-600/4-82-023, June 1982.

5. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9, 1971.

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7. Webb, R.G. and A.C. McCall, "Quantitative PCB Standards for Electron Capture Gas Chromatography," Journal of Chromatographic Science, 11, 366, 1973.

8. Millar, J.D., R.E. Thomas and H.J. Schattenberg, "EPA Method Study 18, Method 608: Organochlorine Pesticides and PCBs," U.S. EPA/EMSL, Research Triangle Park, NC, EPA-600/4-84-061, 1984.

9. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

11. U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. 1, June 1979.

12. Sawyer, L.D., JAOAC, 56, 1015-1023 (1973), 61 272-281 (1978), 61 282-291 (1978).

13. Stewart, J. "EPA Verification Experiment for Validation of the SOXTEC® PCB Extraction Procedure"; Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138; October 1988.

TABLE 1.
GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs[a]

Analyte	Retention time (min) Col. 1	Col. 2	Method Detection limit (μg/L)
Aldrin	2.40	4.10	0.004
α-BHC	1.35	1.82	0.003
β-BHC	1.90	1.97	0.006
δ-BHC	2.15	2.20	0.009
γ-BHC (Lindane)	1.70	2.13	0.004
Chlordane (technical)	e	e	0.014
4,4′-DDD	7.83	9.08	0.011
4,4′-DDE	5.13	7.15	0.004
4,4′-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.003
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
Toxaphene	e	e	0.24
PCB-1016	e	e	nd
PCB-1221	e	e	nd
PCB-1232	e	e	nd
PCB-1242	e	e	0.065
PCB-1248	e	e	nd
PCB-1254	e	e	nd
PCB-1260	e	e	nd

[a]U.S. EPA. Method 617. Organochlorine Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

a EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Analyte	Test conc. (μg/L)	Limit for s (μg/L)	Range for $\bar{x}$ (μg/L)	Range P, P_s (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	0.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in μg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in μg/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Analyte	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Aldrin	0.81C+0.04	0.16$\bar{x}$-0.04	0.20$\bar{x}$-0.01
α-BHC	0.84C+0.03	0.13$\bar{x}$+0.04	0.23$\bar{x}$-0.00
β-BHC	0.81C+0.07	0.22$\bar{x}$+0.02	0.33$\bar{x}$-0.95
δ-BHC	0.81C+0.07	0.18$\bar{x}$+0.09	0.25$\bar{x}$+0.03
γ-BHC	0.82C-0.05	0.12$\bar{x}$+0.06	0.22$\bar{x}$+0.04
Chlordane	0.82C-0.04	0.13$\bar{x}$+0.13	0.18$\bar{x}$+0.18
4,4′-DDD	0.84C+0.30	0.20$\bar{x}$-0.18	0.27$\bar{x}$-0.14
4,4′-DDE	0.85C+0.14	0.13$\bar{x}$+0.06	0.28$\bar{x}$-0.09
4,4′-DDT	0.93C-0.13	0.17$\bar{x}$+0.39	0.31$\bar{x}$-0.21
Dieldrin	0.90C+0.02	0.12$\bar{x}$+0.19	0.16$\bar{x}$+0.16
Endosulfan I	0.97C+0.04	0.10$\bar{x}$+0.07	0.18$\bar{x}$+0.08
Endosulfan II	0.93C+0.34	0.41$\bar{x}$-0.65	0.47$\bar{x}$-0.20
Endosulfan Sulfate	0.89C-0.37	0.13$\bar{x}$+0.33	0.24$\bar{x}$+0.35
Endrin	0.89C-0.04	0.20$\bar{x}$+0.25	0.24$\bar{x}$+0.25
Heptachlor	0.69C+0.04	0.06$\bar{x}$+0.13	0.16$\bar{x}$+0.08
Heptachlor epoxide	0.89C+0.10	0.18$\bar{x}$-0.11	0.25$\bar{x}$-0.08
Toxaphene	0.80C+1.74	0.09$\bar{x}$+3.20	0.20$\bar{x}$+0.22
PCB-1016	0.81C+0.50	0.13$\bar{x}$+0.15	0.15$\bar{x}$+0.45
PCB-1221	0.96C+0.65	0.29$\bar{x}$-0.76	0.35$\bar{x}$-0.62
PCB-1232	0.91C+10.79	0.21$\bar{x}$-1.93	0.31$\bar{x}$+3.50
PCB-1242	0.91C+10.79	0.21$\bar{x}$-1.93	0.31$\bar{x}$+3.50
PCB-1248	0.91C+10.79	0.21$\bar{x}$-1.93	0.31$\bar{x}$+3.50
PCB-1254	0.91C+10.79	0.21$\bar{x}$-1.93	0.31$\bar{x}$+3.50
PCB-1260	0.91C+10.79	0.21$\bar{x}$-1.93	0.31$\bar{x}$+3.50

x′ = Expected recovery for one or more measurements of a sample containing concentration C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

Figure 1
Gas Chromatogram of Pesticides

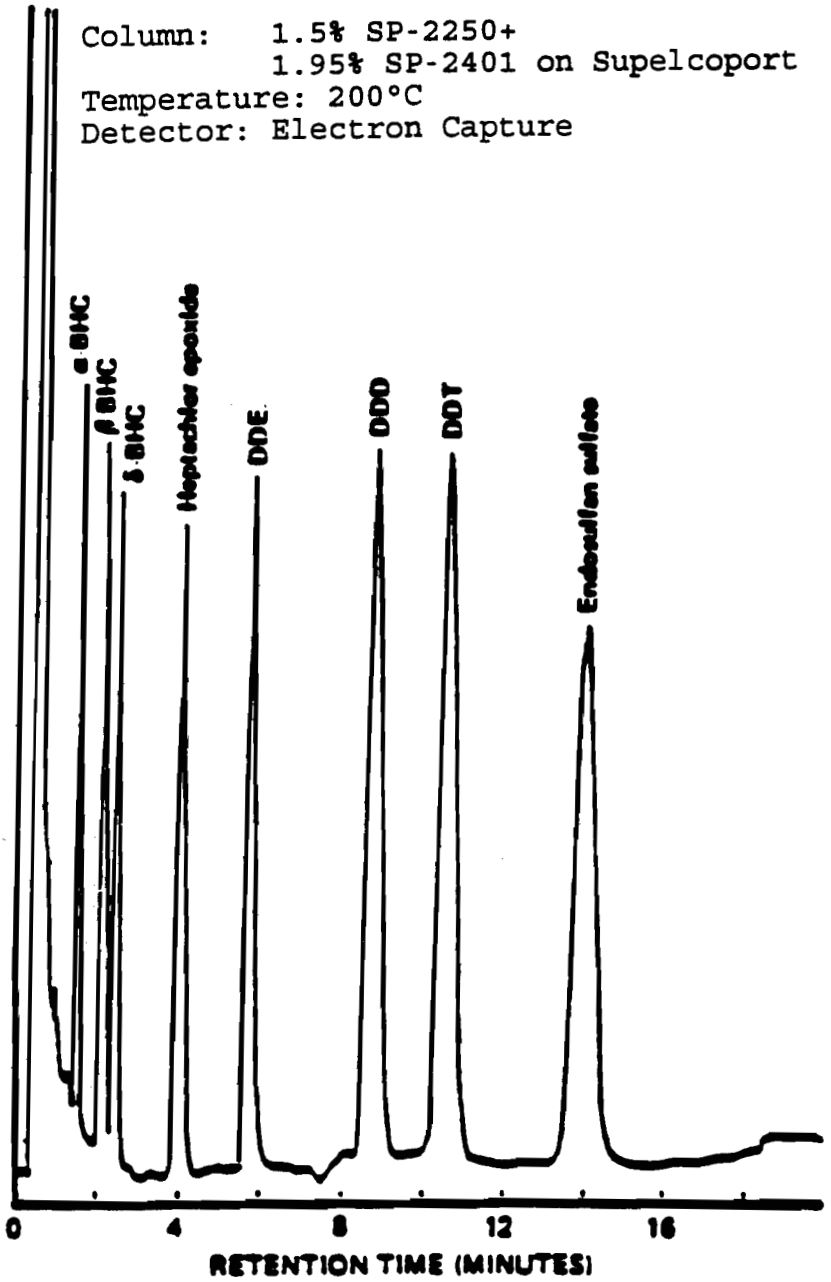


Figure 2
Gas Chromatogram of Chlordane

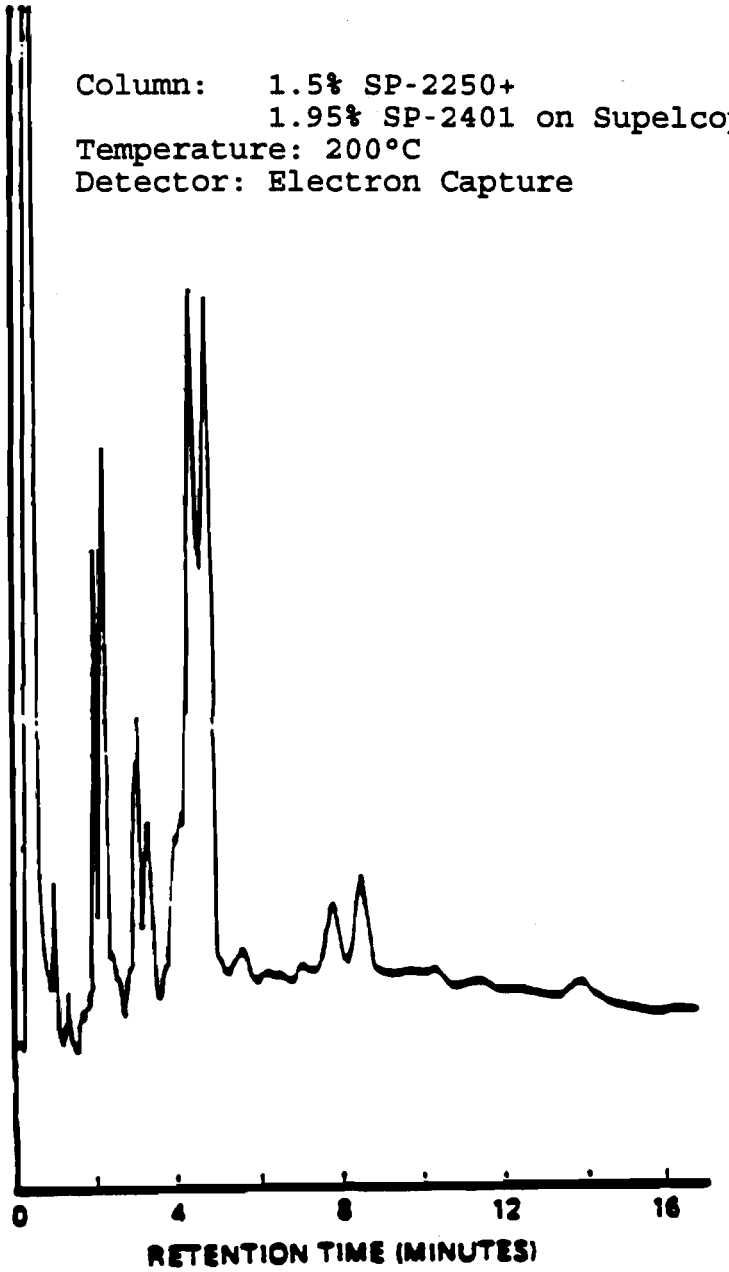


Figure 3
Gas Chromatogram of Toxaphene

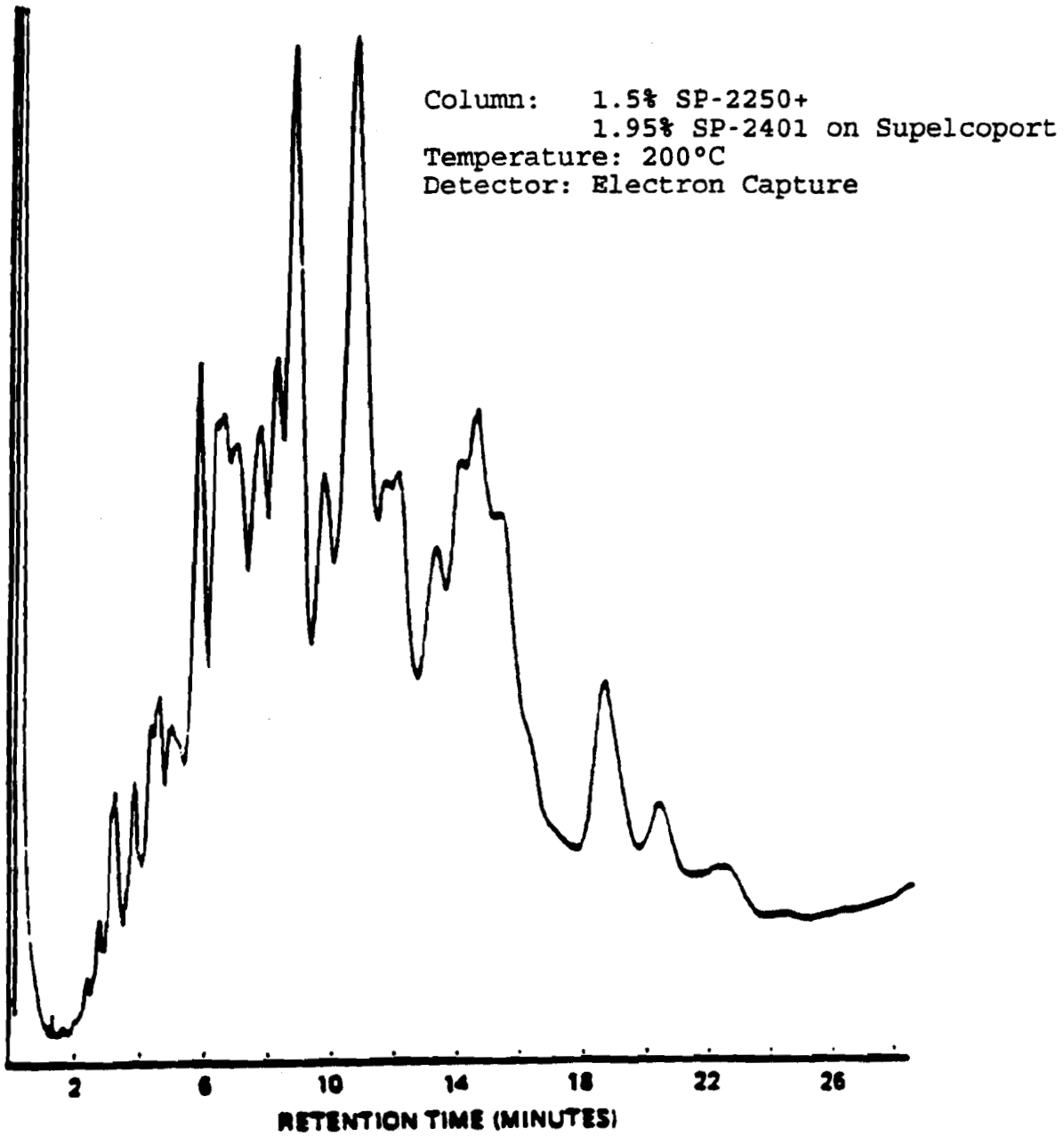


Figure 4
Gas Chromatogram of Aroclor 1254

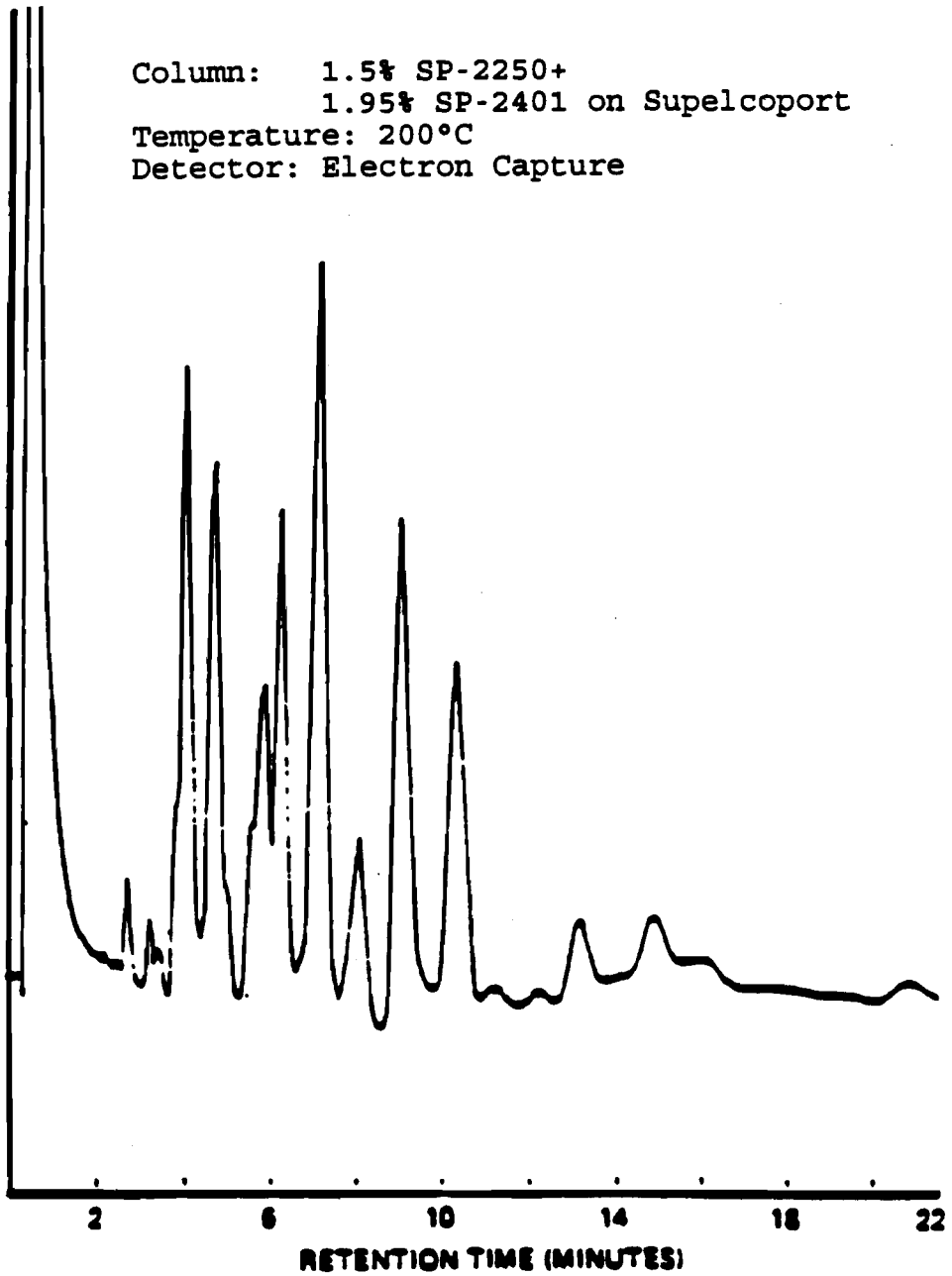


Figure 5
Gas Chromatogram of Aroclor 1260

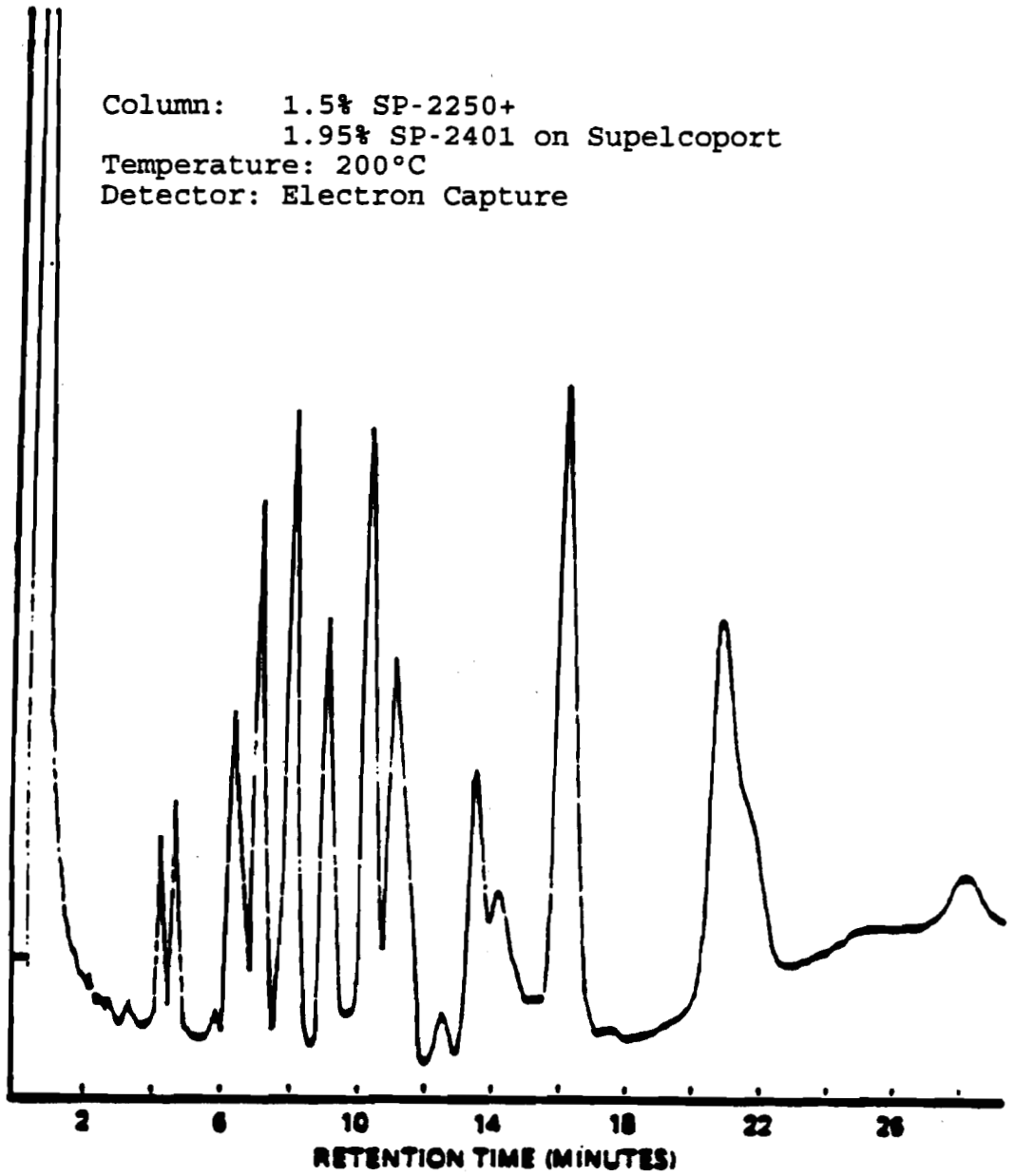


Figure 6

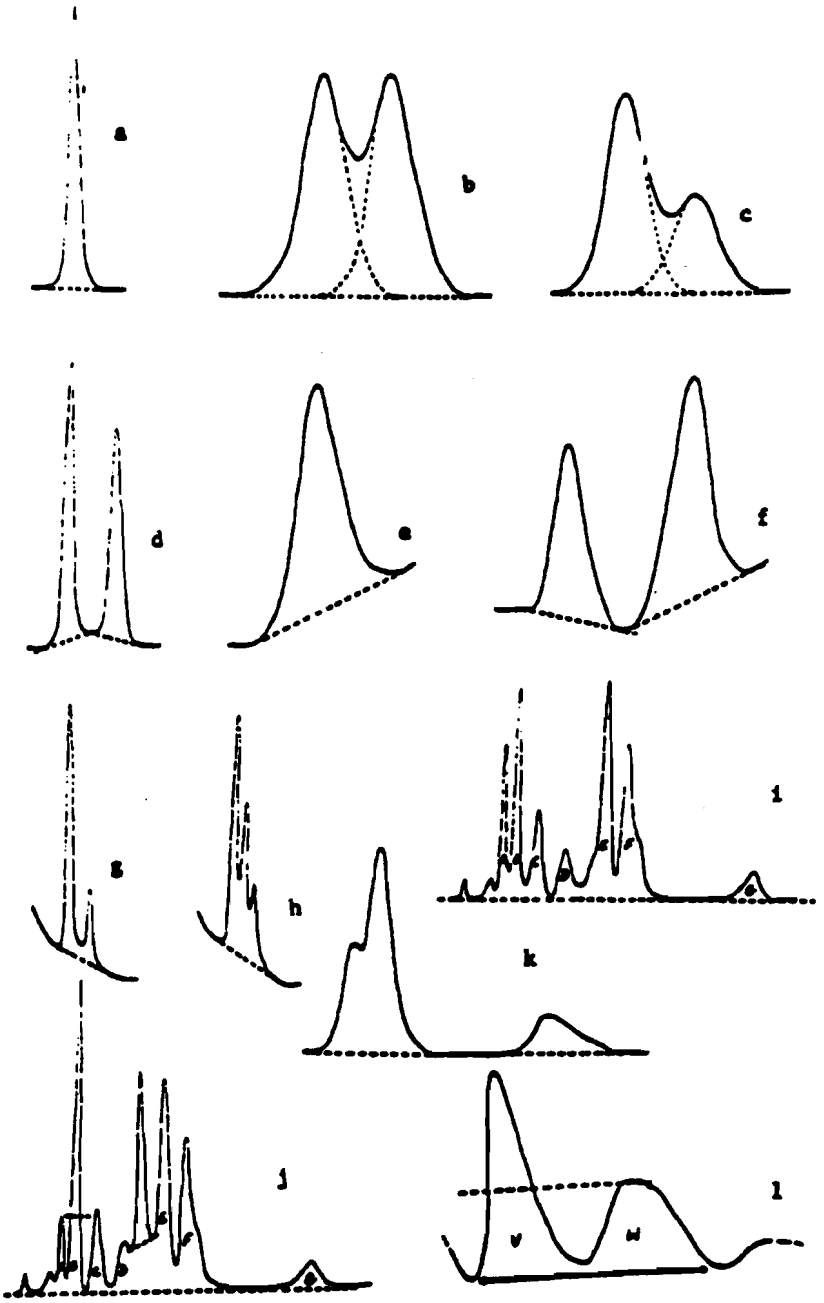


Fig.6--Baseline construction for some typical gas chromotagraphic peaks. a: symmetrical separated flat baseline; b and c: overlapp flat baseline; d: separated (pen does not return to baseline between peaks); e: separated sloping baseline; f: separated (pen goes below baseline between peaks); g: α- and γ-BHC sloping baseline; h: α-,β- and γ-BHC sloping baseline; i: chlordane flat baseline; j: heptachlor and heptachlor epoxide superimposed on chlordane; k: chair-shaped peaks, unsymmetrical peak; l: p,p'-DDT superimposed on toxaphene.

Figure 7

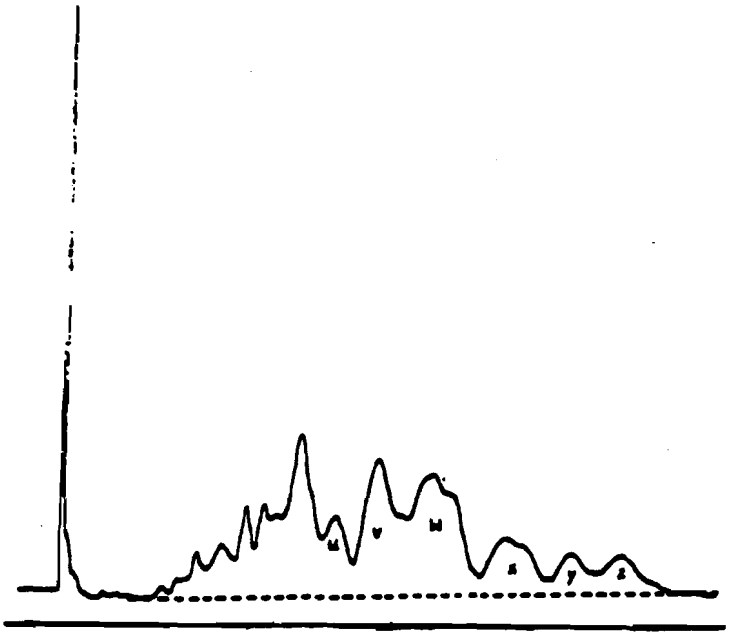


Fig.- 7a -- Baseline construction for multiple residues with standard toxaphene.

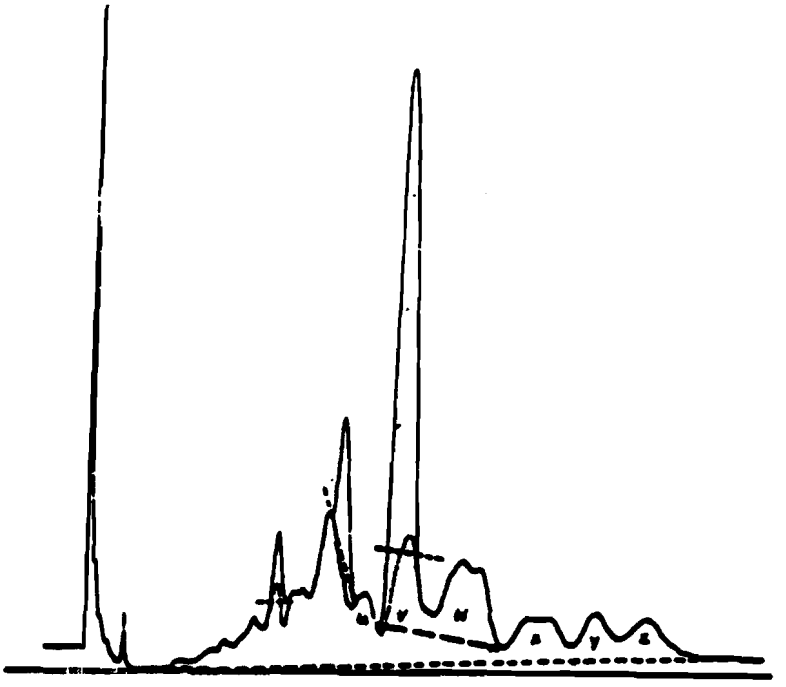


Fig.- 7b -- Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT

Figure 8

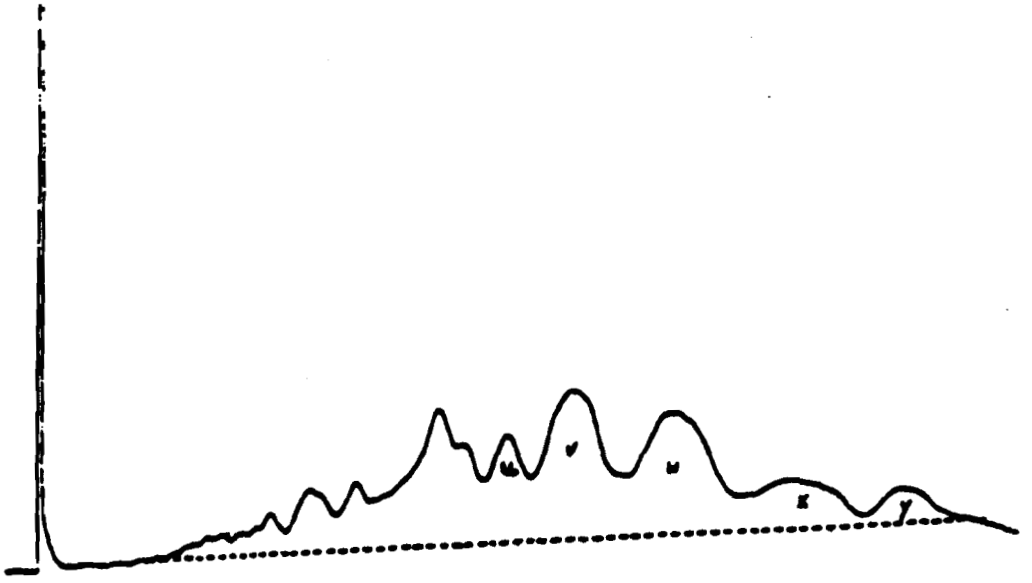


Fig.- 8a -- Baseline construction for multiple residues: standard toxaphene.

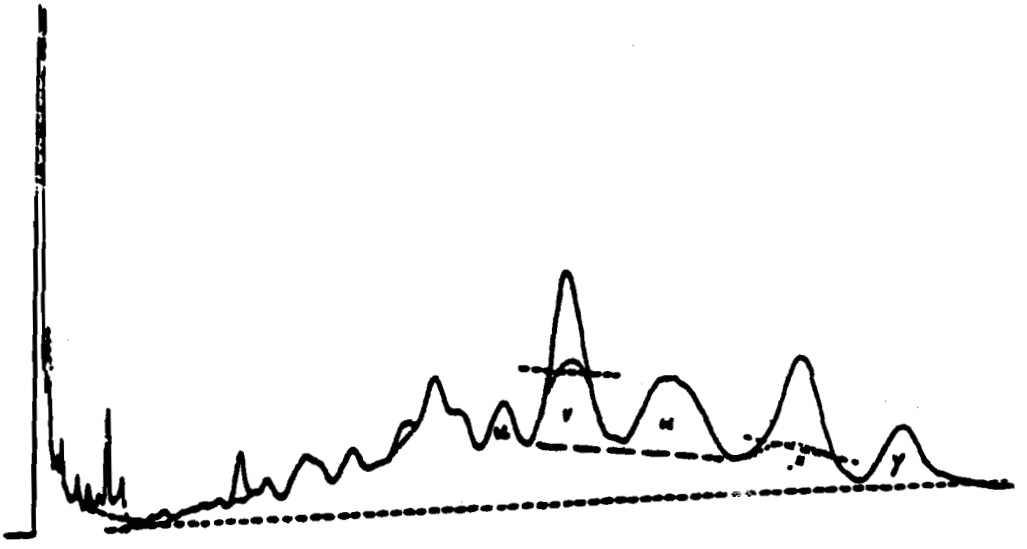


Fig.- 8b -- Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

Figure 9

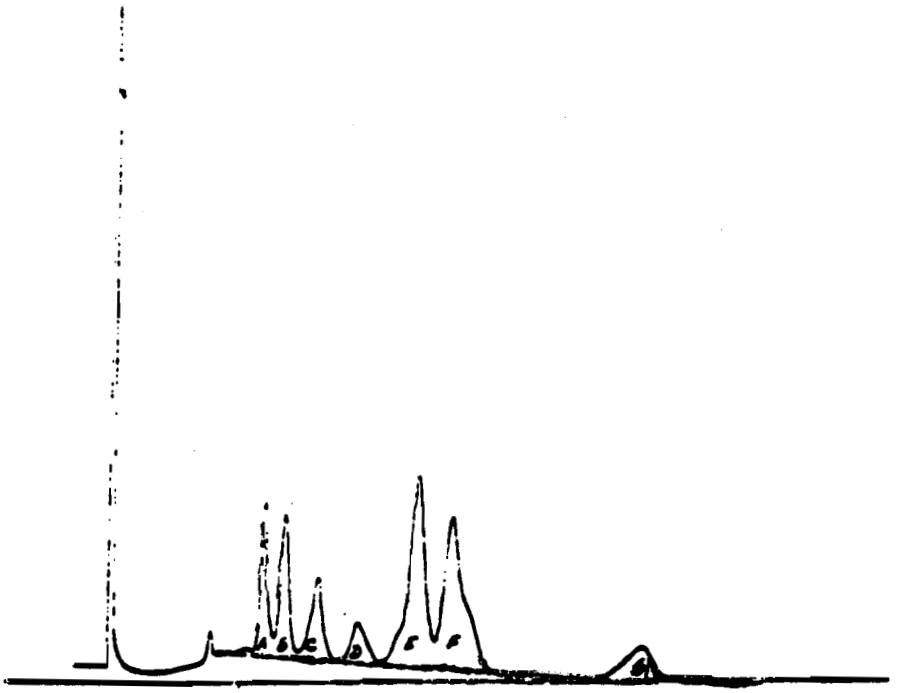


Fig.- 9a -- Baseline construction for multiple residues: standard chlordane.

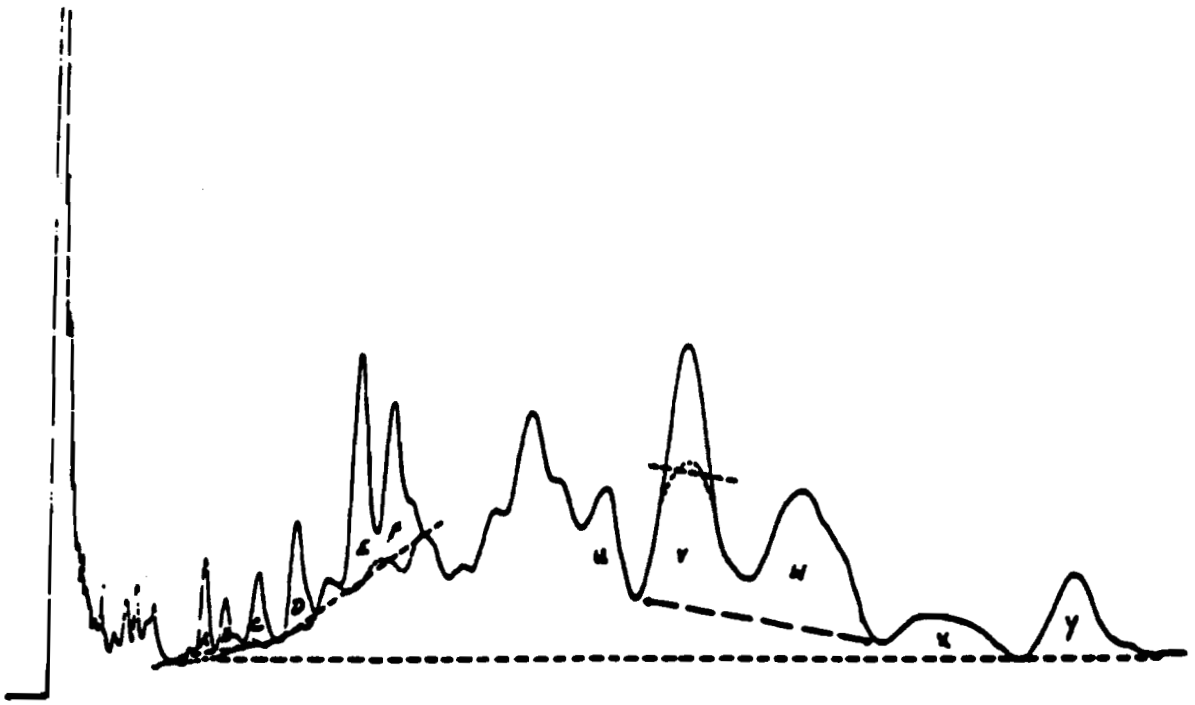
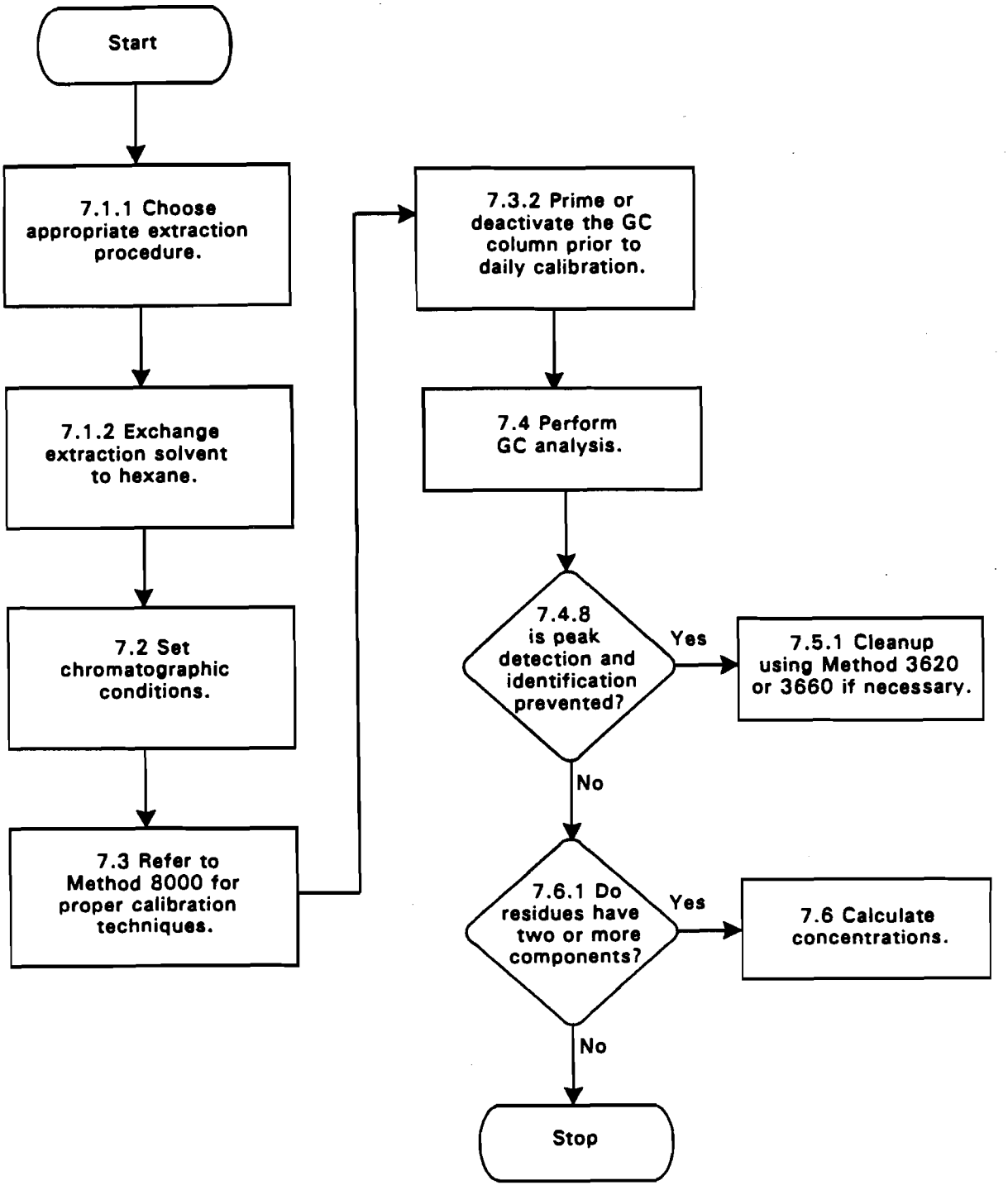


Fig.- 9b -- Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.


Start
7.1.1 Choose appropriate extraction procedure.
7.1.2 Exchange extraction solvent to hexane.
7.2 Set chromatographic conditions.
7.3 Refer to Method 8000 for proper calibration techniques.
7.3.2 Prime or deactivate the GC column prior to daily calibration.
7.4 Perform GC analysis.
7.4.8 is peak detection and identification prevented?
Yes
7.5.1 Cleanup using Method 3620 or 3660 if necessary.
No
7.6.1 Do residues have two or more components?
Yes
7.6 Calculate concentrations.
No
Stop

METHOD 8081

ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides and polychlorinated biphenyls (PCBs) as Aroclors, in extracts from solid and liquid matrices. Open-tubular, capillary columns were employed with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). When compared to the packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The list below is annotated to show whether a single- or dual-column analysis system was used to identify each target analyte.

Compound Name	CAS Registry No.
Aldrin[a,b]	309-00-2
Aroclor-1016[a,b]	12674-11-2
Aroclor-1221[a,b]	1104-28-2
Aroclor-1232[a,b]	11141-16-5
Aroclor-1242[a,b]	53469-21-9
Aroclor-1248[a,b]	12672-29-6
Aroclor-1254[a,b]	11097-69-1
Aroclor-1260[a,b]	11096-82-5
α-BHC[a,b]	319-84-6
β-BHC[a,b]	319-85-7
γ-BHC (Lindane)[a,b]	58-89-9
δ-BHC[a,b]	319-86-8
Chlorobenzilate[b]	510-15-6
α-Chlordane[b]	5103-71-9
γ-Chlordane[a,b]	5103-74-2
DBCP[b]	96-12-8
4,4′-DDD[a,b]	72-54-8
4,4′-DDE[a,b]	72-55-9
4,4′-DDT[a,b]	50-29-3
Diallate[b]	2303-16-4
Dieldrin[a,b]	60-57-1
Endosulfan I[a,b]	959-98-8
Endosulfan II[a,b]	33213-65-9
Endosulfan sulfate[a,b]	1031-07-8
Endrin[a,b]	72-20-8
Endrin aldehyde[a,b]	7421-93-4
Endrin ketone[b]	53494-70-5

Compound Name	CAS Registry No.
Heptachlor[a,b]	76-44-8
Heptachlor epoxide[a,b]	1024-57-3
Hexachlorobenzene[b]	118-74-1
Hexachlorocyclopentadiene[b]	77-47-4
Isodrin[b]	465-73-6
Kepone[b]	143-50-0
Methoxychlor[a,b]	72-43-5
Toxaphene[a,b]	8001-35-2

[a] Single-column analysis
[b] Dual-column analysis

1.2 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.).

1.3 Although performance data are presented for many of the listed chemicals, it is unlikely that all of them could be determined in a single analysis. This limitation results because the chemical and chromatographic behavior of many of these chemicals can result in co-elution. Several cleanup/fractionation schemes are provided in this method and in Method 3600. Any chemical is a potential method interference when it is not a target analyte.

1.4 Several multi-component mixtures (i.e., Aroclors and Toxaphene) are listed as target compounds. When samples contain more than one multi-component analyte, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in "weathered" Aroclors (or any other multi-component mixtures) that may have significant differences in peak patterns than those of standards. In these cases, individual congener analyses may be preferred over total mixture analyses.

1.5 Compound identification based on single column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique if sensitivity permits (Sec. 8).

1.6 This method describes a dual column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual column analysis.

Analysts are cautioned that the dual column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when contaminated samples are analyzed.

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.8 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141). Some extracts may also be suitable for triazine herbicide analysis, if low recoveries (normally samples taken for triazine analysis must be preserved) are not a problem.

1.9 The following compounds may also be determined using this method:

Compound Name	CAS Registry No.
Alachlor[a,b]	15972-60-8
Captafol[b]	2425-06-1
Captan[b]	133-06-2
Chloroneb[b]	2675-77-6
Chloropropylate[b]	99516-95-7
Chlorothalonil[b]	1897-45-6
DCPA[b]	1861-32-1
Dichlone[b]	117-80-6
Dicofol[b]	115-32-2
Etridiazole[b]	2593-15-9
Halowax-1000[b]	58718-66-4
Halowax-1001[b]	58718-67-5
Halowax-1013[b]	12616-35-2
Halowax-1014[b]	12616-36-3
Halowax-1051[b]	2234-13-1
Halowax-1099[b]	39450-05-0
Mirex[b]	2385-85-5
Nitrofen[b]	1836-75-5
PCNB[b]	82-68-8
Perthane[b]	72-56-0
Propachlor[b]	1918-16-17
Strobane[b]	8001-50-1
trans-Nonachlor[b]	39765-80-5
trans-Permethrin[b]	51877-74-8
Trifluralin[b]	1582-09-8

[a] Single-column analysis
[b] Dual-column analysis

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate sample extraction technique. Liquid samples are extracted at neutral pH with methylene chloride using either a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using either Soxhlet extraction (Method 3540), Automated Soxhlet (Method 3541), or Ultrasonic Extraction (Method 3550). A variety of cleanup steps may be applied to the extract, depending on (1) the nature of the coextracted matrix interferences and (2) the target analytes. After cleanup, the extract is analyzed by injecting a 1-μL sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3, in particular), 3600, and 8000.

3.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials may be removed prior to analysis using Gel Permeation Cleanup - pesticide option (Method 3640) or as Fraction III of the silica gel cleanup procedure (Method 3630). Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry in an oven at 130°C for several hours or rinse with methanol and drain. Store dry glassware in a clean environment.

3.5 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur

contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur. Since the recovery of Endrin aldehyde (using the TBA procedure) is drastically reduced, this compound must be determined prior to sulfur cleanup.

3.6 Waxes, lipids, and other high molecular weight co-extractables can be removed by Gel-Permeation Cleanup (Method 3640).

3.7 It may be difficult to quantitate Aroclor patterns and single component pesticides together. Some pesticides can be removed by sulfuric acid/permanganate cleanup (Method 3665) and silica fractionation (Method 3630). Guidance on the identification of PCBs is given in Sec. 7.

3.8 The following target analytes coelute using single column analysis:

DB 608	Trifluralin/Diallate isomers PCNP/Dichlone/Isodrin DDD/Endosulfan II
DB 1701	Captan/Chlorobenzilate Captafol/Mirex DDD/Endosulfan II Methoxychlor/Endosulfan sulfate

3.8.1 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Certain co-eluting organophosphorus pesticides are eliminated by the Gel Permeation Chromatography cleanup - pesticide option (Method 3640). Co-eluting chlorophenols are eliminated by Silica gel (Method 3630), Florisil (Method 3620), or Alumina (Method 3610) cleanup.

3.9 The following compounds coelute using the dual column analysis. Two temperature programs are provided for the same pair of columns as option 1 and option 2 for dual column analysis. In general, the DB-5 column resolves fewer compounds that the DB-1701:

3.9.1 DB-5/DB-1701, thin film, slow ramp: See Sec. 7 and Table 6.

DB-5 *trans*-Permethrin/Heptachlor epoxide
Endosulfan I/α-Chlordane
Perthane/Endrin
Endosulfan II/Chloropropylate/Chlorobenzilate
4,4'-DDT/Endosulfan sulfate
Methoxychlor/Dicofol

Perthane/Endrin and Chlorobenzilate/Endosulfan II/Chloropropylate will also co-elute on DB-5 after moderate deterioration in column performance.

DB-1701	Chlorothalonil/ß-BHC δ-BHC/DCPA/*trans*-Permethrin α-Chlordane/*trans*-Nonachlor Captan/Dieldrin Chlorobenzilate/Chloropropylate

Chlorothalonil/ß-BHC and α-Chlordane/*trans*-Nonachlor will co-elute on the DB-1701 column after moderate deterioration in column performance.

Nitrofen, Dichlone, Carbophenothion, Dichloran and Kepone were removed from the composite mixture because of extensive peak tailing on both columns. Simazine and Atrazine give poor responses on the ECD detector. Triazine compounds should be analyzed using Method 8141 (NPD option).

3.9.2 DB-5/DB-1701, thick film, fast ramp: See Sec. 7 and Table 7.

DB-5	Diallate/α-BHC Perthane/Endosulfan II Chlorobenzilate/Chloropropylate Endrin/Nitrofen 4,4'-DDT/Endosulfan sulfate Methoxychlor/Dicolfol
DB-1701	α-Chlordane/*trans*-Nonachlor (partially resolved) 4,4'-DDD/Endosulfan II (partially resolved)

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: an analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.

The columns listed in this section were used to develop the method performance data. Their specification is not intended to prevent laboratories from using columns that are developed after promulgation of the method. Laboratories may use other capillary columns if they document method performance data (e.g. chromatographic resolution, analyte breakdown, and MDLs) equal to or better than those provided with the method.

4.1.1 Single-column Analysis:

4.1.1.1 Narrow-bore columns:

4.1.1.1.1 Column 1 - 30 m x 0.25 or 0.32 mm internal diameter (ID) fused silica capillary column chemically bonded with SE-54 (DB 5 or equivalent), 1 μm film thickness.

4.1.1.1.2 Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl

methylpolysiloxane (DB 608, SPB 608, or equivalent), 25 µm coating thickness, 1 µm film thickness.

4.1.1.1.3 Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.1.1.2 Wide-bore columns

4.1.1.2.1 Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

4.1.1.2.2 Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB 1701, or equivalent), 1.0 µm film thickness.

4.1.1.2.3 Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB 5, SPB 5, RTx5, or equivalent), 1.5 µm film thickness.

4.1.1.2.4 Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.1.2 Dual Column Analysis:

4.1.2.1 Column pair 1:

4.1.2.1.1 J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733) or Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405), or equivalent.

4.1.2.1.2 30 m x 0.53 m ID DB-5 (J&W Scientific), 1.5 µm film thickness, or equivalent.

4.1.2.1.3 30 m x 0.53 mm ID DB-1701 (J&W Scientific), 1.0 µm film thickness, or equivalent.

4.1.2.2 Column pair 2:

4.1.2.2.1 Splitter 2 - Supelco 8 in. glass injection tee, deactivated (Supelco, Catalog no. 2-3665M), or equivalent.

4.1.2.2.2 30 m x 0.53 m ID DB-5 (J&W Scientific), 0.83 µm film thickness, or equivalent.

4.1.2.2.3 30 m x 0.53 mm ID DB-1701 (J&W Scientific), 1.0 µm film thickness, or equivalent.

4.1.3 Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.2 Glassware (see Methods 3510, 3520, 3540, 3541, 3550, 3630, 3640, 3660, and 3665 for specifications).

4.3 Kuderna-Danish (K-D) apparatus. See extraction methods for specifics.

5.0 REAGENTS

5.1 Reagent or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC (Sec. 8) indicates a problem. All other standard solutions must be replaced after six months or sooner if routine QC (Sec. 8) indicates a problem.

5.2 Solvents and reagents: As appropriate for Method 3510, 3520, 3540, 3541, 3550, 3630, 3640, 3660, or 3665: n-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free. Solvents must be exchanged to hexane or isooctane prior to analysis.

5.2.1 Organic-free reagent water: All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L): Can be prepared from pure standard materials or can be purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 ß-BHC, Dieldrin, and some other standards may not be adequately soluble in isooctane. A small amount of acetone or toluene should be used to dissolve these compounds during the preparation of the stock standard solutions.

5.4 Composite stock standard: Can be prepared from individual stock solutions. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 1 mg/25 mL. This composite solution can be further diluted to obtain the desired concentrations. For composite stock standards containing more than 25 components, use volumetric flasks of the appropriate volume (e.g., 50 mL, 100 mL).

5.5 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.5.1 Although all single component analytes can be resolved on a new 35 percent phenyl methyl silicone column (e.g., DB-608), two calibration mixtures should be prepared for the single component analytes of this method.

5.5.2 This procedure is established to (1) minimize potential resolution and quantitation problems on confirmation columns or on older 35 percent phenyl methyl silicone (e.g. DB-608) columns and (2) allow determination of Endrin and DDT breakdown for method QC (Sec. 8).

5.5.3 Separate calibration standards are required for each multi-component target analyte, with the exception of Aroclors 1016 and 1260, which can be run as a mixture.

5.6 Internal standard (optional):

5.6.1 Pentachloronitrobenzene is suggested as an internal standard for the single column analysis, when it is not considered to be a target analyte. 1-Bromo-2-nitrobenzene is a suggested option. Prepare the standard to complement the concentrations found in Sec. 5.5.

5.6.2 Make a solution of 1000 mg/L of 1-bromo-2-nitrobenzene for dual-column analysis. Dilute it to 500 ng/μL for spiking, then use a spiking volume of 10 μL/mL of extract.

5.7 Surrogate standards: The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards.

5.7.1 For the single column analysis, use decachlorobiphenyl as the primary surrogate. However, if recovery is low, or late-eluting compounds interfere with decachlorobiphenyl, then tetrachloro-m-xylene should be evaluated as a surrogate. Proceed with corrective action when both surrogates are out of limits for a sample (Sec. 8.2). Method 3500, Sec. 5, indicates the proper procedure for preparing these surrogates.

5.7.2 For the dual column analysis make a solution of 1000 mg/L of 4-chloro-3-nitrobenzotrifluoride and dilute to 500 ng/μL. Use a spiking volume of 100 μL for a 1 L aqueous sample. Store the spiking solutions at 4°C in Teflon-sealed containers in the dark.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 See Chapter 4, Organic Analytes, Sec. 4.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with hexane-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541) or ultrasonic extraction (Method 3550) procedures.

NOTE: Hexane/acetone (1:1) may be more effective as an extraction solvent for organochlorine pesticides and PCBs in some environmental and waste matrices than is methylene chloride/acetone (1:1). Use of hexane/acetone generally reduces the amount of co-extracted interferences and improves signal/noise.

7.1.2 Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample type must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample (Sec. 5). See Method 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 Cleanup/Fractionation:

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

7.2.1.1 If a sample is of biological origin, or contains high molecular weight materials, the use of GPC cleanup/pesticide option (Method 3640) is recommended. Frequently, one of the

adsorption chromatographic cleanups may also be required following the GPC cleanup.

7.2.1.2 If only PCBs are to be measured in a sample, the sulfuric acid/permanganate cleanup (Method 3665) is recommended. Additional cleanup/fractionation by Alumina Cleanup (Method 3610), Silica-Gel Cleanup (Method 3630), or Florisil Cleanup (Method 3620), may be necessary.

7.2.1.3 If both PCBs and pesticides are to be measured in the sample, isolation of the PCB fraction by Silica Cleanup (Method 3630) is recommended.

7.2.1.4 If only pesticides are to be measured, cleanup by Method 3620 or Method 3630 is recommended.

7.2.1.5 Elemental sulfur, which may appear in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660, Sulfur Cleanup.

7.3 GC Conditions: This method allows the analyst to choose between a single column or a dual column configuration in the injector port. Either wide- or narrow-bore columns may be used. Identifications based on retention times from a single column must be confirmed on a second column or with an alternative qualitative technique.

7.3.1 Single Column Analysis:

7.3.1.1 This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow-bore) or 0.53 mm ID capillary columns (wide-bore). Performance data are provided for both options. Figures 1-6 provide example chromatograms.

7.3.1.2 The use of narrow-bore columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm) are suitable for more complex environmental and waste matrices.

7.3.1.3 For the single column method of analysis, using wide-bore capillary columns, Table 1 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices. For the single column method of analysis, using narrow-bore capillary columns, Table 2 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices. The MDLs for the components of a specific sample may differ from those listed in Tables 1 and 2 because they are dependent upon the nature of interferences in the sample matrix. Table 3 lists the Estimated Quantitation Limits (EQLs) for other matrices. Table 4 lists the GC operating conditions for the single column method of analysis.

7.3.2 Dual Column Analysis:

7.3.2.1 The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors. Retention times for the organochlorine analytes on dual columns are in Table 5. The GC operating conditions for the compounds in Table 5 are in Table 6. Multicomponent mixtures of Toxaphene and Strobane were analyzed separately (Figures 7 and 8) using the GC operating conditions found in Table 7. Seven Aroclor mixtures and six Halowax mixtures were analyzed under the conditions outlined in Table 7 (Figures 9 through 21). Figure 22 is a sample chromatogram for a mixture of organochlorine pesticides. The retention times of the individual components detected in these mixtures are given in Tables 8 and 9.

7.3.2.1.1 Operating conditions for a more heavily loaded DB-5/DB-1701 pair are given in Table 7. This column pair was used for the detection of multicomponent organochlorine compounds.

7.3.2.1.2 Operating conditions for a DB-5/DB-1701 column pair with thinner films, a different type of splitter, and a slower temperature programming rate are provided in Table 6. These conditions gave better peak shapes for compounds such as Nitrofen and Dicofol. Table 5 lists the retention times for the compounds detected on this column pair.

7.4 Calibration:

7.4.1 Prepare calibration standards using the procedures in Sec. 5. Refer to Method 8000 (Sec. 7) for proper calibration techniques for both initial calibration and calibration verification. The procedure for either internal or external calibration may be used, however, in most cases external standard calibration is used with Method 8081. This is because of the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may co-elute on any single column, analysts should use two calibration mixtures (see Sec. 3.8). The specific mixture should be selected to minimize the problem of peak overlap.

<u>NOTE</u>: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.1.1 Method 8081 has many multi-component target analytes. For this reason, the target analytes chosen for calibration should be limited to those specified in the project plan. For instance, some sites may require analysis for the organochlorine pesticides only or the PCBs only. Toxaphene and/or technical Chlordane may not be specified at certain sites. In addition, where PCBs are specified in the project plan, a mixture of

Aroclors 1016 and 1260 will suffice for the initial calibration of all Aroclors, since they include all congeners present in the different regulated Aroclors. A mid-point calibration standard of all Aroclors (for Aroclor pattern recognition) must be included with the initial calibration so that the analyst is familiar with each Aroclor pattern and retention times on each column.

7.4.1.2 For calibration verification (each 12 hr shift) all target analytes required in the project plan must be injected with the following exception for the Aroclors. For sites that require PCB analysis, include only the Aroclors that are expected to be found at the site. If PCBs are required, but it is unknown which Aroclors may be present, the mid-concentration Aroclors 1016/1260 mixture only, may be injected. However, if specific Aroclors are found at the site during the initial screening, it is required that the samples containing Aroclors be reinjected with the proper mid-concentration Aroclor standards.

7.4.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

CAUTION: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

7.4.3 Retention time windows:

7.4.3.1 Before establishing the retention time windows, make sure the gas chromatographic system is within optimum operating conditions. The width of the retention time window should be based upon actual retention times of standards measured over the course of 72 hours. See Method 8000 for details.

7.4.3.2 Retention time windows shall be defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of the chromatograms. For multicomponent standards (i.e., PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition. Sec. 7.5.4 provides guidance on the establishment of absolute retention time windows.

7.4.3.3 Certain analytes, particularly Kepone, are subject to changes in retention times. Dry Kepone standards prepared in hexane or isooctane can produce gaussian peaks. However, Kepone extracted from samples or standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard (0-1 minute). This shift is presumably the result of the formation

of a hemi-acetal from the ketone functionality. Method 8270 is recommended for Kepone.

7.5 Gas chromatographic analysis:

7.5.1 Set up the GC system using the conditions described in Tables 4, 6, or 7. An initial oven temperature at or below 140-150°C is required to resolve the four BHC isomers. A final temperature of 240-270°C is required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

7.5.2 Verify calibration each 12 hour shift by injecting calibration verification standards prior to conducting any analyses. See Sec. 7.4.1.2 for special guidance on calibration verification of PCBs. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated must not exceed a ±15 percent difference when compared to the initial calibration curve. When this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements (Sec. 8.2) based on the last initial calibration, then a new initial calibration must be performed.

7.5.2.1 Analysts should use high and low concentrations of mixtures of single-component analytes and multi-component analytes for calibration verification.

7.5.3 Sample injection may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is recommended that standards be analyzed after every 10 (required after every 20 samples), and at the end of a set. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.5.3.1 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12 hr shift), or calibration standards interspersed within the samples. All samples that were injected after the standard that last met the QC criteria must be reinjected.

7.5.3.2 Although analysis of a single mid-concentration standard (standard mixture or multi-component analyte) will satisfy the minimum requirements, analysts are urged to use different calibration verification standards during organochlorine pesticide/PCB analyses. Also, multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

7.5.4 Establish absolute retention time windows for each analyte. Use the absolute retention time for each analyte from standards analyzed during that 12 hour shift as the midpoint of the window. The daily retention time window equals the midpoint ± three times the standard deviations.

7.5.4.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

7.5.4.2 Validation of gas chromatographic system qualitative performance: Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.5.5 Record the volume injected to the nearest 0.05 µL and the resulting peak size in area units. Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.5.5.1 If the responses exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.5.5.2 If partially overlapping or coeluting peaks are found, change columns or try GC/MS quantitation, see Sec. 8 and Method 8270.

7.5.5.3 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5.6 Identification of mixtures (i.e. PCBs and Toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures.

7.5.7 Quantitation of the target compounds is based on: 1) a reproducible response of the ECD or ELCD within the calibration range; and 2) a direct proportionality between the magnitude of response of the detector to peaks in the sample extract and the calibration standards. Proper quantitation requires the appropriate selection of a baseline from which the area or height of the characteristic peak(s) can be determined.

7.5.8 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.6 Quantitation of Multiple Component Analytes:

7.6.1 Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handing Toxaphene, Chlordane, PCBs, DDT, and BHC.

7.6.2 Toxaphene: Toxaphene is manufactured by the chlorination of camphenes, whereas Strobane results from the chlorination of a mixture of camphenes and pinenes. Quantitative calculation of Toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate Toxaphene on GC/ECD: (a) adjust the sample size so that the major Toxaphene peaks are 10-70% of full-scale deflection (FSD); (b) inject a Toxaphene standard that is estimated to be within $\pm$10 ng of the sample; (c) quantitate using the five major peaks or the total area of the Toxaphene pattern.

7.6.2.1 To measure total area, construct the baseline of standard Toxaphene between its extremities; and construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide. This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard.

7.6.2.2 A series of Toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the area of the last four peaks only, in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating Toxaphene in a sample where the early eluting portion of the Toxaphene chromatogram shows interferences from other substances such as DDT.

7.6.3 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. *Trans*- and *cis*-Chlordane (α and γ, respectively), are the two major components of technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

7.6.3.1 The GC pattern of a Chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of Chlordane can consist of almost any combination of: constituents from the technical Chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

7.6.3.2 Whenever possible, when a Chlordane residue does not resemble technical Chlordane, the analyst should quantitate the peaks of α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report the individual residues.

7.6.3.3 When the GC pattern of the residue resembles that of technical Chlordane, the analyst may quantitate Chlordane residues by comparing the total area of the Chlordane chromatogram using the five major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation of the residue. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area. (Note that octachloro epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.)

7.6.3.4 To measure the total area of the Chlordane chromatogram, inject an amount of technical Chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

7.6.4 Polychlorinated biphenyls (PCBs): Quantitation of residues of PCBs involves problems similar to those encountered in the quantitation of Toxaphene, Strobane, and Chlordane. In each case, the material is made up of numerous compounds which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.

7.6.4.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish. The Aroclors most commonly found in the environment are 1242, 1254, and 1260.

7.6.4.2 PCB residues are generally quantitated by comparison to the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.6.4.3 PCB Quantitation option #1- Quantitate the PCB residues by comparing the total area of the chlorinated biphenyl peaks to the total area of peaks from the appropriate Aroclor reference material. Measure the total area or height response from the common baseline under all the peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. Option #1 should not be used if there are interference peaks within the Aroclor pattern, especially if they overlap PCB congeners.

7.6.4.4 PCB Quantitation option #2- Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using an individual response factor for each of the major peaks. The results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. Late-eluting Aroclor peaks are generally the most stable in the environment.

7.6.4.5 When samples appear to contain weathered PCBs, treated PCBs, or mixtures of Aroclors, the use of Aroclor standards is not appropriate. Several diagnostic peaks useful for identifying non-Aroclor PCBs are given in Table 10. Analysts should examine chromatograms containing these peaks carefully, as these samples may contain PCBs. PCB concentrations may be estimated from specific congeners by adding the concentration of the congener peaks listed in Table 11. The congeners are analyzed as single components. This approach will provide reasonable accuracy for Aroclors 1016, 1232, 1242 and 1248 but will underestimate the concentrations of Aroclors 1254, 1260 and 1221. It is highly recommended that heavily weathered, treated, or mixed Aroclors be analyzed using GC/MS if concentration permits.

7.6.5 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

7.6.6 DDT: Technical DDT consists primarily of a mixture of 4,4′-DDT (approximately 75%) and 2,4′-DDT (approximately 25%). As DDT weathers, 4,4′-DDE, 2,4′-DDE, 4,4′-DDD, and 2,4′-DDD are formed. Since the 4,4′-isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by US EPA and should be quantitated against standards of the respective pure isomer.

7.7 Suggested chromatography maintenance: Corrective measures may require any one or more of the following remedial actions.

7.7.1 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector (J&W Scientific or Restek), clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.7.1.1 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to Endrin aldehyde, Endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 0.5 M of the column and remount it. Check the injector temperature and lower it to 205°C, if required. Endrin and DDT breakdown is less of a problem when ambient on-column injectors are used.

7.7.2 Metal injector body: Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catch the rinsate in the beaker.

7.7.2.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, rinse the injector body with toluene, methanol, acetone, then hexane. Reassemble the injector and replace the columns.

7.7.3 Column rinsing: The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone; methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures including matrix spikes, duplicates and blanks. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If an extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control requirements for the GC system, including calibration and corrective actions, are found in Method 8000. The following steps are recommended as additional method QC.

8.2.1 The QC Reference Sample concentrate (Method 3500) should contain the organochlorine pesticides at 10 mg/L for water samples. If this method is to be used for analysis of Aroclors, Chlordane, or Toxaphene only, the QC Reference Sample should contain the most representative multi-component mixture at a concentration of 50 mg/L in acetone. The frequency of analysis of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples. If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.2.2 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

If recovery is not within limits, the following are required:

8.2.2.1 Confirm that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.2.2.2 Examine chromatograms for interfering peaks and for integrated areas.

8.2.2.3 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.2.2.4 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.2.3 Include a calibration standard after each group of 20 samples (it is recommended that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.2.4 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.3 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding with calibration.

8.3.1 Calculate percent breakdown as follows:

$$\text{\% breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{peak areas (DDT + DDE + DDD)}} \times 100$$

$$\text{\% breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (Endrin aldehyde + Endrin ketone)}}{\text{peak areas (Endrin + aldehyde + ketone)}} \times 100$$

8.3.2 The breakdown of DDT and Endrin should be measured before samples are analyzed and at the beginning of each 12 hour shift. Injector maintenance and recalibration should be completed if the breakdown is greater than 15% for either compound (Sec. 8.2.3).

8.4 GC/MS confirmation may be used for single column analysis. In addition, any compounds confirmed by two columns should also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS.

8.4.1 Full-scan GC/MS will normally require a minimum concentration near 10 ng/μL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a minimum concentration near 1 ng/μL.

8.4.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis.

8.4.3 GC/MS may not be used for single column confirmation when concentrations are below 1 ng/μL.

8.4.4 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the associated blank.

8.4.5 Use of the base/neutral-acid extract and associated blank may be used if the surrogates and internal standards do not interfere and it is demonstrated that the analyte is stable during acid/base partitioning. However, if the compounds are not detected in the base/neutral-acid extract even though the concentrations are high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.6 A QC reference sample of the compound must also be analyzed by GC/MS. The concentration of the QC reference standard must demonstrate the ability to confirm the pesticides/Aroclors identified by GC/ECD.

8.5 Whenever silica gel (Method 3630) or Florisil (Method 3620) cleanup is used, the analyst must demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel material or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides and PCBs. When compounds are found in two fractions, add the concentrations in the fractions, and corrections for any additional dilution.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Tables 1 and 2 were obtained using organic-free reagent water and sandy loam soil.

9.2 The chromatographic separations in this method have been tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix.

9.3 This method has been applied in a variety of commercial laboratories for environmental and waste matrices. Performance data were obtained for a limited number of target analytes spiked into sewage sludge and dichloroethene still bottoms at high concentration levels. These data are provided in Tables 12 and 13.

9.4 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

9.5 Single laboratory accuracy data were obtained for organochlorine pesticides in a clay soil. The spiking concentration was 500 µg/kg. The spiking solution was mixed into the soil and then immediately transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data represent a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8081 for the organochlorine pesticides. These data are listed in Table 14 and were taken from Reference 14.

9.6 Single laboratory recovery data were obtained for PCBs in clay and soil. Oak Ridge National Laboratory spiked Aroclors 1254 and 1260 at concentrations of 5 and 50 ppm into portions of clay and soil samples and extracted these spiked samples using the procedure outlined in Method 3541. Multiple extractions using two different extractors were performed. The extracts were analyzed by Method 8081. The data are listed in Table 15 and were taken from Reference 15.

9.7 Multi-laboratory accuracy and precision data were obtained for PCBs in soil. Eight laboratories spiked Aroclors 1254 and 1260 into three portions of 10 g of Fuller's Earth on three non-consecutive days, followed by immediate extraction using Method 3541. Six of the laboratories spiked each Aroclor at 5 and 50 mg/kg and two laboratories spiked each Aroclor at 50 and 500 mg/kg. All extracts were analyzed by Oak Ridge National Laboratory, Oak Ridge, TN, using Method 8081. These data are listed in Table 16 and were taken from Reference 13.

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TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS USING WIDE-BORE CAPILLARY COLUMNS SINGLE COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[b]	DB 1701[b]	MDL[a] Water (µg/L)	MDL[a] Soil (µg/kg)
Aldrin	11.84	12.50	0.034	2.2
α-BHC	8.14	9.46	0.035	1.9
ß-BHC	9.86	13.58	0.023	3.3
δ-BHC	11.20	14.39	0.024	1.1
γ-BHC (Lindane)	9.52	10.84	0.025	2.0
α-Chlordane	15.24	16.48	0.008	
γ-Chlordane	14.63	16.20	0.037	1.5
4,4'-DDD	18.43	19.56	0.050	4.2
4,4'-DDE	16.34	16.76	0.058	2.5
4,4'-DDT	19.48	20.10	0.081	3.6
Dieldrin	16.41	17.32	0.044	NA
Endosulfan I	15.25	15.96	0.030	2.1
Endosulfan II	18.45	19.72	0.040	2.4
Endosulfan Sulfate	20.21	22.36	0.035	3.6
Endrin	17.80	18.06	0.039	3.6
Endrin aldehyde	19.72	21.18	0.050	1.6
Heptachlor	10.66	11.56	0.040	2.0
Heptachlor epoxide	13.97	15.03	0.032	2.1
Methoxychlor	22.80	22.34	0.086	5.7
Toxaphene	MR	MR	NA	NA
Aroclor-1016	MR	MR	0.054	57.0
Aroclor-1221	MR	MR	NA	NA
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Water = Organic-free reagent water.
Soil = Sandy loam soil.
MR = Multiple peak responses.
NA = Data not available.

[a] MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, silica gel cleanup, and GC/ECD analysis). MDL = t(n-1, 0.99) x SD, where t(n-1, 0.99) is the Student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.

[b] See Table 4 for GC operating conditions.

TABLE 2

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS USING NARROW-BORE CAPILLARY COLUMNS SINGLE COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[b]	DB 5[b]	MDL[a] Water (μg/L)	MDL[a] Soil (μg/kg)
Aldrin	14.51	14.70	0.034	2.2
α-BHC	11.43	10.94	0.035	1.9
ß-BHC	12.59	11.51	0.023	3.3
δ-BHC	13.69	12.20	0.024	1.1
γ-BHC (Lindane)	12.46	11.71	0.025	2.0
α-Chlordane				
γ-Chlordane	17.34	17.02	0.037	1.5
4,4'-DDD	21.67	20.11	0.050	4.2
4,4'-DDE	19.09	18.30	0.058	2.5
4,4'-DDT	23.13	21.84	0.081	3.6
Dieldrin	19.67	18.74	0.044	NA
Endosulfan I	18.27	17.62	0.030	2.1
Endosulfan II	22.17	20.11	0.040	2.4
Endosulfan sulfate	24.45	21.84	0.035	3.6
Endrin	21.37	19.73	0.039	3.6
Endrin aldehyde	23.78	20.85	0.050	1.6
Heptachlor	13.41	13.59	0.040	2.0
Heptachlor epoxide	16.62	16.05	0.032	2.1
Methoxychlor	28.65	24.43	NA	NA
Toxaphene	MR	MR	0.086	5.7
Aroclor-1016	MR	MR	NA	NA
Aroclor-1221	MR	MR	0.054	57.0
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Water = Organic-free reagent water.
Soil = Sandy loam soil.
MR = Multiple peak responses.
NA = Data not available.

TABLE 2
(Continued)

[a] MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, cleanup, and GC/ECD analysis). MDL = t(n-1, 0.99) x SD, where t(n-1, 0.99) is the Student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.

[b] 30 m x 0.25 mm ID DB-608 1 μm film thickness, see Table 4 for GC operating conditions.

[c] 30 m x 0.25 mm ID DB-5 1 μm film thickness, see Table 4 for GC operating conditions.

TABLE 3

DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a] EQL = [Method detection limit for water (see Table 1 or Table 2) wide-bore or narrow-bore options] x [Factor found in this table]. For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs to be determined herein are provided for guidance and may not always be achievable.

TABLE 4
GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE COLUMN ANALYSIS

Narrow-bore columns:

Narrow-bore Column 1 - 30 m x 0.25 or 0.32 mm internal diameter (ID) fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Narrow-bore Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 25 µm coating thickness, 1 µm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

Wide-bore columns:

Wide-bore Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Wide-bore Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Carrier gas (He)	5-7 mL/minute
Makeup gas	
argon/methane (P-5 or P-10) or N_2	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

(continued)

TABLE 4 (Continued)
GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE COLUMN ANALYSIS

Wide-bore Columns (continued)

Wide-bore Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 μm film thickness.

Carrier gas (He)	6 mL/minute
Makeup gas	
argon/methane (P-5 or P-10) or N_2	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 5
RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL COLUMN METHOD OF ANALYSIS

Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
DBCP	96-12-8	2.14	2.84
Hexachlorocyclopentadiene	77-47-4	4.49	4.88
Etridiazole	2593-15-9	6.38	8.42
Chloroneb	2675-77-6	7.46	10.60
Hexachlorobenzene	118-74-1	12.79	14.58
Diallate	2303-16-4	12.35	15.07
Propachlor	1918-16-17	9.96	15.43
Trifluralin	1582-09-8	11.87	16.26
α-BHC	319-84-6	12.35	17.42
PCNB	82-68-8	14.47	18.20
γ-BHC	58-89-9	14.14	20.00
Heptachlor	76-44-8	18.34	21.16
Aldrin	309-00-2	20.37	22.78
Alachlor	15972-60-8	18.58	24.18
Chlorothalonil	1897-45-6	15.81	24.42
Alachlor	15972-60-8	18.58	24.18
β-BHC	319-85-7	13.80	25.04
Isodrin	465-73-6	22.08	25.29
DCPA	1861-32-1	21.38	26.11
δ-BHC	319-86-8	15.49	26.37
Heptachlor epoxide	1024-57-3	22.83	27.31
Endosulfan-I	959-98-8	25.00	28.88
γ-Chlordane	5103-74-2	24.29	29.32
α-Chlordane	5103-71-9	25.25	29.82
trans-Nonachlor	39765-80-5	25.58	30.01
4,4′-DDE	72-55-9	26.80	30.40
Dieldrin	60-57-1	26.60	31.20
Captan	133-06-2	23.29	31.47
Perthane	72-56-0	28.45	32.18
Endrin	72-20-8	27.86	32.44
Chloropropylate	99516-95-7	28.92	34.14
Chlorobenzilate	510-15-6	28.92	34.42
Nitrofen	1836-75-5	27.86	34.42
4,4′-DDD	72-54-8	29.32	35.32
Endosulfan II	33213-65-9	28.45	35.51
4,4′-DDT	50-29-3	31.62	36.30
Endrin aldehyde	7421-93-4	29.63	38.08
Mirex	2385-85-5	37.15	38.79
Endosulfan sulfate	1031-07-8	31.62	40.05

continued

TABLE 5
(Continued)

Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
Methoxychlor	72-43-5	35.33	40.31
Captafol	2425-06-1	32.65	41.42
Endrin ketone	53494-70-5	33.79	42.26
trans-Permethrin	51877-74-8	41.50	45.81
Kepone	143-50-0	31.10	b
Dicofol	115-32-2	35.33	b
Dichlone	117-80-6	15.17	b
α,α'-Dibromo-m-xylene		9.17	11.51
2-Bromobiphenyl		8.54	12.49

[a]The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83-μm film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0-μm film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 140°C (2-min hold) to 270°C (1-min hold) at 2.8°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.
[b]Not detected at 2 ng per injection.

TABLE 6
GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR DUAL COLUMN METHOD OF ANALYSIS
LOW TEMPERATURE, THIN FILM

Column 1:

Type: DB-1701 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (μm): 1.0

Column 2:

Type: DB-5 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (μm): 0.83

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 μL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 64 (DB-1701)/32 (DB-5)

Type of splitter: Supelco 8 in injection tee

TABLE 7
GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1:

Type: DB-1701 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 1.0 μm

Column 2:

Type: DB-5 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 1.5 μm

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 μL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 64 (DB-1701)/64 (DB-5)

Type of splitter: J&W Scientific press-fit Y-shaped inlet splitter

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TABLE 8 SUMMARY OF RETENTION TIMES (MIN) OF AROCLORS ON THE DB-5 COLUMN[a] DUAL SYSTEM OF ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
1		5.85	5.85					
2		7.63	7.64	7.57				
3	8.41	8.43	8.43	8.37				
4	8.77	8.77	8.78	8.73				
5	8.98	8.99	9.00	8.94	8.95			
6	9.71			9.66				
7	10.49	10.50	10.50	10.44	10.45			
8	10.58	10.59	10.59	10.53				
9	10.90		10.91	10.86	10.85			
10	11.23	11.24	11.24	11.18	11.18			Chlorothalonil (11.18)
11	11.88		11.90	11.84	11.85			
12	11.99		12.00	11.95				
13	12.27	12.29	12.29	12.24	12.24			
14	12.66	12.68	12.69	12.64	12.64			
15	12.98	12.99	13.00	12.95	12.95			
16	13.18		13.19	13.14	13.15			
17	13.61		13.63	13.58	13.58	13.59	13.59	
18	13.80		13.82	13.77	13.77	13.78		
19	13.96		13.97	13.93	13.93	13.90		
20	14.48		14.50	14.46	14.45	14.46		
21	14.63		14.64	14.60	14.60			
22	14.99		15.02	14.98	14.97	14.98		
23	15.35		15.36	15.32	15.31	15.32		
24	16.01			15.96				
25			16.14	16.08	16.08	16.10		
26	16.27		16.29	16.26	16.24	16.25	16.26	Captan (16.21)
27						16.53		
28			17.04		16.99	16.96	16.97	gamma-Chlordane (16.95)
29			17.22	17.19	17.19	17.19	17.21	
30			17.46	17.43	17.43	17.44		
31					17.69	17.69		
32				17.92	17.91	17.91		
33				18.16	18.14	18.14		
34			18.41	18.37	18.36	18.36	18.37	4,4'-DDE (18.38)
35			18.58	18.56	18.55	18.55		Dieldrin (18.59)
36							18.68	
37			18.83	18.80	18.78	18.78	18.79	
38			19.33	19.30	19.29	19.29	19.29	
39						19.48	19.48	
40						19.81	19.80	
41			20.03	19.97	19.92	19.92		Chloropropylate (19.91) Endosulfan II (19.91)
42						20.28	20.28	
43				20.46	20.45			
44						20.57	20.57	
45				20.85	20.83	20.83	20.83	
46			21.18	21.14	21.12	20.98		Kepone (20.99)
47					21.36	21.38	21.38	
48						21.78	21.78	4,4'-DDT (21.75) Endosulfan sulfate (21.75)
49				22.08	22.05	22.04	22.03	
50						22.38	22.37	
51						22.74	22.73	Captafol (22.71)
52						22.96	22.95	
53						23.23	23.23	
54							23.42	
55						23.75	23.73	Endrin ketone (23.73)

(continued)

[a]The GC operating conditions are given in Table 7.

TABLE 8 CONTINUED

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
56						23.99	23.97	
57							24.16	
58						24.27		Methoxychlor (24.29) Dicofol (24.29)
59							24.45	
60						24.61	24.62	
61						24.93	24.91	
62							25.44	
63						26.22	26.19	Mirex (26.19)
64							26.52	
65							26.75	
66							27.41	
67							28.07	
68							28.35	
69							29.00	

[a]The GC operating conditions are given in Table 7.
[b]These are sequentially numbered from elution order and are not isomer numbers

TABLE 9 SUMMARY OF RETENTION TIMES (MIN) OF AROCLORS ON THE DB-1701 COLUMN[a] DUAL SYSTEM OF ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
1		4.45	4.45					
2		5.38						
3		5.78						
4		5.86	5.86					
5	6.33	6.34	6.34	6.28				
6	6.78	6.78	6.79	6.72				
7	6.96	6.96	6.96	6.90	6.91			Trifluralin (6.96)
8	7.64			7.59				
9	8.23	8.23	8.23	8.15	8.16			
10	8.62	8.63	8.63	8.57				
11	8.88		8.89	8.83	8.83			
12	9.05	9.06	9.06	8.99	8.99			
13	9.46		9.47	9.40	9.41			
14	9.77	9.79	9.78	9.71	9.71			
15	10.27	10.29	10.29	10.21	10.21			
16	10.64	10.65	10.66	10.59	10.59			
17				10.96	10.95	10.95		
18	11.01		11.02	11.02	11.03			
19	11.09		11.10					
20	11.98		11.99	11.94	11.93	11.93		
21	12.39		12.39	12.33	12.33	12.33		
22			12.77	12.71	12.69			
23	12.92			12.94	12.93			
24	12.99		13.00	13.09	13.09	13.10		
25	13.14		13.16					
26						13.24		
27	13.49		13.49	13.44	13.44			
28	13.58		13.61	13.54	13.54	13.51	13.52	
29				13.67		13.68		
30			14.08	14.03	14.03	14.03	14.02	
31			14.30	14.26	14.24	14.24	14.25	
32					14.39	14.36		
33			14.49	14.46	14.46			
34						14.56	14.56	
35					15.10	15.10		
36			15.38	15.33	15.32	15.32		Chlordane (15.32)
37			15.65	15.62	15.62	15.61	16.61	4,4'-DDE (15.67)
38			15.78	15.74	15.74	15.74	15.79	
39			16.13	16.10	16.10	16.08		
40							16.19	
41						16.34	16.34	
42						16.44	16.45	
43						16.55		
44			16.77	16.73	16.74	16.77	16.77	Perthane (16.71)
45			17.13	17.09	17.07	17.07	17.08	
46						17.29	17.31	
47				17.46	17.44	17.43	17.43	
48				17.69	17.69	17.68	17.68	
49					18.19	18.17	18.18	
50				18.48	18.49	18.42	18.40	
51						18.59		
52						18.86	18.86	
53				19.13	19.13	19.10	19.09	Endosulfan II (19.05)
54						19.42	19.43	

(continued)

[a]The GC operating conditions are given in Table 7.

TABLE 9 CONTINUED

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
55						19.55	19.59	4,4'-DDT (19.54)
56						20.20	20.21	
57						20.34		
58							20.43	
59					20.57	20.55		
60						20.62	20.66	Endrin aldehyde (20.69)
61						20.88	20.87	
62							21.03	
63						21.53	21.53	
64						21.83	21.81	
65						23.31	23.27	
66							23.85	
67							24.11	
68							24.46	
69							24.59	
70							24.87	
71							25.85	
72							27.05	
73							27.72	

[a]The GC operating conditions are given in Table 7.
[b]These are sequentially numbered from elution order and are not isomer numbers

TABLE 10
PEAKS DIAGNOSTIC OF PCBs OBSERVED IN 0.53 mm ID COLUMN
SINGLE COLUMN ANALYSIS

Peak No.[c]	RT on DB 608[a]	RT on DB 1701[a]	Aroclor[b]	Elution Order
I	4.90	4.66	1221	Before TCmX
II	7.15	6.96	1221, 1232, 1248	Before α-BHC
III	7.89	7.65	1061, 1221, 1232, 1242,	Before α-BHC
IV	9.38	9.00	1016, 1232, 1242, 1248,	just after α-BHC on DB-1701;just before γ-BHC on DB-608
V	10.69	10.54	1016, 1232, 1242,	1248 α-BHC and heptachlor on DB-1701; just after heptachlor on DB-608
VI	14.24	14.12	1248, 1254	γ-BHC and heptachlor epoxide on DB-1701; heptachlor epoxide and γ-Chlordane on DB-608
VII	14.81	14.77	1254	Heptachlor epoxide and γ-Chlordane on DB-1701; α- and γ-Chlordane on DB-608
VIII	16.71	16.38	1254	DDE and Dieldrin on DB-1701; Dieldrin and Endrin on DB-608
IX	19.27	18.95	1254, 1260	Endosulfan II on DB-1701; DDT on DB-608

Continued

TABLE 10 (Continued)
PEAKS DIAGNOSTIC OF PCBs OBSERVED IN 0.53 mm ID COLUMN
SINGLE COLUMN ANALYSIS

Peak No.	RT on DB 608[a]	RT on DB 1701[a]	Aroclor[b]	Elution Order
X	21.22	21.23	1260	Endrin aldehyde and Endosulfan sulfate on DB-1701; Endosulfan sulfate and Methoxychlor on on DB-608
XI	22.89	22.46	1260	Just before endrin ketone on DB-1701; after endrin ketone on DB-608

[a] Temperature program: T_i = 150°C, hold 30 seconds; increase temperature at 5°C/minutes to 275°C.

[b] Underlined Aroclor indicates the largest peak in the pattern.

[c] These are sequentially numbered from elution order and are not isomer numbers

TABLE 11 SPECIFIC PCB CONGENERS IN AROCLORS

Congener	IUPAC number	Aroclor 1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2CB	1	X	X	X	X			
23DCB	5	X	X	X	X	X		
34DCB	12	X		X	X	X		
244'TCB	28*	X		X	X	X	X	
22'35'TCB	44			X	X	X	X	
23'44'TCB	66*					X	X	X
233'4'6PCB	110						X	
23'44'5PCB	118*						X	X
22'44'55'HCB	153							X
22'344'5'HCB	138							X
22'344'55'HpCB	180							X
22'33'44'5HpCB	170							X

*apparent co-elution of two major peaks:

28 with 31 (2,4',5 trichloro)
66 with 95 (2,2',3,5',6 pentachloro)
118 with 149 (2,2',3,4',5',6 hexachloro)

TABLE 12 ANALYTE RECOVERY FROM SEWAGE SLUDGE

Compound	Sonication		Soxhlet	
	%Recovery	%RSD	%Recovery	%RSD
Hexachloroethane	80	7	79	1
2-Chloronapthalene	50	56	67	8
4-Bromodiphenyl ether	118	14	nd	
α-BHC	88	25	265	18
γ-BHC	55	9	155	29
Heptachlor	60	13	469	294
Aldrin	92	33	875	734
β-BHC	351	71	150	260
δ-BHC	51	11	57	2
Heptachlor epoxide	54	11	70	3
Endosulfan I	52	11	70	4
γ-Chlordane	50	9	65	1
α-Chlordane	49	8	66	0
DDE	52	11	74	1
Dieldrin	89	19	327	7
Endrin	56	10	92	15
Endosulfan II	52	10	88	11
DDT	57	10	95	17
Endrin aldehyde	45	6	42	10
DDD	57	11	99	8
Tetrachloro-m-xylene	71	19	82	1
Decachlorobiphenyl	26	23	28	48

Concentration spiked in the sample: 500-1000 ng/g
Three replicates/sample

Extraction solvent, Method 3540 - methylene chloride
Extraction solvent, Method 3550 - methylene chloride/acetone (1:1)

Cleanup - Method 3640

GC column - DB-608, 30M X 0.53 mm ID

TABLE 13 ANALYTE RECOVERY FROM DCE STILL BOTTOMS

Compound	Sonication		Soxhlet	
	%Recovery	%RSD	%Recovery	%RSD
Hexachloroethane	70	2	50	30
2-Chloronapthalene	59	3	35	35
4-Bromodiphenyl ether	159	14	128	137
α-BHC	55	7	47	25
β-BHC	43	6	30	30
Heptachlor	48	6	55	18
Aldrin	48	5	200	258
β-BHC	51	7	75	42
δ-BHC	43	4	119	129
Heptachlor epoxide	47	6	66	34
Endosulfan I	47	4	41	18
γ-Chlordane	48	5	47	13
α-Chlordane	45	5	37	21
DDE	45	4	70	40
Dieldrin	45	5	58	24
Endrin	50	6	41	23
Endosulfan II	49	5	46	17
DDT	49	4	40	29
Endrin aldehyde	40	4	29	20
DDD	48	5	35	21
Tetrachloro-m-xylene	49	2	176	211
Decachlorobiphenyl	17	29	104	93

Concentration spiked in the sample: 500-1000 ng/g
Three replicates/sample

Extraction solvent, Method 3540 - methylene chloride
Extraction solvent, Method 3550 - methylene chloride/acetone (1:1)

Cleanup - Method 3640

GC column - DB-608, 30M X 0.53 mm ID

TABLE 14
SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound Name	Spike Level µg/kg	% Recovery	
		DB-5	DB-1701
α-BHC	500	89	94
β-BHC	500	86	b
Heptachlor	500	94	95
Aldrin	500	b	92
Heptachlor epoxide	500	97	97
trans-Chlordane	500	94	95
Endosulfan I	500	92	92
Dieldrin	500	b	113
Endrin	500	111	104
Endosulfan II	500	104	104
4,4′-DDT	500	b	b
Mirex	500	108	102

a The operating conditions for the automated Soxhlet were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil, extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

b Not able to determine because of interference.

Data taken from Reference 14.

TABLE 15
SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF
PCBS FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Compound	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	Aroclor-1254	5	1	87.0
			2	92.7
			3	93.8
			4	98.6
			5	79.4
			6	28.3
Clay	Aroclor-1254	50	1	65.3
			2	72.6
			3	97.2
			4	79.6
			5	49.8
			6	59.1
Clay	Aroclor-1260	5	1	87.3
			2	74.6
			3	60.8
			4	93.8
			5	96.9
			6	113.1
Clay	Aroclor-1260	50	1	73.5
			2	70.1
			3	92.4
			4	88.9
			5	90.2
			6	67.3
Soil	Aroclor-1254	5	1	69.7
			2	89.1
			3	91.8
			4	83.2
			5	62.5
Soil	Aroclor-1254	50	1	84.0
			2	77.5
			3	91.8
			4	66.5
			5	82.3
			6	61.6

(continued)

TABLE 15
(continued)

Matrix	Compound	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	Aroclor-1260	5	1	83.9
			2	82.8
			3	81.6
			4	96.2
			5	93.7
			6	93.8
			7	97.5
Soil	Aroclor-1260	50	1	76.9
			2	69.4
			3	92.6
			4	81.6
			5	83.1
			6	76.0

a The operating conditions for the automated Soxhlet were as follows: immersion time 60 min; reflux time 60 min.

b Multiple results from two different extractors.

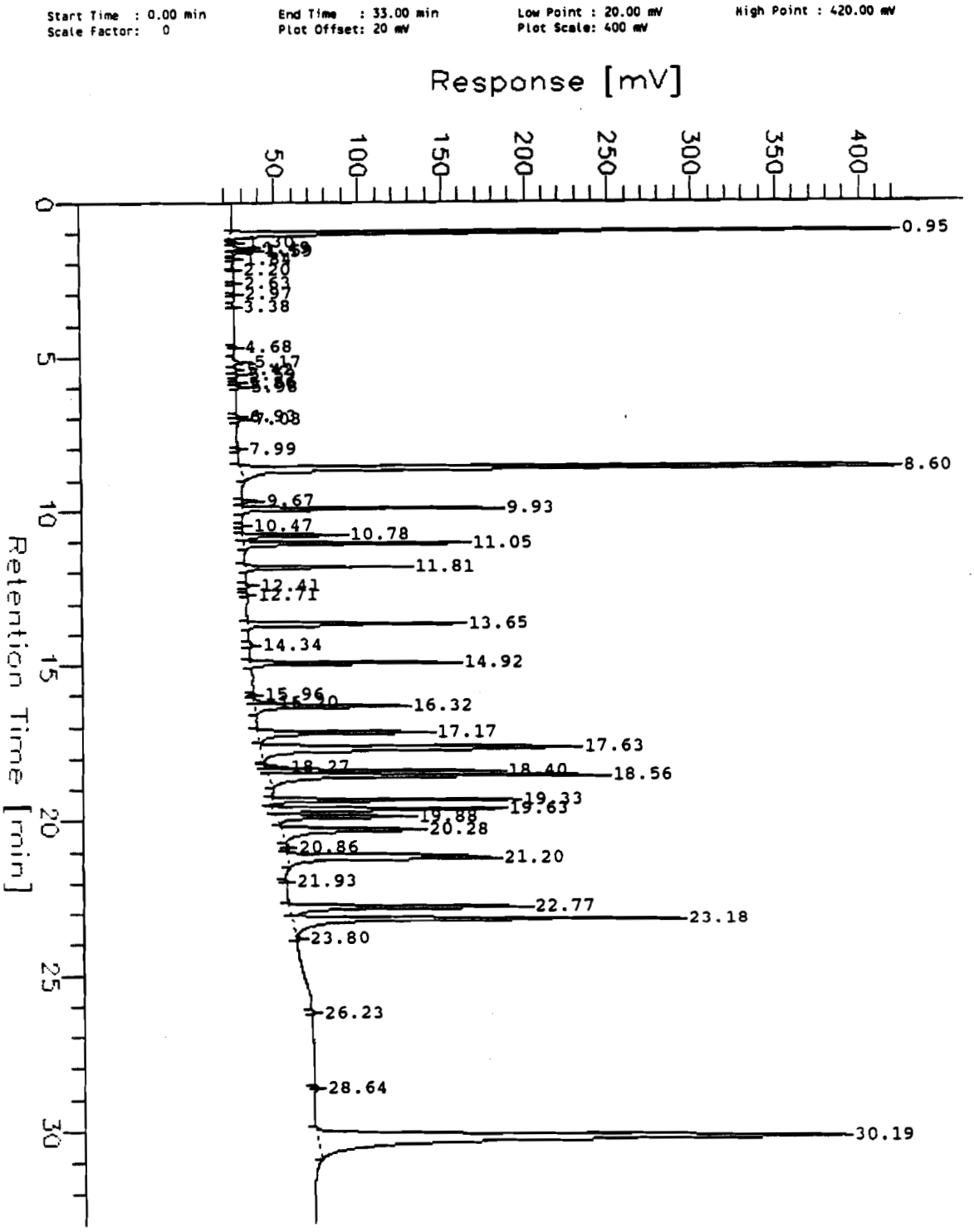
Data from Reference 15.

TABLE 16. MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR THE EXTRACTION OF PCBS FROM SPIKED SOIL BY METHOD 3541 (AUTOMATED SOXHLET)

		PCB Percent Recovery						
		Aroclor						
		1254			1260			
		PCB Level			PCB Level			All Levels
Laboratory		5	50	500	5	50	500	
Lab 1	Num	3.0	3.0		3.0	3.0		12.0
	Average	101.2	74.0		83.9	78.5		84.4
	St Dev	34.9	41.8		7.4	7.4		26.0
Lab 2	Num		6.0	6.0		6.0	6.0	24.0
	Average		56.5	66.9		70.1	74.5	67.0
	St Dev		7.0	15.4		14.5	10.3	13.3
Lab 3	Num	3.0	3.0		3.0	3.0		12.0
	Average	72.8	63.3		70.6	57.2		66.0
	St Dev	10.8	8.3		2.5	5.6		9.1
Lab 4	Num	6.0	6.0		6.0	6.0		24.0
	Average	112.6	144.3		100.3	84.8		110.5
	St Dev	18.2	30.4		13.3	3.8		28.5
Lab 5	Num		3.0	3.0		3.0	3.0	12.0
	Average		97.1	80.1		79.5	77.0	83.5
	St Dev		8.7	5.1		3.1	9.4	10.3
Lab 6	Num	2.0	3.0		3.0	4.0		12.0
	Average	140.9	127.7		138.7	105.9		125.4
	St Dev	4.3	15.5		15.5	7.9		18.4
Lab 7	Num	3.0	3.0		3.0	3.0		12.0
	Average	100.1	123.4		82.1	94.1		99.9
	St Dev	17.9	14.6		7.9	5.2		19.0
Lab 8	Num	3.0	3.0		3.0	3.0		12.0
	Average	65.0	38.3		92.8	51.9		62.0
	St Dev	16.0	21.9		36.5	12.8		29.1
All Laboratories	Num	20.0	30.0	9.0	21.0	31.0	9.0	120.0
	Average	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	St Dev	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Data from Reference 13.

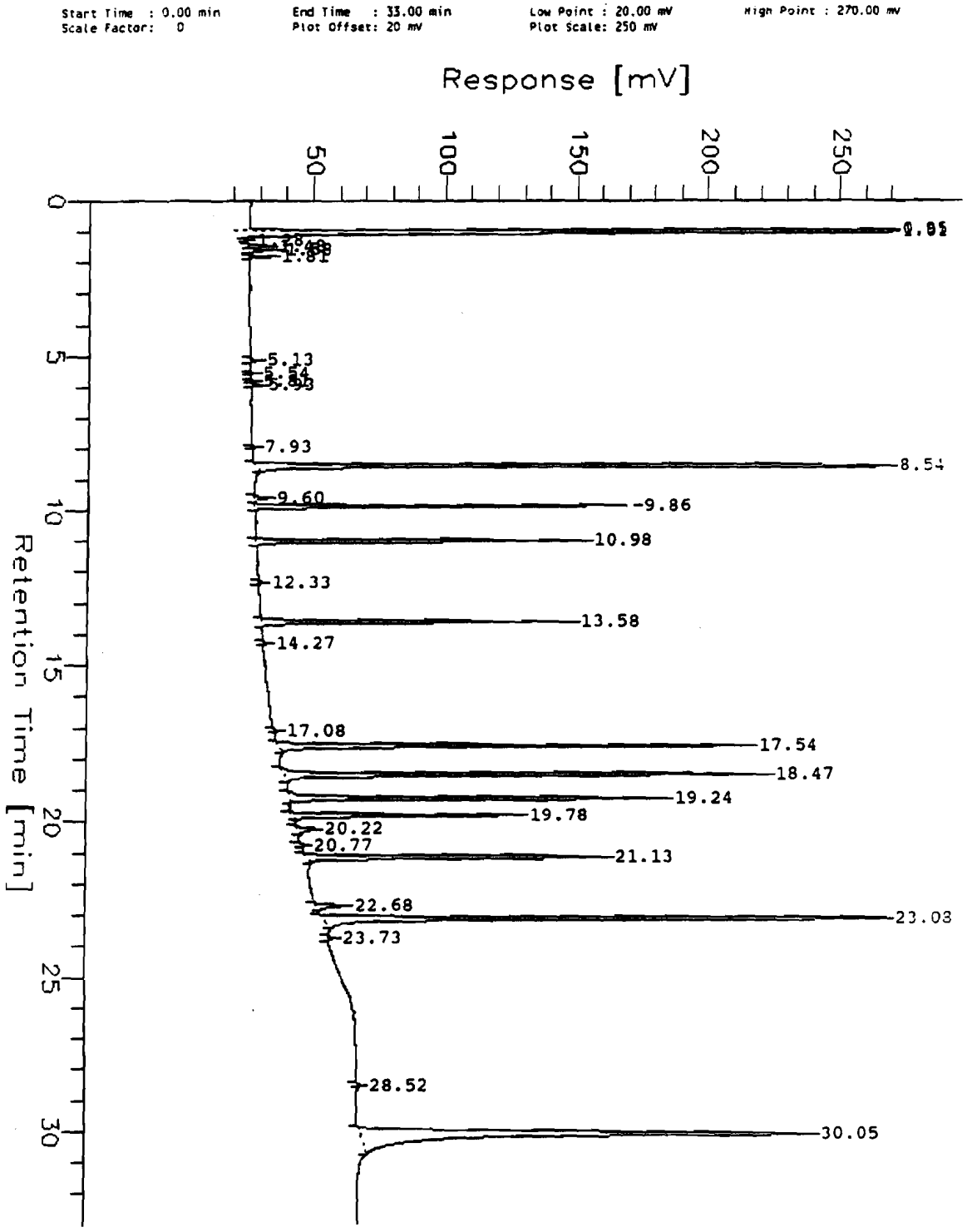
FIGURE 1.
GAS CHROMATOGRAM OF THE MIXED ORGANOCHLORINE PESTICIDE STANDARD



Column: 30 m x 0.25 mm ID, DB-5

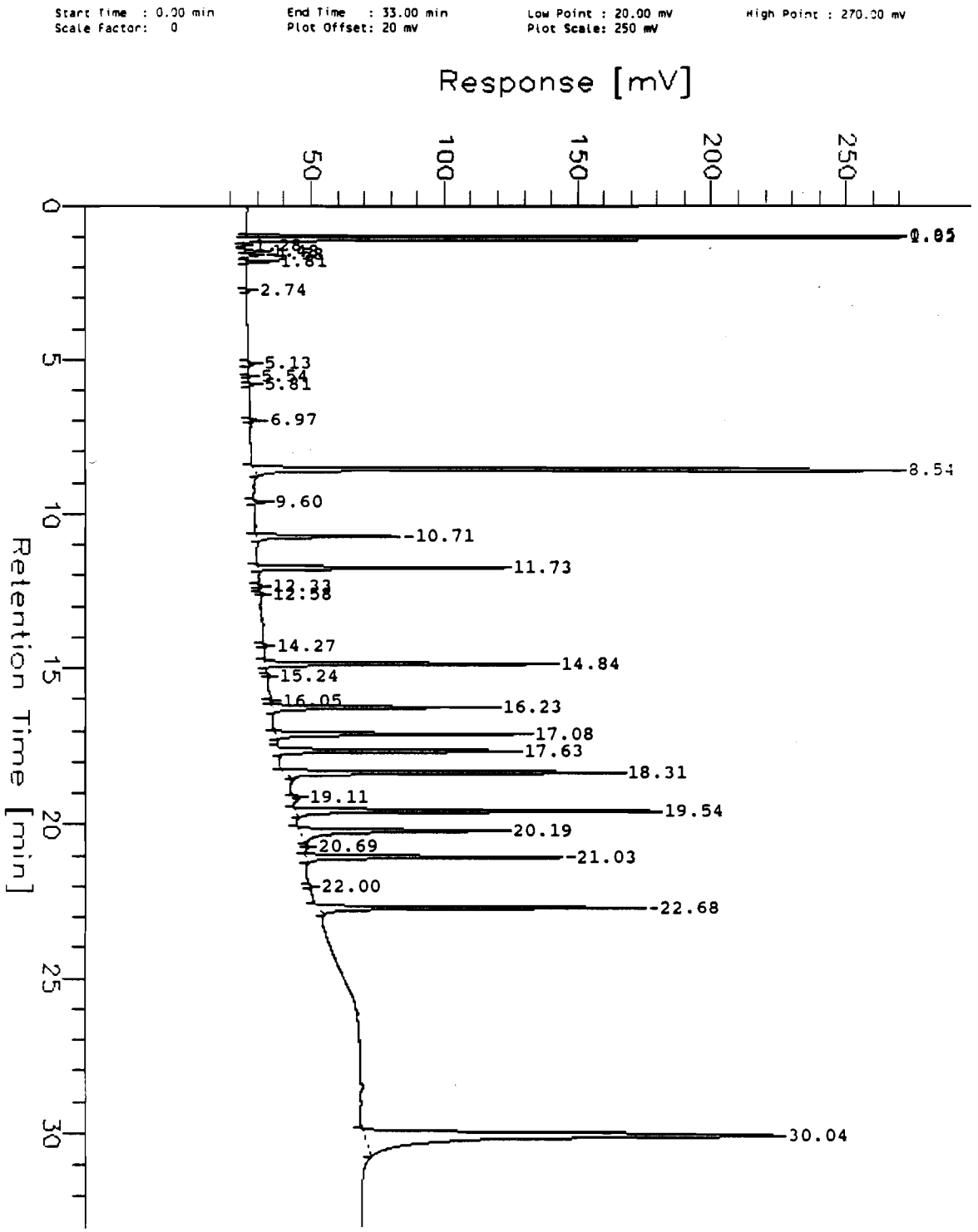
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 2.
GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A



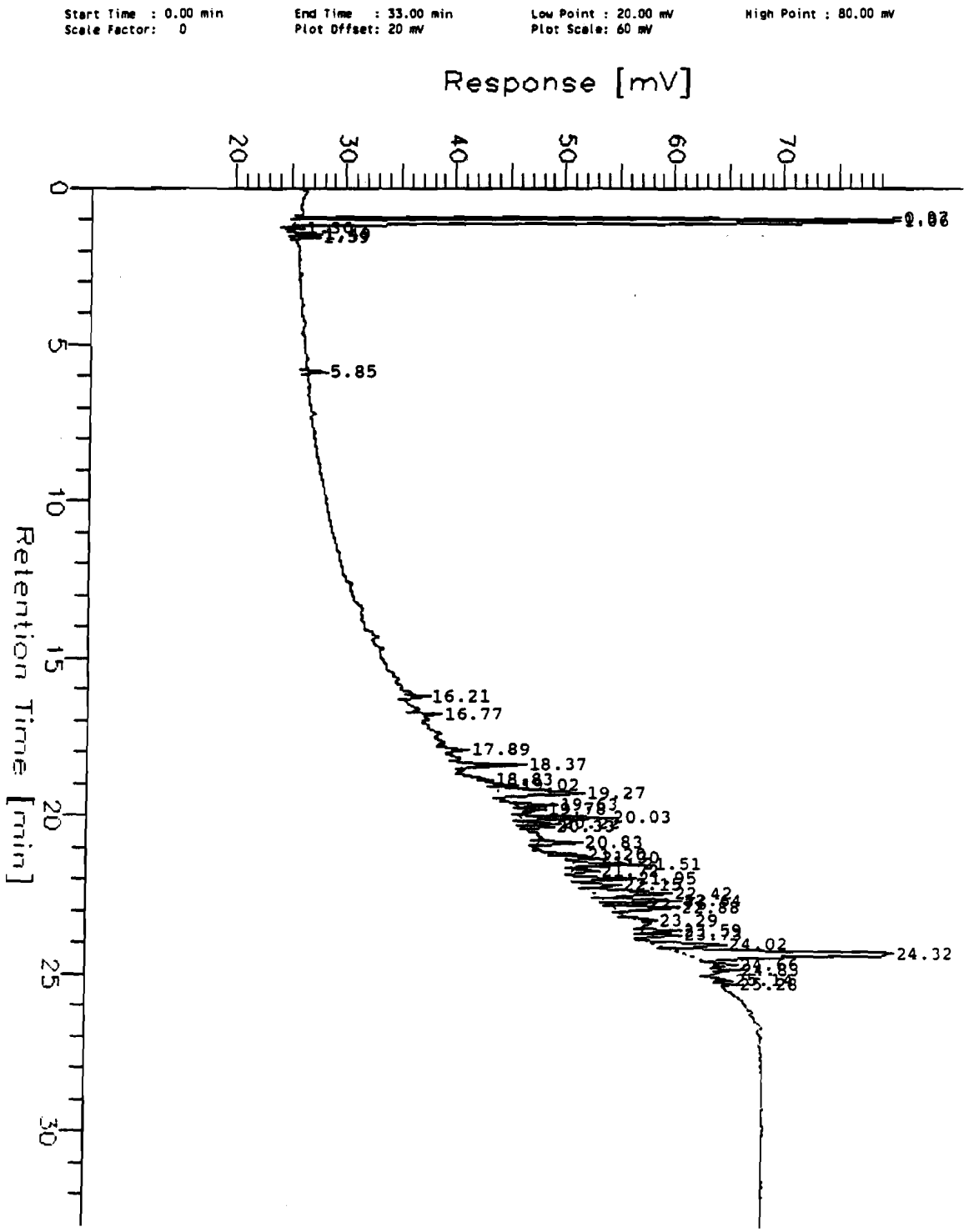
Column: 30 m x 0.25 mm ID, DB-5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 3
GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B



Column: 30 m x 0.25 mm ID, DB-5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

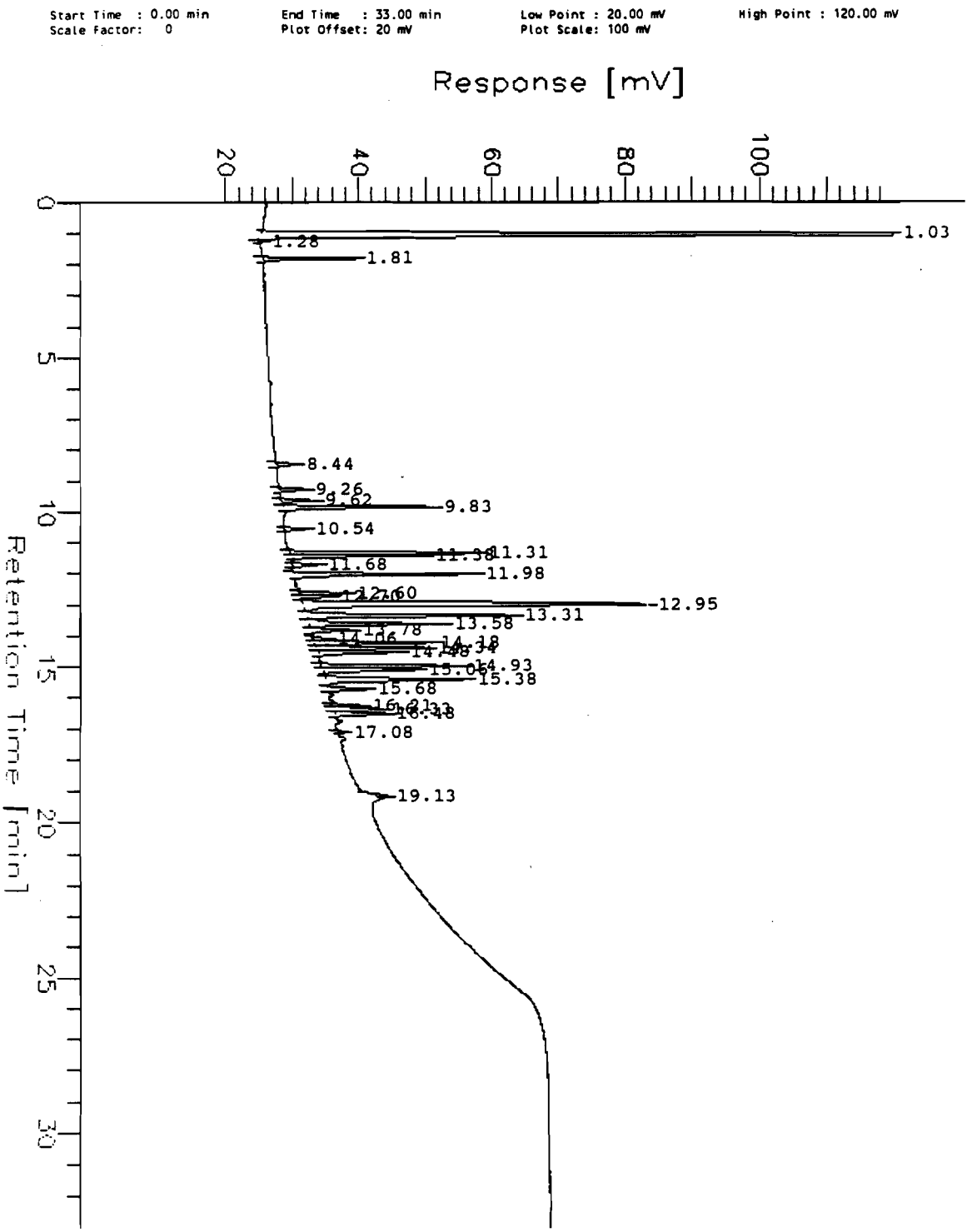
FIGURE 4.
GAS CHROMATOGRAM OF THE TOXAPHENE STANDARD



Column: 30 m x 0.25 mm ID, DB-5

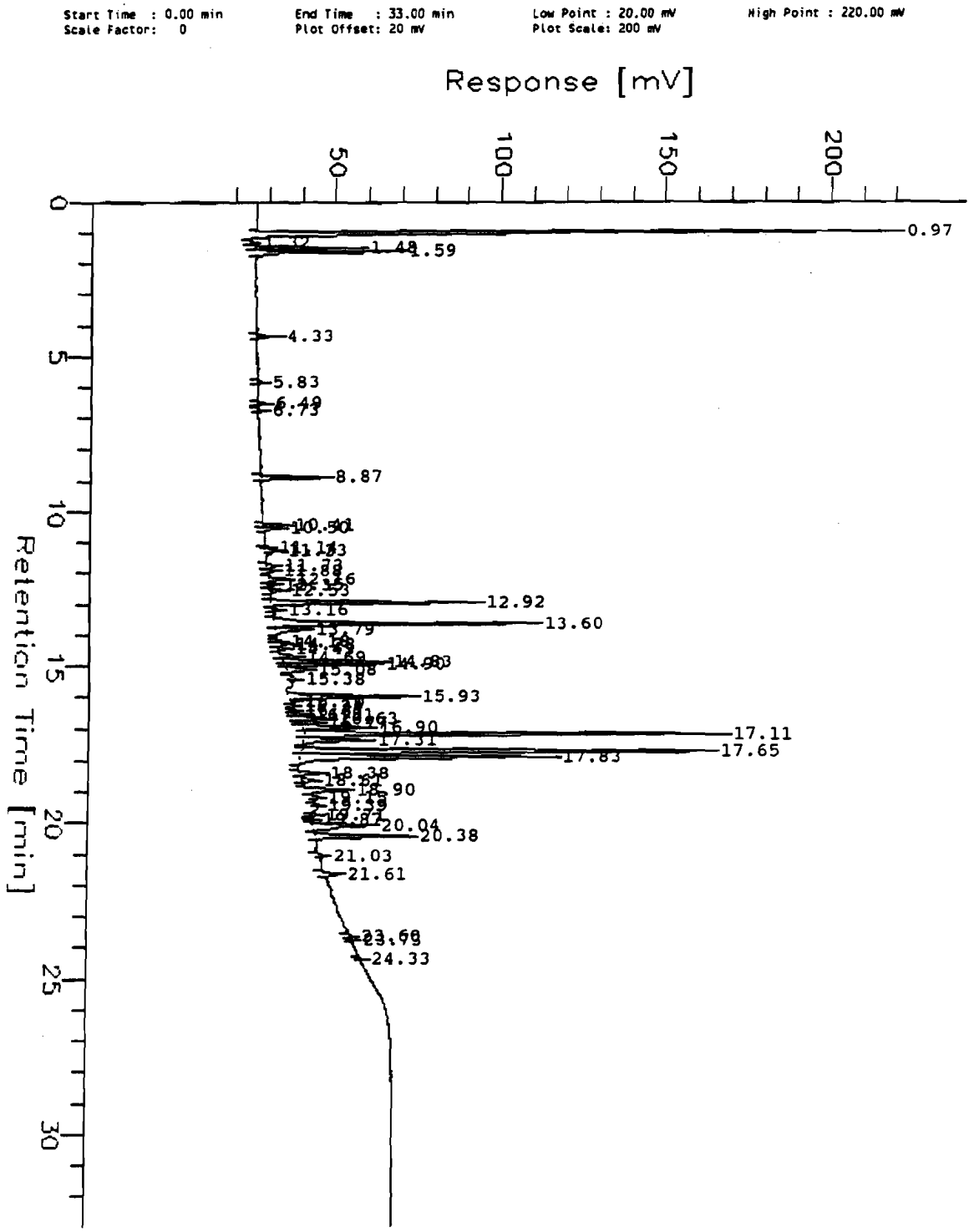
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 5.
GAS CHROMATOGRAM OF THE AROCLOR-1016 STANDARD



Column: 30 m x 0.25 mm ID DB-5 fused silica capillary.
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 6.
GAS CHROMATOGRAM OF THE TECHNICAL CHLORDANE STANDARD



Column: 30 m x 0.25 mm ID DB-5 fused silica capillary.
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

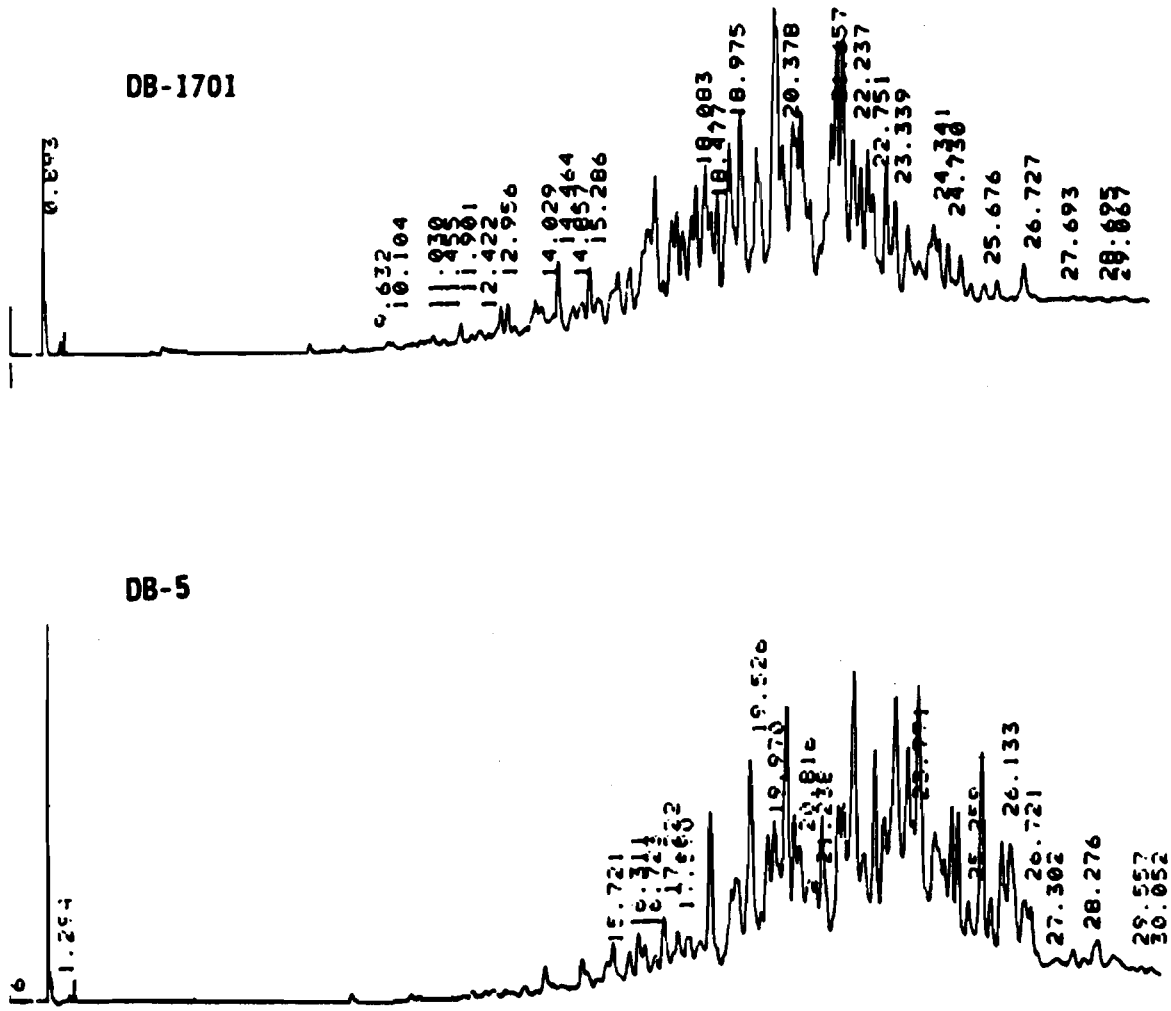


FIGURE 7. GC/ECD chromatogram of Toxaphene analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

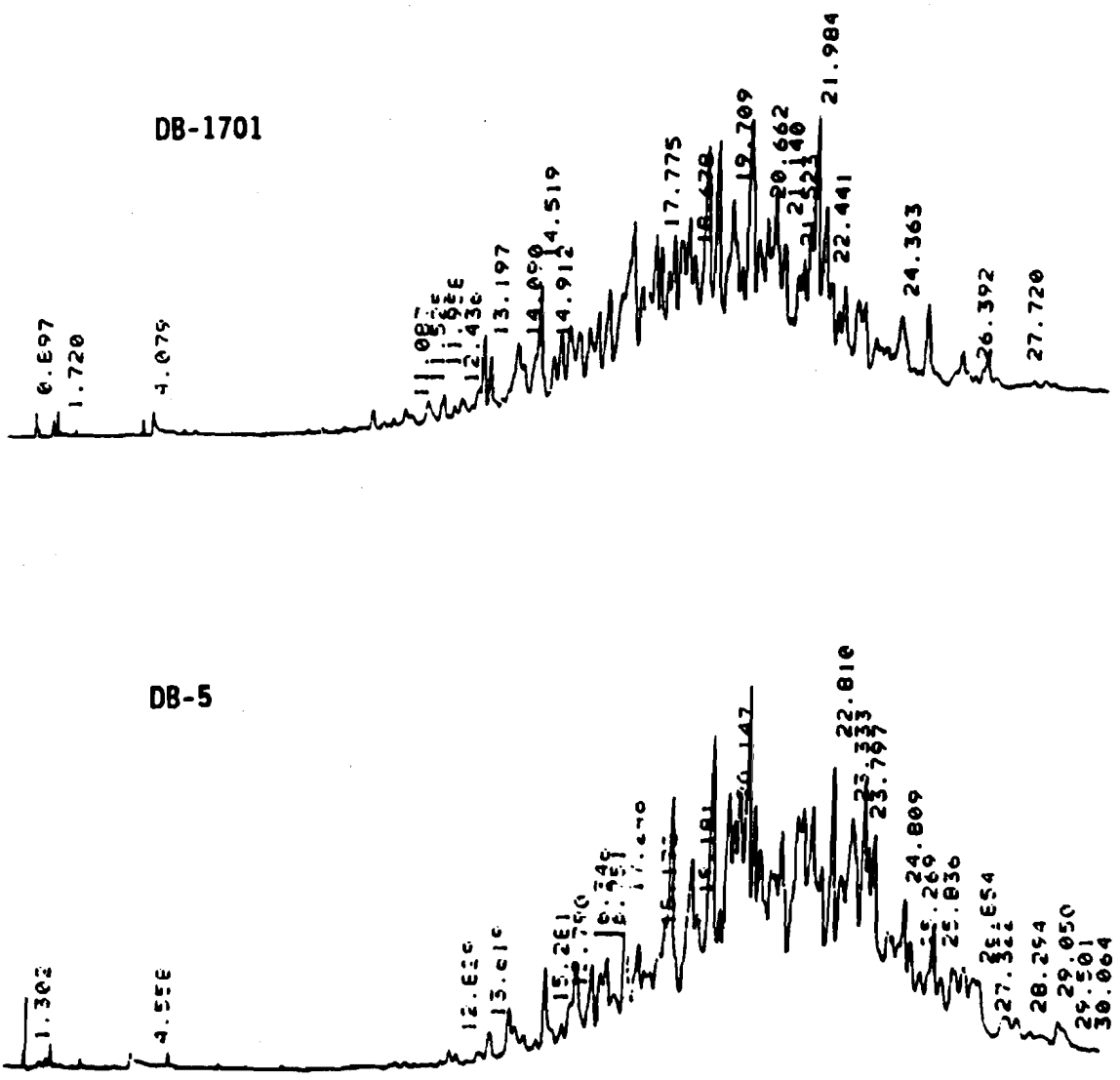


FIGURE 8. GC/ECD chromatogram of Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

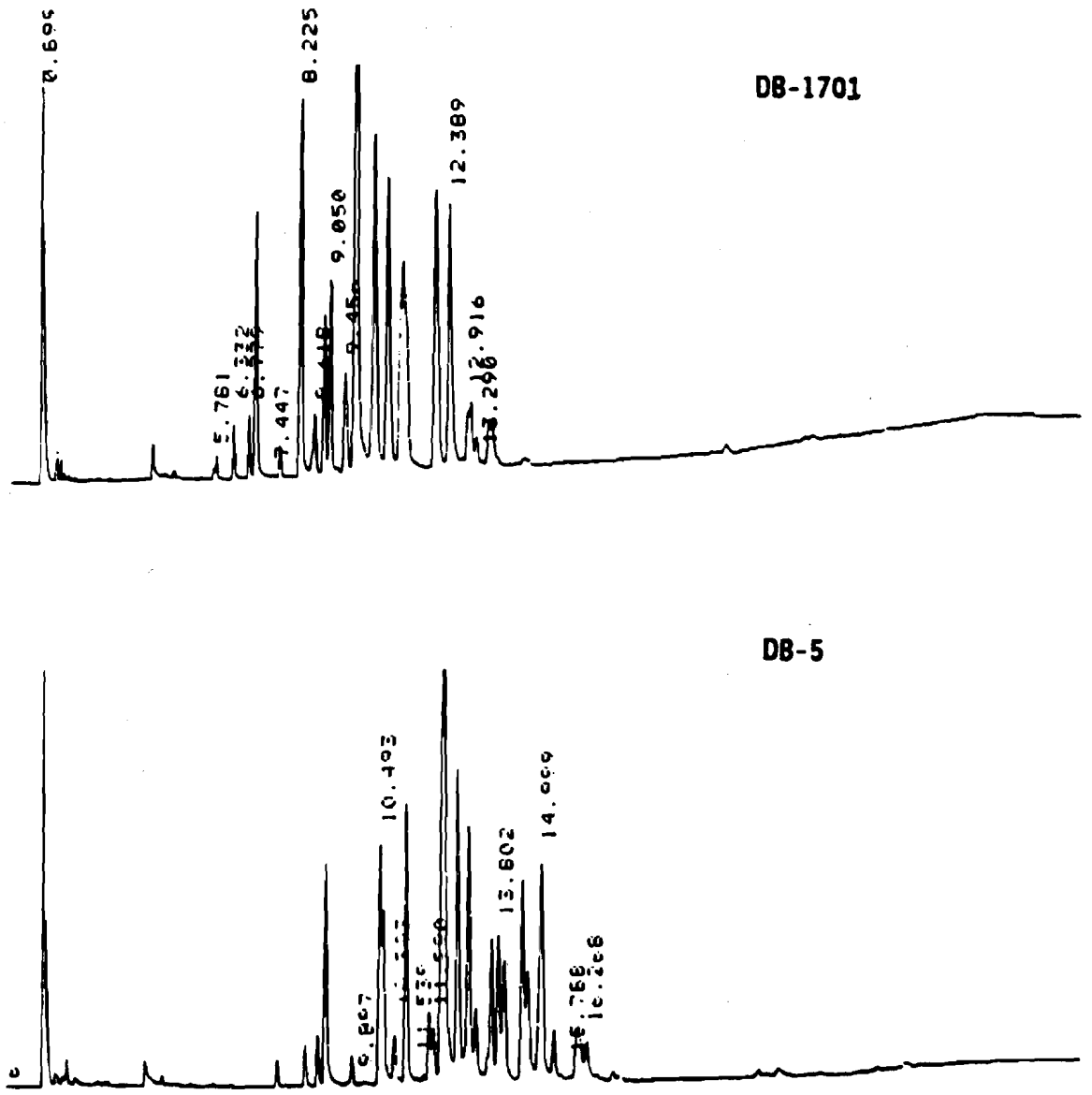


FIGURE 9. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

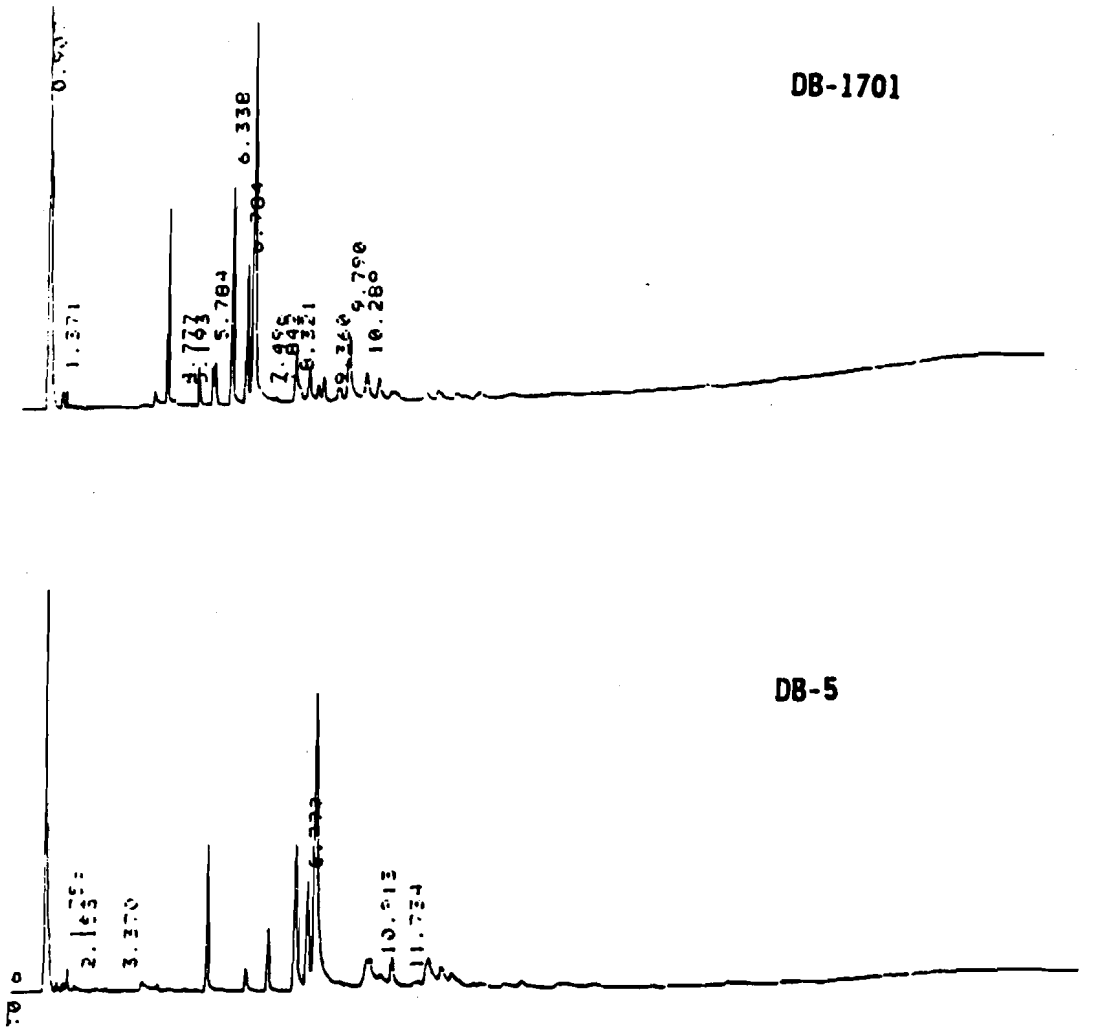


FIGURE 10. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

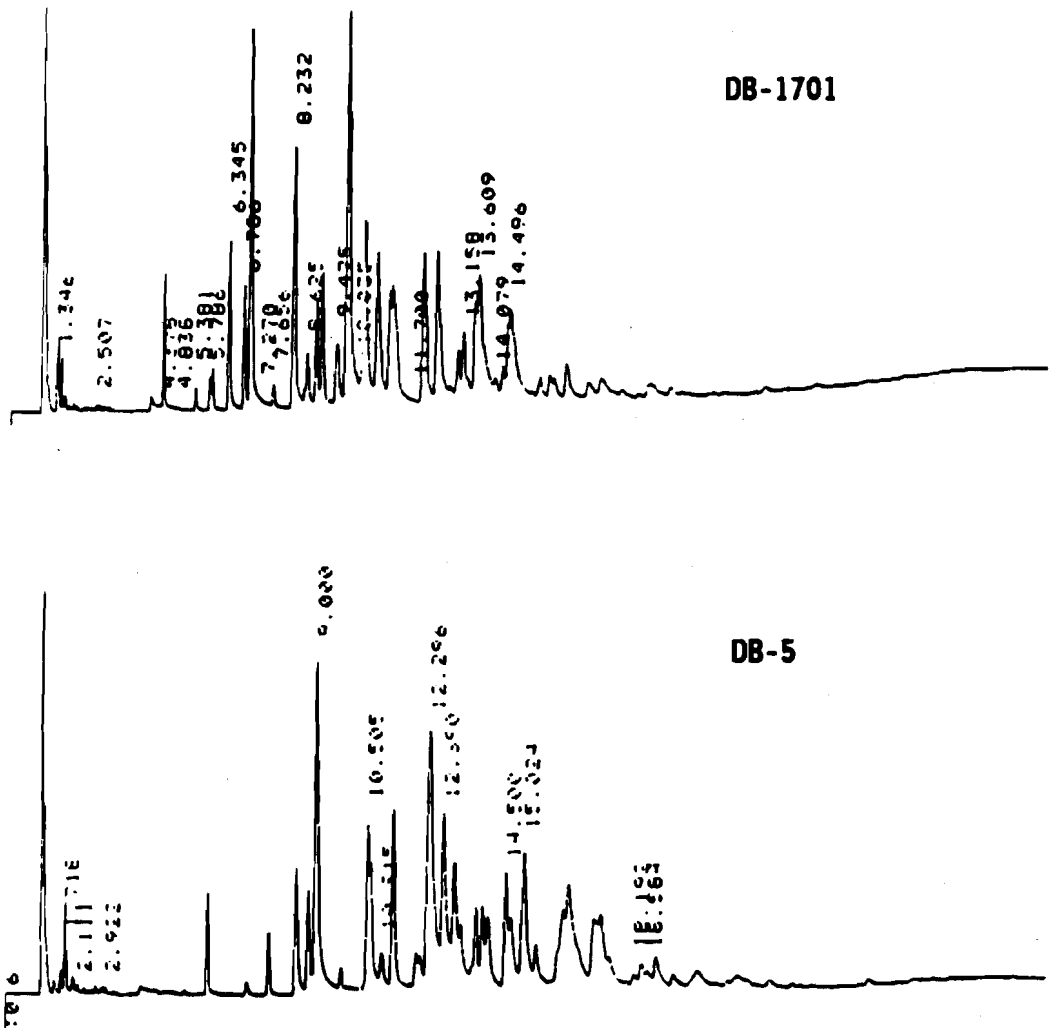


FIGURE 11. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

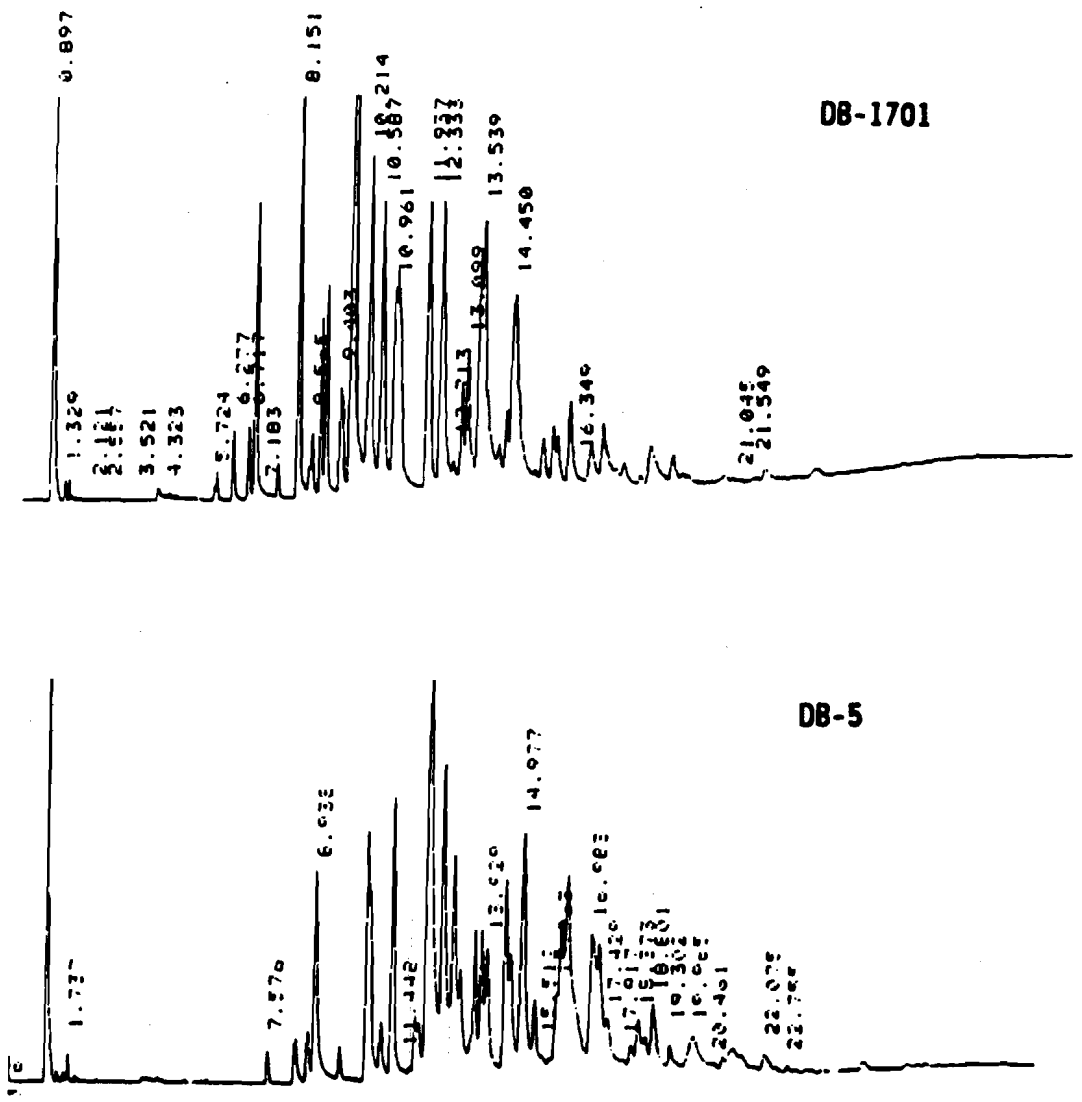


FIGURE 12. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

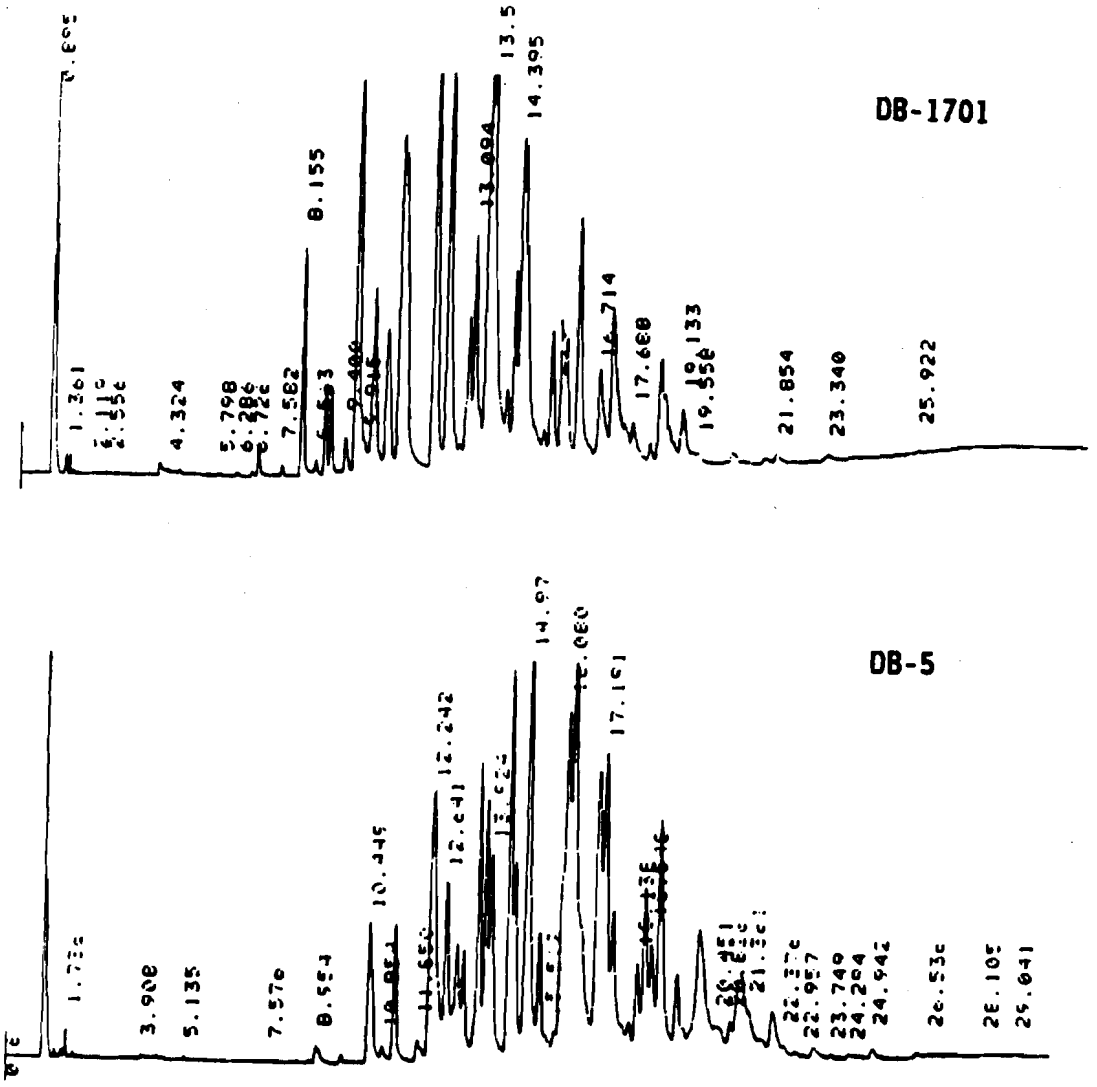


FIGURE 13. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

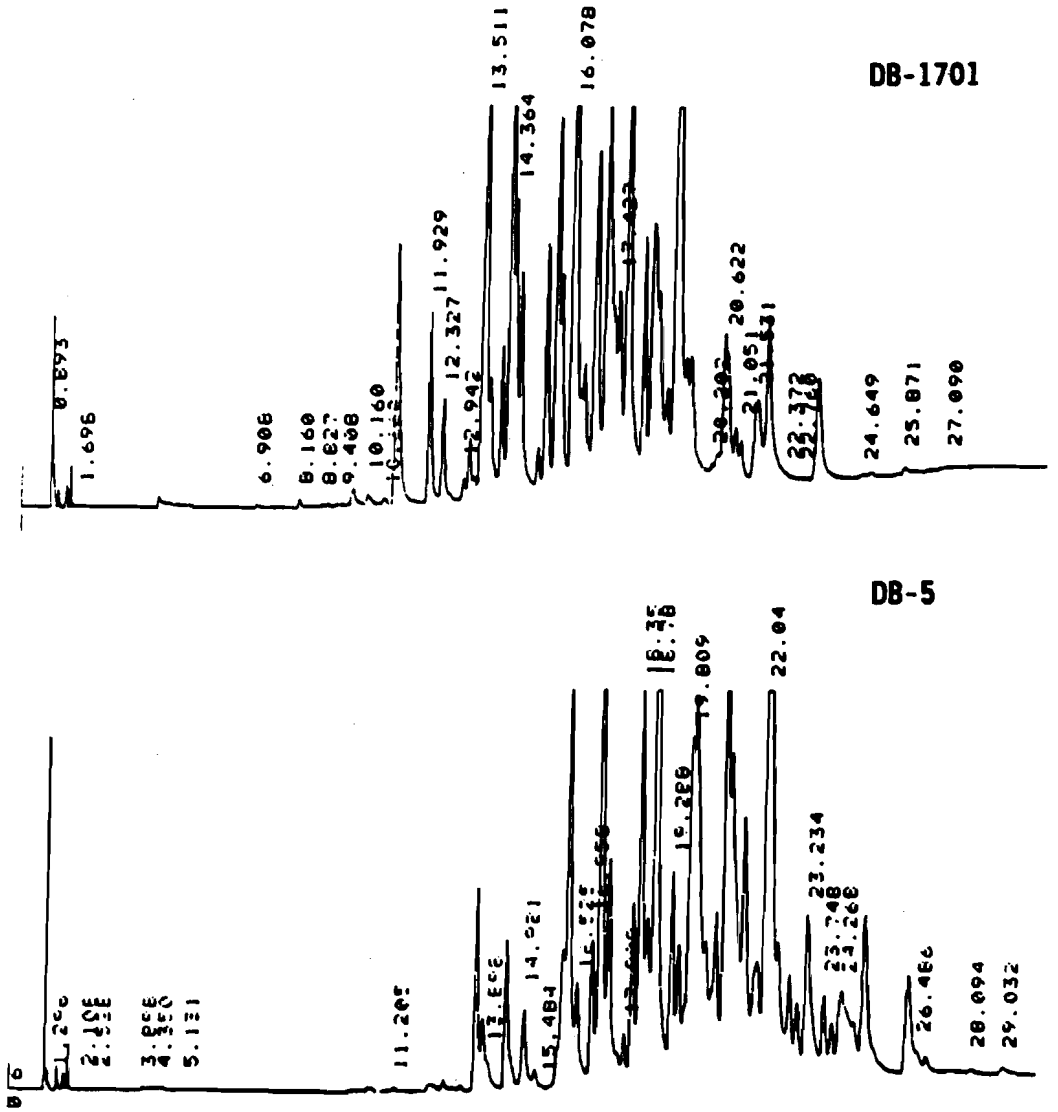


FIGURE 14. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

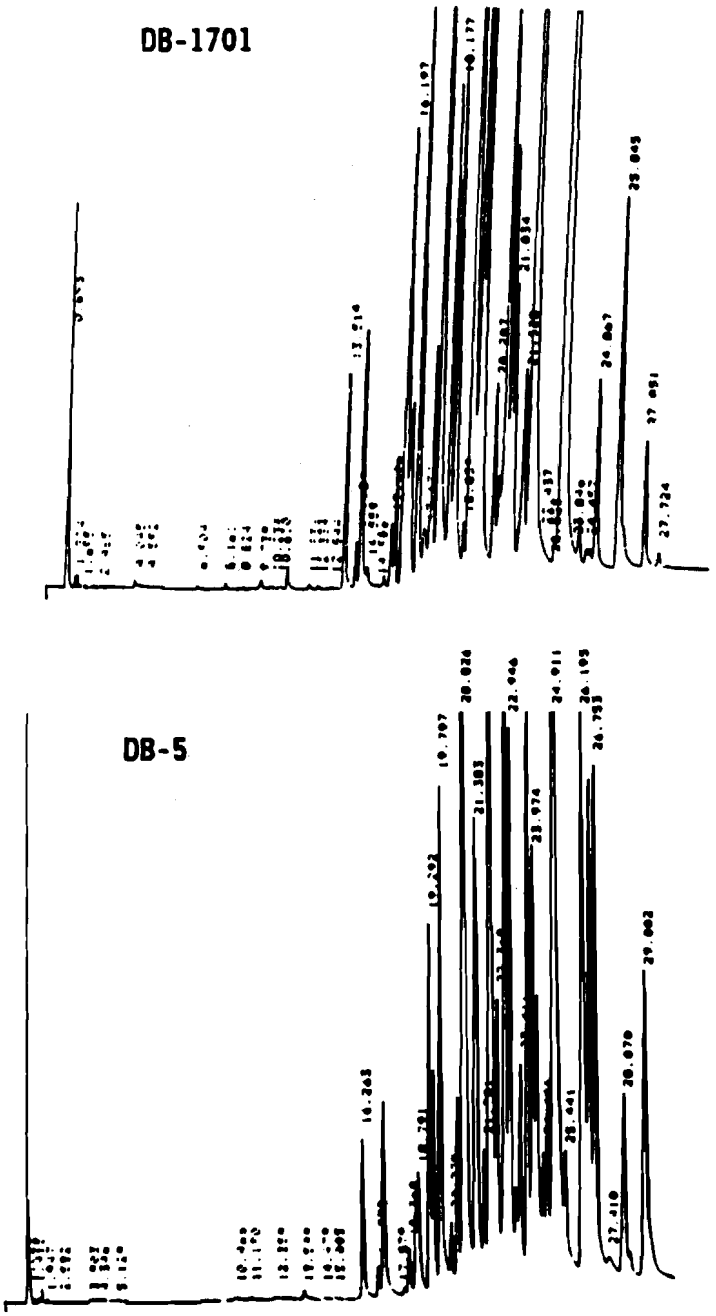


FIGURE 15. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

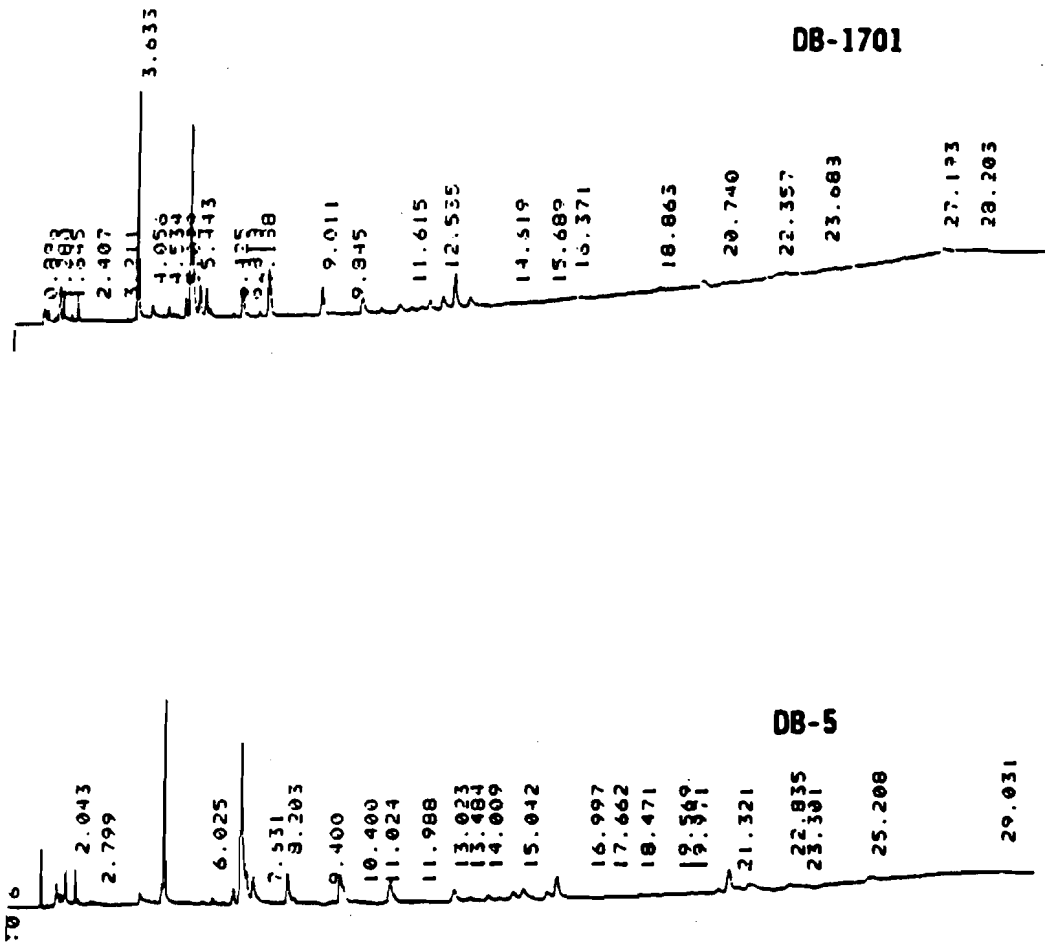


FIGURE 16. GC/ECD chromatogram of Halowax 1000 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

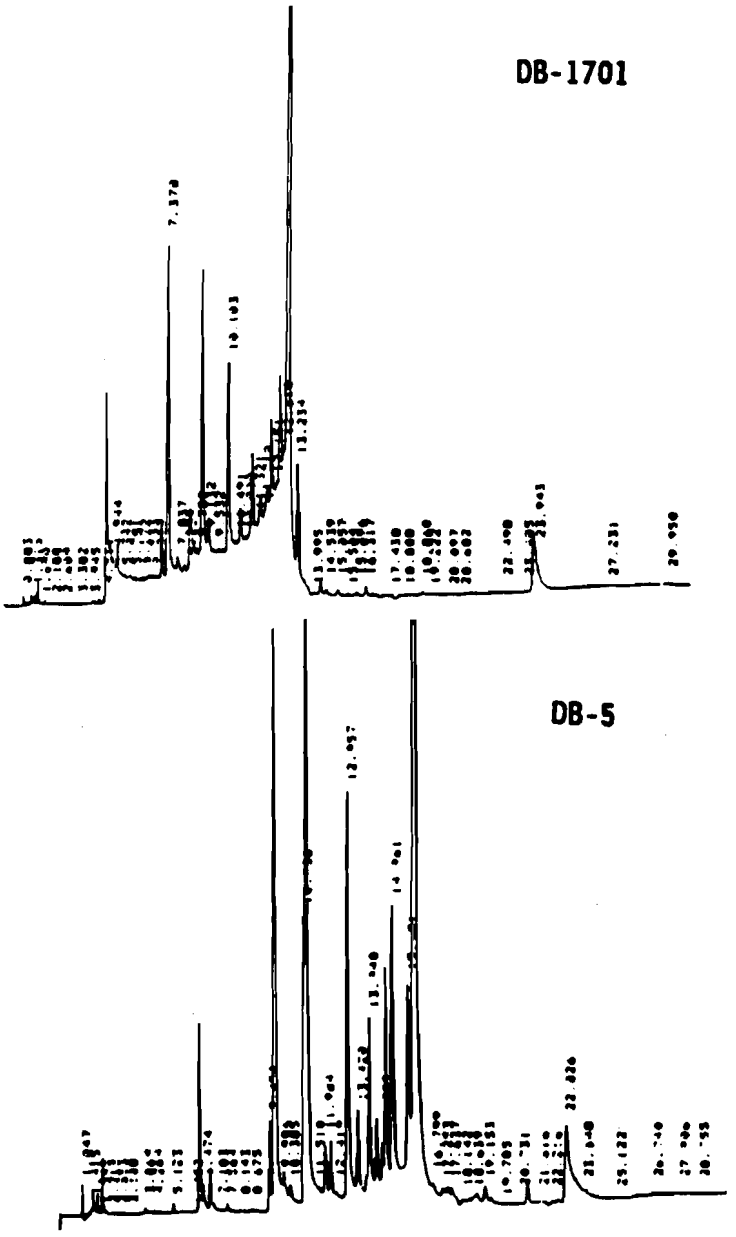


FIGURE 17. GC/ECD chromatogram of Halowax 1001 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

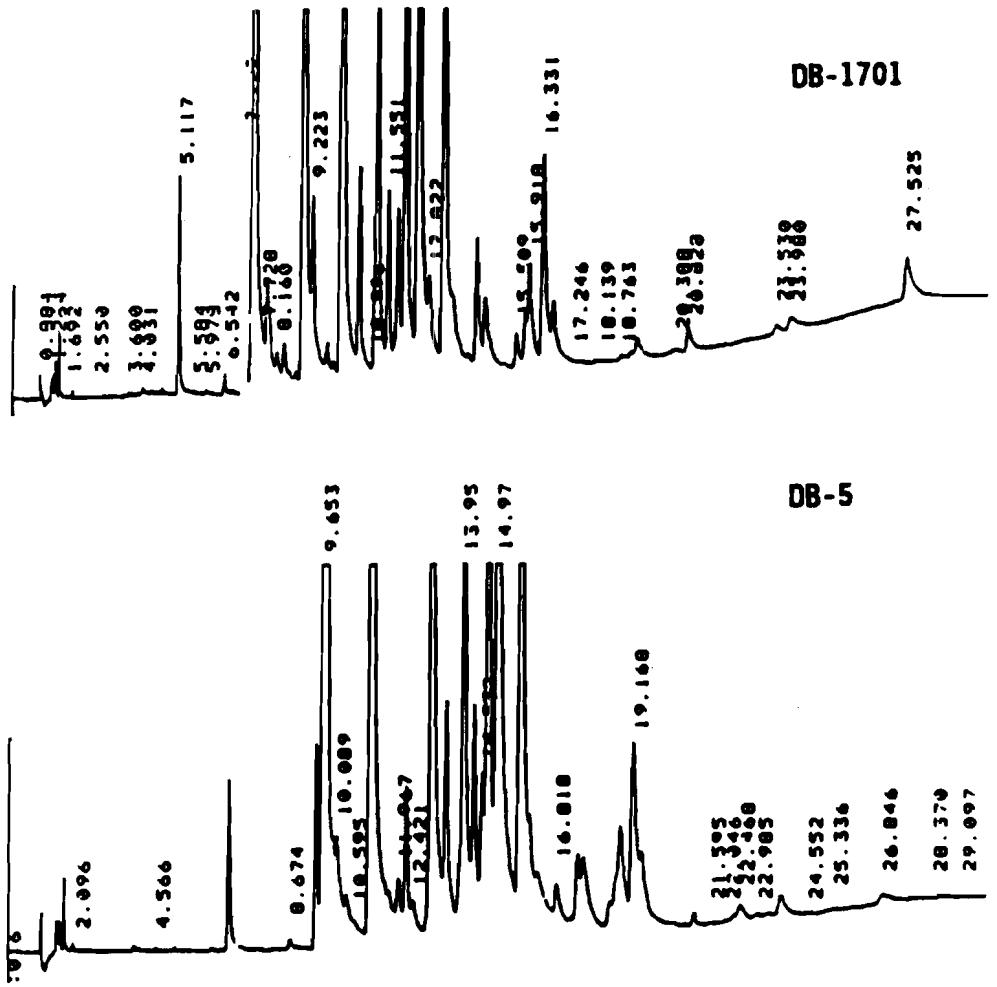


FIGURE 18. GC/ECD chromatogram of Halowax 1099 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

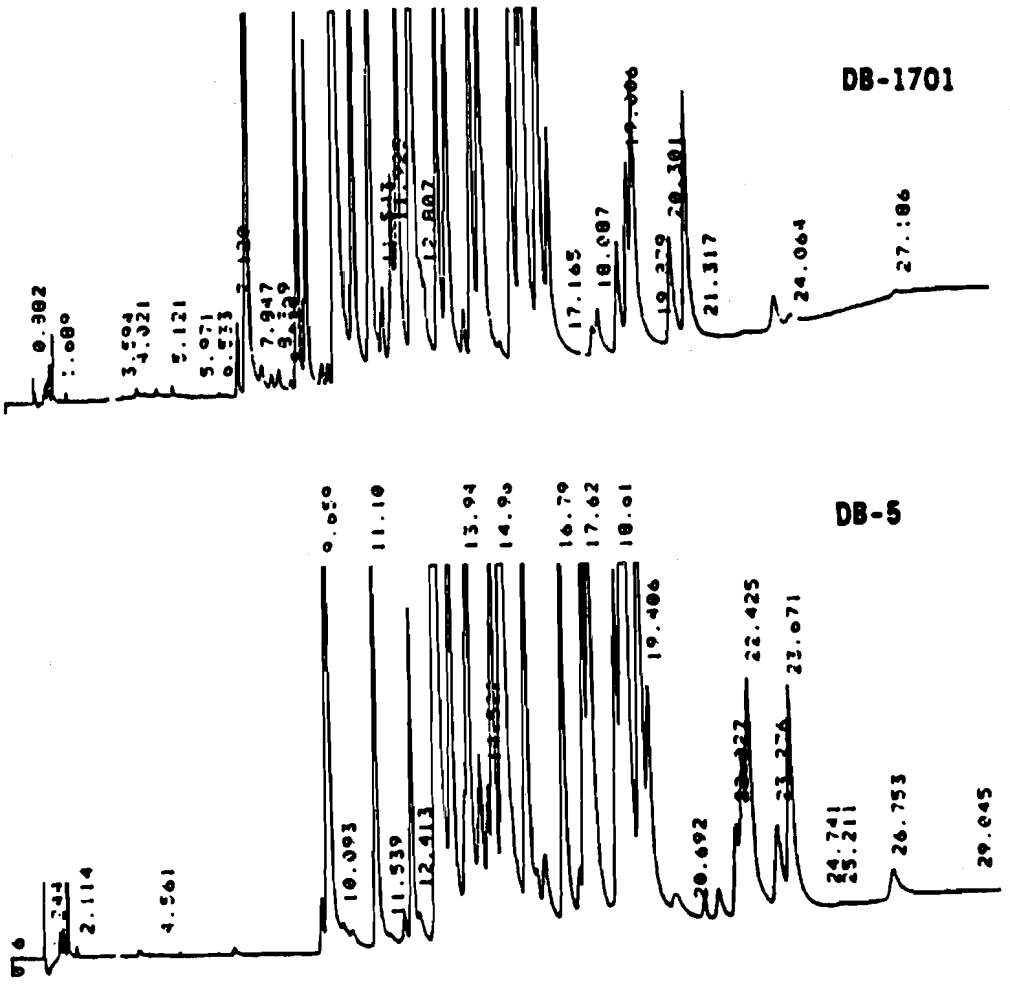


FIGURE 19. GC/ECD chromatogram of Halowax 1013 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

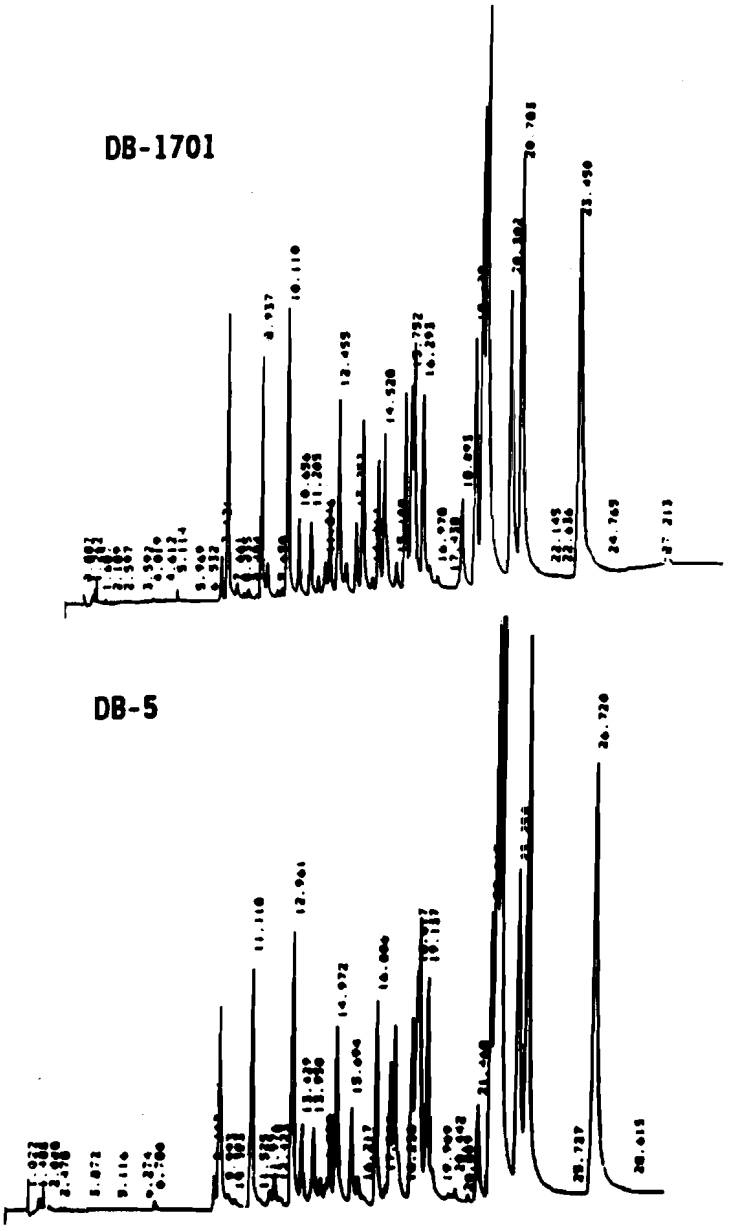


FIGURE 20. GC/ECD chromatogram of Halowax 1014 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

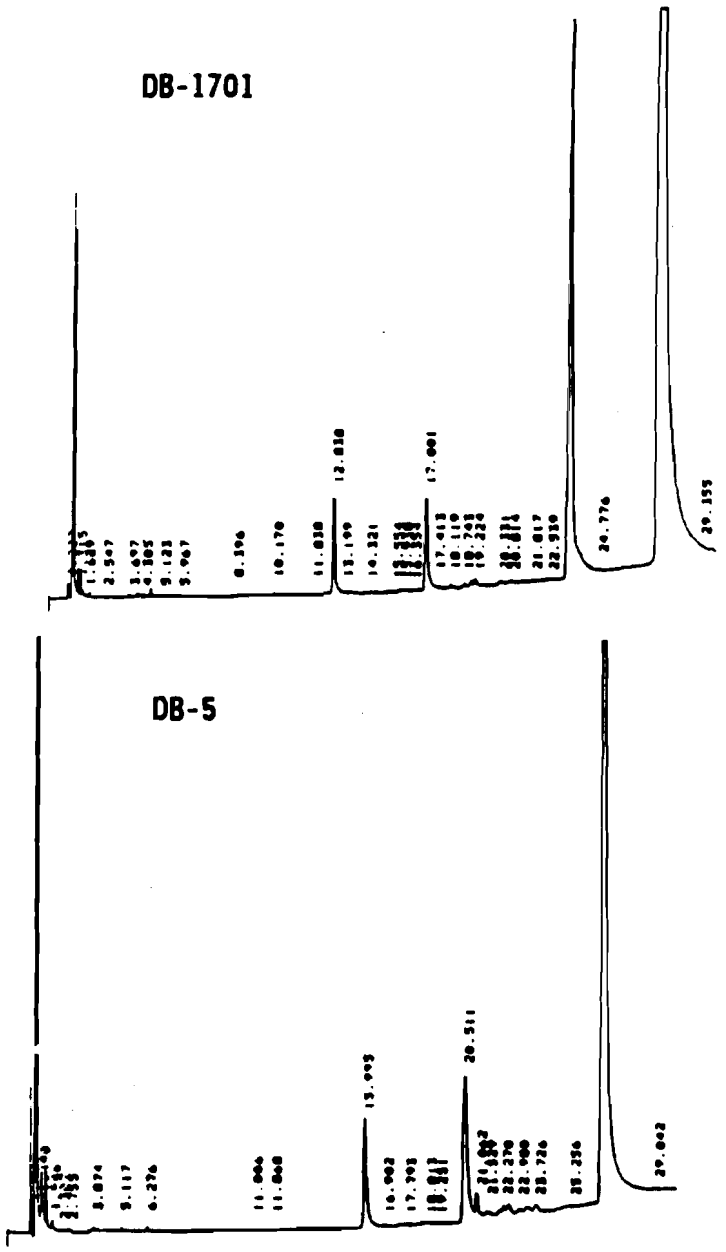


FIGURE 21. GC/ECD chromatogram of Halowax 1051 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

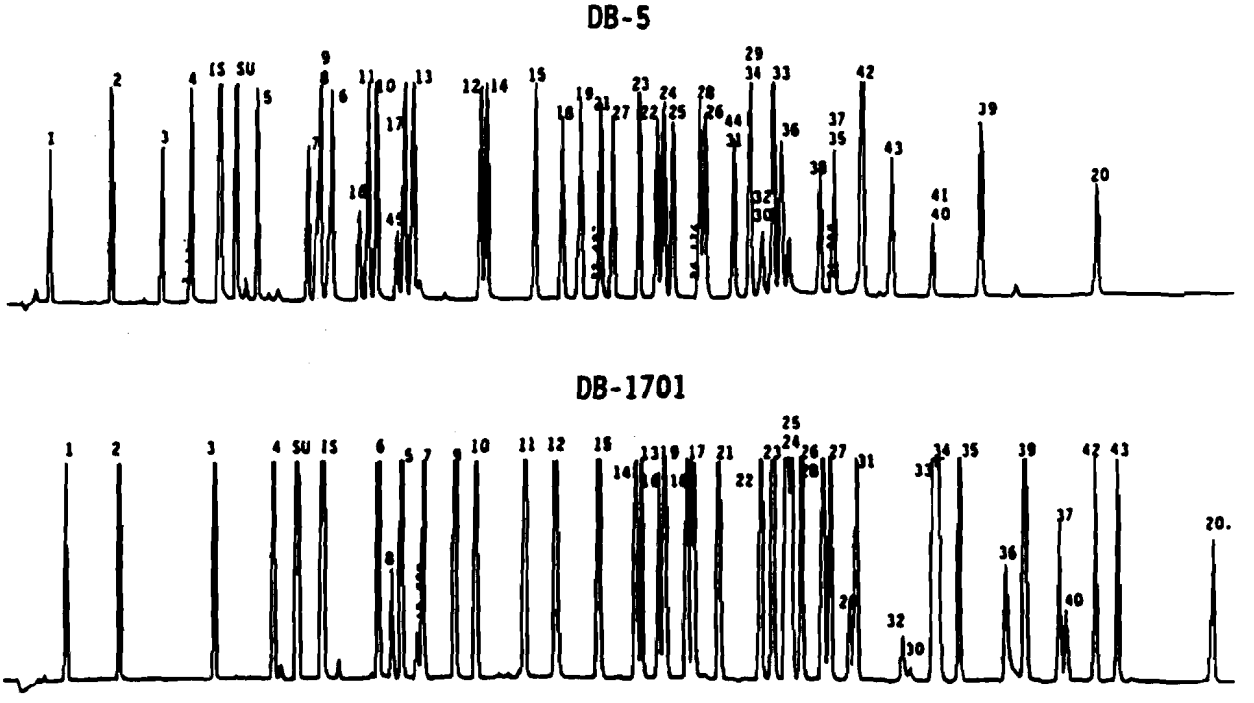


FIGURE 22. GC/ECD chromatogram of the organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min.

ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

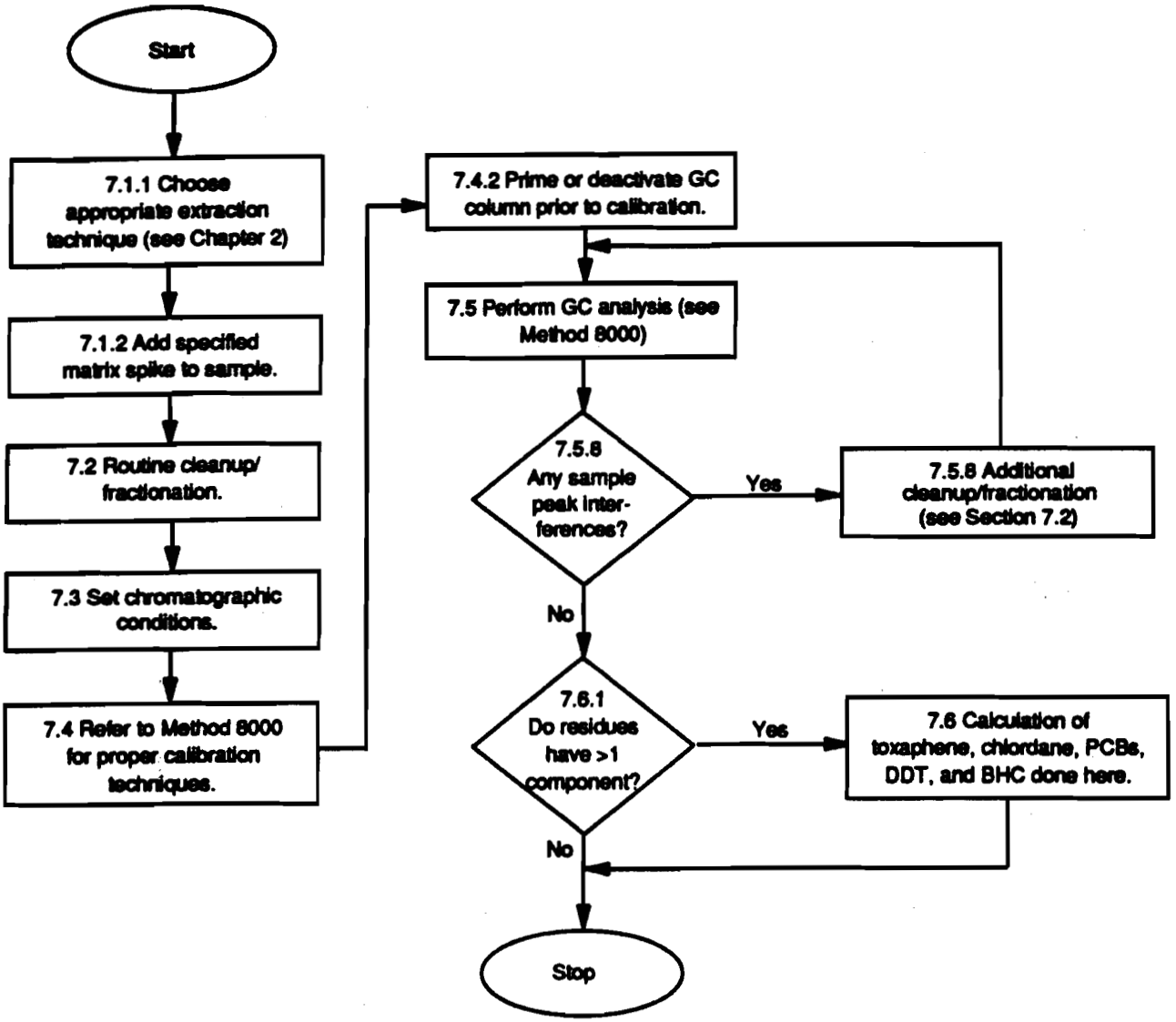


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Table 16 Multi-laboratory Precision and Accuracy Data for the Extraction of PCBs from Spiked Soil by Method 3541 (Automated Soxhlet)

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Figure 2. GC of Individual Organochlorine Pesticide Standard Mix A. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 3. GC of Individual Organochlorine Pesticide Standard Mix B. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 4. GC of the Toxaphene Standard. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 5. GC of the Aroclor-1016 Standard. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused silica capillary column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 6. GC of the Technical Chlordane Standard. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused silica capillary column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 7. GC/ECD chromatogram of Toxaphene analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 8. GC/ECD chromatogram of Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 9. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 10. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 11. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 12. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 13. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 14. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 15. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 16. GC/ECD chromatogram of Halowax 1000 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 17. GC/ECD chromatogram of Halowax 1001 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 18. GC/ECD chromatogram of Halowax 1099 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 19. GC/ECD chromatogram of Halowax 1013 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 20. GC/ECD chromatogram of Halowax 1014 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 21. GC/ECD chromatogram of Halowax 1051 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 22. GC/ECD chromatogram of the organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-μm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min.

METHOD 8090

NITROAROMATICS AND CYCLIC KETONES

1.0 SCOPE AND APPLICATION

1.1 Method 8090 is used to determine the concentration of various nitroaromatic and cyclic ketone compounds. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8090 provides gas chromatographic conditions for the detection of ppb levels of nitroaromatic and cyclic ketone compounds. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a flame ionization detector (FID). The dinitrotoluenes are determined using ECD, whereas the other compounds amenable to this method are determined using FID.

2.2 If interferences prevent proper detection of the analytes, the method may also be performed on extracts that have undergone cleanup.

3.0 INTERFERENCES

3.1 Refer to Method 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. GAS CHROMATOGRAPHY OF NITROAROMATICS AND ISOPHORONE

Compound	Retention time (min)		Method detection limit (ug/L)	
	Col. 1[a]	Col. 2[b]	ECD	FID
Isophorone	4.49	5.72	15.7	5.7
Nitrobenzene	3.31	4.31	13.7	3.6
2,4-Dinitrotoluene	5.35	6.54	0.02	-
2,6-Dinitrotoluene	3.52	4.75	0.01	-
Dinitrobenzene				
Naphthoquinone				

[a]Column 1: Gas-Chrom Q (80/100 mesh) coated with 1.95% QF-1/1.5% OV-17 packed in a 1.2-m x 2-mm or 4-mm I.D. glass column. A 2-mm I.D. column and nitrogen gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by GC/FID. The column temperature was held isothermal at 85°C. A 4-mm I.D. column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used when determining the dinitrotoluenes by GC/ECD. The column temperature was held isothermal at 145°C.

[b]Column 2: Gas-Chrom Q (80/100 mesh) coated with 3% OV-101 packed in a 3.0-m x 2-mm or 4-mm I.D. glass column. A 2-mm I.D. column and nitrogen carrier gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by GC/FID. The column temperature was held isothermal at 100°C. A 4-mm I.D. column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used to determine the dinitrotoluenes by GC/ECD. The column temperature was held isothermal at 150°C.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]Multiply the Method Detection Limits in Table 1 by the Factor to determine the PQL for each analyte in the matrix to be analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns:

4.1.2.1 Column 1: 1.2-m x 2- or 4-mm I.D. glass column packed with 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or equivalent.

4.1.2.2 Column 2: 3.0-m x 2- or 4-mm I.D. glass column packed with 3% OV-101 on Gas-Chrom Q (80/100 mesh) or equivalent.

4.1.3 Detectors: Flame ionization (FID) or electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.2.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: hexane, acetone (pesticide quality or equivalent.)

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in hexane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared through dilution of the stock standards with hexane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each

sample, standard, and reagent water blank with one or two surrogates (e.g., 2-fluorobiphenyl) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH between 5 to 9 with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange may be performed in one of two ways, depending on the data requirements. If the detection limits cited in Table 1 must be achieved, the exchange should be performed as described starting in Section 7.1.4. If these detection limits are not necessary, solvent exchange is performed as outlined in Section 7.1.3.

7.1.3 Solvent exchange when detection limits in Table 1 are not required:

7.1.3.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.3.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. The extract will be handled differently

at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.3.3. If cleanup is needed, proceed to Paragraph 7.1.3.4.

7.1.3.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.3.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.1.4 **Solvent exchange when detection limits listed in Table 1 must be achieved:**

7.1.4.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.4.2 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Add 1-2 mL of hexane, a clean boiling chip, and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.4.3 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. The volume of the extract should be adjusted to 1.0 mL if the extract will be analyzed without cleanup. If the extract will require cleanup, adjust the volume to 2.0 mL with hexane. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with either gas chromatographic analysis or with cleanup, as necessary.

7.2 Gas chromatography conditions (Recommended): The determination of dinitrotoluenes should be performed using GC/ECD. All other compounds amenable to this method are to be analyzed by GC/FID.

7.2.1 **Column 1:** Set 10% methane/90% argon carrier gas flow at 44 mL/min flow rate. For a 2-mm I.D. column, set the temperature at 85°C isothermal. For a 4-mm I.D. column, set the temperature at 145°C isothermal.

7.2.2 **Column 2:** Set 10% methane/90% argon carrier gas flow at 44 mL/min flow rate. For a 2-mm I.D. column, set the temperature at 100°C isothermal. For a 4-mm I.D. column, set the temperature at 150°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.4 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence when using FID and after each group of 5 samples in the analysis sequence when using ECD.

7.4.3 An example of a GC/FID chromatogram for nitrobenzene and isophorone is shown in Figure 1. Figure 2 is an example of a GC/ECD chromatogram of the dinitrotoluenes.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, using the 2-mL hexane extracts obtained from either Paragraph 7.1.3.5 or 7.1.4.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest in acetone at a concentration of 20 ug/mL for each dinitrotoluene and 100 ug/mL for isophorone and nitrobenzene.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

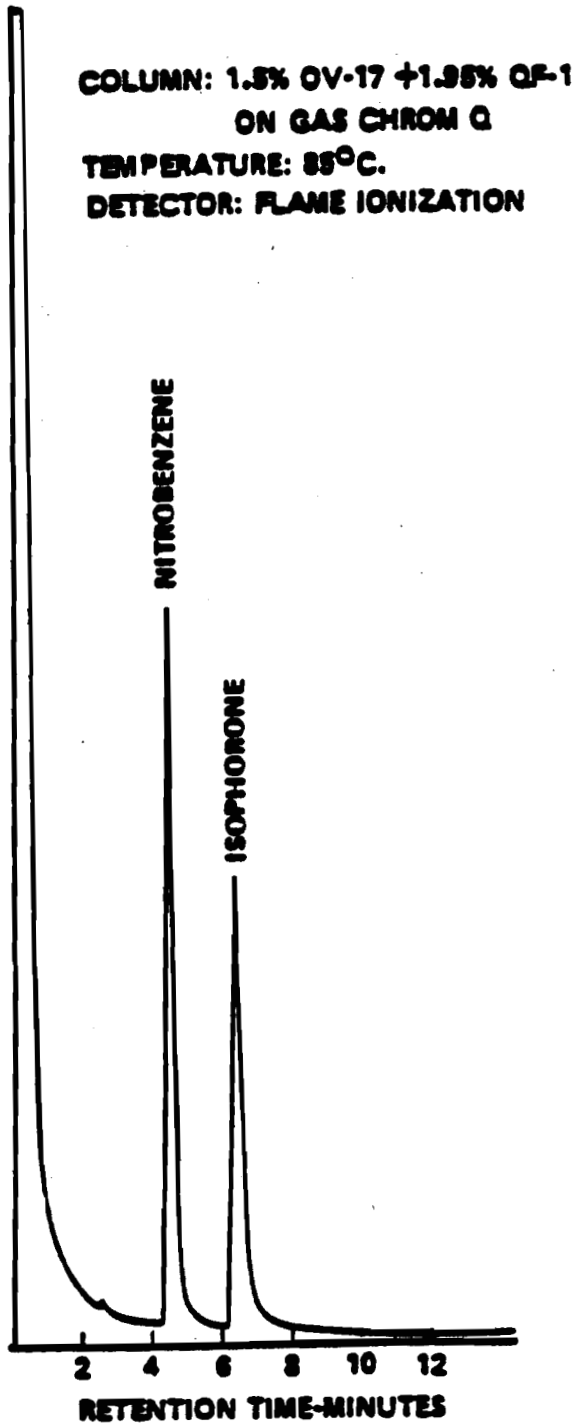


Figure 1. Gas chromatogram of nitrobenzene and isophorone.

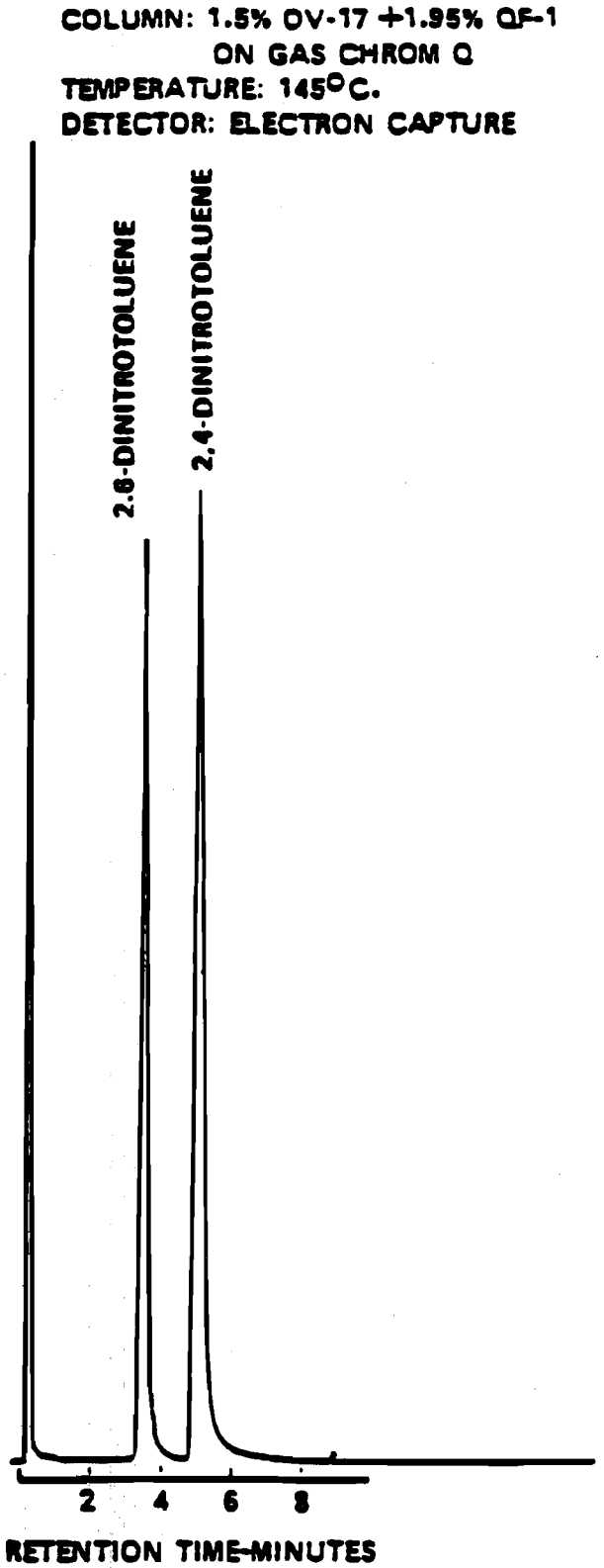


Figure 2. Gas chromatogram of dinitrotoluenes.

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 18 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 515 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 4 - Nitroaromatics and Isophorone,' Report for EPA Contract 68-03-2624 (in preparation).

2. "Determination of Nitroaromatics and Isophorone in Industrial and Municipal Wastewaters," EPA-600/4-82-024, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1982.

3. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. "EPA Method Validation Study 19, Method 609 (Nitroaromatics and Isophorone)," Report for EPA Contract 68-03-2624 (in preparation).

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
2,4-Dinitrotoluene	20	5.1	3.6-22.8	6-125
2,6-Dinitrotoluene	20	4.8	3.8-23.0	8-126
Isophorone	100	32.3	8.0-100.0	D-117
Nitrobenzene	100	33.3	25.7-100.0	6-118

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 609. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
2,4-Dinitrotoluene	0.65C+0.22	0.20$\bar{X}$+0.08	0.37$\bar{X}$-0.07
2,4-Dinitrotoluene	0.66C+0.20	0.19$\bar{X}$+0.06	0.36$\bar{X}$-0.00
Isophorene	0.49C+2.93	0.28$\bar{X}$+2.77	0.46$\bar{X}$+0.31
Nitrobenzene	0.60C+2.00	0.25$\bar{X}$+2.53	0.37$\bar{X}$-0.78

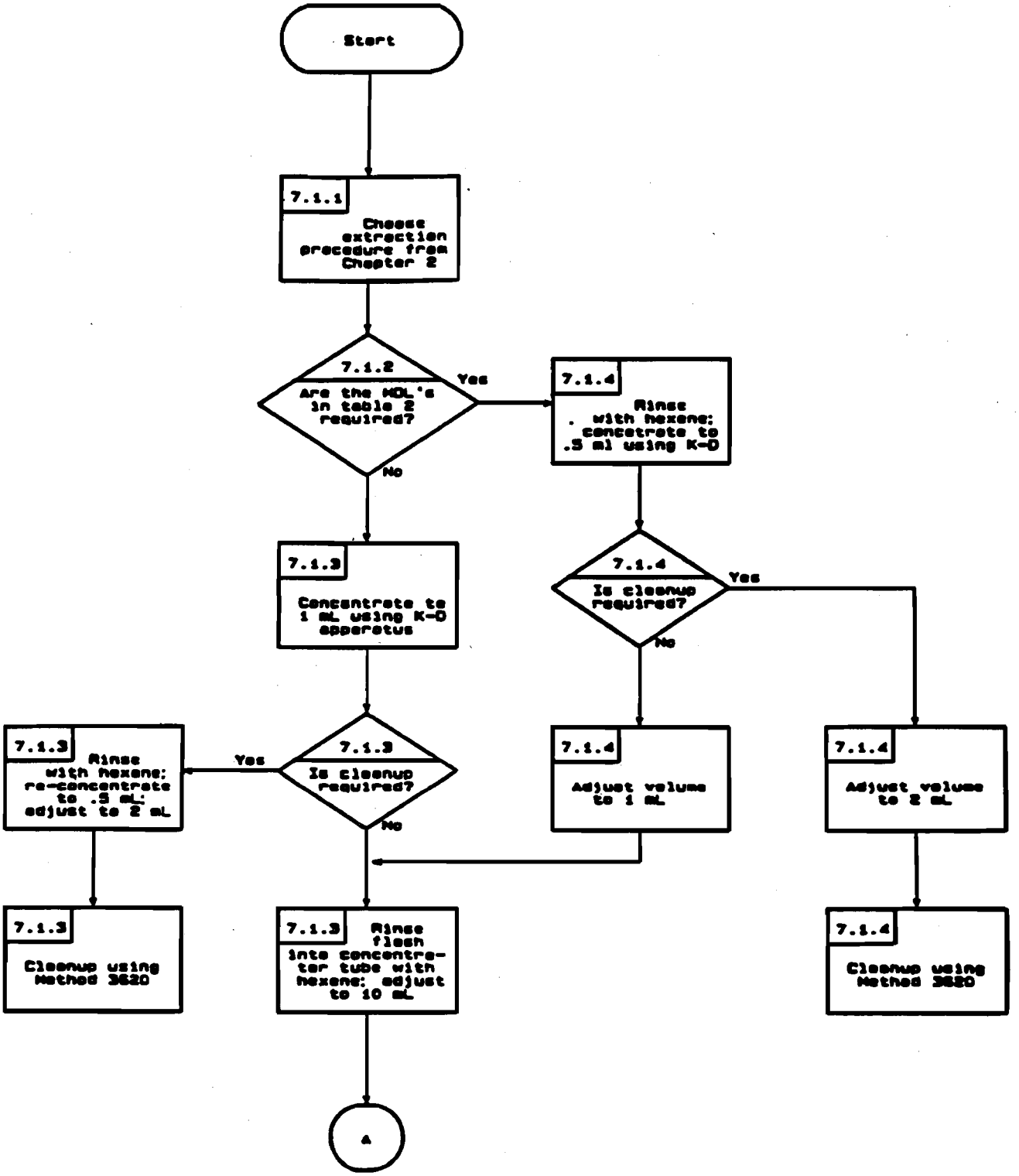
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

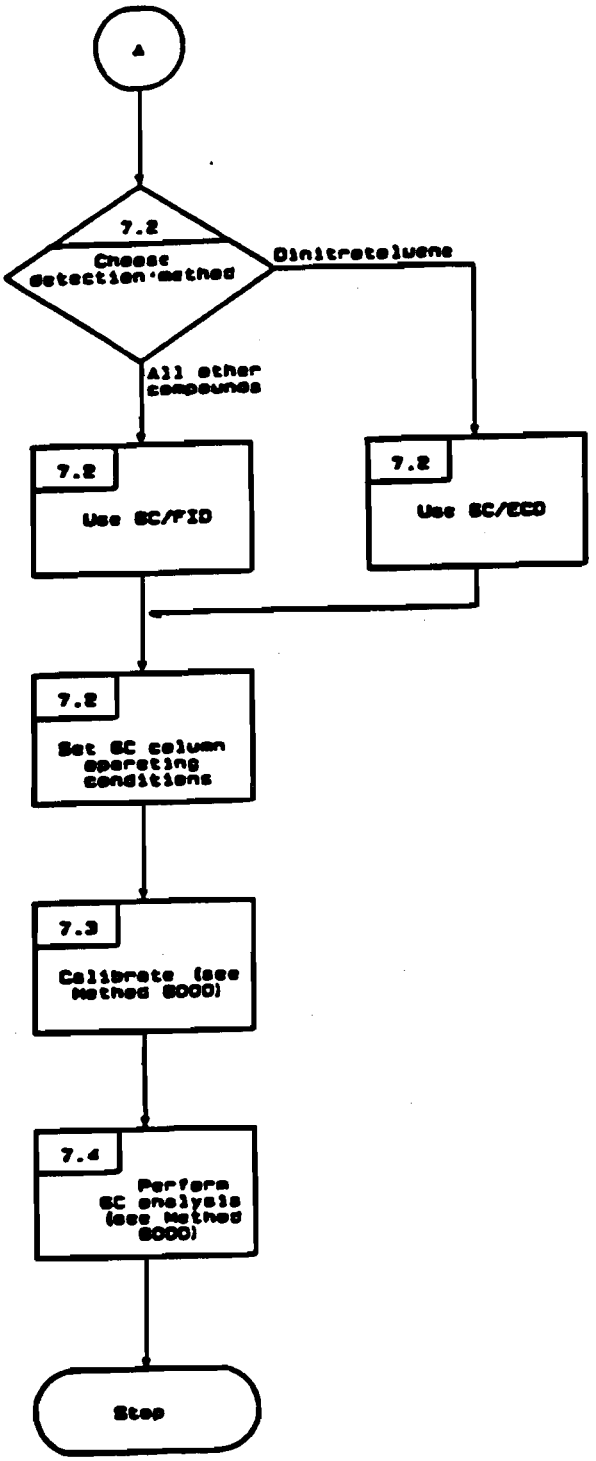
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1
Choose extraction procedure from Chapter 2
7.1.2
Are the MDL's in table 2 required?
Yes
No
7.1.4
Rinse with hexane; concentrate to .5 ml using K-D
7.1.3
Concentrate to 1 mL using K-D apparatus
7.1.4
Is cleanup required?
Yes
No
7.1.3
Is cleanup required?
Yes
No
7.1.3
Rinse with hexane; re-concentrate to .5 mL; adjust to 2 mL
7.1.4
Adjust volume to 1 mL
7.1.4
Adjust volume to 2 mL
7.1.3
Cleanup using Method 3620
7.1.3
Rinse flask into concentrator tube with hexane; adjust to 10 mL
7.1.4
Cleanup using Method 3620
A


A
7.2
Choose detection method
Dinitrotoluene
All other compounds
7.2
Use GC/FID
7.2
Use GC/ECD
7.2
Set GC column operating conditions
7.3
Calibrate (see Method 8000)
7.4
Perform GC analysis (see Method 8000)
Stop

METHOD 8100

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8100 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH). Table 1 indicates compounds that may be determined by this method.

1.2 The packed column gas chromatographic method described here cannot adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, may adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either liquid chromatography (Method 8310) or gas chromatography/mass spectroscopy (Method 8270) should be used for these compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8100 provides gas chromatographic conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. GAS CHROMATOGRAPHY OF POLYNUCLEAR AROMATIC HYDROCARBONS[a]

Compound	Retention time (min)
Acenaphthene	10.8
Acenaphthylene	10.4
Anthracene	15.9
Benzo(a)anthracene	20.6
Benzo(a)pyrene	29.4
Benzo(b)fluoranthene	28.0
Benzo(j)fluoranthene	
Benzo(k)fluoranthene	28.0
Benzo(ghi)perylene	38.6
Chrysene	24.7
Dibenz(a,h)acridine	
Dibenz(a,j)acridine	
Dibenzo(a,h)anthracene	36.2
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	
Dibenzo(a,h)pyrene	
Dibenzo(a,i)pyrene	
Fluoranthene	19.8
Fluorene	12.6
Indeno(1,2,3-cd)pyrene	36.2
3-Methylcholanthrene	
Naphthalene	4.5
Phenanthrene	15.9
Pyrene	20.6

[a]Results obtained using Column 1.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns:

4.1.2.1 Column 1: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.

4.1.2.2 Column 2: 30-m x 0.25-mm I.D. SE-54 fused silica capillary column.

4.1.2.3 Column 3: 30-m x 0.32-mm I.D. SE-54 fused silica capillary column.

4.1.3 Detector: Flame ionization (FID).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.3 Microsyringe: 10-uL.

5.0 REAGENTS

5.1 Solvents: Hexane, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., 2-fluorobiphenyl and 1-fluoronaphthalene) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and must be analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1: Set nitrogen carrier gas flow at 40-mL/min flow rate. Set column temperature at 100°C for 4 min; then program at 8°C/min to a final hold at 280°C.

7.2.2 Column 2: Set helium carrier gas at 20-cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 12 min.

7.2.3 Column 3: Set helium carrier gas at 60 cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 3 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the extract may undergo cleanup using Method 3630.

7.5 Cleanup:

7.5.1 Proceed with Method 3630. Instructions are given in this method for exchanging the solvent of the extract to hexane.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 2 indicates the calibration and QC acceptance criteria for this method. Table 3 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to

the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 3.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (in preparation).

6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 2. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Ideno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

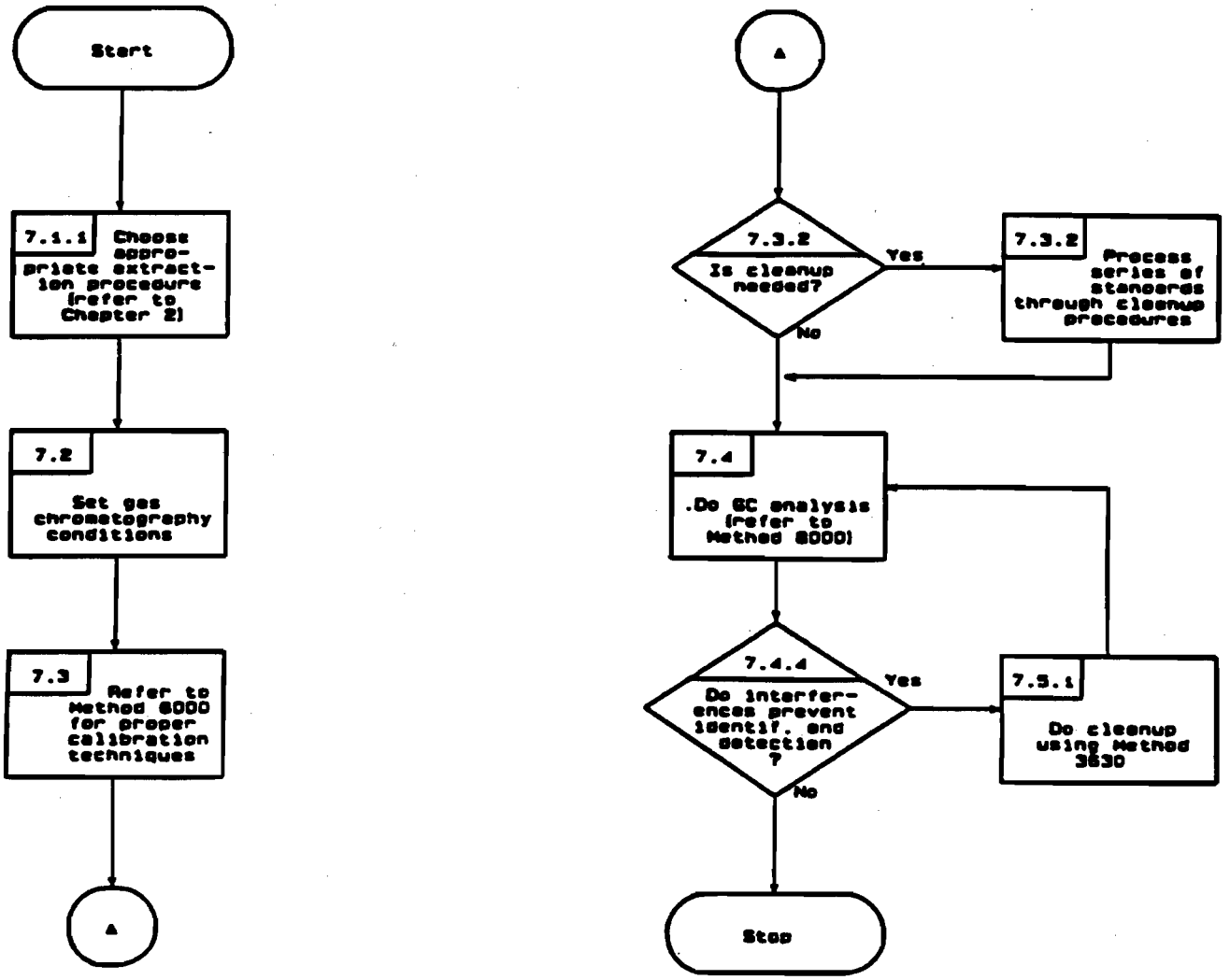
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1
Choose appropriate extraction procedure (refer to Chapter 2)
7.2
Set gas chromatography conditions
7.3
Refer to Method 8000 for proper calibration techniques
A
A
7.3.2
Is cleanup needed?
Yes
No
7.3.2
Process series of standards through cleanup procedures
7.4
Do GC analysis (refer to Method 8000)
7.4.4
Do interferences prevent identif. and detection ?
Yes
No
7.5.1
Do cleanup using Method 3630
Stop

METHOD 8110

HALOETHERS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of certain haloethers. The following compounds can be determined by this method:

		Appropriate Technique				
Compound Name	CAS No.[a]	3510	3520	3540	3550	3580
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X

[a] Chemical Abstract Services Registry Number.
X Greater than 70 percent recovery by this technique.

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions of a second GC column that can be used to confirm measurements made with the primary column. Method 8270 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract from this method.

1.3 The method detection limit (MDL, defined in Section 9.1) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from that listed, depending upon the nature of interferences in the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.5 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also

be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. GC conditions are described which permit the separation and measurement of the compounds in the extract using a halide specific detector.

2.2 Method 8110 provides gas chromatographic conditions for the detection of ppb concentrations of haloethers. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 µL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electrolytic conductivity detector (HECD).

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 7.3 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Dichlorobenzenes are known to coelute with haloethers under some gas chromatographic conditions. If these materials are present in a sample, it may be necessary to analyze the extract with two different column packings to completely resolve all of the compounds.

3.4 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is

recommended for measuring peak areas.

4.1.2 Columns

4.1.2.1 Column 1 - 1.8 m x 2 mm ID pyrex glass, packed with Supelcoport, (100/120 mesh) coated with 3% SP-1000 or equivalent. This column was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate column packings are provided in Section 7.3.1.

4.1.2.2 Column 2 - 1.8 m x 2 mm ID pyrex glass, packed with 2,6-diphenylene oxide polymer (Tenax-GC 60/80 mesh) or equivalent.

4.1.3 Detector - Electrolytic conductivity or microcoulometric. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope of this method. The Hall conductivity detector (HECD) was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate detectors are provided in Section 7.3.1. Although less selective, an electron capture detector (ECD) is an acceptable alternative.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Vials - Amber glass, 10 to 15 mL capacity, with Teflon lined screw-cap or crimp top.

4.4 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Balance - Analytical, 0.0001 g.

4.7 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.4 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.5 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.6 Stock standard solutions (1000 mg/L) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.6.1 Prepare stock standard solutions by accurately weighing 0.1000 ± 0.0010 g of pure material. Dissolve the material in pesticide quality acetone and dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.7 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.8 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.8.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.7.

5.8.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.8.3 Analyze each calibration standard according to Section 7.0.

5.9 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with one or two surrogates (e.g. haloethers that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored at 4°C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

NOTE: Some of the haloethers are very volatile and significant losses will occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D apparatus from the hot water bath.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder

column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Section 7.1.2.3. If cleanup is needed, proceed to Section 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon lined screw-cap vial. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5 mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.2 Cleanup

7.2.1 Proceed with Method 3620, using the 2 mL hexane extracts obtained from Section 7.1.2.5.

7.2.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.3 Gas Chromatography Conditions

7.3.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDLs that

were obtained under these conditions. Examples of the parameter separations achieved by these columns are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

7.4 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.4.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.5 Gas chromatographic analysis

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.5.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration check standard after each group of 10 samples in the analysis sequence.

7.5.3 Examples of GC/HECD chromatograms for haloethers are shown in Figures 1 and 2.

7.5.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.5.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Method 8000 for calculation equations.

7.5.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control (QC) reference sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at 20 mg/L.

8.2.2 Table 1 indicates the recommended operating conditions, retention times, and MDLs that were obtained under these conditions. Table 2 gives method accuracy and precision for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 This method has been tested for linearity of recovery from spiked organic-free reagent water and has been demonstrated to be applicable for the concentration range from 4 x MDL to 1000 x MDL.

9.2 In a single laboratory (Monsanto Research Center), using spiked wastewater samples, the average recoveries presented in Table 2 were obtained. Each spiked sample was analyzed in triplicate on three separate occasions. The standard deviation of the percent recovery is also included in Table 2.

10.0 REFERENCES

1. Fed. Regist. 1984, 49, 43234; October 26.

2. Mills, P.A. "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns"; Journal of the Association of Official Analytical Chemists 1968, 51, 29.

3. Handbook of Analytical Quality Control in Water and Wastewater Laboratories; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1979; EPA-600/4-79-019.

4. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

5. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects"; Journal of the Association of Official Analytical Chemists 1965, 48, 1037.

6. "EPA Method Validation Study 21 Methods 611 (Haloethers)," Report for EPA Contract 68-03-2633.

7. "Determination of Haloethers in Industrial and Municipal Wastewaters"; Report for EPA Contract 68-03-2633 (In preparation).

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Analyte	Retention Time (minutes) Column 1	Column 2	Method Detection Limit (μg/L)
Bis(2-chloroisopropyl) ether	8.4	9.7	0.8
Bis(2-chloroethyl) ether	9.4	9.1	0.3
Bis(2-chloroethoxy)methane	13.1	10.0	0.5
4-Chlorophenyl phenyl ether	19.4	15.0	3.9
4-Bromophenyl phenyl ether	21.2	16.2	2.3

Column 1 conditions:

Carrier gas (He) flow rate:	40 mL/min
Initial temperature:	60°C, hold for 2 minutes
Temperature program:	60°C to 230°C at 8°C/min
Final temperature:	230°C, hold for 4 minutes

Under these conditions the retention time for aldrin is 22.6 minutes.

Column 2 conditions:

Carrier gas (He) flow rate:	40 mL/min
Initial temperature:	150°C, hold for 4 minutes
Temperature program:	150°C to 310°C at 16°C/min
Final temperature:	310°C

Under these conditions the retention time for aldrin is 18.4 minutes.

TABLE 2.
SINGLE OPERATOR ACCURACY AND PRECISION

Analyte	Average Percent Recovery	Standard Deviation %	Spike Range (µg/L)	Number of Analyses	Matrix Types
Bis(2-chloroethoxy)methane	62	5.3	138	27	3
Bis(2-chloroethyl) ether	59	4.5	97	27	3
Bis(2-chloroisopropyl) ether	67	4.0	54	27	3
4-Bromophenyl phenyl ether	78	3.5	14	27	3
4-Chlorophenyl phenyl ether	73	4.5	30	27	3

FIGURE 1.
GAS CHROMATOGRAM OF HALOETHERS

Column: 3% SP-1000 on Supelcoport
Program: 60°C.-2 minutes 8°/minute to 230°C.
Detector: Hall electrolytic conductivity

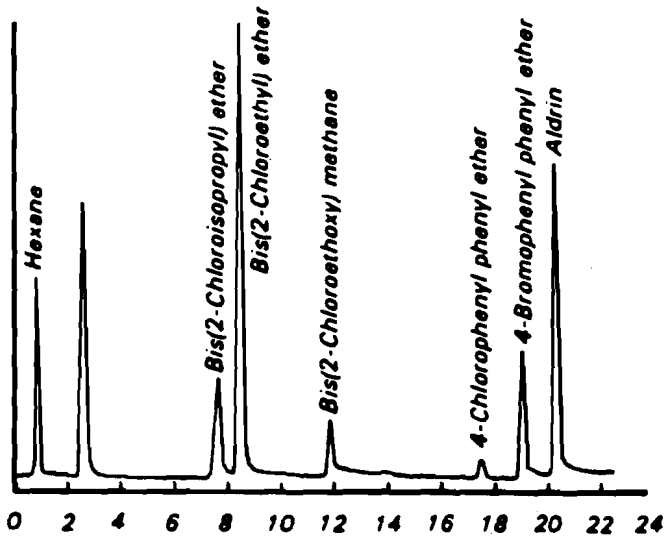
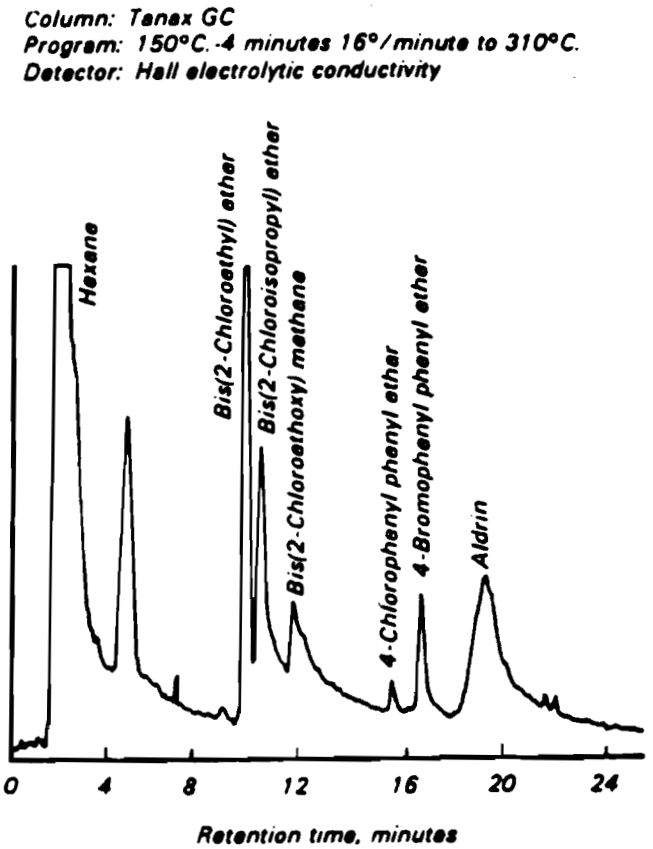
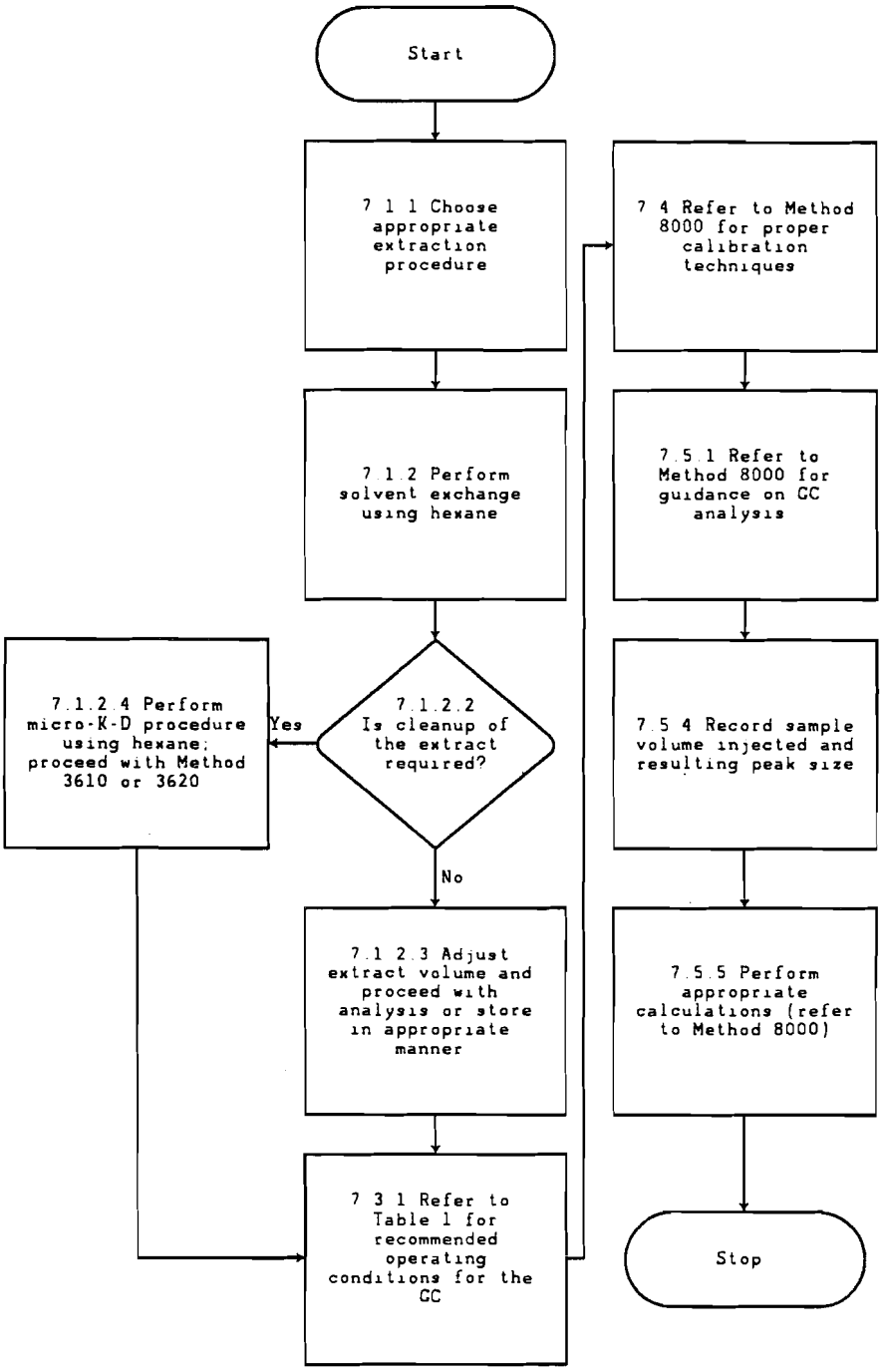


FIGURE 2.
GAS CHROMATOGRAM OF HALOETHERS




Start
7 1 1 Choose appropriate extraction procedure
7 1 2 Perform solvent exchange using hexane
7.1.2.2 Is cleanup of the extract required?
Yes
7.1.2.4 Perform micro-K-D procedure using hexane; proceed with Method 3610 or 3620
No
7.1 2.3 Adjust extract volume and proceed with analysis or store in appropriate manner
7 3 1 Refer to Table 1 for recommended operating conditions for the GC
7 4 Refer to Method 8000 for proper calibration techniques
7.5.1 Refer to Method 8000 for guidance on GC analysis
7.5 4 Record sample volume injected and resulting peak size
7.5.5 Perform appropriate calculations (refer to Method 8000)
Stop

METHOD 8120A

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons. The following compounds can be determined by this method:

		Appropriate Preparation Techniques				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
2-Chloronaphthalene	91-58-7	X	X	X	X	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclohexane	608-73-1	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Pentachlorohexane	--	X	X	X	X	X
Tetrachlorobenzenes	--	X	ND	ND	ND	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X

a Chemical Abstract Services Registry Number.
x Greater than 70 percent recovery by this technique
ND Not determined.

1.2 Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8120 provides gas chromatographic conditions for the detection of ppb concentrations of certain chlorinated hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 μL aliquot of the extract is injected into a gas chromatograph (GC), and compounds in the GC effluent are detected by an electron capture detector (ECD).

2.2 If interferences are encountered in the analysis, Method 8120 may also be performed on extracts that have undergone cleanup using Method 3620.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 1.8 m x 2 mm ID glass column packed with 1% SP-1000 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2 - 1.8 m x 2 mm ID glass column packed with 1.5% OV-1/2.4% OV-225 on Supelcoport (80/100 mesh) or equivalent.

4.1.3 Detector - Electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.5 Volumetric flasks - 10, 50, and 100 mL, with ground glass stoppers.

4.6 Microsyringe - 10 µL.

4.7 Syringe - 5 mL.

4.8 Vials - Glass, 2, 10, and 20 mL capacity with Teflon lined screw-caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.3.2 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.3.3 Isooctane, C_8H_{18}. Pesticide quality or equivalent.

5.4 Stock standard solutions

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane or hexane and diluting to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with isooctane or hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Sec. 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane or hexane.

5.6.3 Analyze each calibration standard according to Sec. 7.0.

5.7 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two surrogates (e.g. chlorinated hydrocarbons that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Methods 3540/3541 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Sec. 7.1.2.3. If cleanup is needed, proceed to Sec. 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw cap or crimp top. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5 mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 minutes. At the proper rate of

distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min
Column temperature = 65°C isothermal, unless otherwise specified (see Table 1).

7.2.2 Column 2

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min
Column temperature = 75°C isothermal, unless otherwise specified (see Table 1).

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injecting.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for certain chlorinated hydrocarbons are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup: If required, the samples may be cleaned up using the Methods presented in Chapter 4.

7.5.1 Proceed with Method 3620 using the 2 mL hexane extracts obtained from Sec. 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at the following concentrations in acetone: hexachloro-substituted hydrocarbon, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons, and Category 8 - Phenols," Report for EPA Contract 68-03-2625.

2. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

3. "EPA Method Validation Study 22, Method 612 (Chlorinated Hydrocarbons)," Report for EPA Contract 68-03-2625.

4. "Method Performance for Hexachlorocyclopentadiene by Method 612," Memorandum from R. Slater, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 7, 1983.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625.

TABLE 1.
GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min) Col. 1	Col. 2	Method Detection limit (μg/L)
2-Chloronaphthalene	2.7[a]	3.6[b]	0.94
1,2-Dichlorobenzene	6.6	9.3	1.14
1,3-Dichlorobenzene	4.5	6.8	1.19
1,4-Dichlorobenzene	5.2	7.6	1.34
Hexachlorobenzene	5.6[a]	10.1[b]	0.05
Hexachlorobutadiene	7.7	20.0	0.34
Hexachlorocyclohexane			
Hexachlorocyclopentadiene	ND	16.5[c]	0.40
Hexachloroethane	4.9	8.3	0.03
Pentachlorohexane	--	--	--
Tetrachlorobenzenes	--	--	--
1,2,4-Trichlorobenzene	15.5	22.3	0.05

ND = Not determined.

[a]150°C column temperature.

[b]165°C column temperature.

[c]100°C column temperature.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

a EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet weight basis. Sample EQLs are highly matrix dependent. The EQLs to be determined herein are provided for guidance and may not always be achievable.

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (μg/L)	Limit for s (μg/L)	Range for $\bar{x}$ (μg/L)	Range P, P_s (%)
2-Chloronaphthalene	100	37.3	29.5-126.9	9-148
1,2-Dichlorobenzene	100	28.3	23.5-145.1	9-160
1,3-Dichlorobenzene	100	26.4	7.2-138.6	D-150
1,4-Dichlorobenzene	100	20.8	22.7-126.9	13-137
Hexachlorobenzene	10	2.4	2.6-14.8	15-159
Hexachlorobutadiene	10	2.2	D-12.7	D-139
Hexachlorocyclopentadiene	10	2.5	D-10.4	D-111
Hexachloroethane	10	3.3	2.4-12.3	8-139
1,2,4-Trichlorobenzene	100	31.6	20.2-133.7	5-149

s = Standard deviation of four recovery measurements, in μg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in μg/L.

P,P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 612. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S' (μg/L)
Chloronaphthalene	$0.75C+3.21$	$0.28\bar{x}-1.17$	$0.38\bar{x}-1.39$
1,2-Dichlorobenzene	$0.85C-0.70$	$0.22\bar{x}-2.95$	$0.41\bar{x}-3.92$
1,3-Dichlorobenzene	$0.72C+0.87$	$0.21\bar{x}-1.03$	$0.49\bar{x}-3.98$
1,4-Dichlorobenzene	$0.72C+2.80$	$0.16\bar{x}-0.48$	$0.35\bar{x}-0.57$
Hexachlorobenzene	$0.87C-0.02$	$0.14\bar{x}+0.07$	$0.36\bar{x}-0.19$
Hexachlorobutadiene	$0.61C+0.03$	$0.18\bar{x}+0.08$	$0.53\bar{x}-0.12$
Hexachlorocyclopentadiene[a]	$0.47C$	$0.24\bar{x}$	$0.50\bar{x}$
Hexachloroethane	$0.74C-0.02$	$0.23\bar{x}+0.07$	$0.36\bar{x}-0.00$
1,2,4-Trichlorobenzene	$0.76C+0.98$	$0.23\bar{x}-0.44$	$0.40\bar{x}-1.37$

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

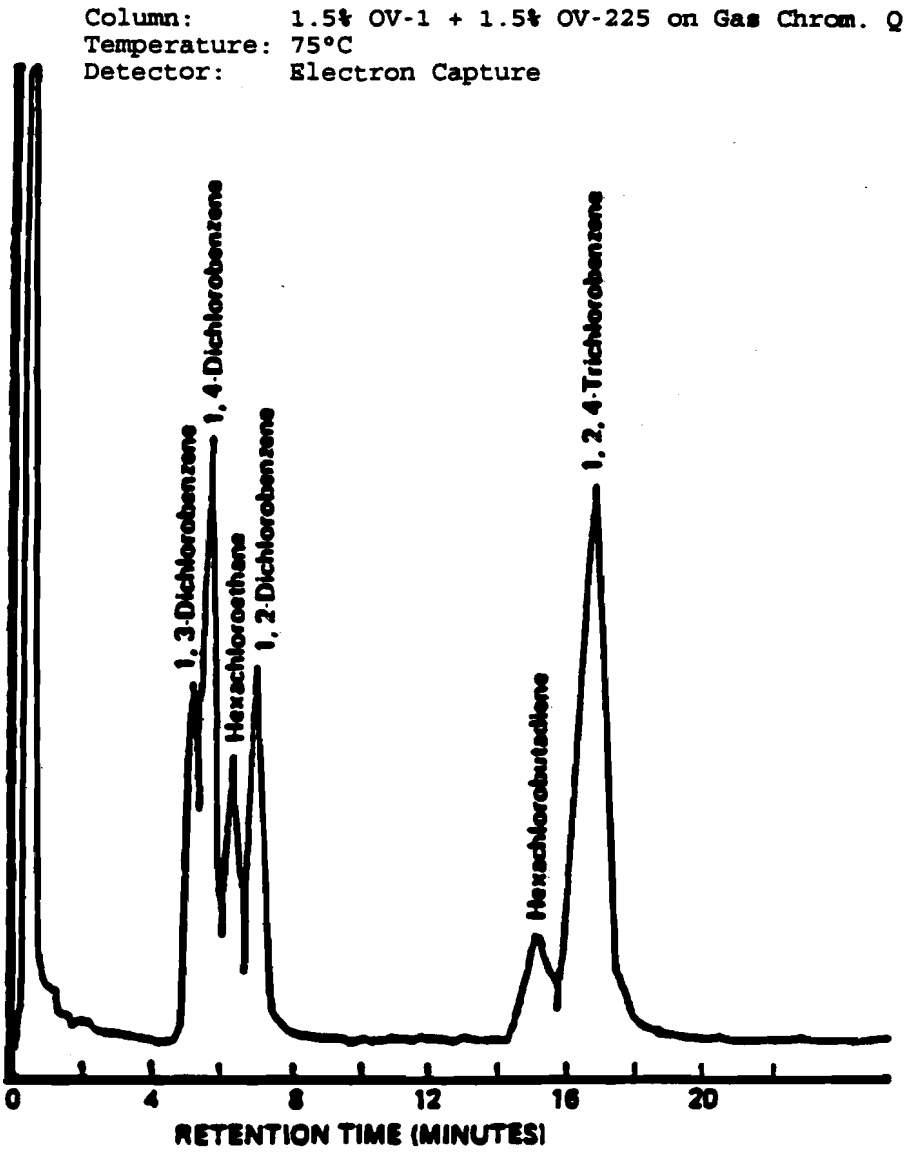
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

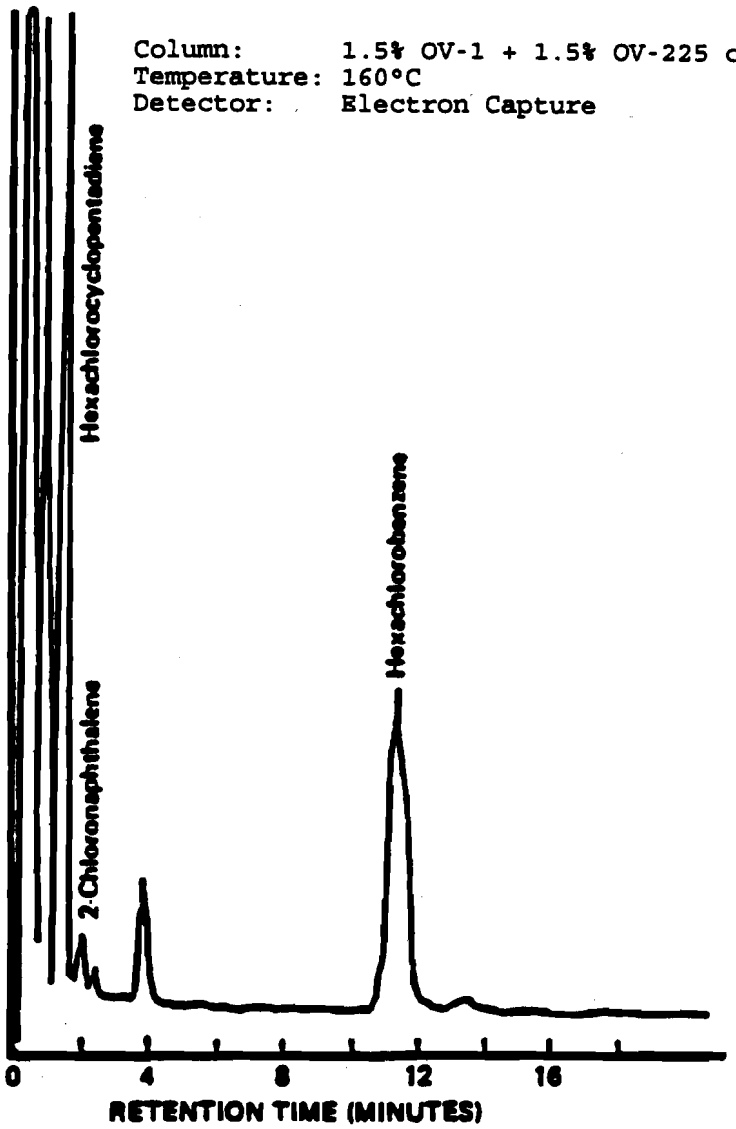
a Estimates based upon the performance in a single laboratory.

FIGURE 1

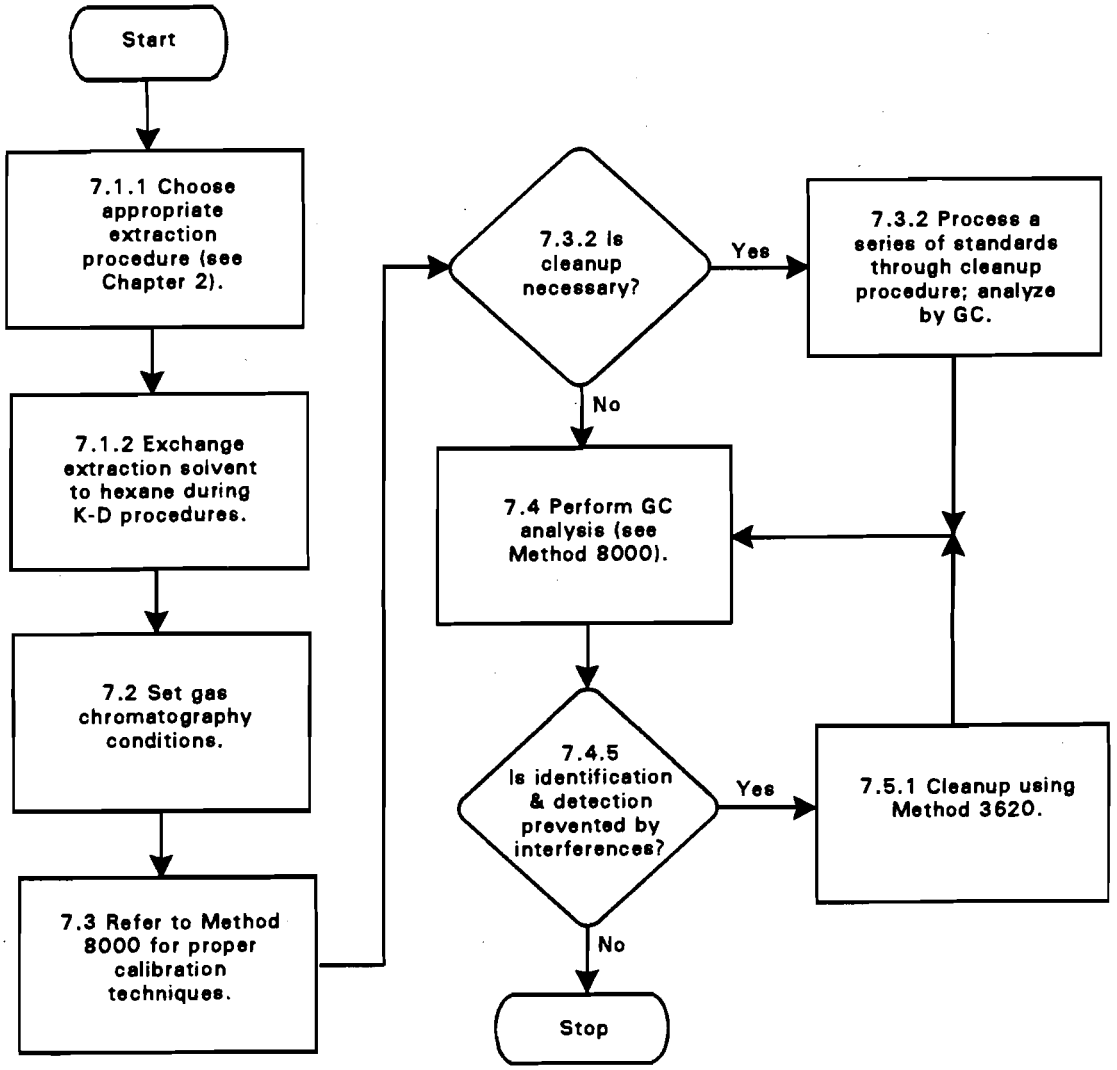


Gas chromatagram of chlorinated hydrocarbons (high molecular weight compounds).

FIGURE 2



Gas chromatagram of chlorinated hydrocarbons (low molecular weight compounds).


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2).
7.1.2 Exchange extraction solvent to hexane during K-D procedures.
7.2 Set gas chromatography conditions.
7.3 Refer to Method 8000 for proper calibration techniques.
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC.
No
7.4 Perform GC analysis (see Method 8000).
7.4.5 Is identification & detection prevented by interferences?
Yes
7.5.1 Cleanup using Method 3620.
No
Stop

METHOD 8121

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8121 describes the determination of chlorinated hydrocarbons in extracts prepared from environmental samples and RCRA wastes. It describes wide-bore open-tubular, capillary column gas chromatography procedures using both single column/single detector and dual-column/dual-detector approaches. The following compounds can be determined by this method:

Compound Name	CAS Registry No.[a]
Benzal chloride	98-87-3
Benzotrichloride	98-07-7
Benzyl chloride	100-44-7
2-Chloronaphthalene	91-58-7
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-1
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
α-Hexachlorocyclohexane (α-BHC)	319-84-6
β-Hexachlorocyclohexane (β-BHC)	319-85-7
γ-Hexachlorocyclohexane (γ-BHC)	58-89-9
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Pentachlorobenzene	608-93-5
1,2,3,4-Tetrachlorobenzene	634-66-2
1,2,4,5-Tetrachlorobenzene	95-94-2
1,2,3,5-Tetrachlorobenzene	634-90-2
1,2,4-Trichlorobenzene	120-82-1
1,2,3-Trichlorobenzene	87-61-6
1,3,5-Trichlorobenzene	108-70-3

[a] Chemical Abstract Services Registry Number.

1.2 The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and two identical detectors. When compared to the packed columns, the megabore fused-silica open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis.

1.3 Table 1 lists method detection limits (MDL) for each compound in an organic-free reagent water matrix. The MDLs for the compounds of a specific sample may differ from those listed in Table 1 because they are dependent upon

the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.4 Table 3 lists the compounds that have been determined by this method and their retention times using the single column technique. Table 4 lists dual column/dual detector retention time data. Figures 1 and 2 are chromatograms showing the single column technique. Figure 3 shows a chromatogram of the target analytes eluted from a pair of DB-5/DB-1701 columns and detected with electron capture detectors (ECD) under the prescribed GC conditions listed in Table 2.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8121 provides gas chromatographic conditions for the detection of ppb concentrations of chlorinated hydrocarbons in water and soil or ppm concentrations in waste samples. Prior to use of this method, appropriate sample extraction techniques must be used for environmental samples (refer to Chapt. 2). Both neat and diluted organic liquids (Method 3580) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Analysis is accomplished by gas chromatography utilizing an instrument equipped with wide bore capillary columns and single or dual electron capture detectors.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 The electron capture detector responds to all electronegative compounds. Therefore, interferences are possible by other halogenated compounds, as well as phthalates and other oxygenated compounds, and, organonitrogen, organosulfur and organophosphorus compounds. Second column confirmation or GC/MS confirmation are necessary to ensure proper analyte identification unless previous characterization of the sample source will ensure proper identification.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the syringe used for injection must be rinsed out between samples with solvent. Whenever an extract concentration exceeds that of the highest calibration standard, it should be followed by the analysis of a solvent blank to check for cross-contamination. Additional solvent blanks interspersed with the sample extracts should be considered whenever the analysis of a solvent blank indicates cross-contamination problems.

3.4 Phthalate esters, if present in a sample, will interfere only with the BHC isomers because they elute in Fraction 2 of the Florisil procedure described in Method 3620. The presence of phthalate esters can usually be minimized by avoiding contact with any plastic materials and by following standard decontamination procedures of reagents and glassware.

3.5 The presence of elemental sulfur will result in large peaks, and can often mask the region of compounds eluting after 1,2,4,5-tetrachlorobenzene. The tetrabutylammonium (TBA)-sulfite procedure (Method 3660) works well for the removal of elemental sulfur.

3.6 In certain cases some compounds coelute on either one or both columns. In these cases the compounds must be reported as coeluting. The mixture can be reanalyzed by GC/MS techniques, see Sec. 8.7 and Method 8270.

3.6.1 Using the dual column system of analysis the following compounds coeluted:

DB-5	1,4-dichlorobenzene/benzyl chloride 1,2,3,5-tetrachlorobenzene/1,2,4,5-tetrachlorobenzene 1,2,3,4-tetrachlorobenzene/2-chloronaphthalene
DB-1701	benzyl chloride/1,2-dichlorobenzene/hexachloroethane benzal chloride/1,2,4-trichlorobenzene/ hexachlorobutadiene

Some of the injections showed a separation of 1,2,4-trichlorobenzene from the other two compounds, however, this is not always the case, so the compounds are listed as coeluting.

3.7 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection, and all required accessories, including syringes, analytical columns, gases, and two electron capture detectors. A data system for measuring peak areas, and dual display of chromatograms is recommended. A GC equipped with a single GC column and detector are acceptable, however, second column confirmation is obviously more time consuming. Following are the single and dual column configurations used for developing the retention time data presented in the method. The columns listed in the dual column configuration may also be used for single column analysis.

4.1.1 Single Column Analysis:

4.1.1.1 Column 1 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone (DB-210 or equivalent).

4.1.1.2 Column 2 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol (DB-WAX or equivalent).

4.1.2 Dual Column Analysis:

4.1.2.1 Column 1 - 30 m x 0.53 mm ID fused-silica open-tubular column, crosslinked and chemically bonded with 95 percent dimethyl and 5 percent diphenyl-polysiloxane (DB-5, RT_x-5, SPB-5, or equivalent), 0.83 µm or 1.5 µm film thickness.

4.1.2.2 Column 2 - 30 m x 0.53 mm ID fused-silica open-tubular column crosslinked and chemically bonded with 14 percent cyanopropylphenyl and 86 percent dimethyl-polysiloxane (DB-1701, RT_x-1701, or equivalent), 1.0 µm film thickness.

4.1.3 Splitter: If the splitter approach to dual column injection is chosen, following are three suggested splitters. An equivalent splitter is acceptable. See Sec. 7.5.1 for a caution on the use of splitters.

4.1.3.1 Splitter 1 - J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

4.1.3.2 Splitter 2 - Supelco 8 in. glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

4.1.3.3 Splitter 3 - Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405).

4.1.4 Column rinsing kit (optional): Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.1.5 Microsyringes - 100 µL, 50 µL, 10 µL (Hamilton 701 N or equivalent), and 50 µL (Blunted, Hamilton 705SNR or equivalent).

4.1.6 Balances - Analytical, 0.0001 g.

4.1.7 Volumetric flasks, Class A - 10 mL to 1000 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the chemicals are of sufficiently high purity to permit their use without affecting the accuracy of the determinations.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. All standard solutions must be replaced after six months or sooner if routine QC (Sec. 8) indicates a problem.

5.2 Solvents

5.2.1 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.2.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.2.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.3 Stock standard solutions (1000 mg/L): Can be prepared from pure standard materials or can be purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10 mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 For those compounds which are not adequately soluble in hexane or isooctane, mixtures of acetone and hexane are recommended.

5.4 Composite stock standard: Can be prepared from individual stock solutions. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25 mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 40 mg/L. This composite solution can be further diluted to obtain the desired concentrations.

5.5 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. A suggested list of calibration solution standards is found in Table 7.

5.6 Recommended internal standard: Make a solution of 1000 mg/L of 1,3,5-tribromobenzene. (Two other internal standards, 2,5-dibromotoluene and alpha,alpha'-dibromo-m-xylene, are suggested if matrix interferences are a problem.) For spiking, dilute this solution to 50 ng/μL. Use a spiking volume of 10 μL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards. Store the internal standard spiking solutions at 4°C in Teflon-sealed containers in the dark.

5.7 Recommended surrogate standards: Monitor the performance of the method using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. Make a solution of 1000 mg/L of 1,4-dichloronaphthalene and dilute it to 100 ng/μL. Use a spiking volume of 100 μL for a 1 L aqueous sample. If matrix interferences are a

problem, two alternative surrogates are: alpha, 2,6-trichlorotoluene or 2,3,4,5,6-pentachlorotoluene.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

6.2 Extracts must be stored at 4 °C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction and Cleanup:

7.1.1 Refer to Chapter Two and Method 3500 for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Methods 3540, 3541, or 3550 with methylene chloride/acetone (1:1) as the extraction solvent.

7.1.2 If required, the samples may be cleaned up using Method 3620 (Florisil) and/or Method 3640 (Gel Permeation Chromatography). See Chapter Two, Sec. 2.3.2 and Method 3600 for general guidance on cleanup and method selection. Method 3660 is used for sulfur removal.

7.1.3 Prior to gas chromatographic analysis, the extraction solvent must exchanged into hexane using the Kuderna-Danish concentration step found in any of the extraction methods. Any methylene chloride remaining in the extract will cause a very broad solvent peak.

7.2 Gas Chromatographic Conditions:

7.2.1 Retention time information for each of the analytes is presented in Tables 3 and 4. The recommended GC operating conditions are provided in Tables 5 and 6. Figures 1, 2 and 3 illustrate typical chromatography of the method analytes for both the single column approach and the dual column approach when operated at the conditions specified in Tables 5 and 6.

7.3 Calibration:

7.3.1 Prepare calibration standards using the procedures in Sec. 5.0. Refer to Method 8000 for proper calibration procedures. The procedure for internal or external calibration may be used.

7.3.2 Refer to Method 8000 for the establishment of retention time windows.

7.4 Gas chromatographic analysis:

7.4.1 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.4.2 Automatic injections of 1 μL are recommended. Hand injections of no more than 2 μL may be used if the analyst demonstrates quantitation precision of $\leq$ 10 percent relative standard deviation. The solvent flush technique may be used if the amount of solvent is kept at a minimum. If the internal standard calibration technique is used, add 10 μL of the internal standard to each mL of sample extract prior to injection.

7.4.3 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

7.4.4 Validation of gas chromatographic system qualitative performance: Use the midconcentration standards interspersed throughout the analysis sequence (Sec. 7.3) to evaluate this criterion. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it (see Sec. 7.5).

7.4.5 Record the volume injected to the nearest 0.05 μL and the resulting peak size in peak height or area units. Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.4.6 If the responses exceed the linear range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.4.7 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique (see Sec. 8.7 and Method 8270). Interferences that prevent analyte identification and/or quantitation may be removed by the cleanup techniques mentioned above.

7.4.8 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5 Instrument Maintenance:

7.5.1 Injection of sample extracts from waste sites often leaves a high boiling residue in: the injection port area, splitters when used, and the injection port end of the chromatographic column. This residue effects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.) and, therefore, instrument maintenance

is very important. Residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Proper cleanup techniques will minimize the problem and instrument QC will indicate when instrument maintenance is required.

7.5.2 Suggested chromatograph maintenance: Corrective measures may require any one or more of the following remedial actions. Also see Sec. 7 in Method 8000 for additional guidance on corrective action for capillary columns and the injection port.

7.5.2.1 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000, Sec. 8.3.

8.3 Calculate surrogate standard recoveries for all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Sec. 8). If the recovery is not within limits, the following are required:

8.3.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.3 Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentrations".

8.4 Data from systems that automatically identify target analytes on the basis of retention time or retention time indices should be reviewed by an experienced analyst before they are reported.

8.5 When using the internal standard calibration technique, an internal standard peak area check must be performed on all samples. The internal standard

must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 50 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within ± 15 percent of the average values for the multiconcentration calibration. When the response factors fall outside that limit, all samples analyzed after that mid-concentration calibration standard must be reanalyzed after performing instrument maintenance to correct the usual source of the problem. If this fails to correct the problem, a new calibration curve must be established.

8.7 GC/MS confirmation:

8.7.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270. Ensure that there is sufficient concentration of the analyte(s) to be confirmed, in the extract for GC/MS analysis.

8.7.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.7.3 To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The identification criteria specified in Method 8270 must be met for qualitative confirmation.

8.7.3.1 Should the MS procedure fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional sample cleanup.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs listed in Table 1 were obtained by using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDLs actually achieved in a given analysis will vary since they depend on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using organic-free reagent water, sandy loam samples and extracts which were spiked with the test compounds at one concentration. Single-operator precision and method accuracy were found to be related to the concentration of compound and the type of matrix.

9.3 Single laboratory accuracy data were obtained for chlorinated hydrocarbons in a clay soil. The spiking concentrations ranged from 500 to 5000 µg/kg, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediatly transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8121 for the chlorinated hydrocarbons. These data are listed in Table 9 and were taken from Reference 4.

10.0 REFERENCES

1. Lopez-Avila, V., N.S. Dodhiwala, and J. Milanes, "Single Laboratory Evaluation of Method 8120, Chlorinated Hydrocarbons", 1988, EPA Contract Numbers 68-03-3226 and 68-03-3511.

2. Glazer, J.A., G.D. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15:1426-1431, 1981.

3. Lopez-Avila, V.; Baldin, E.; Benedicto, J; Milanes, J.; Beckert, W. F. "Application of Open-Tubular Columns to SW 846 GC Methods"; final report to the U.S. Environmental Protection Agency on Contract 68-03-3511; Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

4. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

TABLE 1
METHOD DETECTION LIMITS FOR CHLORINATED HYDROCARBONS
SINGLE COLUMN METHOD OF ANALYSIS

Compound name	CAS Reg. No.	MDL[a] (ng/L)
Benzal chloride	98-87-3	2-5[b]
Benzotrichloride	98-07-7	6.0
Benzyl chloride	100-44-7	180
2-Chloronaphthalene	91-58-7	1,300
1,2-Dichlorobenzene	95-50-1	270
1,3-Dichlorobenzene	541-73-1	250
1,4-Dichlorobenzene	106-46-1	890
Hexachlorobenzene	118-74-1	5.6
Hexachlorobutadiene	87-68-3	1.4
α-Hexachlorocyclohexane (α-BHC)	319-84-6	11
β-Hexachlorocyclohexane (β-BHC)	319-85-7	31
γ-Hexachlorocyclohexane (γ-BHC)	58-89-9	23
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8	20
Hexachlorocyclopentadiene	77-47-4	240
Hexachloroethane	67-72-1	1.6
Pentachlorobenzene	608-93-5	38
1,2,3,4-Tetrachlorobenzene	634-66-2	11
1,2,4,5-Tetrachlorobenzene	95-94-2	9.5
1,2,3,5-Tetrachlorobenzene	634-90-2	8.1
1,2,4-Trichlorobenzene	120-82-1	130
1,2,3-Trichlorobenzene	87-61-6	39
1,3,5-Trichlorobenzene	108-70-3	12

[a] MDL is the method detection limit for organic-free reagent water. MDL was determined from the analysis of eight replicate aliquots processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis).

$$MDL = T/DC_{(n-1, \alpha = .99)}(s)$$

where $t_{(n-1,0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the eight replicate measurements.

[b] Estimated from the instrument detection limit.

TABLE 2

ESTIMATED QUANTITATION LIMIT (EQL) FACTORS FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Waste not miscible with water	100,000

[a] EQL = [Method detection limit (see Table 1)] x [Factor found in this table]. For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

TABLE 3
GAS CHROMATOGRAPHIC RETENTION TIMES FOR CHLORINATED HYDROCARBONS: SINGLE COLUMN METHOD OF ANALYSIS

Compound name	Retention time (min) DB-210[a]	DB-WAX[b]
Benzal chloride	6.86	15.91
Benzotrichloride	7.85	15.44
Benzyl chloride	4.59	10.37
2-Chloronaphthalene	13.45	23.75
1,2-Dichlorobenzene	4.44	9.58
1,3-Dichlorobenzene	3.66	7.73
1,4-Dichlorobenzene	3.80	8.49
Hexachlorobenzene	19.23	29.16
Hexachlorobutadiene	5.77	9.98
α-BHC	25.54	33.84
γ-BHC	24.07	54.30
δ-BHC	26.16	33.79
Hexachlorocyclopentadiene	8.86	c
Hexachloroethane	3.35	8.13
Pentachlorobenzene	14.86	23.75
1,2,3,4-Tetrachlorobenzene	11.90	21.17
1,2,4,5-Tetrachlorobenzene	10.18	17.81
1,2,3,5-Tetrachlorobenzene	10.18	17.50
1,2,4-Trichlorobenzene	6.86	13.74
1,2,3-Trichlorobenzene	8.14	16.00
1,3,5-Trichlorobenzene	5.45	10.37
Internal Standards		
2,5-Dibromotoluene	9.55	18.55
1,3,5-Tribromobenzene	11.68	22.60
α,α'-Dibromo-meta-xylene	18.43	35.94
Surrogates		
α,2,6-Trichlorotoluene	12.96	22.53
1,4-Dichloronaphthalene	17.43	26.83
2,3,4,5,6-Pentachlorotoluene	18.96	27.91

[a] GC operating conditions: 30 m x 0.53 mm ID DB-210 fused-silica capillary column; 1 μm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

[b] GC operating conditions: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1 μm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

[c] Compound decomposes on-column.

TABLE 4
RETENTION TIMES OF THE CHLORINATED HYDROCARBONS[a]
DUAL COLUMN METHOD OF ANALYSIS

Compound	DB-5 RT(min)	DB-1701 RT(min)
1,3-Dichlorobenzene	5.82	7.22
1,4-Dichlorobenzene	6.00	7.53
Benzyl chloride	6.00	8.47
1,2-Dichlorobenzene	6.64	8.58
Hexachloroethane	7.91	8.58
1,3,5-Trichlorobenzene	10.07	11.55
Benzal chloride	10.27	14.41
1,2,4-Trichlorobenzene	11.97	14.54
1,2,3-Trichlorobenzene	13.58	16.93
Hexachlorobutadiene	13.88	14.41
Benzotrichloride	14.09	17.12
1,2,3,5-Tetrachlorobenzene	19.35	21.85
1,2,4,5-Tetrachlorobenzene	19.35	22.07
Hexachlorocyclopentadiene	19.85	21.17
1,2,3,4-Tetrachlorobenzene	21.97	25.71
2-Chloronaphthalene	21.77	26.60
Pentachlorobenzene	29.02	31.05
α-BHC	34.64	38.79
Hexachlorobenzene	34.98	36.52
β-BHC	35.99	43.77
γ-BHC	36.25	40.59
δ-BHC	37.39	44.62
Internal Standard		
1,3,5-Tribromobenzene	11.83	13.34
Surrogate		
1,4-Dichloronaphthalene	15.42	17.71

[a] The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-μm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0 μm film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min then to 240°C (2 min hold) at 5°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

TABLE 5
GC OPERATING CONDITIONS FOR CHLOROHYDROCARBONS
SINGLE COLUMN METHOD OF ANALYSIS

Column 1: DB-210 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone

Carrier gas (He)	10 mL/min	
Column temperature:		
	Initial temperature	65°C
	Temperature program	65°C to 175°C at 4°C/min
	Final temperature	175°C, hold 20 minutes.
Injector temperature	220°C	
Detector temperature	250°C	
Injection volume	1-2 μL	

Column 2: DB-WAX 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol

Carrier gas (He)	10 mL/min	
Column temperature:		
	Initial temperature	60°C
	Temperature program	60°C to 170°C at 4°C/min
	Final temperature	170°C, hold 30 minutes.
Injector temperature	200°C	
Detector temperature	230°C	
Injection volume	1-2 μL	

TABLE 6
GC OPERATING CONDITIONS FOR CHLORINATED HYDROCARBONS
DUAL COLUMN METHOD OF ANALYSIS

Column 1:

Type: DB-1701 (J&W Scientific) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 1.0 (μm)

Column 2:

Type: DB-5 (J&W Scientific) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness: 0.83 (μm)

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min then to 240°C (2 min hold) at 5°C/min.

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 μL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 32 (DB-1701)/32 (DB-5)

Type of splitter: Supelco 8-in injection tee

TABLE 7

SUGGESTED CONCENTRATIONS FOR THE CALIBRATION SOLUTIONS[a]

	Concentration (ng/μL)				
Benzal chloride	0.1	0.2	0.5	0.8	1.0
Benzotrichloride	0.1	0.2	0.5	0.8	1.0
Benzyl chloride	0.1	0.2	0.5	0.8	1.0
2-Chloronaphthalene	2.0	4.0	10	16	20
1,2-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,3-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,4-Dichlorobenzene	1.0	2.0	5.0	8.0	10
Hexachlorobenzene	0.01	0.02	0.05	0.08	0.1
Hexachlorobutadiene	0.01	0.02	0.05	0.08	0.1
α-BHC	0.1	0.2	0.5	0.8	1.0
β-BHC	0.1	0.2	0.5	0.8	1.0
γ-BHC	0.1	0.2	0.5	0.8	1.0
δ-BHC	0.1	0.2	0.5	0.8	1.0
Hexachlorocyclopentadiene	0.01	0.02	0.05	0.08	0.1
Hexachloroethane	0.01	0.02	0.05	0.08	0.1
Pentachlorobenzene	0.01	0.02	0.05	0.08	0.1
1,2,3,4-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,3,5-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
Surrogates					
α,2,6-Trichlorotoluene	0.02	0.05	0.1	0.15	0.2
1,4-Dichloronaphthalene	0.2	0.5	1.0	1.5	2.0
2,3,4,5,6-Pentachlorotoluene	0.02	0.05	0.1	0.15	0.2

[a] One or more internal standards should be spiked prior to GC/ECD analysis into all calibration solutions. The spike concentration of the internal standards should be kept constant for all calibration solutions.

TABLE 8

ELUTION PATTERNS OF CHLORINATED HYDROCARBONS
FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1)
AND 1:1 PETROLEUM ETHER/DIETHYL ETHER (FRACTION 2)

Compound	Amount (µg)	Recovery (percent)[a]	
		Fraction 1[b]	Fraction 2[c]
Benzal chloride[d]	10	0	0
Benzotrichloride	10	0	0
Benzyl chloride	100	82	16
2-Chloronaphthalene	200	115	
1,2-Dichlorobenzene	100	102	
1,3-Dichlorobenzene	100	103	
1,4-Dichlorobenzene	100	104	
Hexachlorobenzene	1.0	116	
Hexachlorobutadiene	1.0	101	
α-BHC	10		95
β-BHC	10		108
γ-BHC	10		105
δ-BHC	10		71
Hexachlorocyclopentadiene	1.0	93	
Hexachloroethane	1.0	100	
Pentachlorobenzene	1.0	129	
1,2,3,4-Tetrachlorobenzene	10	104	
1,2,4,5-Tetrachlorobenzene[e]	10	102	
1,2,3,5-Tetrachlorobenzene[e]	10	102	
1,2,4-Trichlorobenzene	10	59	
1,2,3-Trichlorobenzene	10	96	
1,3,5-Trichlorobenzene	10	102	

[a] Values given represent average values of duplicate experiments.

[b] Fraction 1 was eluted with 200 mL petroleum ether.

[c] Fraction 2 was eluted with 200 mL petroleum ether/diethyl ether (1:1).

[d] This compound coelutes with 1,2,4-trichlorobenzene; separate experiments were performed with benzal chloride to verify that this compound is not recovered from the Florisil cleanup in either fraction.

[e] This pair cannot be resolved on the DB-210 fused-silica capillary columns.

TABLE 9
SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF CHLORINATED HYDROCARBONS FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound Name	Spike Level	% Recovery	
	µg/kg	DB-5	DB-1701
1,3-Dichlorobenzene	5000	b	39
1,2-Dichlorobenzene	5000	94	77
Benzal chloride	500	61	66
Benzotrichloride	500	48	53
Hexachlorocyclopentadiene	500	30	32
Pentachlorobenzene	500	76	73
alpha-BHC	500	89	94
delta-BHC	500	86	b
Hexachlorobenzene	500	84	88

a The operating conditions for the automated Soxhlet were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil, extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

b Not able to determine because of interference.

Data taken from Reference 4.

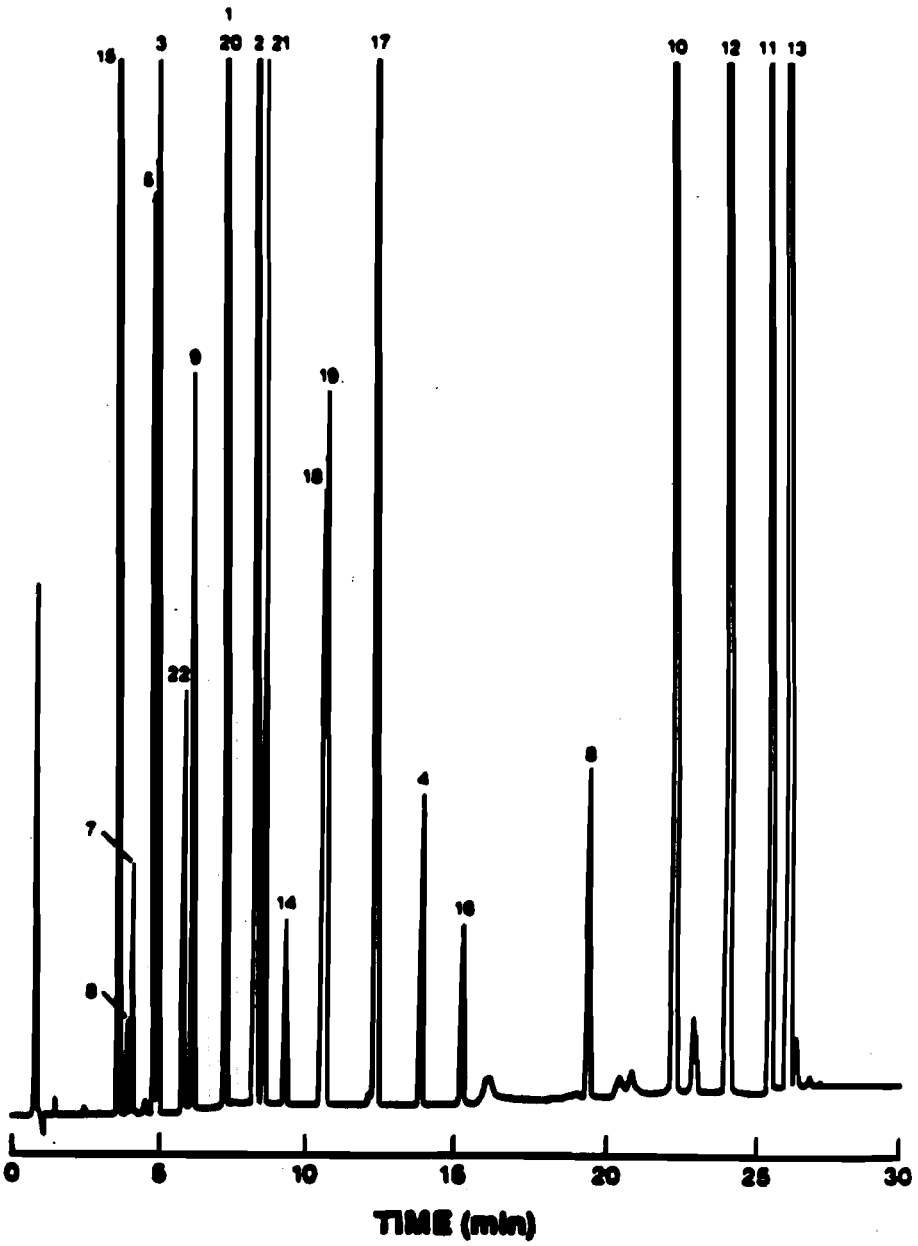


Figure 1. GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-210 fused-silica capillary column. GC operating conditions are given in Section 7.4. See Table 3 for compound identification.

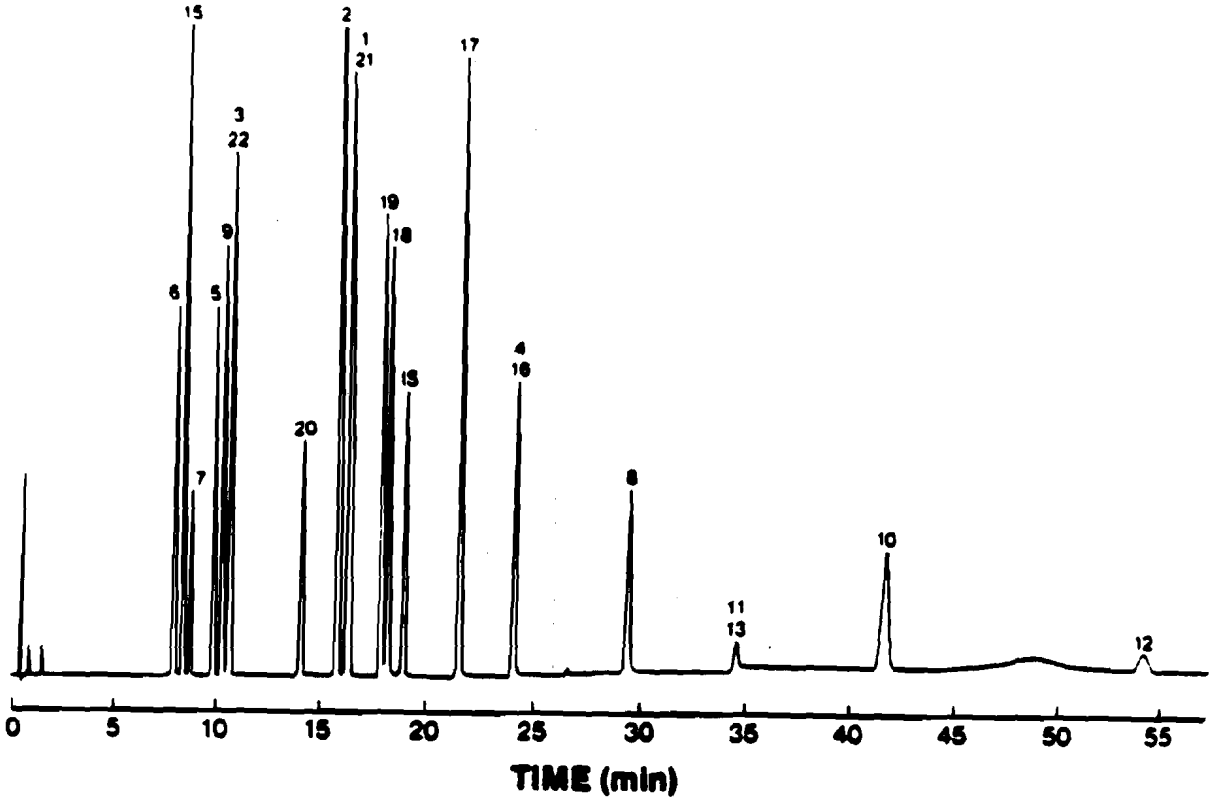


Figure 2. GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-WAX fused-silica capillary column. GC operating conditions are given in Section 7.4. See Table 3 for compound identification.

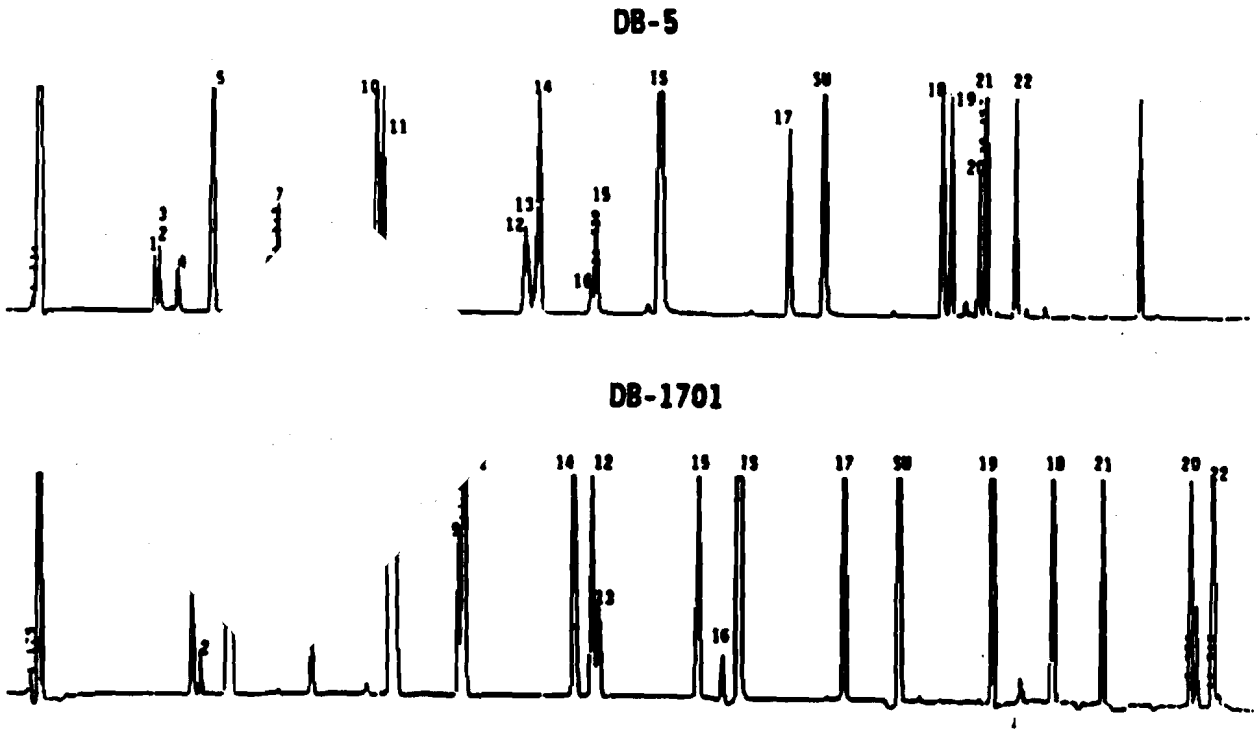
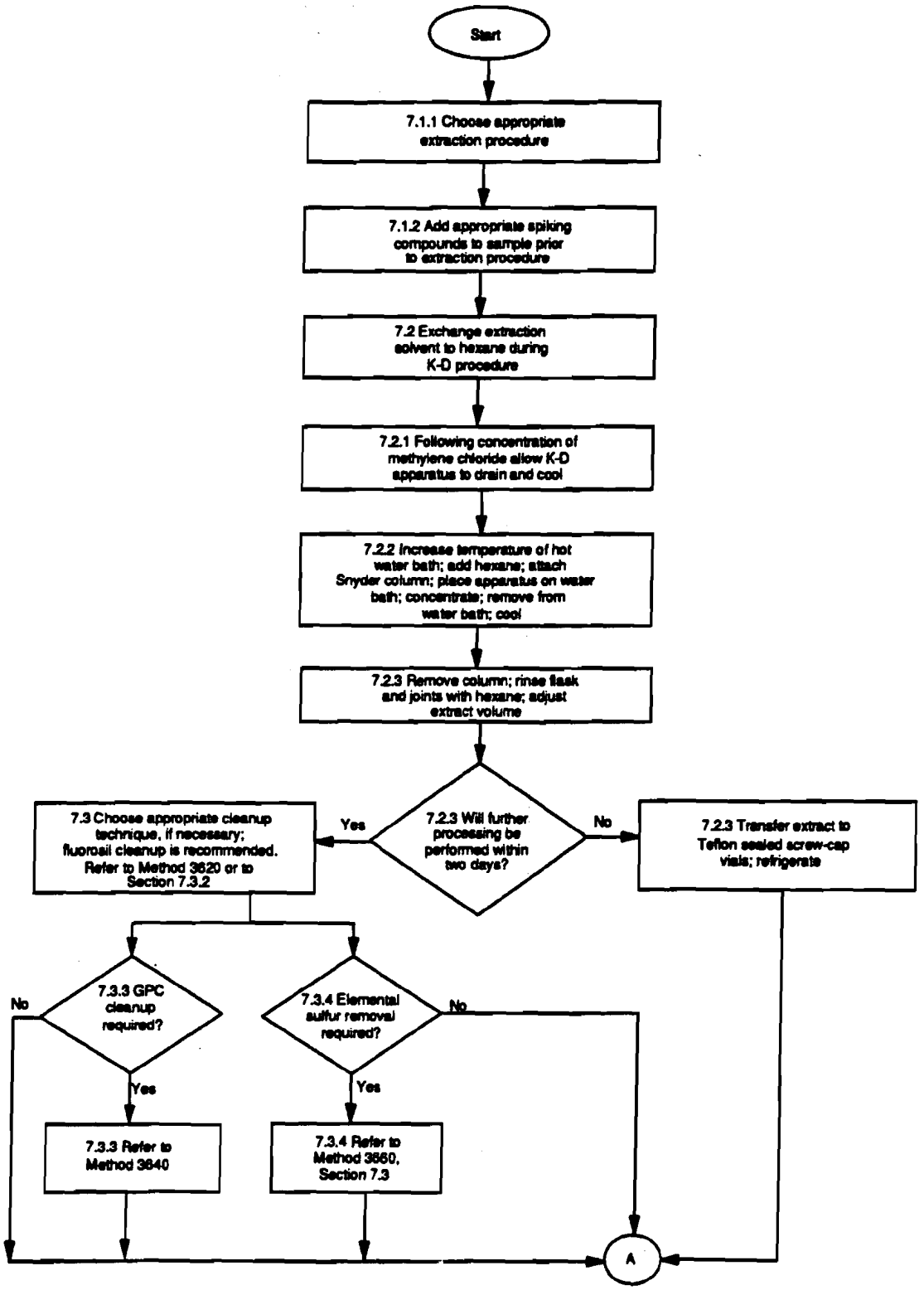
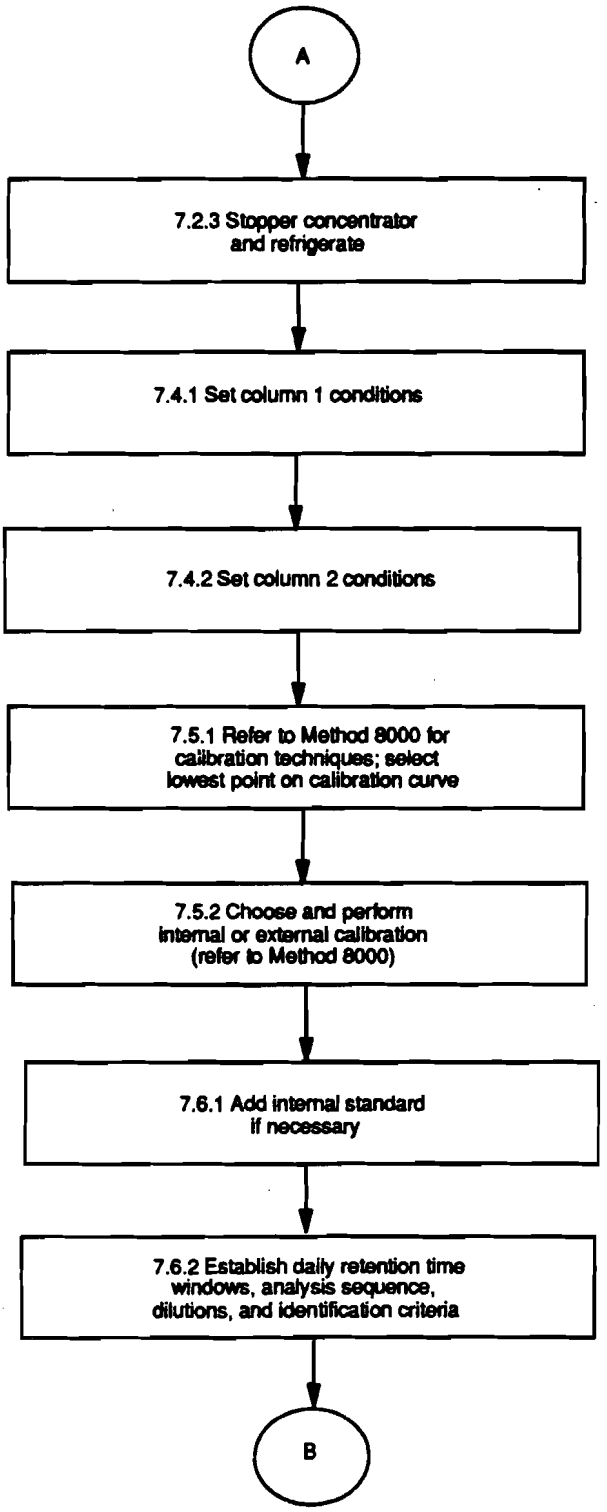
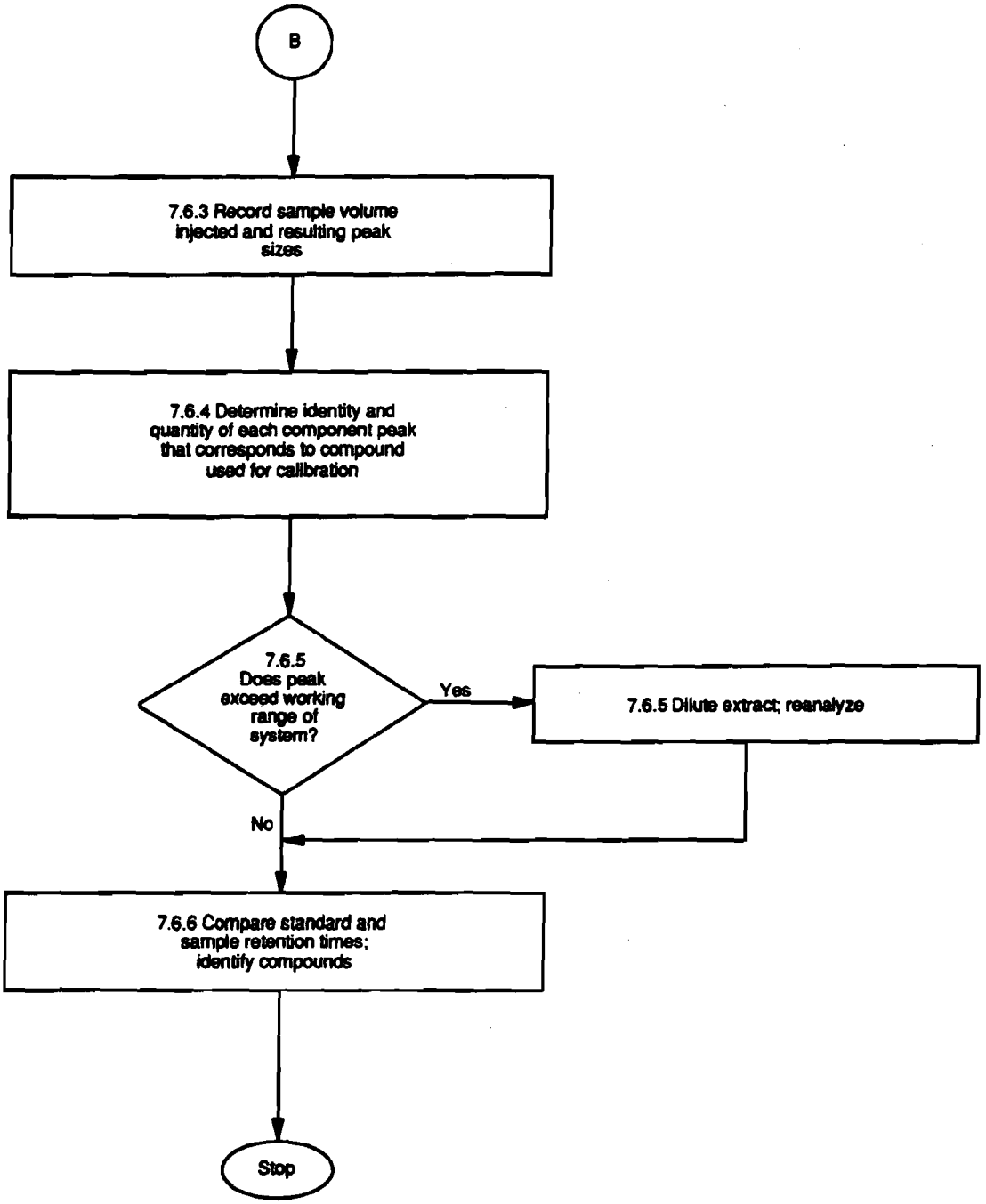


Figure 3. GC/ECD chromatogram of chlorinated hydrocarbons analyzed on a DB 5/DB 1701 fused-silica, open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB 5 (0.83 μm film thickness) and 30 m x 0.53 mm ID DB 1701 (1.0 μm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min, then to 240°C (2 min hold) at 5°C/min.

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE




A
7.2.3 Stopper concentrator and refrigerate
7.4.1 Set column 1 conditions
7.4.2 Set column 2 conditions
7.5.1 Refer to Method 8000 for calibration techniques; select lowest point on calibration curve
7.5.2 Choose and perform internal or external calibration (refer to Method 8000)
7.6.1 Add internal standard if necessary
7.6.2 Establish daily retention time windows, analysis sequence, dilutions, and identification criteria
B


B
7.6.3 Record sample volume injected and resulting peak sizes
7.6.4 Determine identity and quantity of each component peak that corresponds to compound used for calibration
7.6.5 Does peak exceed working range of system?
Yes
7.6.5 Dilute extract; reanalyze
No
7.6.6 Compare standard and sample retention times; identify compounds
Stop

METHOD 8140

ORGANOPHOSPHORUS PESTICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8140 is a gas chromatographic (GC) method used to determine the concentration of various organosphosphorus pesticides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least two additional qualitative techniques if mass spectroscopy is not employed. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

2.0 SUMMARY OF METHOD

2.1 Method 8140 provides gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. Prior to analysis, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph, and compounds in the GC effluent are detected with a flame photometric or thermionic detector.

2.2 If interferences are encountered in the analysis, Method 8140 may also be performed on extracts that have undergone cleanup using Method 3620 and/or Method 3660.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 The use of Florisil cleanup materials (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorous pesticides as a function of Florisil fractions. Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

TABLE 1. GAS CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR ORGANOPHOSPHOROUS PESTICIDES[a]

Compound	GC column[b]	Retention time (min)	Method detection limit (ug/L)
Azinphos methyl	1a	6.80	1.5
Bolstar	1a	4.23	0.15
Chlorpyrifos	2	6.16	0.3
Coumaphos	1a	11.6	1.5
Demeton-O	1a	2.53	0.25
Demeton-S	1a	1.16	0.25
Diazinon	2	7.73	0.6
Dichlorvos	1b, 3	0.8, 1.50	0.1
Disulfoton	1a	2.10	0.20
Ethoprop	2	3.02	0.25
Fensulfothion	1a	6.41	1.5
Fenthion	1a	3.12	0.10
Merphos	2	7.45	0.25
Mevinphos	1b	2.41	0.3
Naled	3	3.28	0.1
Parathion methyl	2	3.37	0.03
Phorate	1a	1.43	0.15
Ronnel	2	5.57	0.3
Stirophos (Tetrachlorvinphos)	1b, 3	8.52, 5.51	5.0
Tokuthion (Prothiofos)	1a	3.40	0.5
Trichloronate	1a	2.94	0.15

[a]Development of Analytical Test Procedures for Organic Pollutants in Wastewater; Report for EPA Contract 68-03-2711 (in preparation).

[b]See Sections 4.2.1 and 7.2 for column descriptions and conditions.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

3.3 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus. Elemental sulfur, however, may interfere with the determination of certain organophosphorus pesticides by flame photometric gas chromatography. Sulfur cleanup using Method 3660 may alleviate this interference.

3.4 A halogen-specific detector (i.e., electrolytic conductivity or microcoulometric) is very selective for the halogen-containing pesticides and is recommended for use with dichlorvos, naled, and stirophos.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 2-mm I.D. glass, packed with 5% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

4.1.1.2 Column 2: 1.8-m x 2-mm I.D. glass, packed with 3% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

4.1.1.3 Column 3: 50-cm x 1/8-in O.D. Teflon, packed with 15% SE-54 on Gas Chrom Q, 100/120 mesh (or equivalent).

4.1.2 **Detectors:** The following detectors have proven effective in analysis for the analytes listed in Table 1 and were used to develop the accuracy and precision statements in Section 9.0.

4.1.2.1 Phosphorus-specific: Nitrogen/Phosphorus (N/P), operated in phosphorus-sensitive mode.

4.1.2.2 Flame Photometric (FPD): FPD is more selective for phosphorus than the N/P.

4.1.2.3 Halogen-specific: Electrolytic conductivity or microcoulometric. These are very selective for those pesticides containing halogen substituents.

4.2 Balance: analytical, capable of accurately weighing to the nearest 0.0001 g.

4.3 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw-cap.

4.4 Kuderna-Danish (K-D) apparatus:

4.4.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.4.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.4.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

4.9 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection

limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane or other suitable solvent.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., organophosphorous pesticides not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent may be exchanged to hexane. This is recommended if the detector used is halogen-specific. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1a:** Set helium carrier gas flow at 30 mL/min flow rate. Column temperature is set at 150°C for 1 min and then programmed at 25°C/min to 220°C and held.

7.2.2 **Column 1b:** Set nitrogen carrier gas flow at 30 mL/min flow rate. Column temperature is set at 170°C for 2 min and then programmed at 20°C/min to 220°C and held.

7.2.3 **Column 2:** Set helium carrier gas at 25 mL/min flow rate. Column temperature is set at 170°C for 7 min and then programmed at 10°C/min to 250°C and held.

7.2.4 **Column 3:** Set nitrogen carrier gas at 30 mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 25°C/min to 200°C and held.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of chromatograms for various organophosphorous pesticides are shown in Figures 1 through 4.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10-mL hexane extracts obtained from Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

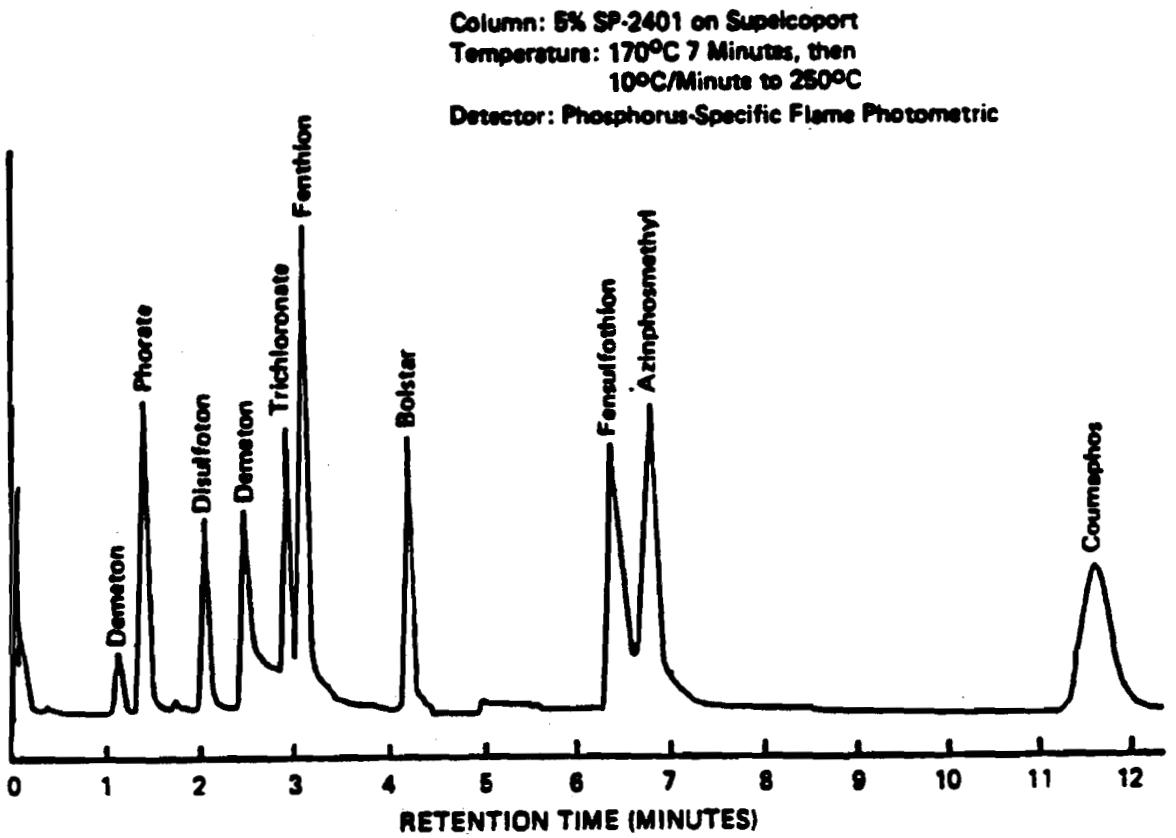


Figure 1. Gas chromatogram of organophosphorus pesticides (Example 1).

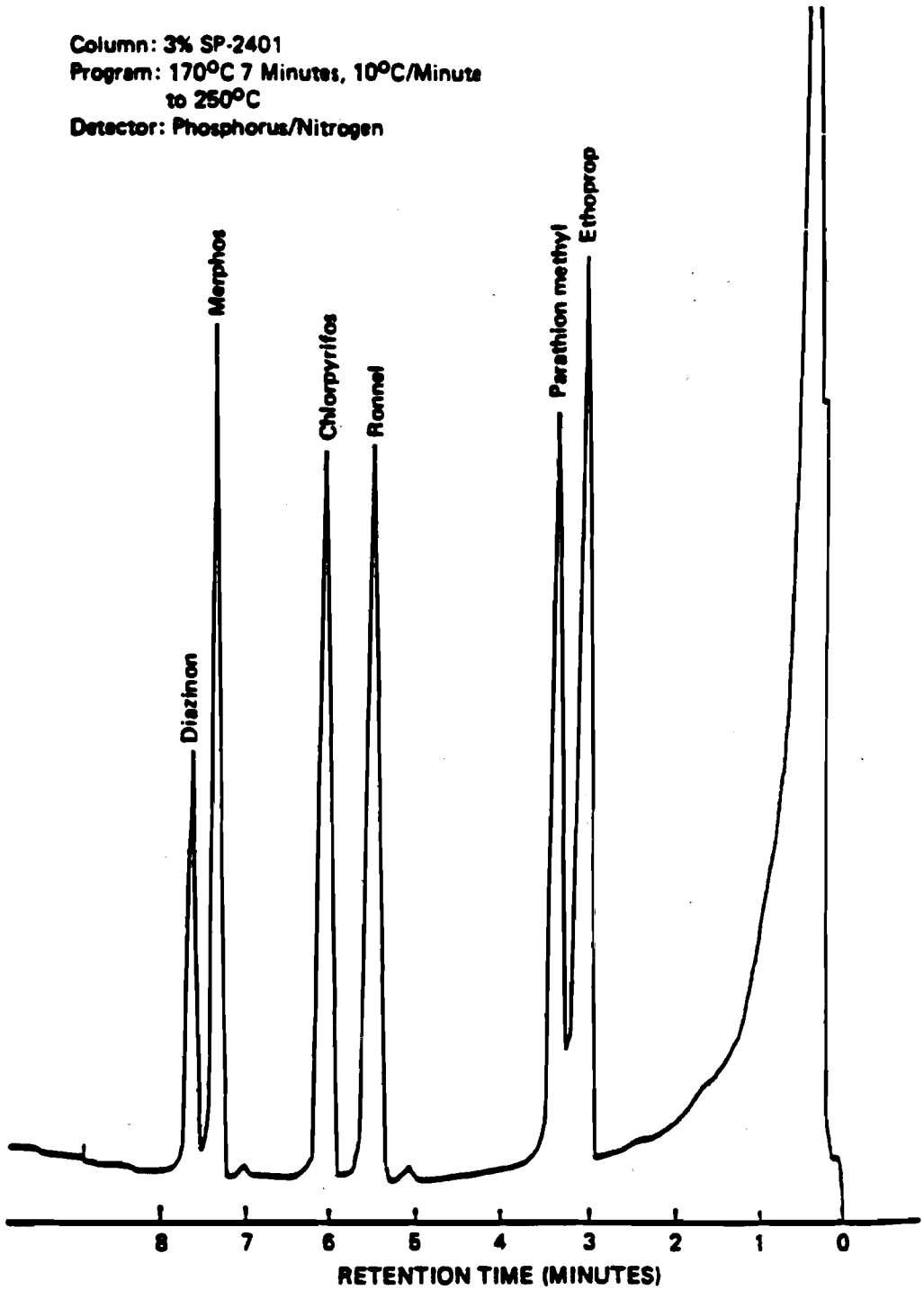


Figure 2. Gas chromatogram of organophosphorus pesticides (Example 2).

Figure 3. Gas chromatogram of organophosphorus pesticides (Example 3).

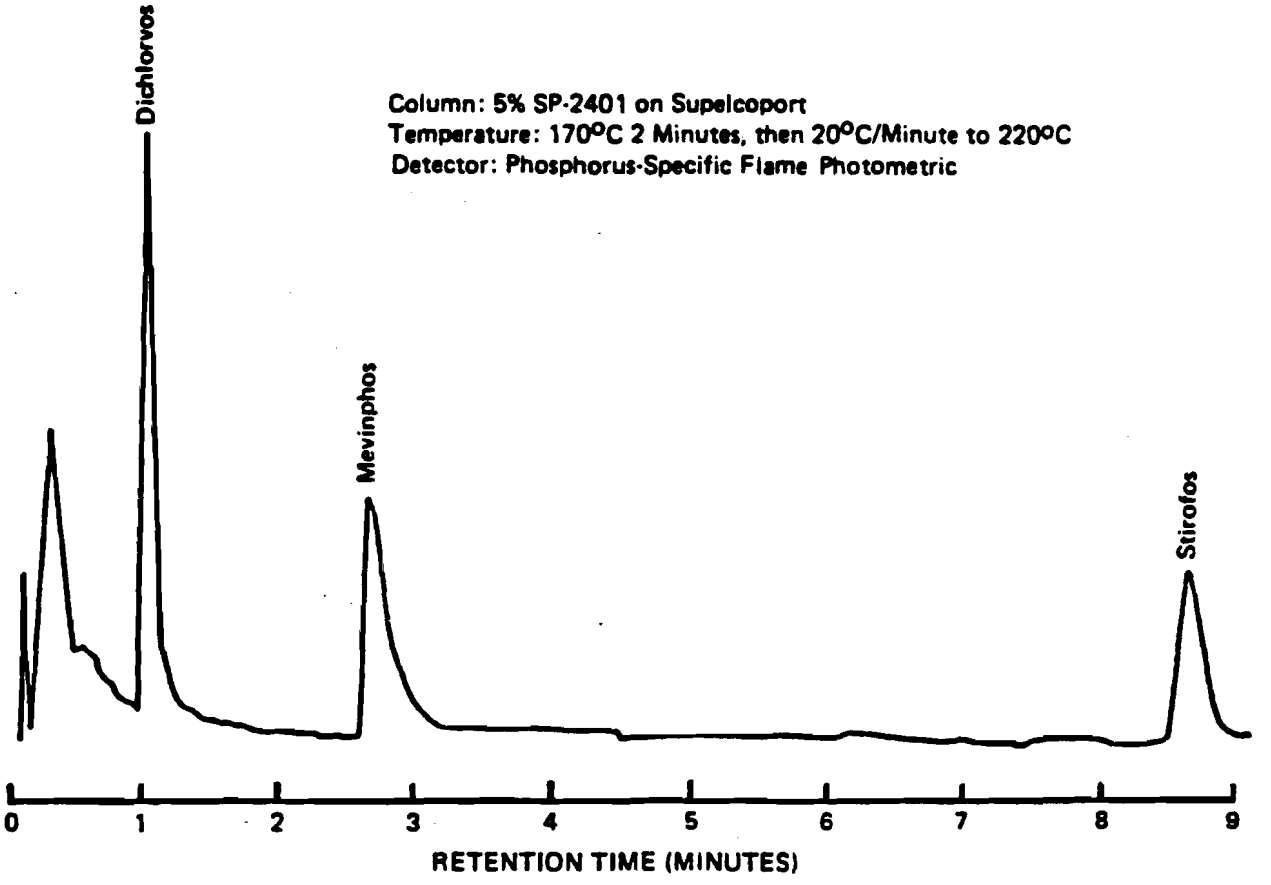


Figure 4. Gas chromatogram of organophosphorus pesticides (Example 4).

8.2.1 Select a representative spike concentration for each analyte to be measured. The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The GC/MS operating conditions and procedures for analysis are those specified in Method 8270.

8.4.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns and additional cleanup.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision studies have been conducted using spiked wastewater samples. The results of these studies are presented in Table 3.

10.0 REFERENCES

1. Pressley, T.A. and J.E. Longbottom, "The Determination of Organophosphorus Pesticides in Industrial and Municipal Wastewater: Method 614," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-82-004, 1982.

2. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists 48, 1037, 1965.

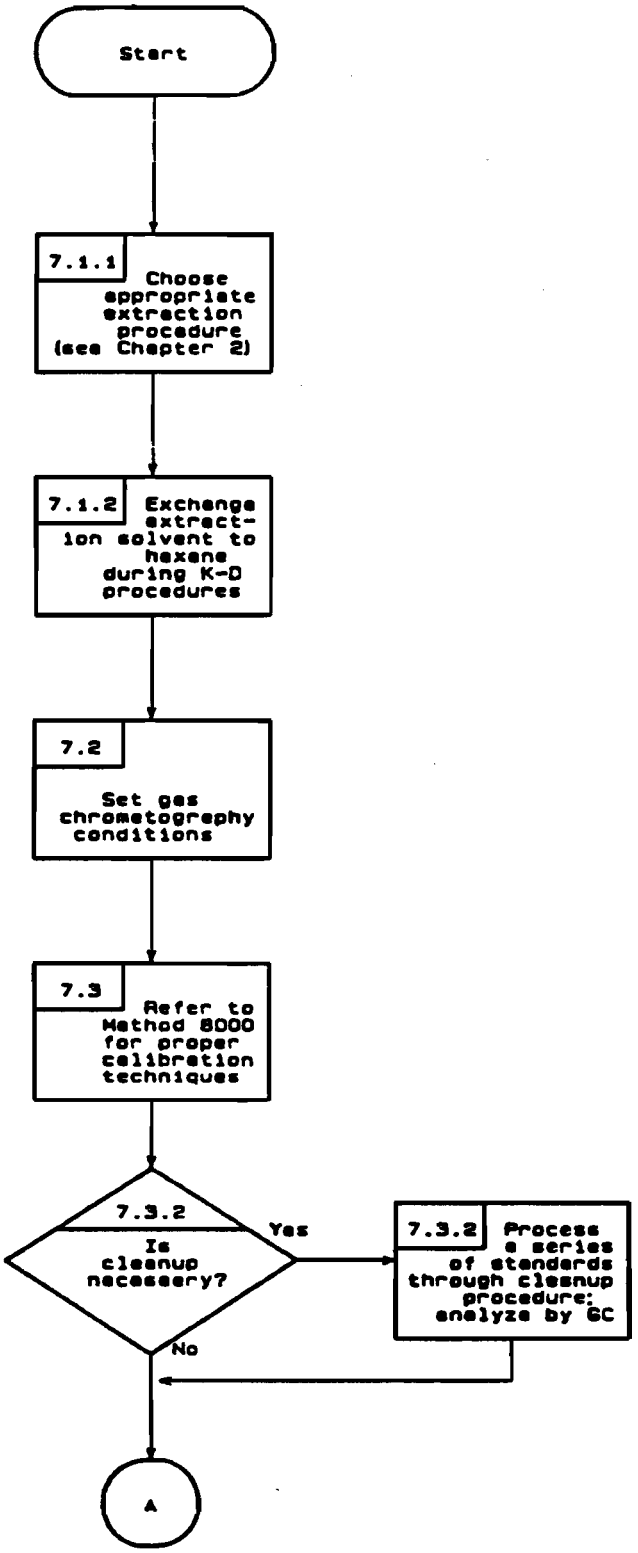
3. U.S. EPA, "Analysis of Volatile Hazardous Substances by GC/MS: Pesticide Methods Evaluation," Letter Reports 6, 12A, and 14, EPA Contract 68-03-2697, 1982.

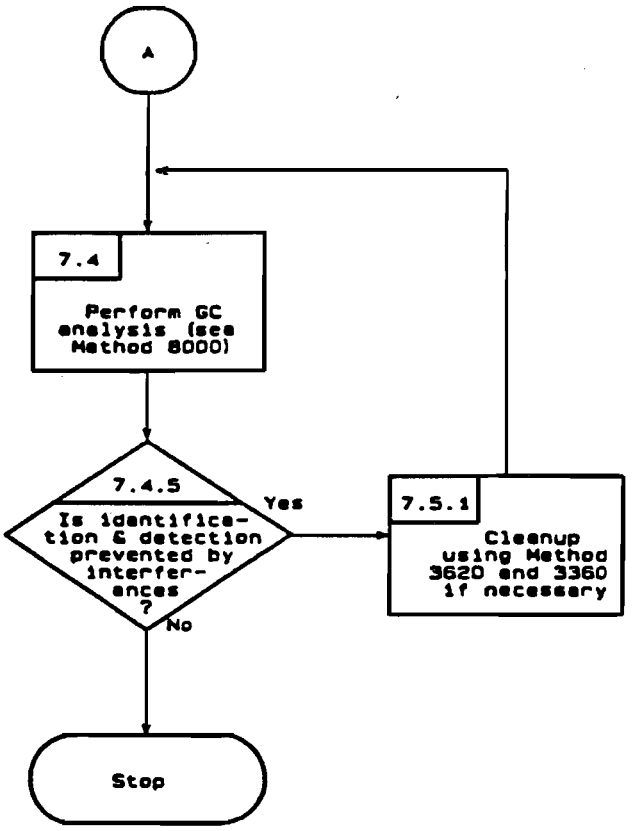
4. U.S. EPA, "Method 622, Organophosphorous Pesticides," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Average recovery (%)	Standard deviation (%)	Spike range (ug/L)	Number of analyses
Azinphos methyl	72.7	18.8	21-250	17
Bolstar	64.6	6.3	4.9-46	17
Chlorpyrifos	98.3	5.5	1.0-50.5	18
Coumaphos	109.0	12.7	25-225	17
Demeton	67.4	10.5	11.9-314	17
Diazinon	67.0	6.0	5.6	7
Dichlorvos	72.1	7.7	15.6-517	16
Disulfoton	81.9	9.0	5.2-92	17
Ethoprop	100.5	4.1	1.0-51.5	18
Fensulfothion	94.1	17.1	23.9-110	17
Fenthion	68.7	19.9	5.3-64	17
Merphos	120.7	7.9	1.0-50	18
Mevinphos	56.5	7.8	15.5-520	16
Naled	78.0	8.1	25.8-294	16
Parathion methyl	96.0	5.3	0.5-500	21
Phorate	62.7	8.9	4.9-47	17
Ronnel	99.2	5.6	1.0-50	18
Stirophos	66.1	5.9	30.3-505	16
Tokuthion	64.6	6.8	5.3-64	17
Trichloronate	105.0	18.6	20	3

[a]Information taken from Reference 4.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
No
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
A


A
7.4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences ?
Yes
No
7.5.1 Cleanup using Method 3620 and 3360 if necessary
Stop

METHOD 8141A

ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8141 is a capillary gas chromatographic (GC) method used to determine the concentration of organophosphorus (OP) compounds. The fused-silica, open-tubular columns specified in this method offer improved resolution, better selectivity, increased sensitivity, and faster analysis than packed columns. The compounds listed in the table below can be determined by GC using capillary columns with a flame photometric detector (FPD) or a nitrogen-phosphorus detector (NPD). Triazine herbicides can also be determined with this method when the NPD is used. Although performance data are presented for each of the listed chemicals, it is unlikely that all of them could be determined in a single analysis. This limitation results because the chemical and chromatographic behavior of many of these chemicals can result in co-elution. The analyst must select columns, detectors and calibration procedures for the specific analytes of interest in a study. Any listed chemical is a potential method interference when it is not a target analyte.

Compound Name	CAS Registry No.
OP Pesticides	
Aspon,[b]	3244-90-4
Azinphos-methyl	86-50-0
Azinphos-ethyl[a]	2642-71-9
Bolstar (Sulprofos)	35400-43-2
Carbophenothion[a]	786-19-6
Chlorfenvinphos[a]	470-90-6
Chlorpyrifos	2921-88-2
Chlorpyrifos methyl[a]	5598-13-0
Coumaphos	56-72-4
Crotoxyphos[a]	7700-17-6
Demeton-O[c]	8065-48-3
Demeton-S[c]	8065-48-3
Diazinon	333-41-5
Dichlorofenthion[a]	97-17-6
Dichlorvos (DDVP)	62-73-7
Dicrotophos[a]	141-66-2
Dimethoate	60-51-5
Dioxathion[a,c]	78-34-2
Disulfoton	298-04-4
EPN	2104-64-5
Ethion[a]	563-12-2
Ethoprop	13194-48-4
Famphur[a]	52-85-7
Fenitrothion[a]	122-14-5
Fensulfothion	115-90-2

Compound Name	CAS Registry No.
Fonophos[a]	944-22-9
Fenthion	55-38-9
Leptophos[a,d]	21609-90-5
Malathion	121-75-5
Merphos[c]	150-50-5
Mevinphos[e]	7786-34-7
Monocrotophos	6923-22-4
Naled	300-76-5
Parathion, ethyl	56-38-2
Parathion, methyl	298-00-0
Phorate	298-02-2
Phosmet[a]	732-11-6
Phosphamidon[a]	13171-21-6
Ronnel	299-84-3
Stirophos (Tetrachlorovinphos)	22248-79-9
Sulfotepp	3689-24-5
TEPP[d]	21646-99-1
Terbufos[a]	13071-79-9
Thionazin[a,b] (Zinophos)	297-97-2
Tokuthion[b] (Protothiofos)	34643-46-4
Trichlorfon[a]	52-68-6
Trichloronate[b]	327-98-0
Industrial Chemicals	
Hexamethylphosphoramide[a] (HMPA)	680-31-9
Tri-o-cresylphosphate[a,d] (TOCP)	78-30-8
Triazine Herbicides (NPD only)	
Atrazine[a]	1912-24-9
Simazine[a]	122-34-9

a This analyte has been evaluated using a 30-m column only.
b Production discontinued in the U.S., standard not readily available.
c Standards may have multiple components because of oxidation.
d Compound is extremely toxic or neurotoxic.
e Adjacent major/minor peaks can be observed due to cis/trans isomers.

1.2 A dual-column/dual-detector approach may be used for the analysis of relatively clean extracts. Two 15- or 30-m x 0.53-mm ID fused-silica, open-tubular columns of different polarities are connected to an injection tee and each is connected to a detector. Analysts are cautioned regarding the use of a dual column configuration when their instrument is subject to mechanical stress,

when many samples are analyzed over a short time, or when extracts of contaminated samples are analyzed.

1.3 Two detectors can be used for the listed OP chemicals. The FPD works by measuring the emission of phosphorus- or sulfur-containing species. Detector performance is optimized by selecting the proper optical filter and adjusting the hydrogen and air flows to the flame. The NPD is a flame ionization detector with a rubidium ceramic flame tip which enhances the response of phosphorus- and nitrogen-containing analytes. The FPD is more sensitive and more selective, but is a less common detector in environmental laboratories.

1.4 Table 1 lists method detection limits (MDLs) for the target analytes, using 15-m columns and FPD, for water and soil matrices. Table 2 lists the estimated quantitation limits (EQLs) for other matrices. MDLs and EQLs using 30-m columns will be very similar to those obtained from 15-m columns.

1.5 The use of a 15-m column system has not been fully validated for the determination of the following compounds. The analyst must demonstrate chromatographic resolution of all analytes, recoveries of greater than 70 percent, with precision of no more than 15 percent RSD, before data generated on the 15-m column system can be reported for these, or any additional, analytes:

Azinphos-ethyl	Ethion	Phosmet
Carbophenothion	Famphur	Phosphamidon
Chlorfenvinphos	HMPA	Terbufos
Dioxathion	Leptophos	TOCP

1.6 When Method 8141 is used to analyze unfamiliar samples, compound identifications should be supported by confirmatory analysis. Sec. 8.0 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.7 This method is restricted to use by, or under the supervision of, analysts experienced in the use of capillary gas chromatography and in the interpretation of chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8141 provides gas chromatographic conditions for the detection of ppb concentrations of organophosphorus compounds. Prior to the use of this method, appropriate sample preparation techniques must be used. Water samples are extracted at a neutral pH with methylene chloride by using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet extraction (Method 3540) or automated Soxhlet extraction (Method 3541) using methylene chloride/acetone (1:1) are used for solid samples. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. A gas chromatograph with a flame photometric or nitrogen-phosphorus detector is used for this multiresidue procedure.

2.2 Organophosphorus esters and thioesters can hydrolyze under both acid and base conditions. Samples prepared using acid and base partitioning procedures are not suitable for analysis by Method 8141.

2.3 Ultrasonic Extraction (Method 3550) is not an appropriate sample preparation method for Method 8141 and should not be used because of the potential for destruction of target analytes during the ultrasonic extraction process.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000, as well as to Sec. 1.1.

3.2 The use of Florisil Cleanup (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85 percent and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorus compounds. Use of an FPD often eliminates the need for sample cleanup. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is not less than 85 percent.

3.3 The use of Gel Permeation Cleanup (GPC) (Method 3640) for sample cleanup has been demonstrated to yield recoveries of less than 85 percent for many method analytes because they elute before bis-(2-ethylhexyl) phthalate. Method 3640 is therefore not recommended for use with this method, unless analytes of interest are listed in Method 3640 or are demonstrated to give greater than 85 percent recovery.

3.4 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus or sulfur. Elemental sulfur will interfere with the determination of certain organophosphorus compounds by flame photometric gas chromatography. If Method 3660 is used for sulfur cleanup, only the tetrabutylammonium (TBA)-sulfite option should be employed, since copper and mercury may destroy OP pesticides. The stability of each analyte must be tested to ensure that the recovery from the TBA-sulfite sulfur cleanup step is not less than 85 percent.

3.5 A halogen-specific detector (i.e., electrolytic conductivity or microcoulometry) is very selective for the halogen-containing compounds and may be used for the determination of Chlorpyrifos, Ronnel, Coumaphos, Tokuthion, Trichloronate, Dichlorvos, EPN, Naled, and Stirophos only. Many of the OP pesticides may also be detected by the electron capture detector (ECD); however, the ECD is not as specific as the NPD or FPD. The ECD should only be used when previous analyses have demonstrated that interferences will not adversely effect quantitation, and that the detector sensitivity is sufficient to meet regulatory limits.

3.6 Certain analytes will coelute, particularly on 15-m columns (Table 3). If coelution is observed, analysts should (1) select a second column of different polarity for confirmation, (2) use 30-m x 0.53-mm columns, or (3) use 0.25- or 0.32-mm ID columns. See Figures 1 through 4 for combinations of compounds that do not coelute on 15-m columns.

3.7 The following pairs coeluted on the DB-5/DB-210 30-m column pair:

DB-5 Terbufos/tri-o-cresyl phosphate
Naled/Simazine/Atrazine
Dichlorofenthion/Demeton-O
Trichloronate/Aspon
Bolstar/Stirophos/Carbophenothion
Phosphamidon/Crotoxyphos
Fensulfothion/EPN

DB-210 Terbufos/tri-o-cresyl phosphate
Dichlorofenthion/Phosphamidon
Chlorpyrifos, methyl/Parathion, methyl
Chlorpyrifos/Parathion, ethyl
Aspon/Fenthion
Demeton-O/Dimethoate
Leptophos/Azinphos-methyl
EPN/Phosmet
Famphur/Carbophenothion

See Table 4 for retention times of these compounds on 30-m columns.

3.8 Analytical difficulties encountered for target analytes include:

3.8.1 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate which is readily hydrolyzed in water and is thermally labile (TEPP decomposes at 170°C). Care must be taken to minimize loss during GC analysis and during sample preparation. Identification of bad standard lots is difficult since the electron impact (EI) mass spectrum of TEPP is nearly identical to its major breakdown product, triethyl phosphate.

3.8.2 The water solubility of Dichlorvos (DDVP) is 10 g/L at 20°C, and recovery is poor from aqueous solution.

3.8.3 Naled is converted to Dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample workup. The extent of debromination will depend on the nature of the matrix being analyzed. The analyst must consider the potential for debromination when Naled is to be determined.

3.8.4 Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos (DDVP) and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of Trichlorfon, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.

3.8.5 Demeton (Systox) is a mixture of two compounds; O,O-diethyl O-[2-(ethylthio)ethyl]phosphorothioate (Demeton-O) and O,O-diethyl S-[2-(ethylthio)ethyl]phosphorothioate (Demeton-S). Two peaks are observed in all the chromatograms corresponding to these two isomers. It is recommended that the early eluting compound (Demeton-S) be used for quantitation.

3.8.6 Dioxathion is a single-component pesticide. However, several extra peaks are observed in the chromatograms of standards. These peaks appear to be the result of spontaneous oxygen-sulfur isomerization. Because of this, Dioxathion is not included in composite standard mixtures.

3.8.7 Merphos (tributyl phosphorotrithioite) is a single-component pesticide that is readily oxidized to its phosphorotrithioate (Merphos oxone). Chromatographic analysis of Merphos almost always results two peaks (unoxidized Merphos elutes first). As the relative amounts of oxidation of the sample and the standard are probably different, quantitation based on the sum of both peaks may be most appropriate.

3.8.8 Retention times of some analytes, particularly Monocrotophos, may increase with increasing concentrations in the injector. Analysts should check for retention time shifts in highly contaminated samples.

3.8.9 Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination and are silanized. Columns should be installed and maintained properly.

3.8.10 Performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown and baselines may be improved by column washing (Sec. 7). Oxidation of columns is not reversible.

3.9 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks (Sec. 8.0).

3.10 NP Detector interferences: Triazine herbicides, such as Atrazine and Simazine, and other nitrogen-containing compounds may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: An analytical system complete with a gas chromatograph suitable for on-column or split/splitless injection, and all required accessories, including syringes, analytical columns, gases, suitable detector(s), and a recording device. The analyst should select the detector for the specific measurement application, either the flame photometric detector or the nitrogen-phosphorus detector. A data system for measuring peak areas and dual display of chromatograms is highly recommended.

4.1.1 Capillary Columns (0.53-mm, 0.32-mm, or 0.25-mm ID x 15-m or 30-m length, depending on the resolution required). Columns of 0.53-mm ID are recommended for most environmental and waste analysis applications. Dual-column, single-injector analysis requires columns of equal length and bore. See Sec. 3.0 and Figures 1 through 4 for guidance on selecting the proper length and diameter for the column(s).

4.1.1.1 Column 1 - 15- or 30-m x 0.53-mm wide-bore capillary column, 1.0-μm film thickness, chemically bonded with 50% trifluoropropyl polysiloxane, 50% methyl polysiloxane (DB-210), or equivalent.

4.1.1.2 Column 2 - 15- or 30-m x 0.53-mm wide-bore capillary column, 0.83-μm film thickness, chemically bonded with 35% phenyl methyl polysiloxane (DB-608, SPB-608, RTx-35), or equivalent.

4.1.1.3 Column 3 - 15- or 30-m x 0.53-mm wide-bore capillary column, 1.0 μm film thickness, chemically bonded with 5% phenyl polysiloxane, 95% methyl polysiloxane (DB-5, SPB-5, RTx-5), or equivalent.

4.1.1.4 Column 4 - 15- or 30-m x 0.53-mm ID fused-silica open-tubular column, chemically bonded with methyl polysiloxane (DB-1, SPB-1, or equivalent), 1.0-μm or 1.5-μm film thickness.

4.1.1.5 (optional) Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.1.2 Splitter: If a dual-column, single-injector configuration is used, the open tubular columns should be connected to one of the following splitters, or equivalent:

4.1.2.1 Splitter 1 - J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

4.1.2.2 Splitter 2 - Supelco 8-in glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

4.1.2.3 Splitter 3 - Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405).

4.1.3 Injectors:

4.1.3.1 Packed column, 1/4-in injector port with hourglass liner are recommended for 0.53-mm column. These injector ports can be fitted with splitters (Sec. 4.0) for dual-column analysis.

4.1.3.2 Split/splitless capillary injectors operated in the split mode are required for 0.25-mm and 0.32-mm columns.

4.1.4 Detectors:

4.1.4.1 Flame Photometric Detector (FPD) operated in the phosphorus-specific mode is recommended.

4.1.4.2 Nitrogen-Phosphorus Detector (NPD) operated in the phosphorus-specific mode is less selective but can detect triazine herbicides.

4.1.4.3 Halogen-Specific Detectors (electrolytic conductivity or microcoulometry) may be used only for a limited number of halogenated or sulfur-containing analytes (Sec. 3.0).

4.1.4.4 Electron-capture detectors may be used for a limited number of analytes (Sec. 3.0).

4.1.5 Data system:

4.1.5.1 Data system capable of presenting chromatograms, retention time, and peak integration data is strongly recommended.

4.1.5.2 Use of a data system that allows storage of raw chromatographic data is strongly recommended.

5.0 REAGENTS

5.1 Solvents

5.1.1 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.1.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.1.3 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.1.4 Tetrahydrofuran (THF), C_4H_8O - Pesticide quality or equivalent (for triazine standards only).

5.1.5 Methyl *tert*-butyl-ether (MTBE), $CH_3Ot\text{-}C_4H_9$ - Pesticide quality or equivalent (for triazine standards only).

5.2 Stock standard solutions (1000 mg/L): Can be prepared from pure standard materials or can be purchased as certified solutions.

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compounds. Dissolve the compounds in suitable mixtures of acetone and hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Both Simazine and Atrazine have low solubilities in hexane. If Simazine and Atrazine standards are required, Atrazine should be dissolved in MTBE, and Simazine should be dissolved in acetone/MTBE/THF (1:3:1).

5.2.3 Composite stock standard: This standard can be prepared from individual stock solutions. The analyst must demonstrate that the individual analytes and common oxidation products are resolved by the chromatographic system. For composite stock standards containing less

than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 40 mg/L. This composite solution can be further diluted to obtain the desired concentrations. Composite stock standards containing more than 25 components are not recommended.

5.2.4 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. All standard solutions should be replaced after two months, or sooner if routine QC (Sec. 8.0) indicates a problem. Standards for easily hydrolyzed chemicals including TEPP, Methyl Parathion, and Merphos should be checked every 30 days.

5.2.5 It is recommended that lots of standards be subdivided and stored in small vials. Individual vials should be used as working standards to minimize the potential for contamination or hydrolysis of the entire lot.

5.3 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. Organophosphorus calibration standards should be replaced after one or two months, or sooner if comparison with check samples or historical data indicates that there is a problem. Laboratories may wish to prepare separate calibration solutions for the easily hydrolyzed standards identified above.

5.4 Internal standard: Internal standards should only be used on well-characterized samples by analysts experienced in the technique. Use of internal standards is complicated by co-elution of some OP pesticides and by the differences in detector response to dissimilar chemicals.

5.4.1 FPD response for organophosphorus compounds is enhanced by the presence of sulfur atoms bonded to the phosphorus atom. It has not been established that a thiophosphate can be used as an internal standard for an OP with a different numbers of sulfur atoms (e.g., phosphorothioates [P=S] as an internal standard for phosphates [PO_4]) or phosphorodithioates [$P=S_2$]).

5.4.2 If internal standards are to be used, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

5.4.3 When 15-m columns are used, it may be difficult to fully resolve internal standards from target analytes, method interferences and matrix interferences. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

5.4.4 The following NPD internal standard has been used for a 30-m column pair. Make a solution of 1000 mg/L of 1-bromo-2-nitrobenzene. For spiking, dilute this solution to 5 mg/L. Use a spiking volume of 10 µL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards. Since its FPD response is small, 1-bromo-2-nitrobenzene is not an appropriate internal standard for that detector. No FPD internal standard is suggested.

5.5 Surrogate standard spiking solutions - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g., organophosphorus compounds not expected to be present in the sample). If multiple analytes are to be measured, two surrogates (an early and a late eluter) are recommended. Deuterated analogs of analytes are not appropriate surrogates for gas chromatographic/FPD/NPD analysis.

5.5.1 If surrogates are to be used, the analyst must select one or more compounds that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of a surrogate is not affected by method or matrix interferences. General guidance on the selection and use of surrogates is provided in Sec. 5.0 of Method 3500.

5.5.2 Tributyl phosphate and triphenyl phosphate are used as FPD and NPD surrogates. A volume of 1.0 mL of a 1-µg/L spiking solution (1 ng of surrogate) is added to each water sample and each soil/sediment sample. If there is a co-elution problem, 4-chloro-3-nitrobenzo-trifluoride has also been used as an NPD-only surrogate.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to Chapter Four, "Organic Analytes," Sec. 4.0.

6.2 Extracts are to be refrigerated at 4°C and analyzed within 40 days of extraction. See Sec. 5.2.4 for storage of standards.

6.3 Organophosphorus esters will hydrolyze under acidic or basic conditions. Adjust samples to a pH of 5 to 8 using sodium hydroxide or sulfuric acid solution as soon as possible after sample collection. Record the volume used.

6.4 Even with storage at 4°C and use of mercuric chloride as a preservative, most OPs in groundwater samples collected for the national pesticide survey degraded within a 14-day period. Begin sample extraction within 7 days of collection.

7.0 PROCEDURE

7.1 Extraction and cleanup:

7.1.1 Refer to Chapter Two and Method 8140 for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3541 with methylene chloride/acetone (1:1 v/v) or hexane/acetone (1:1 v/v) as the extraction solvent. Method 3550 is an inappropriate extraction technique for the target analytes of this method (See Sec. 2.3).

7.1.2 Extraction and cleanup procedures that use solutions below pH 4 or above pH 8 are not appropriate for this method.

7.1.3 If required, the samples may be cleaned up using the Methods presented in Chapter Four, Sec. 2. Florisil Column Cleanup (Method 3620) and Sulfur Cleanup (Method 3660, TBA-sulfite option) may have particular application for OPs. Gel Permeation Cleanup (Method 3640) should not generally be used for OP pesticides.

7.1.3.1 If sulfur cleanup by Method 3660 is required, do not use mercury or copper.

7.1.3.2 GPC may only be employed if all target OP pesticides are listed as analytes of Method 3640, or if the laboratory has demonstrated a recovery of greater than 85 percent for target OPs at a concentration not greater than 5 times the regulatory action level. Laboratories must retain data demonstrating acceptable recovery.

7.1.4 Prior to gas chromatographic analysis, the extraction solvent may be exchanged to hexane. The analyst must ensure quantitative transfer of the extract concentrate. Single-laboratory data indicate that samples should not be transferred with 100-percent hexane during sample workup, as the more polar organophosphorus compounds may be lost. Transfer of organophosphorus esters is best accomplished using methylene chloride or a hexane/acetone solvent mixture.

7.1.5 Methylene chloride may be used as an injection solvent with both the FPD and the NPD.

<u>NOTE</u>: Follow manufacturer's instructions as to suitability of using methylene chloride with any specific detector.

7.2 Gas chromatographic conditions:

7.2.1 Four 0.53-mm ID capillary columns are suggested for the determination of organophosphates by this method. Column 1 (DB-210 or equivalent) and Column 2 (SPB-608 or equivalent) of 30-m length are recommended if a large number of organophosphorus analytes are to be determined. If superior chromatographic resolution is not required, 15-m lengths columns may be appropriate. Operating conditions for 15-m columns

are listed in Table 5. Operating conditions for 30-m columns are listed in Table 6.

7.2.2 Retention times for analytes on each set of columns are presented in Tables 3 and 4.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 5 and Table 6 for establishing the proper operating parameters for the set of columns being employed in the analyses.

7.4 Gas chromatographic analysis: Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows and identification criteria.

7.4.1 Automatic injections of 1 μL are recommended. Hand injections of no more than 2 μL may be used if the analyst demonstrates quantitation precision of $\leq$ 10 percent relative standard deviation. The solvent flush technique may be used if the amount of solvent is kept at a minimum. If the internal standard calibration technique is used, add 10 μL of internal standard to each mL of sample prior to injection. Chromatograms of the target organophosphorus compounds are shown in Figures 1 through 4.

7.4.2 Figures 5 and 6 show chromatograms with and without Simazine, Atrazine, and Carbophenothion on 30-m columns.

7.5 Record the sample volume injected to the nearest 0.05 μL and the resulting peak sizes (in area units or peak heights). Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.5.1 If peak detection and identification is prevented by the presence of interferences, the use of an FPD or further sample cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to establish elution patterns and to determine recovery of target compounds. The absence of interference from reagents must be demonstrated by routine processing of reagent blanks through the chosen cleanup procedure. Refer to Sec. 3.0 for interferences.

7.5.2 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off-scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.5.3 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The

analyst should consult with the source of the sample to determine whether further concentration of the sample extract is warranted.

7.5.4 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique. Refer to Sec. 8.0 and Method 8270.

7.6 Suggested chromatograph maintenance: Corrective measures may require any one or more of the following remedial actions.

7.6.1 Refer to Method 8000 for general information on the maintenance of capillary columns and injectors.

7.6.2 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector (J&W Scientific, Restek, or equivalent), clean and deactivate the splitter. Reattach the columns after cleanly cutting off at least one foot from the injection port side of the column using a capillary cutting tool or scribe. The accumulation of high boiling residues can change split ratios between dual columns and thereby change calibration factors.

7.6.3 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperature. Oxygen can enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Polar columns including the DB-210 and DB-608 are more prone to oxidation. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

7.6.4 Peak tailing for all components will be exacerbated by dirty injectors, pre-columns, and glass "Y"s. Additionally, cleaning of this equipment (or replacement/clipping, as appropriate) will greatly reduce the peak tailing. Components such as Fensulfothion, Naled, Azinphos-methyl, and Dimethoate are very good indicators of system performance.

7.7 Detector maintenance:

7.7.1 Older FPDs may be susceptible to stray light in the photomultiplier tube compartment. This stray light will decrease the sensitivity and the linearity of the detector. Analysts can check for leaks by initiating an analysis in a dark room and turning on the lights. A shift in the baseline indicates that light may be leaking into the photomultiplier tube compartment. Additional shielding should be applied to eliminate light leaks and minimize stray light interference.

7.7.2 The bead of the NPD will become exhausted with time, which will decrease the sensitivity and the selectivity of the detector. The collector may become contaminated which decreased detector sensitivity.

7.7.3 Both types of detectors use a flame to generate a response. Flow rates of air and hydrogen should be optimized to give the most sensitive, linear detector response for target analytes.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Include a mid-level check standard after each group of 10 samples in the analysis sequence. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270.

8.3.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.3.3 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

8.3.3.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

8.3.3.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

8.3.3.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

8.3.3.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

8.3.3.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

8.3.3.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

8.3.3.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the

sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

8.3.4 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process because of the extensive fragmentation of organophosphorus pesticides during electron impact MS processes.

8.3.5 Should the MS procedure fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional sample cleanup.

9.0 METHOD PERFORMANCE

9.1 Estimated MDLs and associated chromatographic conditions for water and clean soil (uncontaminated with synthetic organics) are listed in Table 1. As detection limits will vary with the particular matrix to be analyzed, guidance for determining EQLs is given in Table 2. Recoveries for several method analytes are provided in Tables 5, 6, and 7.

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TABLE 1
METHOD DETECTION LIMITS IN A WATER AND A SOIL MATRIX USING 15-m COLUMNS AND A FLAME PHOTOMETRIC DETECTOR

Compound	Reagent Water (3510)[a] (µg/L)	Soil (3540)[b] (µg/kg)
Azinphos-methyl	0.10	5.0
Bolstar (Sulprofos)	0.07	3.5
Chlorpyrifos	0.07	5.0
Coumaphos	0.20	10.0
Demeton, -O, -S	0.12	6.0
Diazinon	0.20	10.0
Dichlorvos (DDVP)	0.80	40.0
Dimethoate	0.26	13.0
Disulfoton	0.07	3.5
EPN	0.04	2.0
Ethoprop	0.20	10.0
Fensulfothion	0.08	4.0
Fenthion	0.08	5.0
Malathion	0.11	5.5
Merphos	0.20	10.0
Mevinphos	0.50	25.0
Naled	0.50	25.0
Parathion, ethyl	0.06	3.0
Parathion, methyl	0.12	6.0
Phorate	0.04	2.0
Ronnel	0.07	3.5
Sulfotepp	0.07	3.5
TEPP[c]	0.80	40.0
Tetrachlorovinphos	0.80	40.0
Tokuthion (Protothiofos)[c]	0.07	5.5
Trichloronate[c]	0.80	40.0

[a] Sample extracted using Method 3510, Separatory Funnel Liquid-Liquid Extraction.

[b] Sample extracted using Method 3540, Soxhlet Extraction.

[c] Purity of these standards not established by the EPA Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC.

TABLE 2
DETERMINATION OF ESTIMATED QUANTITATION LIMITS
(EQLs) FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water (Methods 3510 or 3520)	10[b]
Low-concentration soil by Soxhlet and no cleanup	10[c]
Non-water miscible waste (Method 3580)	1000[c]

[a] EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix dependent. The EQLs to be determined herein are for guidance and may not always be achievable.

[b] Multiply this factor times the reagent water MDL in Table 1.

[c] Multiply this factor times the soil MDL in Table 1.

TABLE 3.
RETENTION TIMES FOR METHOD 8141A ANALYTES
EMPLOYING 15-m COLUMNS

	Capillary Column			
	Compound	DB-5	SPB-608	DB-210
TEPP		6.44	5.12	10.66
Dichlorvos (DDVP)	9.63	7.91	12.79	
Mevinphos	14.18	12.88	18.44	
Demeton, -O and -S	18.31	15.90	17.24	
Ethoprop	18.62	16.48	18.67	
Naled		19.01	17.40	19.35
Phorate	19.94	17.52	18.19	
Monochrotophos	20.04	20.11	31.42	
Sulfotepp	20.11	18.02	19.58	
Dimethoate	20.64	20.18	27.96	
Disulfoton	23.71	19.96	20.66	
Diazinon	24.27	20.02	19.68	
Merphos	26.82	21.73	32.44	
Ronnel	29.23	22.98	23.19	
Chlorpyrifos	31.17	26.88	25.18	
Malathion	31.72	28.78	32.58	
Parathion, methyl	31.84	23.71	32.17	
Parathion, ethyl	31.85	27.62	33.39	
Trichloronate	32.19	28.41	29.95	
Tetrachlorovinphos	34.65	32.99	33.68	
Tokuthion (Protothiofos)	34.67	24.58	39.91	
Fensulfothion	35.85	35.20	36.80	
Bolstar (Sulprofos)	36.34	35.08	37.55	
Famphur*	36.40	36.93	37.86	
EPN		37.80	36.71	36.74
Azinphos-methyl	38.34	38.04	37.24	
Fenthion	38.83	29.45	28.86	
Coumaphos	39.83	38.87	39.47	

*Method 8141A has not been fully validated for Famphur.

Initial temperature	130°C	50°C	50°C
Initial time	3 minutes	1 minute	1 minute
Program 1 rate	5°C/min	5°C/min	5°C/min
Program 1 final temp.	180°C	140°C	140°C
Program 1 hold	10 minutes	10 minutes	10 minutes
Program 2 rate	2°C/min	10°C/min	10°C/min
Program 2 final temp.	250°C	240°C	240°C
Program 2 hold	15 minutes	10 minutes	10 minutes

TABLE 4.
RETENTION TIMES FOR METHOD 8141A ANALYTES
EMPLOYING 30-m COLUMNS[a]

Compound	RT (min) DB-5	DB-210	DB-608	DB-1
Trimethylphosphate	b	2.36		
Dichlorvos (DDVP)	7.45	6.99	6.56	10.43
Hexamethylphosphoramide	b	7.97		
Trichlorfon	11.22	11.63	12.69	
TEPP	b	13.82		
Thionazin	12.32	24.71		
Mevinphos	12.20	10.82	11.85	14.45
Ethoprop	12.57	15.29	18.69	18.52
Diazinon	13.23	18.60	24.03	21.87
Sulfotepp	13.39	16.32	20.04	19.60
Terbufos	13.69	18.23	22.97	
Tri-o-cresyl phosphate	13.69	18.23		
Naled	14.18	15.85	18.92	18.78
Phorate	12.27	16.57	20.12	19.65
Fonophos	14.44	18.38		
Disulfoton	14.74	18.84	23.89	21.73
Merphos	14.89	23.22		26.23
Oxidized Merphos	20.25	24.87	35.16	
Dichlorofenthion	15.55	20.09	26.11	
Chlorpyrifos, methyl	15.94	20.45	26.29	
Ronnel	16.30	21.01	27.33	23.67
Chlorpyrifos	17.06	22.22	29.48	24.85
Trichloronate	17.29	22.73	30.44	
Aspon	17.29	21.98		
Fenthion	17.87	22.11	29.14	24.63
Demeton-S	11.10	14.86	21.40	20.18
Demeton-O	15.57	17.21	17.70	
Monocrotophos[c]	19.08	15.98	19.62	19.3
Dimethoate	18.11	17.21	20.59	19.87
Tokuthion	19.29	24.77	33.30	27.63
Malathion	19.83	21.75	28.87	24.57
Parathion, methyl	20.15	20.45	25.98	22.97
Fenithrothion	20.63	21.42		
Chlorfenvinphos	21.07	23.66	32.05	
Parathion, ethyl	21.38	22.22	29.29	24.82
Bolstar	22.09	27.57	38.10	29.53
Stirophos	22.06	24.63	33.40	26.90
Ethion	22.55	27.12	37.61	

(continued)

TABLE 4. (Continued)

Compound	RT (min) DB-5	DB-210	DB-608	DB-1
Phosphamidon	22.77	20.09	25.88	
Crotoxyphos	22.77	23.85	32.65	
Leptophos	24.62	31.32	44.32	
Fensulfothion	27.54	26.76	36.58	28.58
EPN	27.58	29.99	41.94	31.60
Phosmet	27.89	29.89	41.24	
Azinphos-methyl	28.70	31.25	43.33	32.33
Azinphos-ethyl	29.27	32.36	45.55	
Famphur	29.41	27.79	38.24	
Coumaphos	33.22	33.64	48.02	34.82
Atrazine	13.98	17.63		
Simazine	13.85	17.41		
Carbophenothion	22.14	27.92		
Dioxathion	d	d	22.24	
Trithion methyl			36.62	
Dicrotophos			19.33	
Internal Standard				
1-Bromo-2-nitrobenzene	8.11	9.07		
Surrogates				
Tributyl phosphate			11.1	
Triphenyl phosphate			33.4	
4-Cl-3-nitrobenzotrifluoride	5.73	5.40		

[a] The GC operating conditions were as follows:

DB-5 and DB-210 - 30-m x 0.53-mm ID column, DB-5 (1.50- m film thickness) and DB-210 (1.0- m film thickness). Both connected to a press-fit Y-shaped inlet splitter. Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min; injector temperature 250°C; detector temperature 300°C; bead temperature 400°C; bias voltage 4.0; hydrogen gas pressure 20 psi; helium carrier gas 6 mL/min; helium makeup gas 20 mL/min.

DB-608 - 30-m x 0.53-mm ID column, DB-608 (1.50- m film thickness) installed in an 0.25-in packed-column inlet. Temperature program: 110°C (0.5-min hold) to 250°C (4-min hold) at 3°C/min; injector temperature 250°C; helium carrier gas 5 mL/min; flame photometric detector.

DB-1 30-m x 0.32-mm ID column, DB-1 (0.25- m film thickness) split/splitless with head pressure of 10 psi, split valve closure at 45 sec, injector temp. 250°C, 50°C (1-min hold) to 280°C (2-min hold) at 6°C/min, mass spectrometer full scan 35-550 amu.

[b] Not detected at 20 ng per injection.
[c] Retention times may shift to longer times with larger amounts injected (shifts of over 30 seconds have been observed, Hatcher et. al.)
[d] Shows multiple peaks; therefore, not included in the composite.

TABLE 5.
PERCENT RECOVERY OF 27 ORGANOPHOSPHATES BY SEPARATORY FUNNEL EXTRACTION

Compound	Percent Recovery		
	Low	Medium	High
Azinphos methyl	126	143 + 8	101
Bolstar	134	141 + 8	101
Chlorpyrifos	7	89 + 6	86
Coumaphos	103	90 + 6	96
Demeton	33	67 + 11	74
Diazinon	136	121 + 9.5	82
Dichlorvos	80	79 + 11	72
Dimethoate	NR	47 + 3	101
Disulfoton	48	92 + 7	84
EPN	113	125 + 9	97
Ethoprop	82	90 + 6	80
Fensulfonthion	84	82 + 12	96
Fenthion	NR	48 + 10	89
Malathion	127	92 + 6	86
Merphos	NR	79	81
Mevinphos	NR	NR	55
Monocrotophos	NR	18 + 4	NR
Naled	NR	NR	NR
Parathion, ethyl	101	94 + 5	86
Parathion, methyl	NR	46 + 4	44
Phorate	94	77 + 6	73
Ronnel	67	97 + 5	87
Sulfotep	87	85 + 4	83
TEPP	96	55 + 72	63
Tetrachlorvinphos	79	90 + 7	80
Tokuthion	NR	45 + 3	90
Trichloroate	NR	35	94

NR = Not recovered.

TABLE 6.
PERCENT RECOVERY OF 27 ORGANOPHOSPHATES BY CONTINUOUS LIQUID-LIQUID EXTRACTION

Compound	Percent Recovery		
	Low	Medium	High
Azinphos methyl	NR	129	122
Bolstar	NR	126	128
Chlorpyrifos	13	82 + 4	88
Coumaphos	94	79 + 1	89
Demeton	38	23 + 3	41
Diazinon	NR	128 + 37	118
Dichlorvos	81	32 + 1	74
Dimethoate	NR	10 + 8	102
Disulfoton	94	69 + 5	81
EPN	NR	104 + 18	119
Ethoprop	39	76 + 2	83
Famphur	--	63 + 15	--
Fensulfonthion	90	67 + 26	90
Fenthion	8	32 + 2	86
Malathion	105	87 + 4	86
Merphos	NR	80	79
Mevinphos	NR	87	49
Monocrotophos	NR	30	1
Naled	NR	NR	74
Parathion, ethyl	106	81 + 1	87
Parathion, methyl	NR	50 + 30	43
Phorate	84	63 + 3	74
Ronnel	82	83 + 7	89
Sulfotep	40	77 + 1	85
TEPP	39	18 + 7	70
Tetrachlorvinphos	56	70 + 14	83
Tokuthion	132	32 + 14	90
Trichloroate	NR	NR	21

NR = Not recovered.

TABLE 7.
PERCENT RECOVERY OF 27 ORGANOPHOSPHATES BY SOXHLET EXTRACTION

Compound	Percent Recovery		
	Low	Medium	High
Azinphos methyl	156	110 ± 6	87
Bolstar	102	103 ± 15	79
Chlorpyrifos	NR	66 ± 17	79
Coumaphos	93	89 ± 11	90
Demeton	169	64 ± 6	75
Diazinon	87	96 ± 3	75
Dichlorvos	84	39 ± 21	71
Dimethoate	NR	48 ± 7	98
Disulfoton	78	78 ± 6	76
EPN	114	93 ± 8	82
Ethoprop	65	70 ± 7	75
Fensulfonthion	72	81 ± 18	111
Fenthion	NR	43 ± 7	89
Malathion	100	81 ± 8	81
Merphos	62	53	60
Mevinphos	NR	71	63
Monocrotophos	NR	NR	NR
Naled	NR	48	NR
Parathion, ethyl	75	80 ± 8	80
Parathion, methyl	NR	41 ± 3	28
Phorate	75	77 ± 6	78
Ronnel	NR	83 ± 12	79
Sulfotep	67	72 ± 8	78
TEPP	36	34 ± 33	63
Tetrachlorvinphos	50	81 ± 7	83
Tokuthion	NR	40 ± 6	89
Trichloroate	56	53	53

NR = Not recovered.

TABLE 8.

SUGGESTED OPERATING CONDITIONS FOR 15-m COLUMNS

Columns 1 and 2 (DB-210 and SPB-608 or their equivalent)	
Carrier gas (He) flow rate =	5 mL/min
Initial temperature =	50°C, hold for 1 minute
Temperature program =	50°C to 140°C at 5°C/min, hold for 10 minutes, followed by 140°C to 240°C at 10°C/min, hold for 10 minutes (or a sufficient amount of time for last compound to elute).
Column 3 (DB-5 or equivalent)	
Carrier gas (He) flow rate =	5 mL/min
Initial temperature =	130°C, hold for 3 minutes
Temperature program =	130°C to 180°C at 5°C/min, hold for 10 minutes, followed by 180°C to 250°C at 2°C/min, hold for 15 minutes (or a sufficient amount of time for last compound to elute).

TABLE 9
SUGGESTED OPERATING CONDITIONS FOR 30-m COLUMNS

Column 1:

Type: DB-210
Dimensions: 30-m x 0.53-mm ID
Film Thickness (μm): 1.0

Column 2:

Type: DB-5
Dimensions: 30-m x 0.53-mm ID
Film Thickness (μm): 1.5

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Helium)

Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min

Injector temperature: 250°C

Detector temperature: 300°C

Injection volume: 2 μL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual NPD

Range: 1

Attenuation: 64

Type of splitter: Y-shaped or Tee

Data system: Integrator

Hydrogen gas pressure: 20 psi

Bead temperature: 400°C

Bias voltage: 4

TABLE 10
QUANTITATION AND CHARACTERISTIC IONS FOR OP PESTICIDES

Compound Name	Quantitation ions	Characteristic ions
Azinphos-methyl	160	77,132
Bolstar (Sulprofos)	156	140,143,113,33
Chlorpyrifos	197	97,199,125.314
Coumaphos	109	97,226,362,21
Demeton-S	88	60,114,170
Diazinon	137	179,152,93,199,304
Dichlorvos (DDVP)	109	79,185,145
Dimethoate	87	93,125,58,143
Disulfoton	88	89,60,61,97,142
EPN	157	169,141,63,185
Ethoprop	158	43,97,41,126
Fensulfothion	293	97,125,141,109,308
Fenthion	278	125,109,93,169
Malathion	173	125,127,93,158
Merphos	209	57,153,41,298
Mevinphos	127	109,67,192
Monocrotophos	127	67,97,192,109
Naled	109	145,147,79
Parathion, ethyl	291	97,109,139,155
Parathion, methyl	109	125,263,79
Phorate	75	121,97,47,260
Ronnel	285	125,287,79,109
Stirophos	109	329,331,79
Sulfotepp	322	97,65,93,121,202
TEPP	99	155,127,81,109
Tokuthion	113	43,162,267,309

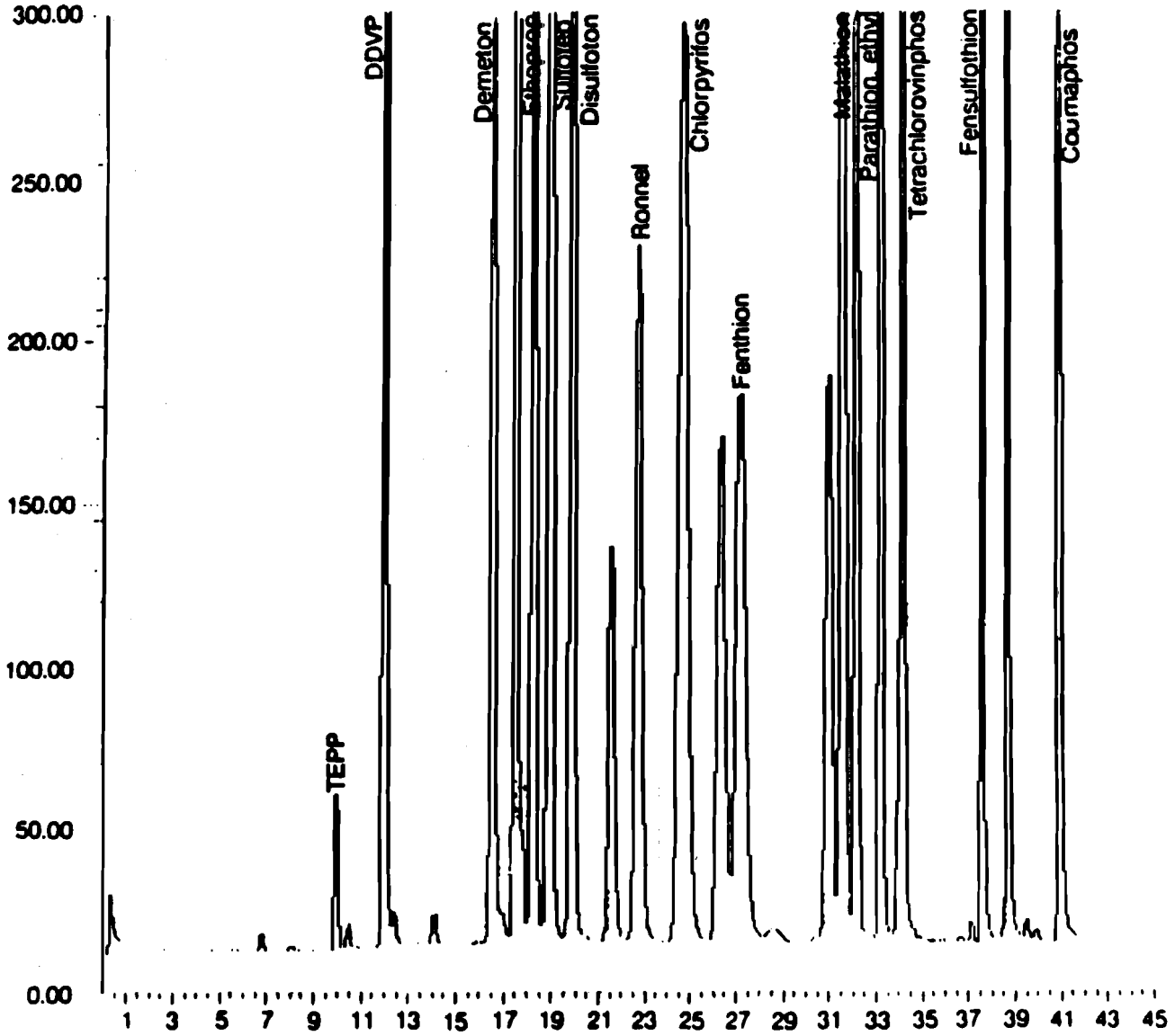


Figure 1. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 2. See Table 3 for retention times.

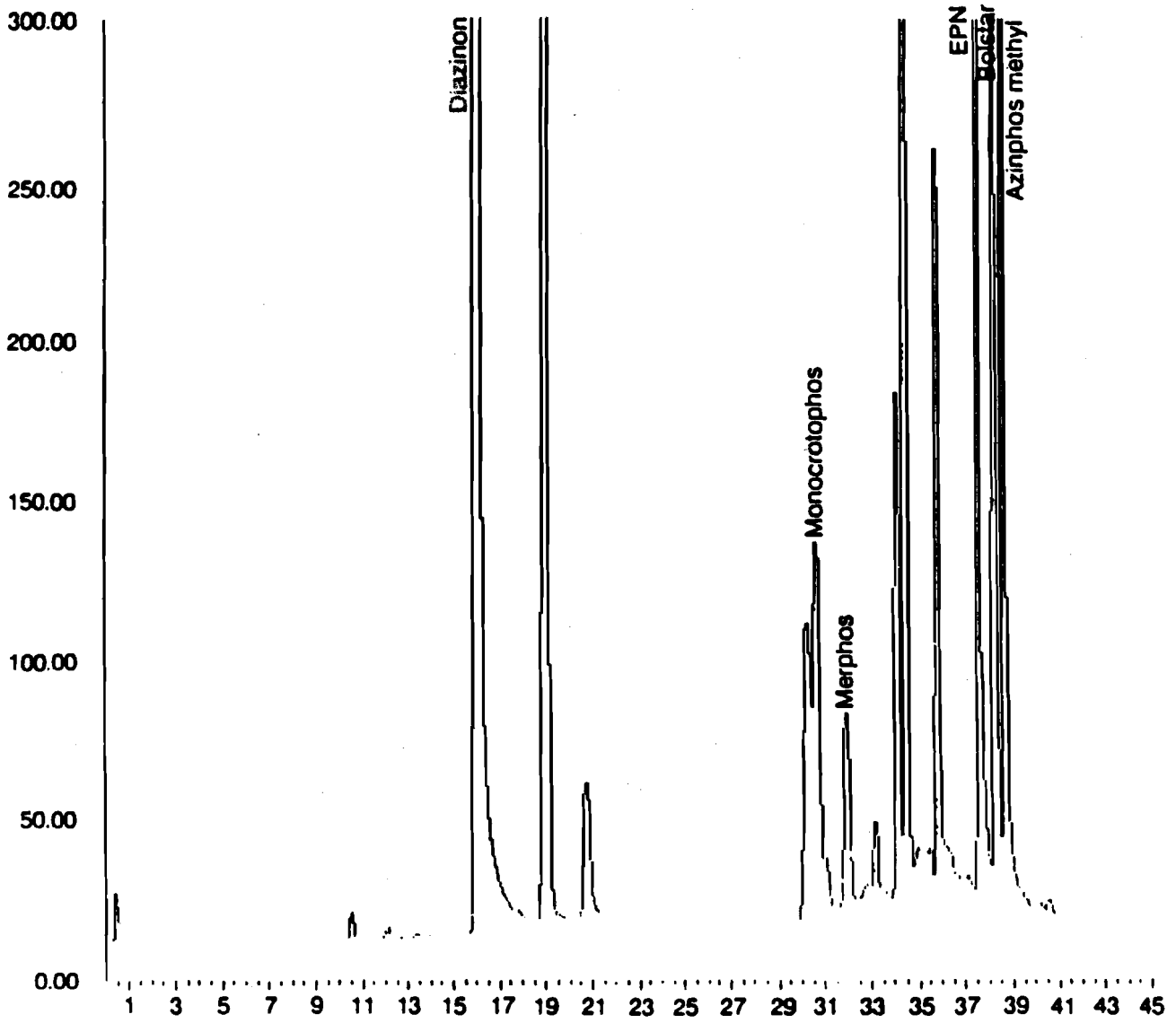


Figure 2. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 1. See Table 3 for retention times.

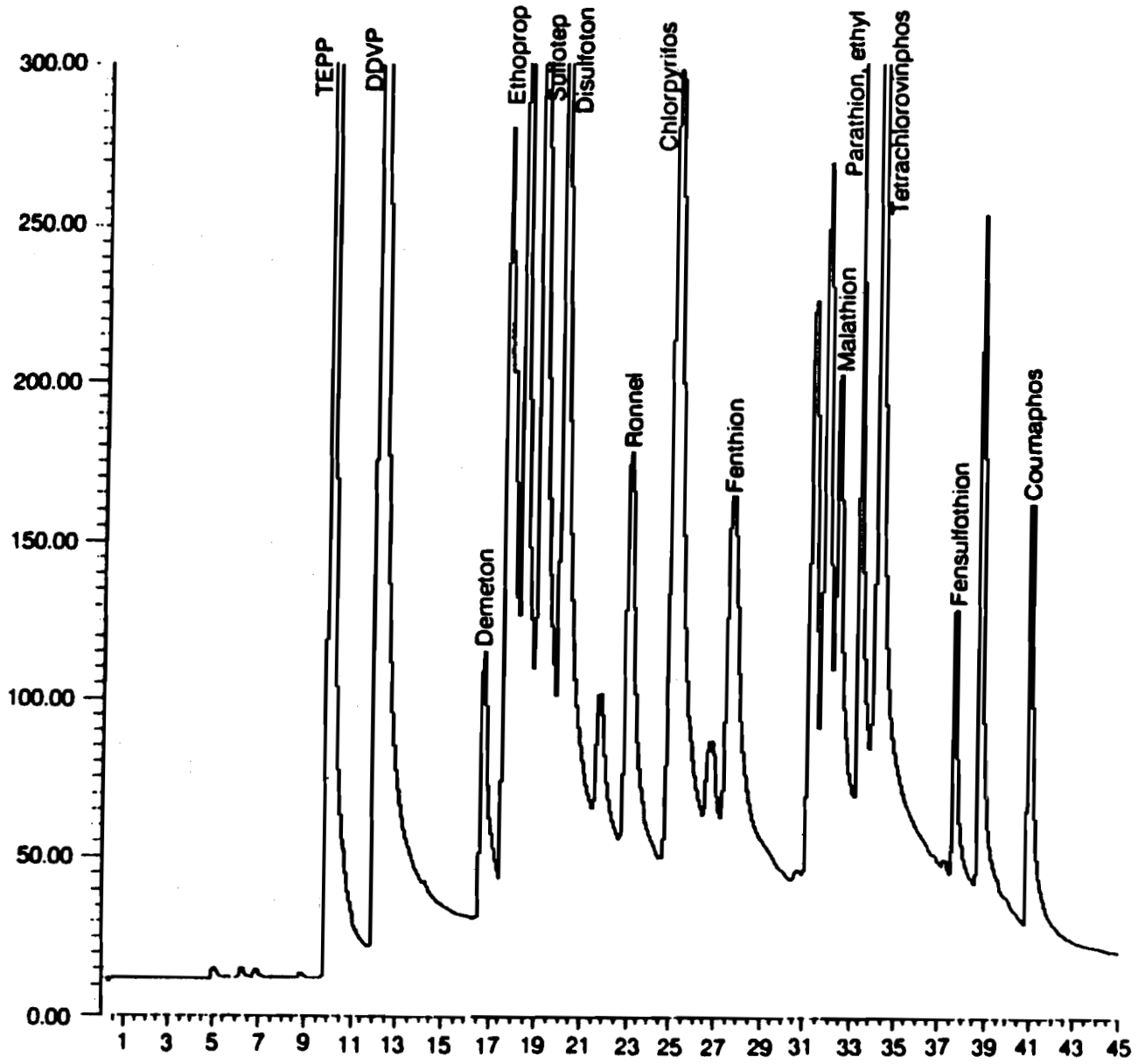


Figure 3. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 4. See Table 3 for retention times.

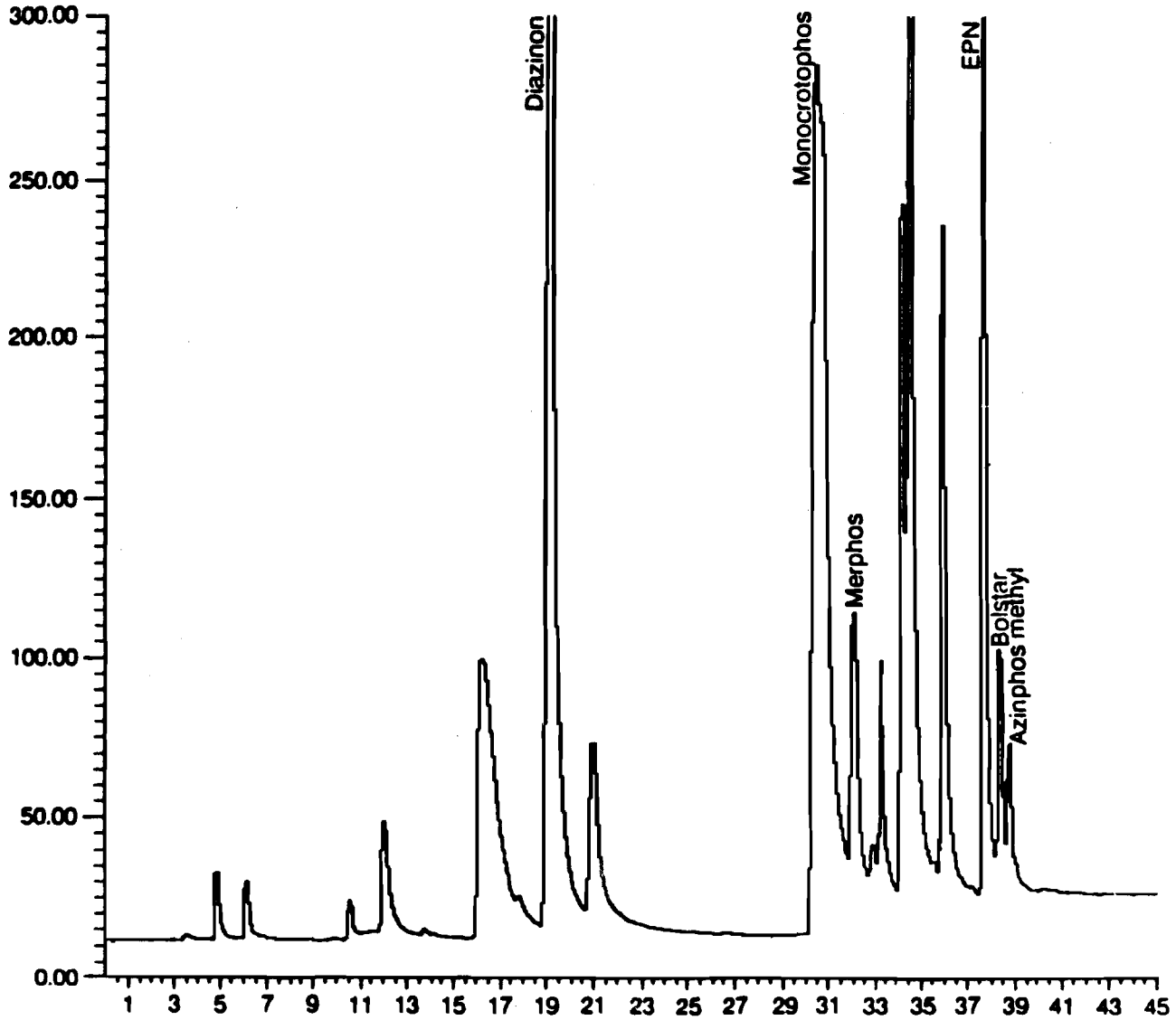


Figure 4. Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 3. See Table 3 for retention times.

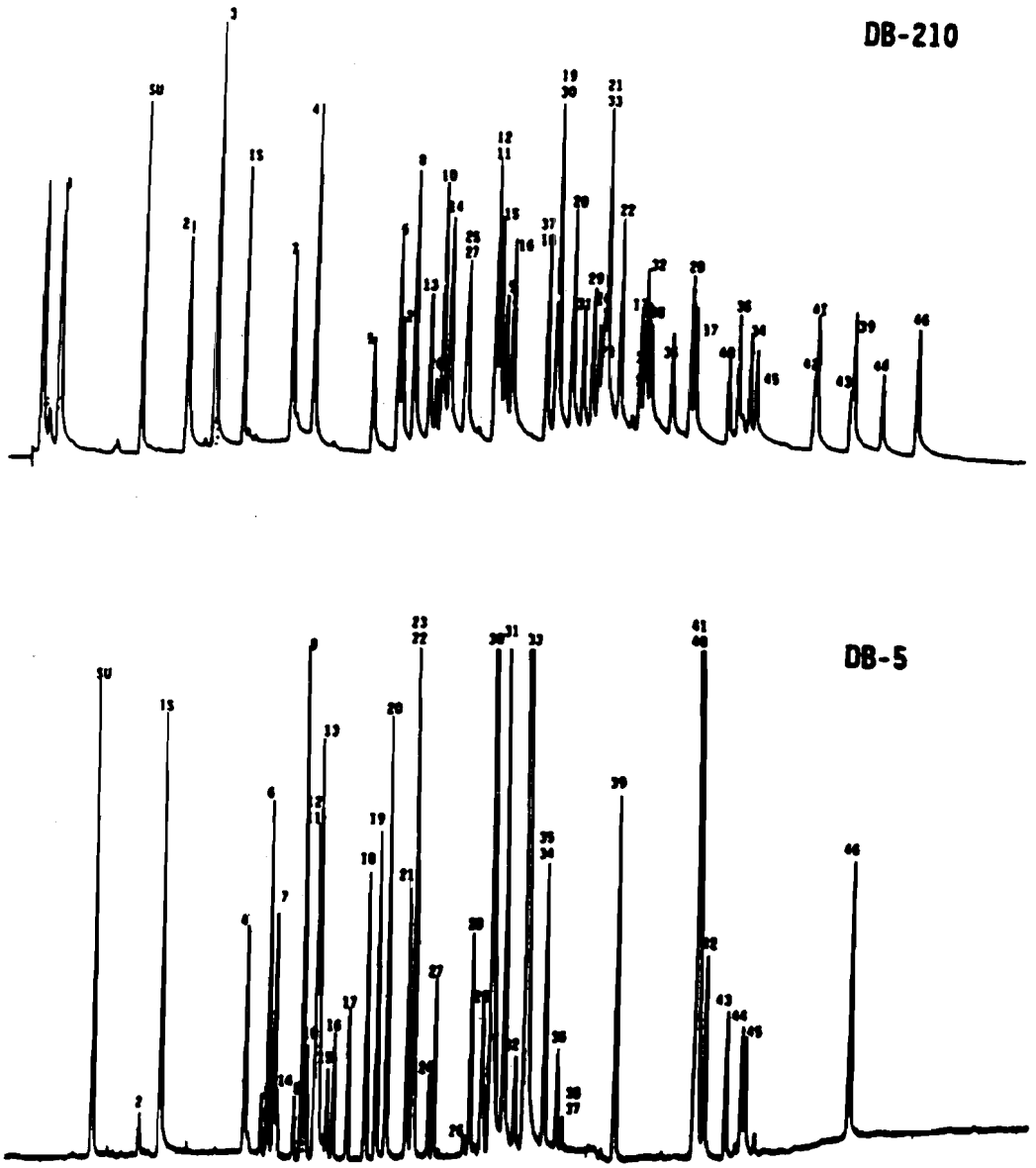


Figure 5. Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, without Simazine, Atrazine and Carbophenothion. See Table 4 for retention times and for GC operating conditions.

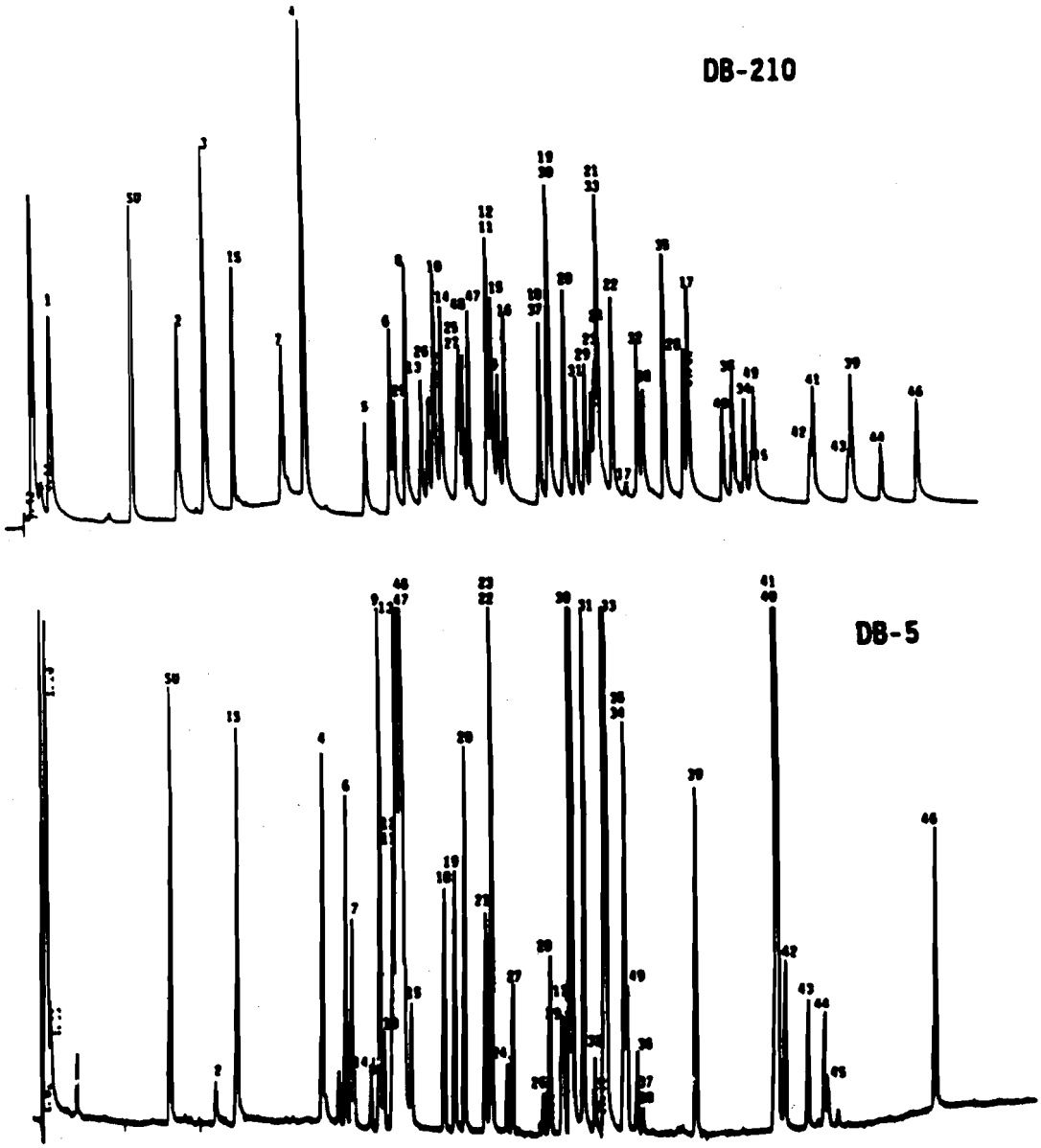
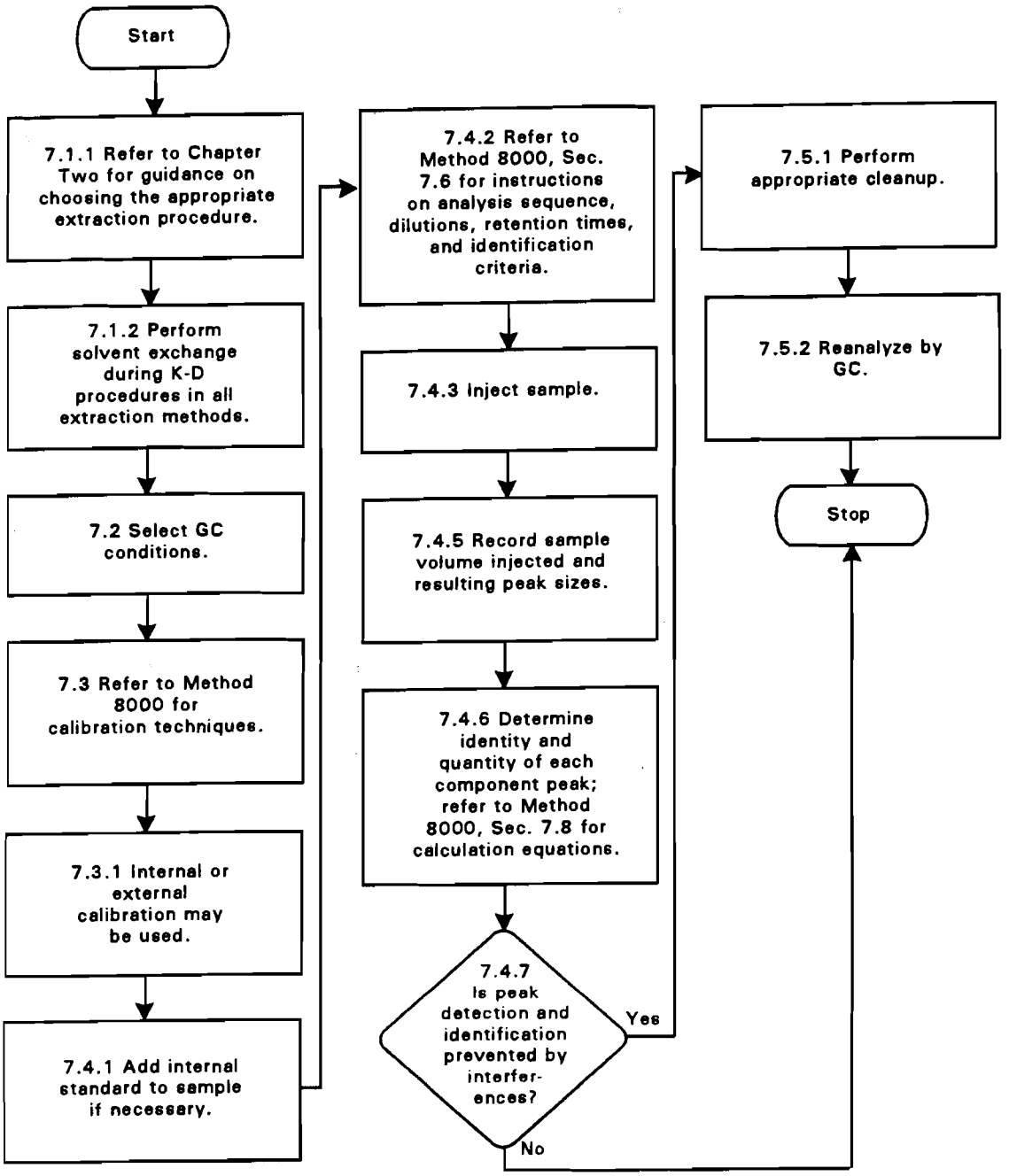


Figure 6. Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, with Simazine, Atrazine and Carbophenothion. See Table 4 for retention times and for GC operating conditions.


Start
7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure.
7.1.2 Perform solvent exchange during K-D procedures in all extraction methods.
7.2 Select GC conditions.
7.3 Refer to Method 8000 for calibration techniques.
7.3.1 Internal or external calibration may be used.
7.4.1 Add internal standard to sample if necessary.
7.4.2 Refer to Method 8000, Sec. 7.6 for instructions on analysis sequence, dilutions, retention times, and identification criteria.
7.4.3 Inject sample.
7.4.5 Record sample volume injected and resulting peak sizes.
7.4.6 Determine identity and quantity of each component peak; refer to Method 8000, Sec. 7.8 for calculation equations.
7.4.7 Is peak detection and identification prevented by interfer-ences?
Yes
No
7.5.1 Perform appropriate cleanup.
7.5.2 Reanalyze by GC.
Stop

METHOD 8150B

CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2

[a] Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

1.3 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Sec. 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.4 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium

hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.7 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1a and 1b - 1.8 m x 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2 - 1.8 m x 4 mm ID glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.2.3 Column 3 - 1.98 m x 2 mm ID glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.3 Detector - Electron capture (ECD).

4.2 Erlenmeyer flasks - 250 and 500 mL Pyrex, with 24/40 ground glass joint.

4.3 Beaker - 500 mL.

4.4 Diazomethane generator - Refer to Sec. 7.4 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 Diazald kit - recommended for the generation of diazomethane using the procedure given in Sec. 7.4.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Sec. 7.4.3.

4.5 Vials - 10 to 15 mL, amber glass, with Teflon lined screw cap or crimp top.

4.6 Separatory funnel - 2000 mL, 125 mL, and 60 mL.

4.7 Drying column - 400 mm x 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.9 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.11 Microsyringe - 10 μL.

4.12 Wrist shaker - Burrell Model 75 or equivalent.

4.13 Glass wool - Pyrex, acid washed.

4.14 Balance - Analytical, capable of accurately weighing to 0.0001 g.

4.15 Syringe - 5 mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid solution

5.3.1 ((1:1) (v/v)) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.3.2 ((1:3) (v/v)) - Slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of organic-free reagent water.

5.4 Hydrochloric acid ((1:9) (v/v)), HCl. Add one volume of concentrated HCl to 9 volumes of organic-free reagent water.

5.5 Potassium hydroxide solution (KOH) - 37% aqueous solution (w/v). Dissolve 37 g potassium hydroxide pellets in organic-free reagent water, and dilute to 100 mL.

5.6 Carbitol (Diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2OH$. Available from Aldrich Chemical Co.

5.7 Solvents

5.7.1 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.7.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.7.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.7.4 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.7.5 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.8 Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store at 130°C.

5.9 N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald), $CH_3C_6H_4SO_2N(CH_3)NO$. Available from Aldrich Chemical Co.

5.10 Silicic acid. Chromatographic grade, nominal 100 mesh. Store at 130°C.

5.11 Stock standard solutions - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the acids in pesticide quality acetone and dissolve the esters in 10% acetone/isooctane (v/v) and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.11.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.11.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.12 Calibration standards - A minimum of five calibration standards for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.13 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.13.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Sec. 5.12.

5.13.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane.

5.13.3 Analyze each calibration standard per Sec. 7.0.

5.14 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample,

standard, and organic-free reagent water blank with one or two herbicide surrogates (e.g. herbicides that are not expected to be present in the sample). The surrogates selected should elute over the range of the temperature program used in this method. 2,4-Dichlorophenylacetic acid (DCAA) is recommended as a surrogate compound. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Preparation of waste samples

7.1.1 Extraction

7.1.1.1 Follow Method 3580 except use diethyl ether as the dilution solvent, acidified anhydrous sodium sulfate, and acidified glass wool.

7.1.1.2 Transfer 1.0 mL (a lesser volume or a dilution may be required if herbicide concentrations are high) to a 250 mL ground glass-stoppered Erlenmeyer flask. Proceed to Sec. 7.2.2 hydrolysis.

7.2 Preparation of soil, sediment, and other solid samples

7.2.1 Extraction

7.2.1.1 To a 500 mL, wide mouth Erlenmeyer flask add 50 g (dry weight as determined in Method 3540, Sec. 7.2.1) of the well mixed, moist solid sample. Adjust the pH to 2 (See Method 9045) with concentrated HCl and monitor the pH for 15 minutes with occasional stirring. If necessary, add additional HCl until the pH remains at 2.

7.2.1.2 Add 20 mL acetone to the flask and mix the contents with the wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.2.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.2.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2 liter separatory funnel containing

250 mL of reagent water. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.2.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500 mL ground glass-stoppered Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask.

7.2.1.6 An alternative extraction procedure using ultrasonic extraction can be found in Sec. 7.2 of Method 8151.

7.2.2 Hydrolysis

7.2.2.1 Add 30 mL of organic-free reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place a three ball Snyder column on the flask, evaporate the diethyl ether on a water bath, and continue to heat until the hydrolysis step is completed (usually 1 to 2 hours).

7.2.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125 mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy-acid herbicides remain soluble in the aqueous phase as potassium salts.

7.2.3 Solvent cleanup

7.2.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.2.3.2 Combine ether extracts in a 125 mL Erlenmeyer flask containing 5-7 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

<u>NOTE</u>: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free=flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few

additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.2.3.3 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.4 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5 mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether. Proceed to Sec. 7.4 for esterification.

7.3 Preparation of aqueous samples

7.3.1 Extraction

7.3.1.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL, and quantitatively transfer it to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.3.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the

solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1 liter Erlenmeyer flask. Collect the solvent extract in a 250 mL ground glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

7.3.1.3 Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1 liter flask with each additional aliquot of extracting solvent.)

7.3.2 Hydrolysis

7.3.2.1 Add one or two clean boiling chips and 15 mL of organic-free reagent water to the 250 mL flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the apparatus on a hot water bath (60°-65°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 minutes, continue heating until the hydrolysis step is completed (usually 1 to 2 hours). Remove the apparatus and let stand at room temperature for at least 10 minutes.

7.3.2.2 Transfer the solution to a 60 mL separatory funnel using 5-10 mL of organic-free reagent water. Wash the basic solution twice by shaking for 1 minute with 20 mL portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.3.3 Solvent cleanup

7.3.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 minutes. Drain the aqueous layer into a 250 mL Erlenmeyer flask, and pour the organic layer into a 125 mL Erlenmeyer flask containing about 5-7 g of acidified sodium sulfate. Repeat the extraction twice more with 10 mL aliquots of diethyl ether, combining all solvent in the 125 mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

<u>NOTE</u>: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing

crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.3.3.2 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.3.3.3 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.3.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5 mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.4 Esterification

7.4.1 Two methods may be used for the generation of diazomethane: the bubbler method (set up shown in Figure 1) and the Diazald kit method. The bubbler method is suggested when small batches (10-15) of samples require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g. aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils

that result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

<u>CAUTION</u>: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C -- EXPLOSION may result.
- Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.
- Store away from alkali metals -- EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.4.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.4.2.1 Add 2 mL of diazomethane solution and let sample stand for 10 minutes with occasional swirling.

7.4.2.2 Rinse inside wall of the ampule with several hundred µL of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

7.4.2.3 Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

7.4.3 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.4.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.4.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.4.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.5 Gas chromatographic conditions (Recommended)

7.5.1 Column 1a

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min
Temperature program: 185°C, isothermal.

7.5.2 Column 1b

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min
Initial temperature: 140°C, hold for 6 minutes
Temperature program: 140°C to 200°C at 10°C/min, hold until last compound has eluted.

7.5.3 Column 2

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min
Temperature program: 185°C, isothermal.

7.5.4 Column 3

Carrier gas (ultra-high purity N_2) flow rate: 25 mL/min
Initial temperature: 100°C, no hold
Temperature program: 100°C to 150°C at 10°C/min, hold until last compound has eluted.

7.6 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.6.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.6.2 The following gas chromatographic columns are recommended for the compounds indicated:

Analyte	Column	Analyte	Column
Dicamba	1a,2	Dalapon	3
2,4-D	1a,2	MCPP	1b
2,4,5-TP	1a,2	MCPA	1b
2,4,5-T	1a,2	Dichloroprop	1b
2,4-DB	1a	Dinoseb	1b

7.7 Gas chromatographic analysis

7.7.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 μL of internal standard to the sample prior to injection.

7.7.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration check standard after each group of 10 samples in the analysis sequence.

7.7.3 Examples of chromatograms for various chlorophenoxy acid herbicides are shown in Figures 2 through 4.

7.7.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.7.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.7.6 If calibration standards have been analyzed in the same manner as the samples (e.g. have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is done using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.7.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1,000 times more concentrated than the selected concentrations.

8.2.2 Table 3 indicates single operator accuracy and precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if none of the above checks reveal a problem.
- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.4 GC/MS confirmation

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using organic-free reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

1. U.S. EPA, National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio, 1971.

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5. "Pesticide Methods Evaluation," Letter Report #33 for EPA Contract No. 68-03-2697. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995, 1975.

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8. Gurka, D.F, Shore, F.L., Pan, S-T, "Single Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Hazardous Waste", JAOAC, 69, 970, 1986.

9. U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS
FOR CHLORINATED HERBICIDES

Compound	Retention time (min)[a]				Method detection limit (μg/L)
	Col.1a	Col.1b	Col.2	Col.3	
2,4-D	2.0	-	1.6	-	1.2
2,4-DB	4.1	-	-	-	0.91
2,4,5-T	3.4	-	2.4	-	0.20
2,4,5-TP (Silvex)	2.7	-	2.0	-	0.17
Dalapon	-	-	-	5.0	5.8
Dicamba	1.2	-	1.0	-	0.27
Dichloroprop	-	4.8	-	-	0.65
Dinoseb	-	11.2	-	-	0.07
MCPA	-	4.1	-	-	249
MCPP	-	3.4	-	-	192

[a]Column conditions are given in Secs. 4.1 and 7.5.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION
LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water (based on one liter sample size)	10
Soil/sediment and other solids	200
Waste samples	100,000

[a]EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet weight basis. Sample EQLs are highly matrix dependent. The EQLs to be determined herein are provided for guidance and may not always be achievable.

TABLE 3.
SINGLE OPERATOR ACCURACY AND PRECISION[a]

Compound	Sample Type	Spike (µg/L)	Mean Recovery (%)	Standard deviation (%)
2,4-D	DW	10.9	75	4
	MW	10.1	77	4
	MW	200	65	5
Dalapon	DW	23.4	66	8
	MW	23.4	96	13
	MW	468	81	9
2,4-DB	DW	10.3	93	3
	MW	10.4	93	3
	MW	208	77	6
Dicamba	DW	1.2	79	7
	MW	1.1	86	9
	MW	22.2	82	6
Dichlorprop	DW	10.7	97	2
	MW	10.7	72	3
	MW	213	100	2
Dinoseb	MW	0.5	86	4
	MW	102	81	3
MCPA	DW	2020	98	4
	MW	2020	73	3
	MW	21400	97	2
MCPP	DW	2080	94	4
	MW	2100	97	3
	MW	20440	95	2
2,4,5-T	DW	1.1	85	6
	MW	1.3	83	4
	MW	25.5	78	5
2,4,5-TP	DW	1.0	88	5
	MW	1.3	88	4
	MW	25.0	72	5

[a]All results based upon seven replicate analyses. Esterification performed using the bubbler method. Data obtained from reference 8.

DW = ASTM Type II
MW = Municipal water

FIGURE 1.
DIAZOMETHANE GENERATOR

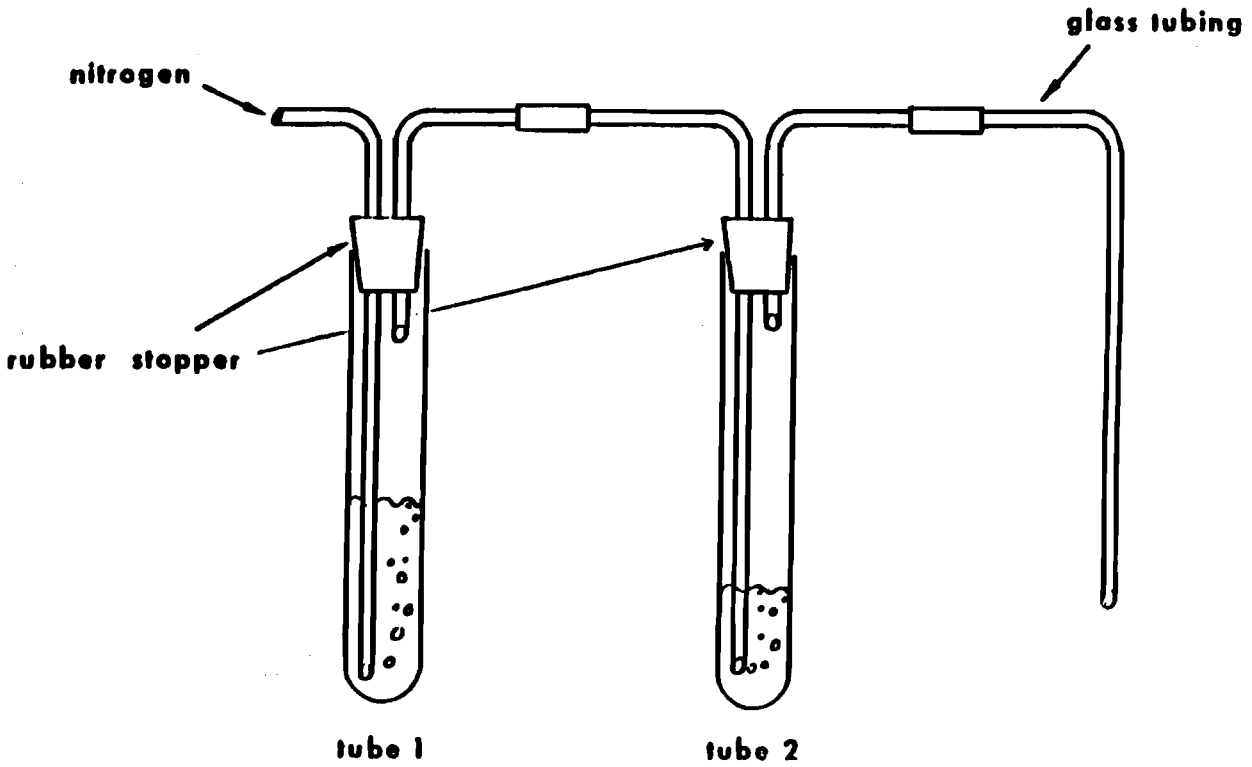


FIGURE 2.
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

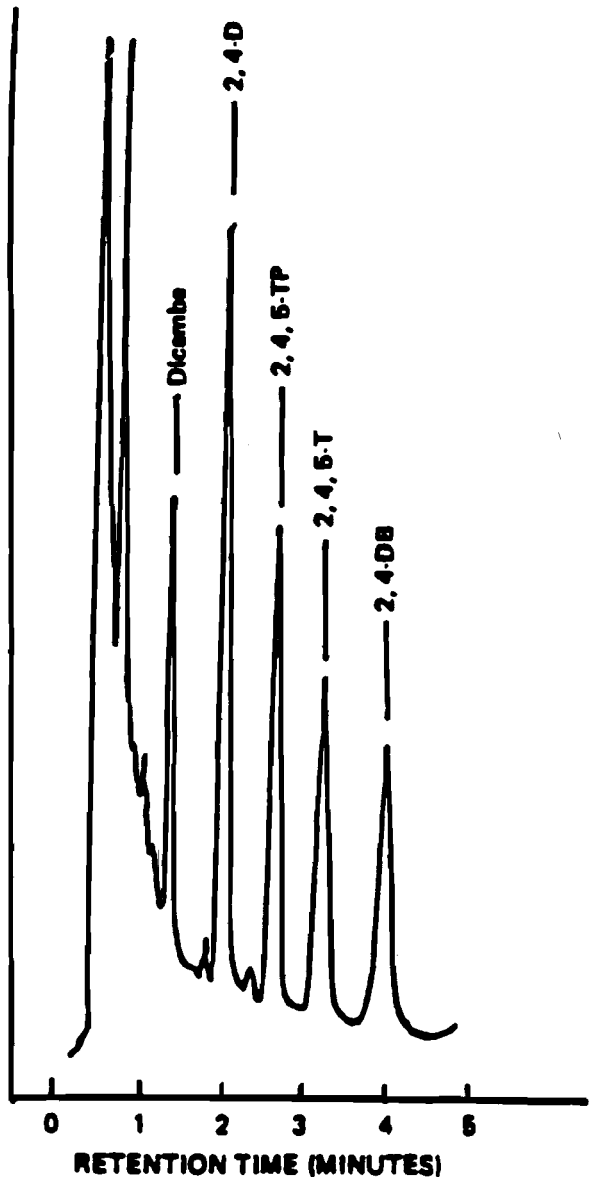


FIGURE 3.
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

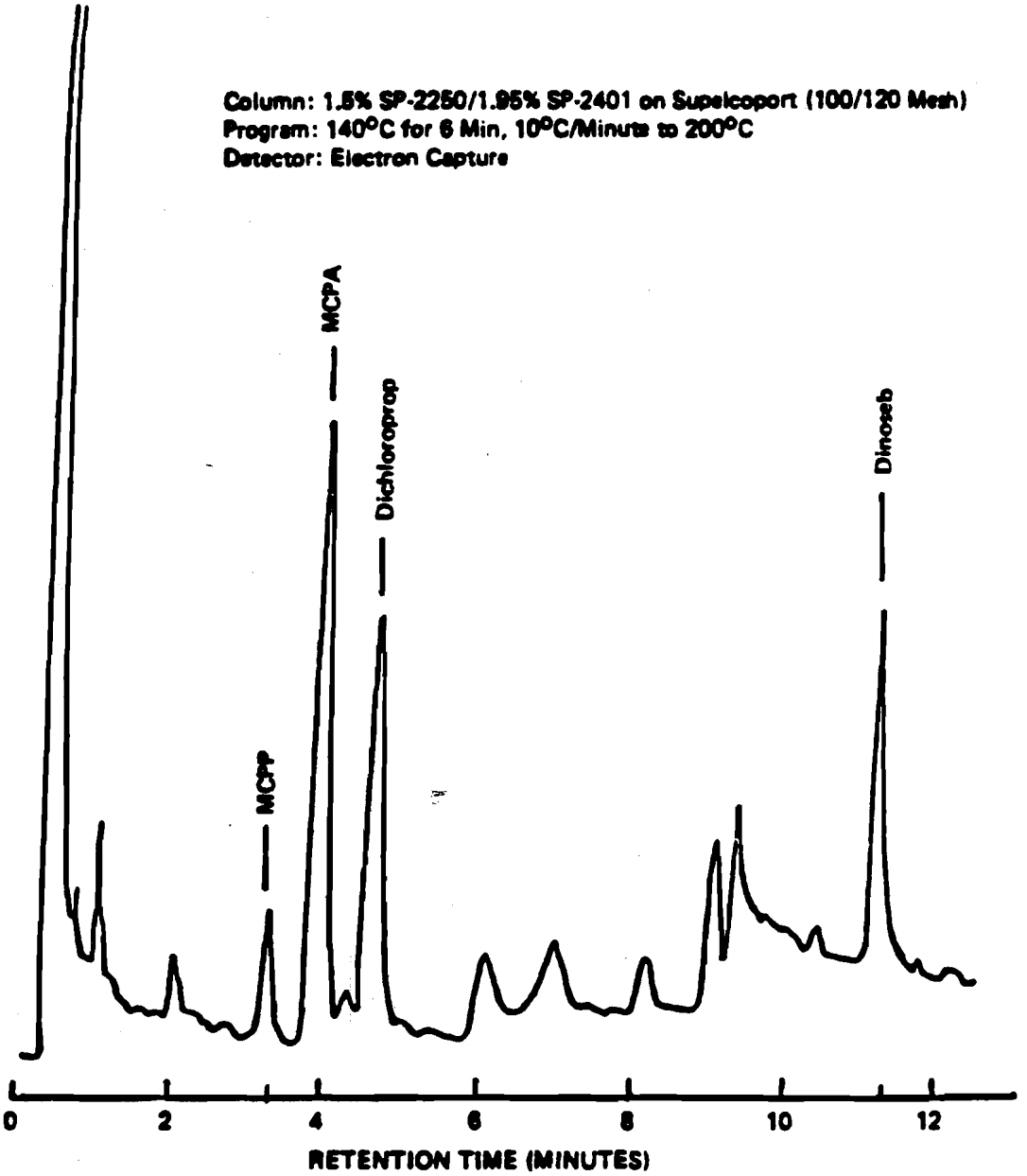
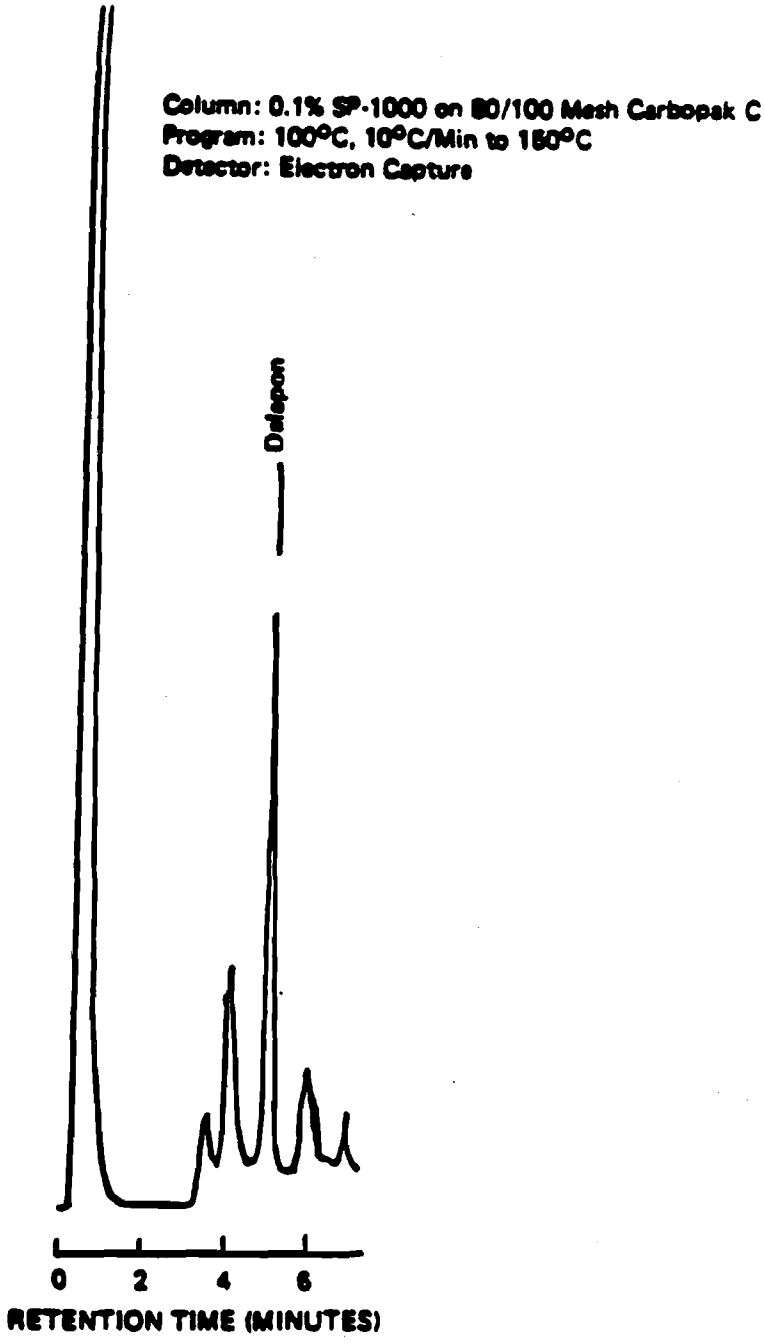
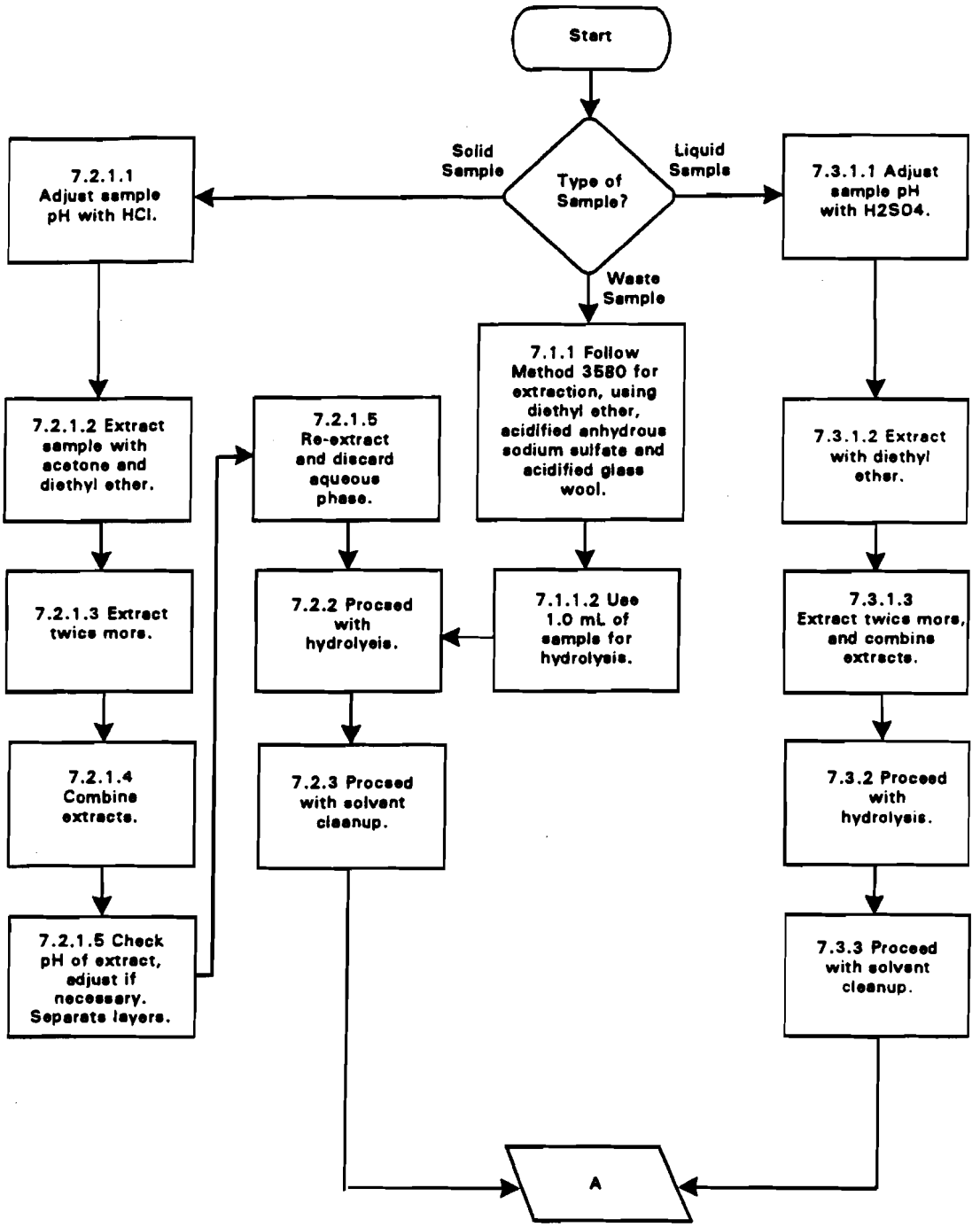
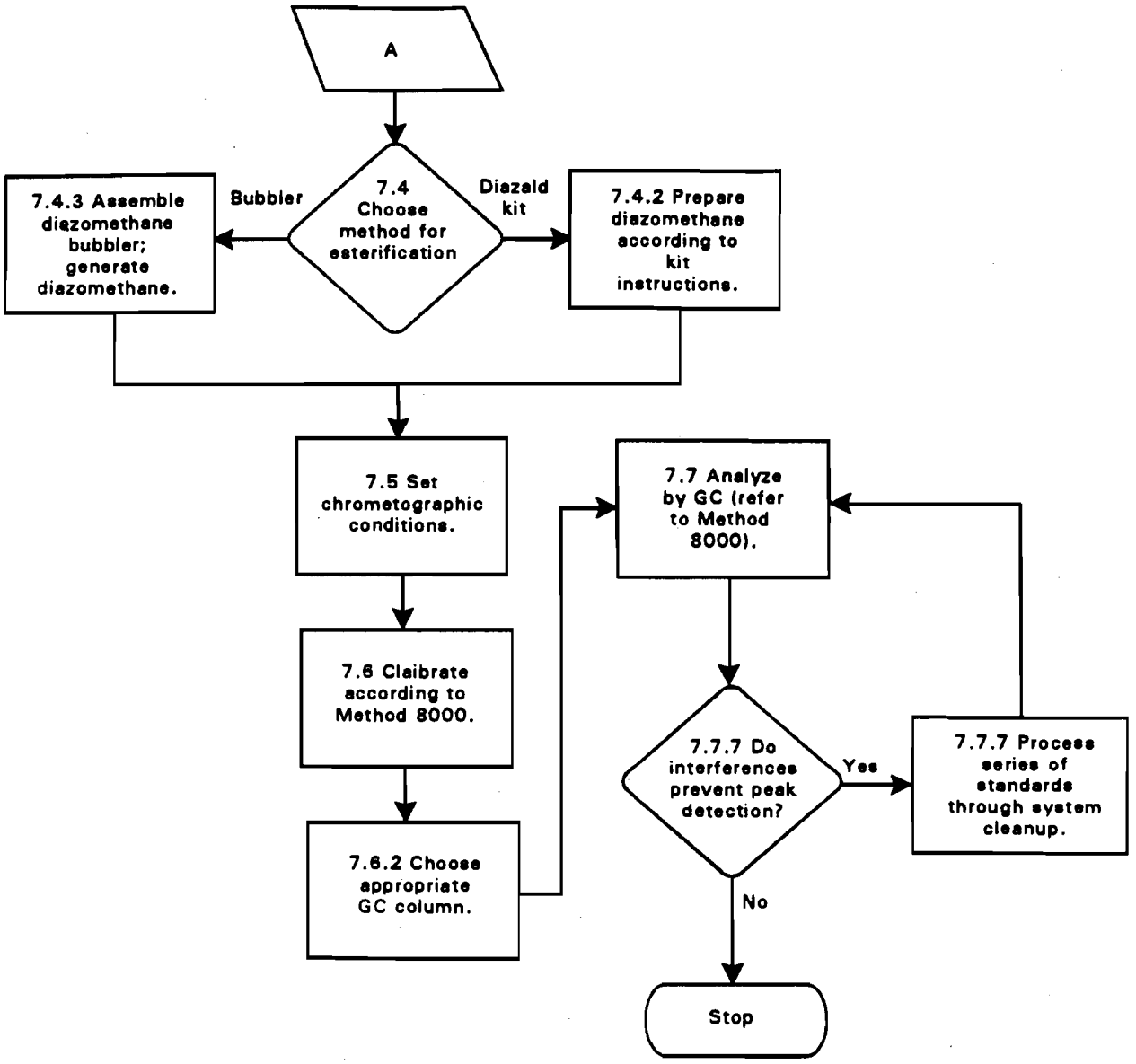


FIGURE 4.
GAS CHROMATOGRAM OF DALAPON, COLUMN 3




Start
Type of Sample?
Solid Sample
Liquid Sample
Waste Sample
7.2.1.1 Adjust sample pH with HCl.
7.3.1.1 Adjust sample pH with H2SO4.
7.1.1 Follow Method 3580 for extraction, using diethyl ether, acidified anhydrous sodium sulfate and acidified glass wool.
7.2.1.2 Extract sample with acetone and diethyl ether.
7.2.1.5 Re-extract and discard aqueous phase.
7.3.1.2 Extract with diethyl ether.
7.2.1.3 Extract twice more.
7.2.2 Proceed with hydrolysis.
7.1.1.2 Use 1.0 mL of sample for hydrolysis.
7.3.1.3 Extract twice more, and combine extracts.
7.2.1.4 Combine extracts.
7.2.3 Proceed with solvent cleanup.
7.3.2 Proceed with hydrolysis.
7.2.1.5 Check pH of extract, adjust if necessary. Separate layers.
7.3.3 Proceed with solvent cleanup.
A


A
7.4 Choose method for esterification
Bubbler
Diazald kit
7.4.3 Assemble diazomethane bubbler; generate diazomethane.
7.4.2 Prepare diazomethane according to kit instructions.
7.5 Set chrometographic conditions.
7.6 Claibrate according to Method 8000.
7.6.2 Choose appropriate GC column.
7.7 Analyze by GC (refer to Method 8000).
7.7.7 Do interferences prevent peak detection?
Yes
7.7.7 Process series of standards through system cleanup.
No
Stop

METHOD 8151

CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8151 is a capillary gas chromatographic (GC) method for determining certain chlorinated acid herbicides and related compounds in aqueous, soil and waste matrices. Specifically, Method 8151 may be used to determine the following compounds:

Compound Name	CAS No.[a]
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol	100-02-1
Pentachlorophenol	87-86-5

[a] Chemical Abstract Services Registry Number.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

1.2 When Method 8151 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Sec. 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 The estimated detection limits for each of the compounds in aqueous and soil matrices are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

1.4 The following compounds may also be determined using this method:

Compound Name	CAS No.[a]
Acifluorfen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
DCPA diacid[b]	2136-79-0
3,5-Dichlorobenzoic acid	51-36-5
5-Hydroxydicamba	7600-50-2
Picloram	1918-02-1

[a] Chemical Abstract Services Registry Number.

[b] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.6 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8151 provides extraction, derivatization, and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil, and waste samples. An option for the hydrolysis of esters is also described.

2.1.1 Water samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.1.2 Soil and waste samples are extracted and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.1.3 If herbicide esters are to be determined using this method, hydrolysis conditions for the esters in water and soil extracts are described.

2.2 The sensitivity of Method 8151 depends on the level of interferences in addition to instrumental limitations. Table 1 lists the GC/ECD and GC/MS detection limits that can be obtained in aqueous and soil matrices in the absence of interferences. Detection limits for a typical waste sample should be higher.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

3.7 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns, and all required accessories including detector, capillary analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Narrow Bore Columns

4.1.2.1.1 Primary Column 1 - 30 m x 0.25 mm, 5% phenyl/95% methyl silicone (DB-5, J&W Scientific, or equivalent), 0.25 μm film thickness.

4.1.2.1.2 Primary Column 1a (GC/MS) - 30 m x 0.32 mm, 5% phenyl/95% methyl silicone, (DB-5, J&W Scientific, or equivalent), 1 μm film thickness.

4.1.2.1.3 Column 2 - 30 m x 0.25 mm DB-608 (J&W Scientific or equivalent) with a 25 μm film thickness.

4.1.2.1.4 Confirmation Column - 30 m x 0.25 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 0.25 μm film thickness.

4.1.2.2 Wide-bore Columns

4.1.2.2.1 Primary Column - 30 m x 0.53 mm DB-608 (J&W Scientific or equivalent) with 0.83 μm film thickness.

4.1.2.2.2 Confirmation Column - 30 m x 0.53 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 1.0 μm film thickness.

4.1.3 Detector - Electron Capture Detector (ECD)

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Diazomethane Generator: Refer to Sec. 7.5 to determine which method of diazomethane generation should be used for a particular generation.

4.3.1 Diazald Kit - Recommended for the generation of diazomethane (Aldrich Chemical Co., Cat No. 210,025-0, or equivalent).

4.3.2 As an alternative, assemble from two 20 mm x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Sec. 7.5.

4.4 Other Glassware

4.4.1 Beaker - 400 mL, thick walled.

4.4.2 Funnel - 75 mm diameter.

4.4.3 Separatory funnel - 500 mL, with Teflon stopcock.

4.4.4 Centrifuge bottle - 500 mL (Pyrex 1260 or equivalent).

4.4.5 Centrifuge bottle - 24/40 500 mL

4.4.6 Continuous Extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915, or equivalent)

4.4.7 Pipet - Pasteur, glass, disposable (140 mm x 5 mm ID).

4.4.8 Vials - 10 mL, glass, with Teflon lined screw-caps.

4.4.9 Volumetric flasks, Class A - 10 mL to 1000 mL.

4.5 Filter paper - 15 cm diameter (Whatman No. 1 or equivalent).

4.6 Glass Wool - Pyrex, acid washed.

4.7 Boiling chips - Solvent extracted with methylene chloride,approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.9 Balance - Analytical, capable of accurately weighing to 0.0001 g.

4.10 Centrifuge.

4.11 Ultrasonic preparation - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.11.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples. Use a 3/4" horn for most samples.

4.12 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.13 pH paper.

4.14 Silica gel cleanup column (Bond Elut™ - Analytichem, Harbor City, CA or equivalent).

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free water, as defined in Chapter One.

5.3 Sodium hydroxide solution (0.1 N), NaOH. Dissolve 4 g NaOH in organic-free reagent water and dilute to 1.0 L.

5.4 Potassium hydroxide solution (37% aqueous solution (w/v)), KOH. Dissolve 37 g potassium hydroxide pellets in organic-free reagent water and dilute to 100 mL.

5.5 Phosphate buffer pH = 2.5 (0.1 M). Dissolve 12 g sodium phosphate (NaH_2PO_4) in organic-free reagent water and dilute to 1.0 L. Add phosphoric acid to adjust the pH to 2.5.

5.6 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald). High purity, available from Aldrich Chemical Co. or equivalent.

5.7 Silicic acid, H_2SiO_5. 100 mesh powder, store at 130°C.

5.8 Potassium carbonate, K_2CO_3.

5.9 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr), $C_6F_5CH_2Br$. Pesticide quality or equivalent.

5.10 Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store the remaining solid at 130°C.

5.11 Solvents

5.11.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.11.2 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.11.3 Methanol, CH_3OH. Pesticide quality or equivalent.

5.11.4 Toluene, $C_6H_5CH_3$. Pesticide quality or equivalent.

5.11.5 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.11.6 Isooctane, $(CH_3)_3CH_2CH(CH_3)_2$. Pesticide quality or equivalent.

5.11.7 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.11.8 Ethanol, absolute. C_2H_5OH

5.11.9 Carbitol (diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2O$ - optional for producing alcohol-free diazomethane.

5.12 Stock standard solutions (1000 mg/L) - Can be prepared from pure standard materials or can be purchased as certified solutions.

5.12.1 Prepare stock standard solutions by accurately weighing about 0.010 g of pure acid. Dissolve the material in pesticide quality acetone and dilute to volume in a 10 mL volumetric flask. Stocks prepared from pure methyl esters are dissolved in 10% acetone/isooctane (v/v). Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.12.2 Transfer the stock standard solutions to vials with Teflon lined screw-caps. Store at 4°C, protected from light. Stock standard solutions should be checked frequently for signs of degradation

or evaporation, especially immediately prior to preparing calibration standards from them.

5.12.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.13 Internal Standard Spiking Solution (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The compound 4,4'-dibromooctafluorobiphenyl (DBOB) has been shown to be an effective internal standard, but other compounds, such as 1,4-dichlorobenzene, may be used if there is a DBOB interference.

5.13.1 Prepare an internal standard spiking solution by accurately weighing approximately 0.0025 g of pure DBOB. Dissolve the DBOB in acetone and dilute to volume in a 10 mL volumetric flask. Transfer the internal standard spiking solution to a vial with a Teflon lined screw-cap, and store at room temperature. Addition of 10 µL of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 µg/L. The solution should be replaced if there is a change in internal standard response greater than 20 percent of the original response recorded.

5.14 Calibration standards - Calibration standards, at a minimum of five concentrations for each parameter of interest, should be prepared through dilution of the stock standards with diethyl ether or hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.14.1 Derivatize each calibration standard prepared from free acids in a 10 mL K-D concentrator tube, according to the procedures beginning at Sec. 7.5.

5.14.2 Add a known, constant amount of one or more internal standards to each derivatized calibration standard, and dilute to volume with the solvent indicated in the derivative option used.

5.15 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and determinative step, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates in gas chromatographic

analysis due to coelution problems. The surrogate standard recommended for use is 2,4-Dichlorophenylacetic acid (DCAA).

5.15.1 Prepare a surrogate standard spiking solution by accurately weighing approximately 0.001 g of pure DCAA. Dissolve the DCAA in acetone, and dilute to volume in a 10 mL volumetric flask. Transfer the surrogate standard spiking solution to a vial with a Teflon lined screw-cap, and store at room temperature. Addition of 50 μL of the surrogate standard spiking solution to 1 L of sample, prior to extraction, results in a final concentration in the extract of 0.5 mg/L.

5.16 pH Adjustment Solutions

5.16.1 Sodium hydroxide, NaOH, 6 N.

5.16.2 Sulfuric acid, H_2SO_4, 12 N.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1. 1 L samples should be collected.

6.2 Extracts must be stored under refrigeration (4°C).

7.0 PROCEDURE

7.1 Preparation of High Concentration Waste Samples

7.1.1 Extraction

7.1.1.1 Follow Method 3580, Waste Dilution, with the following exceptions:

- use diethyl ether as the dilution solvent,
- use acidified anhydrous sodium sulfate, and acidified glass wool,
- spike the sample with surrogate compound(s) according to Sec. 5.16.1.

7.1.1.2 If the sample is to be analyzed for both herbicide esters and acids, then the sample extract must be hydrolyzed. In this case, transfer 1.0 mL (a smaller volume or a dilution may be required if herbicide concentrations are large) to a 250 mL ground glass Erlenmeyer flask. Proceed to Sec. 7.2.1.8. If the analysis is for acid herbicides only, proceed to Sec. 7.4.5 for derivatization by diazomethane (if PFB derivatization is selected, reduce the volume of diethyl ether to 0.1 - 0.5 mL as per Sec. 7.4.2 and then dilute to 4 mL with acetone).

7.2 Preparation of Soil, Sediment, and Other Solid Samples

7.2.1 Extraction

7.2.1.1 To a 400 mL, thick-wall beaker add 30 g (dry weight as determined in Method 3540, Sec. 7.2.1) of the well-mixed solid sample. Adjust the pH to 2 with concentrated hydrochloric acid or acidify solids in each beaker with 85 mL of 0.1 M phosphate buffer (pH = 2.5) and thoroughly mix the contents with a glass stirring rod. Spike the sample with surrogate compound(s) according to Sec. 5.16.1.

7.2.1.2 The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to clay type soils (normally 1:1), or any other solid that is not a free flowing sandy mixture, until a free flowing mixture is obtained.

7.2.1.3 Add 100 mL of methylene chloride/acetone (1:1 v/v) to the beaker. Perform ultrasonic extraction for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Allow the solids to settle. Transfer the organic layer into a 500 mL centrifuge bottle.

7.2.1.4 Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic conditions.

7.2.1.5 Combine the three organic extracts from the sample in the centrifuge bottle and centrifuge 10 minutes to settle the fine particles. Filter the combined extract through filter paper (Whatman #1, or equivalent) containing 7-10 g of acidified sodium sulfate into a 500 mL 24/40 Erlenmeyer flask. Add 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.1.6 that emphasizes the need for a dry extract prior to esterification.

7.2.1.6 Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached. Add boiling chips and attach the macro Snyder column. Evaporate the extract on the water bath to a volume of approximately 5 mL. Remove the flasks from the water bath and allow them to cool.

7.2.1.7 If hydrolysis or additional cleanup is not required and the sample is dry, proceed to Sec. 7.4.4 - Nitrogen Blowdown.

7.2.1.8 Use this step only if herbicide esters in addition to herbicide acids are to be determined:

7.2.1.8.1 Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Add additional boiling chips to the flask. Reflux the mixture on a water bath at 60-65°C until the hydrolysis step is completed (usually 1 to 2 hours). Remove the flasks from the water bath and cool to room temperature. CAUTION - the presence of residual acetone will result in the formation of aldol condensation products which will cause GC interference.

7.2.1.8.2 Transfer the hydrolyzed aqueous solution to a 500 mL separatory funnel and extract the solution three times with 100 mL portions of methylene chloride. Discard the methylene chloride phase. At this point the basic (aqueous) solution contains the herbicide salts.

7.2.1.8.3 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1:3) and extract once with 40 mL of diethyl ether and twice with 20 mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect the dried extracts in a 500 mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.1.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.1.8.4 Proceed to Sec. 7.4, Extract Concentration. If additional cleanup is required, proceed to Sec. 7.2.1.9.

7.2.1.9 Use this step if additional cleanup of the non-hydrolyzed herbicides is required:

7.2.1.9.1 Partition the herbicides by extracting the methylene chloride from 7.2.1.7 (or diethyl ether from 7.2.1.8.4) with 3 x 15 mL portions of aqueous base prepared by carefully mixing 30 mL of reagent water into 15 mL of 37% aqueous potassium hydroxide. Discard the methylene chloride or ether phase. At this point the basic (aqueous) solution contains the herbicide salts.

7.2.1.9.2 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1:3) and extract once with 40 mL of diethyl ether and twice with 20 mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate.

Collect the dried extracts in a 500 mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.1.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.1.9.3 Proceed to section 7.4 for extract concentration.

7.2.1.10 An alternative wrist-shaker extraction procedure can be found in Sec. 7.2 of Method 8150.

7.3 Preparation of Aqueous Samples

7.3.1 Separatory Funnel

7.3.1.1 Using a graduated cylinder, measure out a 1-L sample and transfer it into a 2-L separatory funnel. Spike the sample with surrogate compound(s) according to Sec. 5.15.1.

7.3.1.2 Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

7.3.1.3 Use this step only if herbicide esters in addition to herbicide acids, are to be determined:

7.3.1.3.1 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature until the hydrolysis step is completed (usually 1 to 2 hours), shaking the separatory funnel and contents periodically.

7.3.1.3.2 Add 60 mL of methylene chloride to the sample bottle and rinse both the bottle and the graduated cylinder. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

7.3.1.3.3 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

7.3.1.4 Add 17 mL of cold (4°C) 12 N sulfuric acid to the sample (or hydrolyzed sample), seal, and shake to mix. Check the pH of the sample with pH paper: if the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

7.3.1.5 Add 120 mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum techniques to complete the phase separation depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2 L Erlenmeyer flask and collect the ether phase in a 500 mL Erlenmeyer flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent.

7.3.1.6 Return the aqueous phase to the separatory funnel, add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500 mL Erlenmeyer flask. Perform a third extraction with 60 mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7.3.1.7 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and funnel with 20 to 30 mL of diethyl ether to complete the quantitative transfer. Proceed to Sec. 7.4 for extract concentration.

7.4 Extract Concentration

7.4.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.4.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. The extract may be further concentrated by using either the micro Snyder column technique (Sec. 7.4.3) or nitrogen blowdown technique (Sec. 7.4.4).

7.4.3 Micro Snyder Column Technique

7.4.3.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of diethyl ether to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of diethyl ether and add to the concentrator tube. Proceed to Sec. 7.4.5.

7.4.4 Nitrogen Blowdown Technique

7.4.4.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

<u>CAUTION</u>: Do not use plasticized tubing between the carbon trap and the sample.

7.4.4.2 The internal wall of the tube must be rinsed down several times with diethyl ether during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal

operating conditions, the extract should not be allowed to become dry. Proceed to Sec. 7.4.5.

7.4.5 Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane. If PFB derivation is being performed, dilute to 4 mL with acetone.

7.5 Esterification - For diazomethane derivatization proceed with Sec. 7.5.1. For PFB derivatization proceed with Sec. 7.5.2.

7.5.1 Diazomethane Derivatization - Two methods may be used for the generation of diazomethane: the bubbler method (see Figure 1), Sec. 7.5.1.1, and the Diazald kit method, Sec. 7.5.1.2.

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10-15) require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S.EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.5.1.1 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.5.1.1.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g of Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists.

The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.5.1.1.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.5.1.1.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately. Analyze by gas chromatography.

7.5.1.1.4 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, it is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur.

7.5.1.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.5.1.2.1 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

7.5.1.2.2 Rinse the inside wall of the ampule with 700 µL of diethyl ether. Reduce the sample volume to approximately 2 mL to remove excess diazomethane by allowing the solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg of silicic acid can be added to destroy the excess diazomethane.

7.5.1.2.3 Dilute the sample to 10.0 mL with hexane. Analyze by gas chromatography. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur.

7.5.2 PFB Method

7.5.2.1 Add 30 µL of 10% K_2CO_3 and 200 µL of 3% PFBBr in acetone. Close the tube with a glass stopper and mix on a vortex mixer. Heat the tube at 60°C for 3 hours.

7.5.2.2 Evaporate the solution to 0.5 mL with a gentle stream of nitrogen. Add 2 mL of hexane and repeat evaporation just to dryness at ambient temperature.

7.5.2.3 Redissolve the residue in 2 mL of toluene:hexane (1:6) for column cleanup.

7.5.2.4 Top a silica column (Bond Elut™ or equivalent) with 0.5 cm of anhydrous sodium sulfate. Prewet the column with 5 mL hexane and let the solvent drain to the top of the adsorbent. Quantitatively transfer the reaction residue to the column with several rinsings of the toluene:hexane solution (total 2 - 3 mL).

7.5.2.5 Elute the column with sufficient toluene:hexane to collect 8 mL of eluent. Discard this fraction, which contains excess reagent.

7.5.2.6 Elute the column with toluene:hexane (9:1) to collect 8 mL of eluent containing PFB derivatives in a 10 mL volumetric flask. Dilute to 10 mL with hexane. Analyze by GC/ECD.

7.6 Gas chromatographic conditions (recommended):

7.6.1 Narrow Bore

7.6.1.1 Primary Column 1:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.1.2 Primary Column 1a:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.1.3 Column 2:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.1.4 Confirmation Column:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.2 Wide-bore

7.6.2.1 Primary Column:

Temperature program:	0.5 minute at 150°C, 150°C to 270°C at 5°C/min
Helium carrier flow:	7 mL/min
Injection volume:	1 µL

7.6.2.2 Confirmatory Column:

Temperature program:	0.5 minute at 150°C, 150°C to 270°C at 5°C/min
Helium carrier flow:	7 mL/min
Injection volume:	1 µL

7.7 Calibration

7.7.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 for guidance on selecting the lowest point on the calibration curve.

7.8 Gas chromatographic analysis

7.8.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.8.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.8.3 An example of a chromatogram for a methylated chlorophenoxy herbicide is shown in Figure 2. Tables 2 and 3 present retention times for the target analytes after esterification, using the diazomethane derivatization procedure and the PFB derivatization procedure, respectively.

7.8.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.8.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak

in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.8.6 If calibration standards have been analyzed in the same manner as the samples (e.g. have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is performed using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.8.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate, in acetone, that is 1000 times more concentrated than the selected concentrations. Use this quality control check sample concentrate to prepare quality control check samples.

8.2.2 Tables 4 and 5 present bias and precision data for water and clay matrices, using the diazomethane derivatization procedure. Table 6 presents relative recovery data generated using the PFB derivatization procedure and water samples. Compare the results obtained with the results given in these Tables to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all standards, samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required:

8.3.1.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In single laboratory studies using organic-free reagent water and clay/still bottom samples, the mean recoveries presented in Tables 4 and 5 were obtained for diazomethane derivatization. The standard deviations of the percent recoveries of these measurements are also in Tables 4 and 5.

9.2 Table 6 presents relative recoveries of the target analytes obtained using the PFB derivatization procedure with spiked water samples.

10.0 REFERENCES

1. Fed. Reg. 1971, 38, No. 75, Pt. II.

2. Goerlitz, D. G.; Lamar, W.L., "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography,". U.S. Geol. Survey Water Supply Paper 1967, 1817-C.

3. Burke, J. A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects, J. Assoc. Off Anal. Chem. 1965, 48, 1037.

4. "Extraction and Cleanup Procedures for the Determination of Phenoxy Acid Herbicides in Sediment"; U.S. Environmental Protection Agency. EPA Toxicant and Analysis Center: Bay St. Louis, MS, 1972.

5. Shore, F.L.; Amick, E.N.; Pan, S. T. "Single Laboratory Validation of EPA Method 8151 for the Analysis of Chlorinated Herbicides in Hazardous Waste"; U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Office of Research and Development, Las Vegas, NV, 1985; EPA-60014-85-060.

6. Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector", Revision 4.0, USEPA, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

7. Method 1618, "Organo-halide and Organo-phosphorus Pesticides and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors", Revision A, July 1989, USEPA, Office of Water Regulations and Standards, Washington, DC.

8. Gurka, D.F, Shore, F.L., Pan, S-T, "Single Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Hazardous Waste", JAOAC, 69, 970, 1986.

Figure 1
DIAZOMETHANE GENERATOR

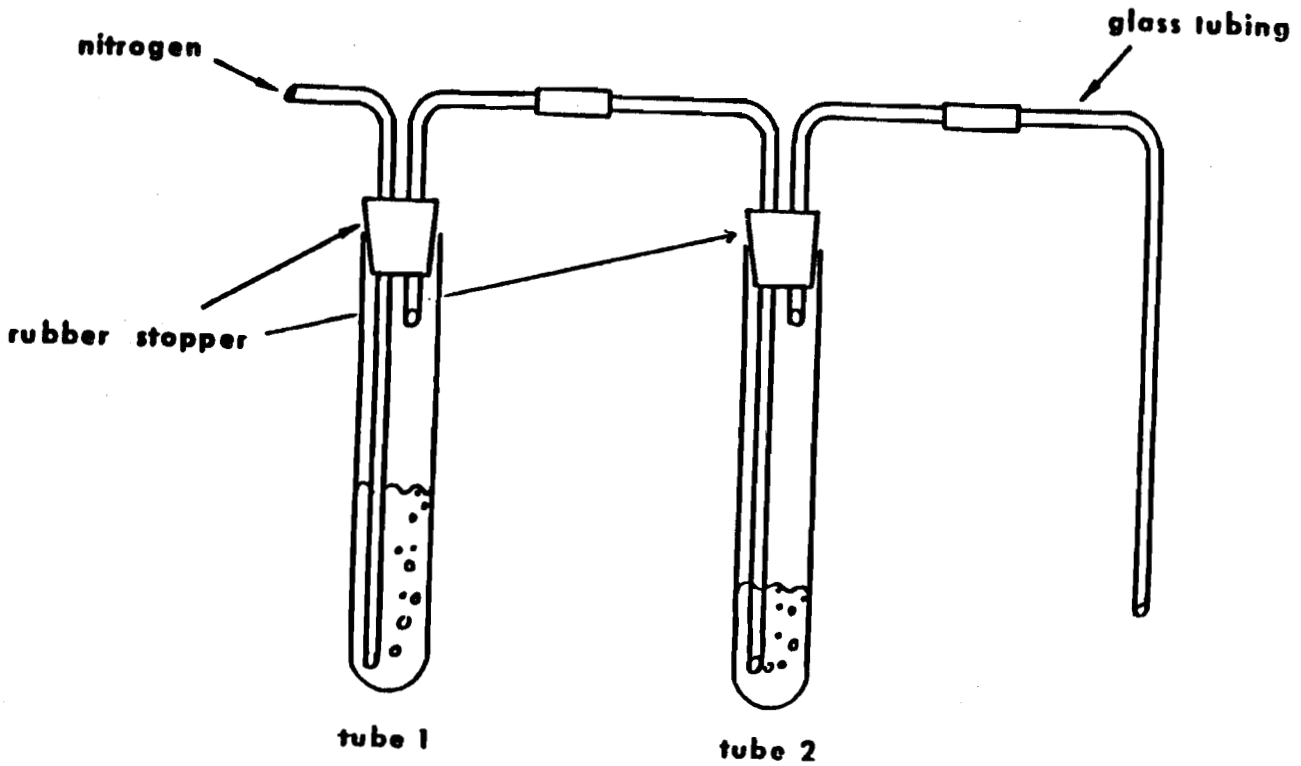


Figure 2
CHROMATOGRAM OF METHYL ESTERS OF CHLOROPHENOXYACIDS

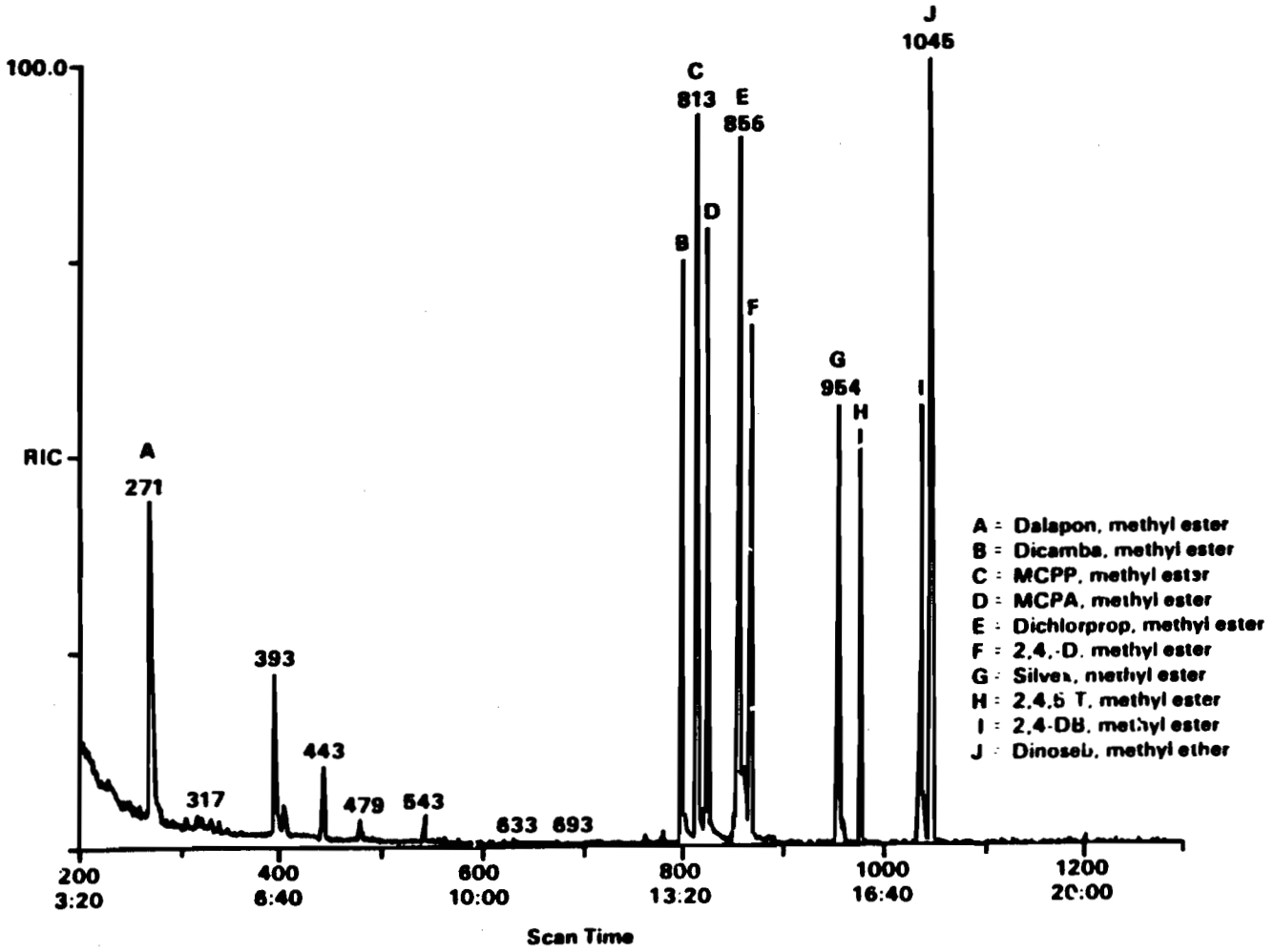


TABLE 1
ESTIMATED METHOD DETECTION LIMITS FOR METHOD 8151,
DIAZOMETHANE DERIVATIZATION

Analyte	Aqueous Samples GC/ECD Estimated Detection Limit[a] (µg/L)	Soil Samples GC/ECD Estimated Detection Limit[b] (µg/kg)	Soil Samples GC/MS Estimated Identification Limit[c] (ng)
Acifluorfen	0.096		
Bentazon	0.2		
Chloramben	0.093	4.0	1.7
2,4-D	0.2	0.11	1.25
Dalapon	1.3	0.12	0.5
2,4-DB	0.8		
DCPA diacid[e]	0.02		
Dicamba	0.081		
3,5-Dichlorobenzoic acid	0.061	0.38	0.65
Dichloroprop	0.26		
Dinoseb	0.19		
5-Hydroxydicamba	0.04		
MCPP	0.09[d]	66	0.43
MCPA	0.056[d]	43	0.3
4-Nitrophenol	0.13	0.34	0.44
Pentachlorophenol	0.076	0.16	1.3
Picloram	0.14		
2,4,5-T	0.08		
2,4,5-TP	0.075	0.28	4.5

a EDL = estimated detection limit; defined as either the MDL (40 CFR Part 136, Appendix B, Revision 1.11), or a concentration of analyte in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

b Detection limits determined from standard solutions corrected back to 50 g samples, extracted and concentrated to 10 mL, with 5 µL injected. Chromatography using narrow bore capillary column, 0.25 µm film, 5% phenyl/95% methyl silicone.

c The minimum amount of analyte to give a Finnigan INCOS FIT value of 800 as the methyl derivative vs. the spectrum obtained from 50 ng of the respective free acid herbicide.

d 40 CFR Part 136, Appendix B (49 FR 43234). Chromatography using wide-bore capillary column.

e DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 2
RETENTION TIMES (MINUTES) OF METHYL DERIVATIVES OF CHLORINATED HERBICIDES

Megabore Columns	Narrow Bore Columns		Wide-bore Columns	
Analyte	Primary[a] Column	Confirmation[a] Column	Primary[b] Column	Confirmation[b] Column
Dalapon	3.4	4.7		
3,5-Dichlorobenzoic acid	18.6	17.7		
4-Nitrophenol	18.6	20.5		
DCAA (surrogate)	22.0	14.9		
Dicamba	22.1	22.6	4.39	4.39
Dichloroprop	25.0	25.6	5.15	5.46
2,4-D	25.5	27.0	5.85	6.05
DBOB (internal std.)	27.5	27.6		
Pentachlorophenol	28.3	27.0		
Chloramben	29.7	32.8		
2,4,5-TP	29.7	29.5	6.97	7.37
5-Hydroxydicamba	30.0	30.7		
2,4,5-T	30.5	30.9	7.92	8.20
2,4-DB	32.2	32.2	8.74	9.02
Dinoseb	32.4	34.1		
Bentazon	33.3	34.6		
Picloram	34.4	37.5		
DCPA diacid[c]	35.8	37.8		
Acifluorfen	41.5	42.8		
MCPP			4.24	4.55
MCPA			4.74	4.94

a Primary Column: 5% phenyl/95% methyl silicone
Confirmation Column: 14% cyanopropyl phenyl silicone
Temperature program: 60°C to 300°C, at 4°C/min
Helium carrier flow: 30 cm/sec
Injection volume: 2 µL, splitless, 45 sec delay
Injector temperature: 250°C
Detector temperature: 320°C

b Primary Column: DB-608
Confirmatory Column: 14% cyanopropyl phenyl silicone
Temperature program: 0.5 minute at 150°C, 150°C to 270°C, at 5°C/min
Helium carrier flow: 7 mL/min
Injection volume: 1 µL

c DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 3
RETENTION TIMES (MINUTES) OF PFB DERIVATIVES OF CHLORINATED HERBICIDES

Herbicide	Gas Chromatographic Column		
	Thin-film DB-5[a]	SP-2250[b]	Thick-film DB-5[c]
Dalapon	10.41	12.94	13.54
MCPP	18.22	22.30	22.98
Dicamba	18.73	23.57	23.94
MCPA	18.88	23.95	24.18
Dichloroprop	19.10	24.10	24.70
2,4-D	19.84	26.33	26.20
Silvex	21.00	27.90	29.02
2,4,5-T	22.03	31.45	31.36
Dinoseb	22.11	28.93	31.57
2,4-DB	23.85	35.61	35.97

a DB-5 capillary column, 0.25 μm film thickness, 0.25 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 17 minutes.

b SP-2550 capillary column, 0.25 μm film thickness, 0.25 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

c DB-5 capillary column, 1.0 μm film thickness, 0.32 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

TABLE 4
ACCURACY AND PRECISION FOR METHOD 8151
DIAZOMETHANE DERIVATIZATION, ORGANIC-FREE REAGENT WATER MATRIX

Analyte	Spike Concentration (µg/L)	Mean[a] Percent Recovery	Standard Deviation of Percent Recovery
Acifluorfen	0.2	121	15.7
Bentazon	1	120	16.8
Chloramben	0.4	111	14.4
2,4-D	1	131	27.5
Dalapon	10	100	20.0
2,4-DB	4	87	13.1
DCPA diacid[b]	0.2	74	9.7
Dicamba	0.4	135	32.4
3,5-Dichlorobenzoic acid	0.6	102	16.3
Dichloroprop	2	107	20.3
Dinoseb	0.4	42	14.3
5-Hydroxydicamba	0.2	103	16.5
4-Nitrophenol	1	131	23.6
Pentachlorophenol	0.04	130	31.2
Picloram	0.6	91	15.5
2,4,5-TP	0.4	117	16.4
2,4,5-T	0.2	134	30.8

a Mean percent recovery calculated from 7-8 determinations of spiked organic-free reagent water.

b DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 5
ACCURACY AND PRECISION FOR METHOD 8151
DIAZOMETHANE DERIVATIZATION, CLAY MATRIX

Analyte	Mean Percent Recovery[a]	Linear Concentration Range[b] (ng/g)	Percent Relative Standard Deviation[c] (n=20)
Dicamba	95.7	0.52 - 104	7.5
MCPP	98.3	620 - 61,800	3.4
MCPA	96.9	620 - 61,200	5.3
Dichloroprop	97.3	1.5 - 3,000	5.0
2,4-D	84.3	1.2 - 2,440	5.3
2,4,5-TP	94.5	0.42 - 828	5.7
2,4,5-T	83.1	0.42 - 828	7.3
2,4-DB	90.7	4.0 - 8,060	7.6
Dinoseb	93.7	0.82 - 1,620	8.7

a Mean percent recovery calculated from 10 determinations of spiked clay and clay/still bottom samples over the linear concentration range.

b Linear concentration range was determined using standard solutions and corrected to 50 g solid samples.

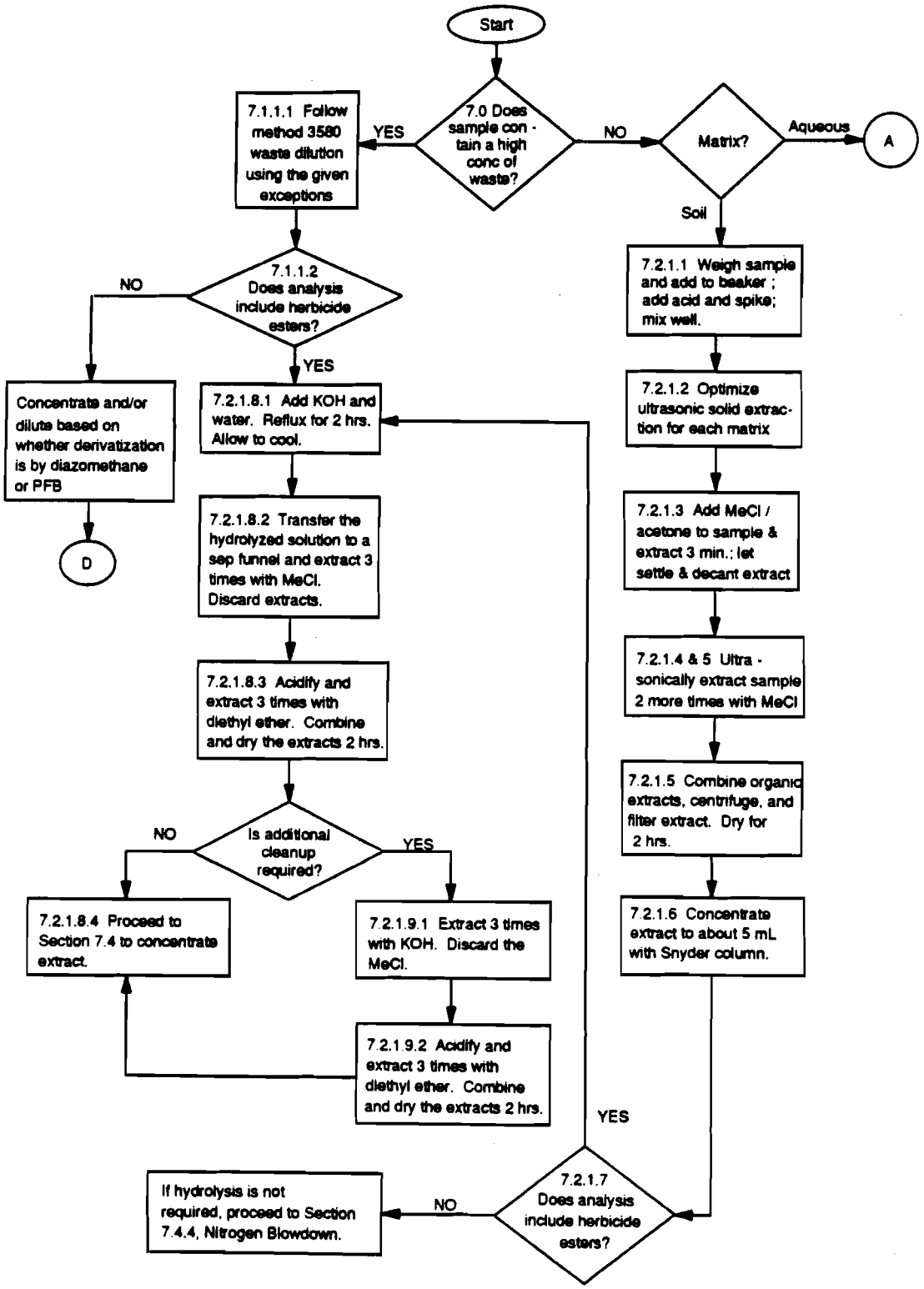
c Percent relative standard deviation was calculated using standard solutions, 10 samples high in the linear concentration range, and 10 samples low in the range.

TABLE 6
RELATIVE RECOVERIES OF PFB DERIVATIVES OF HERBICIDES[a]

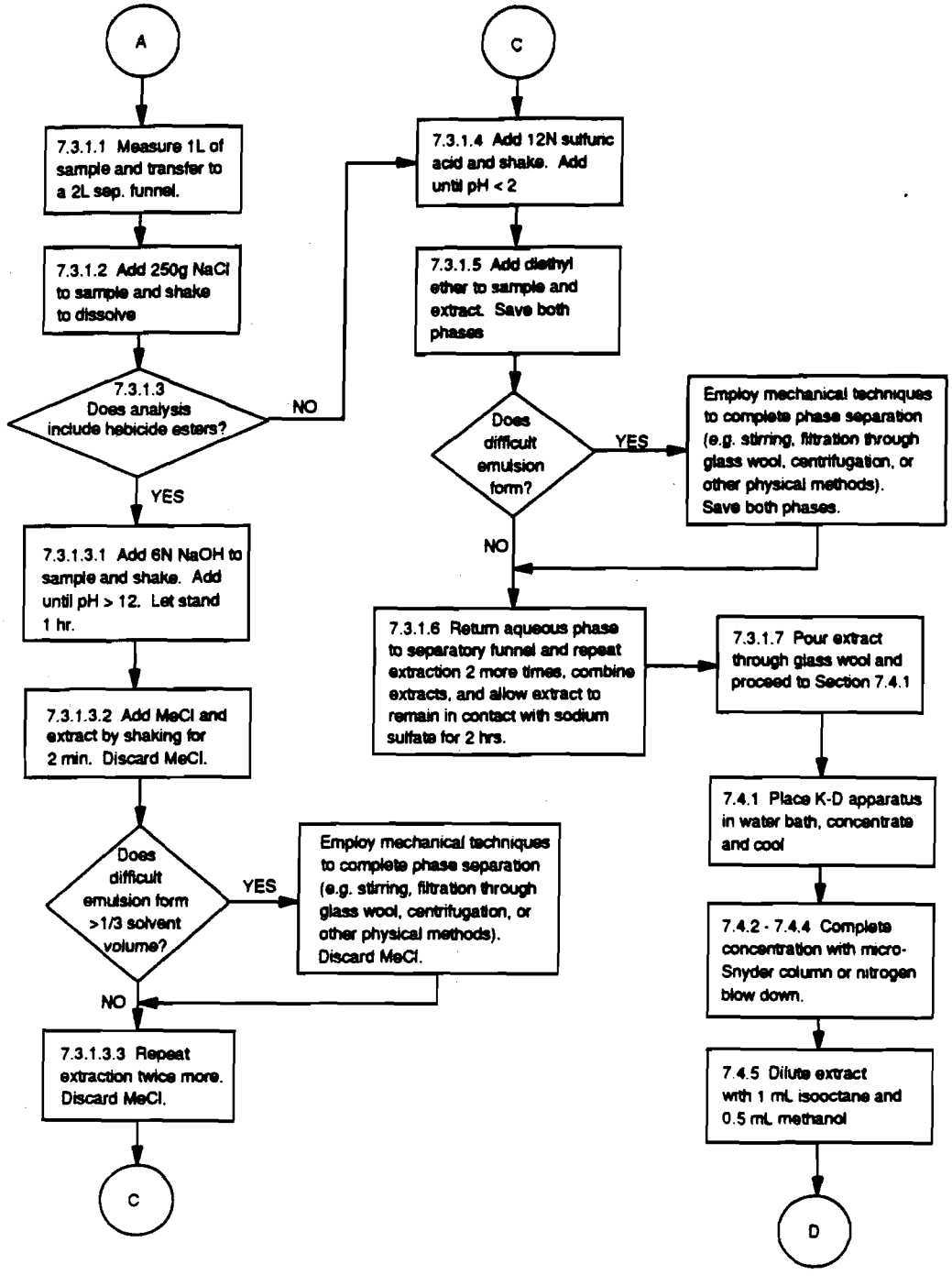
Analyte	Standard Concentration mg/L	Relative recoveries, %								
		1	2	3	4	5	6	7	8	Mean
MCPP	5.1	95.6	88.8	97.1	100	95.5	97.2	98.1	98.2	96.3
Dicamba	3.9	91.4	99.2	100	92.7	84.0	93.0	91.1	90.1	92.7
MCPA	10.1	89.6	79.7	87.0	100	89.5	84.9	92.3	98.6	90.2
Dichloroprop	6.0	88.4	80.3	89.5	100	85.2	87.9	84.5	90.5	88.3
2,4-D	9.8	55.6	90.3	100	65.9	58.3	61.6	60.8	67.6	70.0
Silvex	10.4	95.3	85.8	91.5	100	91.3	95.0	91.1	96.0	93.3
2,4,5-T	12.8	78.6	65.6	69.2	100	81.6	90.1	84.3	98.5	83.5
2,4-DB	20.1	99.8	96.3	100	88.4	97.1	92.4	91.6	91.6	95.0
Mean		86.8	85.7	91.8	93.4	85.3	89.0	87.1	91.4	

a Percent recovery determinations made using eight spiked water samples.

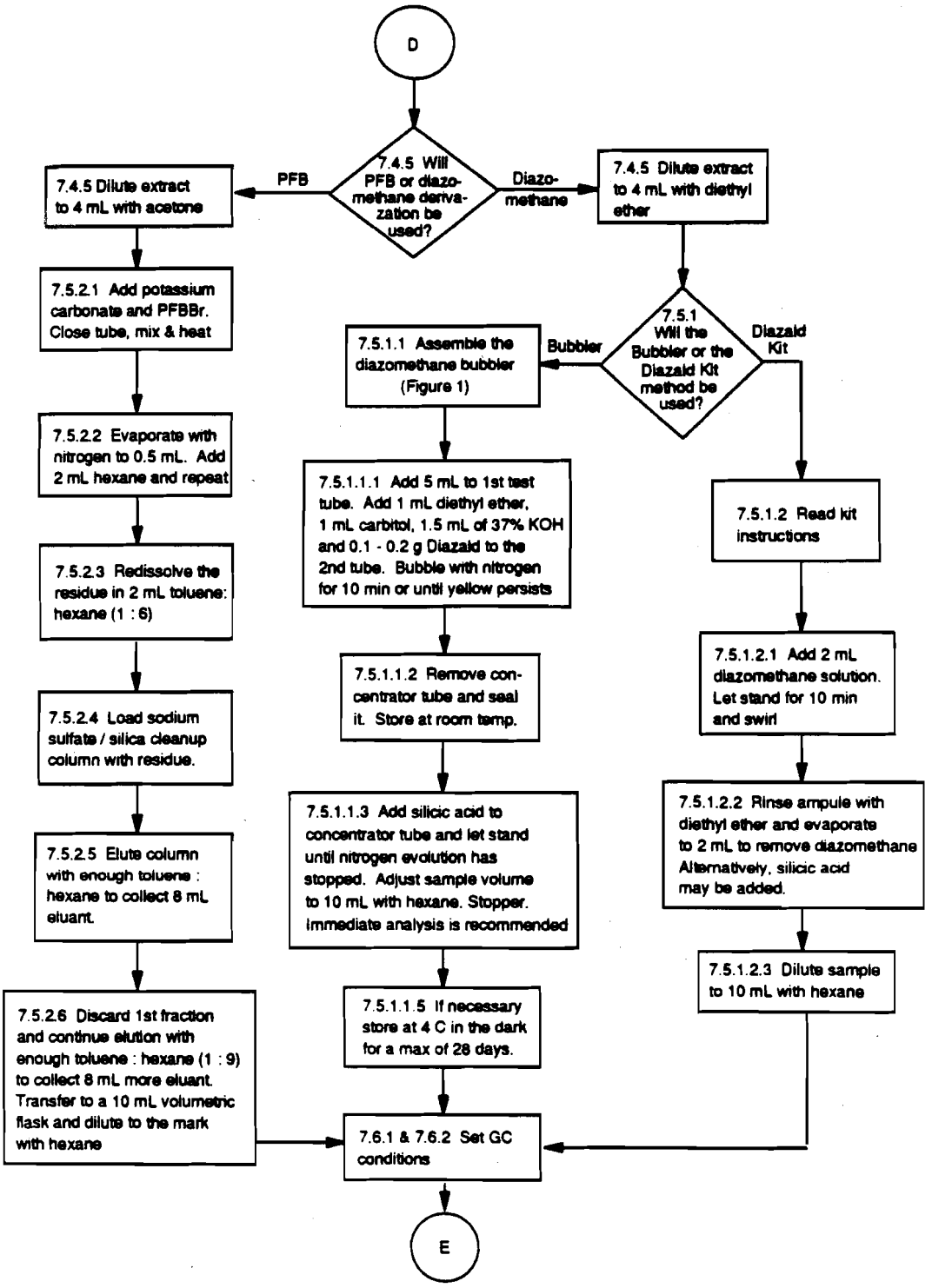
Extraction/Hydrolysis of Waste and Soil Samples



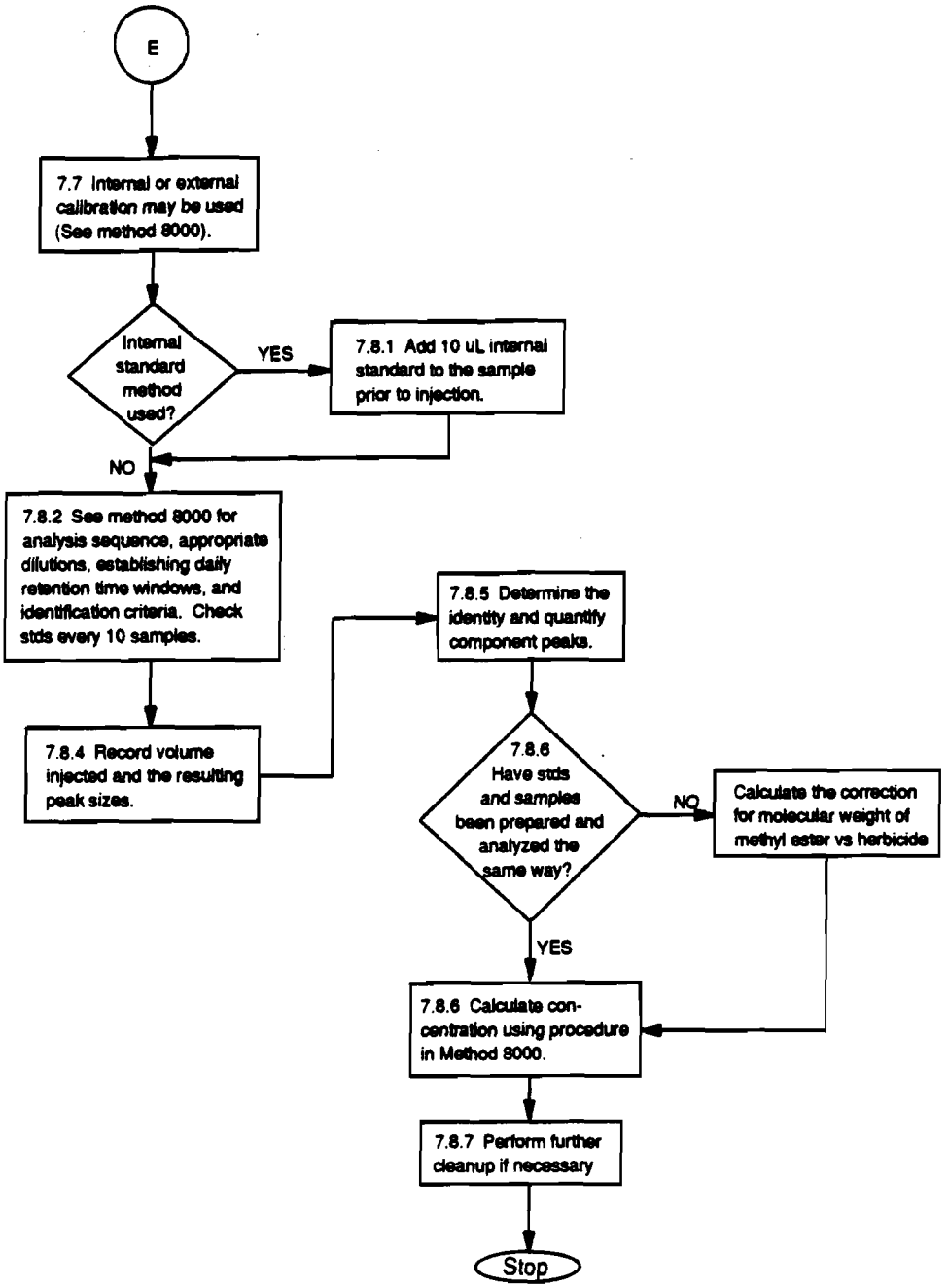
Extraction/Hydrolysis of Aqueous Samples and Extract Concentration



Extract Derivatization



Analysis by Gas Chromatography



4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.2 GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC METHODS

The following methods are included in this section:

Method 8240B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8250A: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8260A: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

Method 8270B: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

Method 8280: The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans

- **Appendix A:** Signal-to-Noise Determination Methods
- **Appendix B:** Recommended Safety and Handling Procedures for PCDDs/PCDFs

Method 8290: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)

METHOD 8240B

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Technique	
Analyte	CAS No.[b]	Purge-and-Trap	Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein (Propenal)	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	pp	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	pp	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
2-Butanone (MEK)	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chloral hydrate	302-17-0	pp	a
Chlorobenzene	108-90-7	a	a
Chlorobenzene-d_5 (I.S.)	3114-55-4	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
bis-(2-Chloroethyl) sulfide	505-60-2	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropionitrile	542-76-7	ND	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a

Analyte	CAS No.[b]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Dibromomethane	74-95-3	a	a
1,4-Dichloro-2-butene	764-41-0	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,2-Dichloroethane-d_4(surr.)	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2,3,4-Diepoxybutane	1464-53-5	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	ND	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone	108-10-1	pp	a
Pentachloroethane	76-01-7	i	pc
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
ß-Propiolactone	57-57-8	pp	a
Propionitrile	107-12-0	pp	a
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
Toluene-d_8 (surr.)	2037-26-5	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a

Analyte	CAS No.[b]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
1,2,3-Trichloropropane	96-18-4	a	a
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
Xylene (Total)	1330-20-7	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
pp Poor purging efficiency resulting in high EQLs.
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.
surr Surrogate
I.S. Internal Standard
ND Not determined

1.2 Method 8240 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The estimated quantitation limit (EQL) of Method 8240 for an individual compound is approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 2). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The

components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with organic-free reagent water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank, prepared from organic-free reagent water and carried through the sampling and handling protocol, can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to check for cross contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-concentration sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running calibration and reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1,000 µL. These syringes should be equipped with a 20 gauge (0.006 in. ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5 mL, gas-tight with shutoff valve.

4.4 Balances - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.5 Glass scintillation vials - 20 mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

4.6 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.7 Vials - 2 mL, for GC autosampler.

4.8 Spatula - Stainless steel.

4.9 Disposable pipets - Pasteur.

4.10 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C

are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning. However, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 Trap Packing Materials

4.11.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, lot #M-2649, by crushing through 26 mesh screen (or equivalent).

4.12 Gas chromatograph/mass spectrometer system

4.12.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 Column - 6 ft x 0.1 in. ID glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer - Capable of scanning from 35-260 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see

Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 Data system - A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Add the assayed reference material, as described below.

5.3.2.1 Liquids - Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture

Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon sealed screw cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.3.5 Prepare fresh stock standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 20% drift.

5.3.6 Optionally, calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.4 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Sec. 5.3, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 μg/10 mL in methanol. Each water sample undergoing GC/MS analysis must be spiked with 10 μL of the surrogate spiking solution prior to analysis.

5.6 Internal standards - The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.3 and 5.4. It is recommended that the secondary dilution standard should be

prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 μg/L.

5.7 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/μL of BFB in methanol should be prepared.

5.8 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Secs. 5.3 and 5.4). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. It is EPA's intent that all target analytes for a particular analysis be included in the calibration standard(s). However, these target analytes may not include the entire List of Analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s). Calibration standards must be prepared daily.

5.9 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 μg/10.0 mL.

5.10 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at -10°C to -20°C in screw cap amber bottles with Teflon liners.

5.11 Methanol, CH_3OH. Pesticide quality or equivalent. Store apart from other solvents.

5.12 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.12.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

<u>CAUTION</u>: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask

equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two stage mechanical pump. The vacuum system is equipped with an all glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 100 mg/L of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw cap bottle in an area that is not contaminated by solvent vapors.

5.12.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.13 Polyethylene glycol, $H(OCH_2CH_2)_nOH$. Free of interferences at the detection limit of the analytes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

Samples may be introduced into the GC by either direct injection or purge-and-trap procedures. Whichever procedure is used, the instrument calibration and sample introduction must be performed by the same procedure.

Regardless of which sample introduction procedure is employed, establish GC/MS operating conditions using the following recommendations as guidance.

Recommended GC/MS operating conditions:

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak, but not to exceed 1 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 minutes.
Column temperature program:	8°C/minute.
Final column temperature:	220°C.
Final column holding time:	15 minutes.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. One such application is for verification of the

alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection using the procedures described in Sec. 7.2,, but bypassing the purge-and-trap device.

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Establish the GC/MS operating conditions, using the recommendations in Sec. 7.0 as guidance.

7.2.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection or purging of 4-bromofluorobenzene (2 µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Sec. 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device (use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5 mL glass syringe fitted with a 15 cm, 20 gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14 gauge needle that forms the sample inlet will permit insertion of the 20 gauge needle. Next, using a 10 µL or 25 µL microsyringe equipped with a long needle (Sec. 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Sec. 5.6). Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10 µL of the internal standard solution (Sec. 5.4). Close the 2 way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Sec. 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that

has a retention time closest to the compound being measured (Sec. 7.5.2). The RF is calculated as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

7.2.8 The average RF must be calculated for each compound using the 5 RF values calculated for each compound from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (>0.10 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 relative to m/z 95 ratio may improve bromoform response.

7.2.8.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.9 Using the RFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RSD = relative standard deviation.
$\overline{RF}$ = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N - 1}}$$

where:

RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%. Late-eluting compounds usually have much better agreement. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.2.9.1 If a %RSD greater than 30 percent is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is required before reattempting calibration.

7.2.10 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.5.2.2).

7.2.10.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Sec. 7.5.2.4). The use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.2.11 These curves are verified each shift by purging a performance standard. Recalibration is required only if calibration and on-going performance criteria cannot be met.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12 hour shift.

7.3.2 The initial calibration curve (Sec. 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS and checking the SPCC (Sec. 7.3.3) and CCC (Sec. 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum relative response factor for volatile SPCCs is 0.300 (>0.10 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Sec. 7.2.9 are used to check the validity of the initial calibration.

Calculate the percent drift using the following equation:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift), for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 20% drift criterion.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last calibration check (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (- 50% to + 100%) from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When

corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (HECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Sec. 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Sec. 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Sec. 7.2.8).

7.4.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Sec. 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5 mL syringe with the diluted sample as in Sec. 7.4.1.6.

7.4.1.8 Add 10.0 µL of surrogate spiking solution (Sec. 5.5) and 10 µL of internal standard spiking solution (Sec. 5.6) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 µg/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 µL of the matrix spike solution (Sec. 5.9) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Secs. 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water miscible liquids

7.4.2.1 Water miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100 mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5 mL gas tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20 µL, but not more than 100 µL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may be used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require

extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-concentration method (> 1 mg/kg).

7.4.3.1 Low-concentration method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5 g sample if the expected concentration is < 0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg.

7.4.3.1.2 The GC/MS system should be set up as in Secs. 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution (Sec. 5.5) and internal standard solution (Sec. 5.6) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 µL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 µg/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Sec. 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent dry weight of the soil/sediment sample. This includes waste samples that are amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.4.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.4.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Secs. 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minute.

7.4.3.1.8 Proceed with the analysis as outlined in Secs. 7.4.1.11-7.4.1.16. Use 5 mL of the same organic-free reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.4.3.1.9 For low-concentration sediment/soils add 10 µL of the matrix spike solution (Sec. 5.9) to the 5 mL of organic-free reagent water (Sec. 7.4.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/kg of each matrix spike standard.

7.4.3.2 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Use a top loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Sec. 7.4.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

NOTE: Secs. 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 µL aliquot of each of these extracts in Sec. 7.4.3.2.6 will give a concentration equivalent to 6,200 µg/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Secs. 7.4.1.2-7.4.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Sec. 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 µL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the organic-free reagent water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Sec. 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 µL of solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Sec. 5.5), and 1.0 mL of matrix spike solution (Sec. 5.9) as in Sec. 7.4.3.2.2. This results in a 6,200 µg/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 µL aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Sec. 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.5.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.5.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.5.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.5.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 5).

7.5.2.2 When linearity exists, as per Sec. 7.2.10, calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(\overline{RF})(V_o)}$$

where:

A_x	=	Area of characteristic ion for compound being measured.
I_s	=	Amount of internal standard injected (ng).
A_{is}	=	Area of characteristic ion for the internal standard.
$\overline{RF}$	=	Mean relative response factor for compound being measured (Sec. 7.2.8).
V_o	=	Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, A_{is}, $\overline{RF}$, = Same as for water.

V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).

V_i = Volume of extract added (μL) for purging.

W_s = Weight of sample extracted or purged (g).

D = % dry weight of sample/100, or 1 for a wet-weight basis.

7.5.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.4 Alternatively, the regression line fitted to the initial calibration (Sec. 7.2.10.1) may be used for determination of analyte concentration.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Sec. 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Sec. 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Step 7.3.3 and the CCC criteria in Sec. 7.3.4, each 12 hours.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC reference sample to contain 20 µg/L of each analyte by adding 200 µL of QC reference sample concentrate to 100 mL of water.

8.5.3 Four 5-mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Sec. 7.4.1.

8.5.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte using the four results.

8.5.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{x}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

<u>NOTE</u>: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the

acceptance criteria when all analytes of a given method are determined.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Sec. 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Sec. 8.5.2.

8.5.6.2 Beginning with Sec. 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Sec. 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a method blank and a spiked replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a specific limit, the spike should be at 20 µg/L or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger. For other matrices, recommended spiking concentration is 10 times the EQL.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Sec. 8.5.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations,

assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Sec. 8.7.

8.7 If any analyte in a water sample fails the acceptance criteria for recovery in Sec. 8.6, a QC reference sample containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference sample will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Sec. 8.6, the probability that the analysis of a QC reference sample will be required is high. In this case, the QC reference sample should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 10 µL of the QC reference sample concentrate (Sec. 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC reference sample needs only to contain the analytes that failed criteria in the test in Sec. 8.6.

8.7.2 Analyze the QC reference sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Sec. 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Sec. 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval

from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g., after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Sec. 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must

be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 This method was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

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TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Ethylene oxide	1.30	44	44, 43, 42
Chloromethane	2.30	50	52, 49
Dichlorodifluoromethane	2.47	85	85, 87, 101, 103
Bromomethane	3.10	94	96, 79
Vinyl chloride	3.80	62	64, 61
Acetonitrile	3.97	41	41, 40, 39
Chloroethane	4.60	64	66, 49
Methyl iodide	5.37	142	142, 127, 141
Methylene chloride	6.40	84	49, 51, 86
Carbon disulfide	7.47	76	76, 78, 44
Trichlorofluoromethane	8.30	101	103, 66
Propionitrile	8.53	54	54, 52, 55, 40
Allyl chloride	8.83	76	76, 41, 39, 78
1,1-Dichloroethene	9.00	96	61, 98
Bromochloromethane (I.S.)	9.30	128	49, 130, 51
Allyl alcohol	9.77	57	57, 58, 39
trans-1,2-Dichloroethene	10.00	96	61, 98
1,2-Dichloroethane	10.10	62	64, 98
Propargyl alcohol	10.77	55	55, 39, 38, 53
Chloroform	11.40	83	85, 47
1,2-Dichloroethane-d_4(surr)	12.10	65	102
2-Butanone	12.20	72	43, 72
Methacrylonitrile	12.37	41	41, 67, 39, 52, 66
Dibromomethane	12.53	93	93, 174, 95, 172, 176
2-Chloroethanol	12.93	49	49, 44, 43, 51, 80
b-Propiolactone	13.00	42	42, 43, 44
Epichlorohydrin	13.10	57	57, 49, 62, 51
1,1,1-Trichloroethane	13.40	97	99, 117
Carbon tetrachloride	13.70	117	119, 121
1,4-Dioxane	13.70	88	88, 58, 43, 57
Isobutyl alcohol	13.80	43	43, 41, 42, 74
Bromodichloromethane	14.30	83	85, 129
Chloroprene	14.77	53	53, 88, 90, 51
1,2:3,4-Diepoxybutane	14.87	55	55, 57, 56
1,2-Dichloropropane	15.70	63	62, 41
Chloral hydrate (b)	15.77	82	44, 84, 86, 111
cis-1,3-Dichloropropene	15.90	75	77, 39
Bromoacetone	16.33	136	43, 136, 138, 93, 95
Trichloroethene	16.50	130	95, 97, 132
Benzene	17.00	78	52, 71
trans-1,3-Dichloropropene	17.20	75	77, 39
1,1,2-Trichloroethane	17.20	97	83, 85, 99
3-Chloropropionitrile	17.37	54	54, 49, 89, 91
1,2-Dibromoethane	18.40	107	107, 109, 93, 188
Pyridine	18.57	79	79, 52, 51, 50

TABLE 1.
(Continued)

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
2-Chloroethyl vinyl ether	18.60	63	65,106
2-Hydroxypropionitrile	18.97	44	44,43,42,53
1,4-Difluorobenzene (I.S.)	19.60	114	63,88
Malononitrile	19.60	66	66,39,65,38
Methyl methacrylate	19.77	69	69,41,100,39
Bromoform	19.80	173	171,175,252
1,1,1,2-Tetrachloroethane	20.33	131	131,133,117,119,95
1,3-Dichloro-2-propanol	21.83	79	79,43,81,49
1,1,2,2-Tetrachloroethane	22.10	83	85,131,133
Tetrachloroethene	22.20	164	129,131,166
1,2,3-Trichloropropane	22.20	75	75,77,110,112,97
1,4-Dichloro-2-butene	22.73	75	75,53,77,124,89
n-Propylamine	23.00	59	59,41,39
2-Picoline	23.20	93	93,66,92,78
Toluene	23.50	92	91,65
Ethyl methacrylate	23.53	69	69,41,99,86,114
Chlorobenzene	24.60	112	114,77
Pentachloroethane[a]	24.83	167	167,130,132,165,169
Ethylbenzene	26.40	106	91
1,2-Dibromo-3-chloropropane	27.23	157	157,75,155,77
4-Bromofluorobenzene (surr.)	28.30	95	174,176
Benzyl chloride	29.50	91	91,126,65,128
Styrene	30.83	104	104,103,78,51,77
bis-(2-Chloroethyl) sulfide(b)	33.53	109	111, 158, 160
Acetone	--	43	58
Acrolein	--	56	55,58
Acrylonitrile	--	53	52,51
Chlorobenzene-d_5 (I.S.)	--	117	82,119
Chlorodibromomethane	--	129	208,206
1,1-Dichloroethane	--	63	65,83
Ethanol	--	31	45,27,46
2-Hexanone	--	43	58,57, 100
Iodomethane	--	142	127,141
4-Methyl-2-pentanone	--	43	58,57,100
Toluene-d_8 (surr.)	--	98	70,100
Vinyl acetate	--	43	86
Xylene (Total)	--	106	91

a The base peak at m/e 117 was not used due to an interference at that mass with a nearly coeluting internal standard, chlorobenzene-d_5.
b Response factor judged to be too low (less than 0.02) for practical use.
(I.S.) = Internal Standard
(surr) = Surrogate

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQL) FOR VOLATILE ORGANICS

Volatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acetone	100	100
Acetonitrile	100	100
Allyl chloride	5	5
Benzene	5	5
Benzyl chloride	100	100
Bromodichloromethane	5	5
Bromoform	5	5
Bromomethane	10	10
2-Butanone	100	100
Carbon disulfide	100	100
Carbon tetrachloride	5	5
Chlorobenzene	5	5
Chlorodibromomethane	5	5
Chloroethane	10	10
2-Chloroethyl vinyl ether	10	10
Chloroform	5	5
Chloromethane	10	10
Chloroprene	5	5
1,2-Dibromo-3-chloropropane	100	100
1,2-Dibromoethane	5	5
Dibromomethane	5	5
1,4-Dichloro-2-butene	100	100
Dichlorodifluoromethane	5	5
1,1-Dichloroethane	5	5
1,2-Dichloroethane	5	5
1,1 Dichloroethene	5	5
trans-1,2-Dichloroethene	5	5
1,2-Dichloropropane	5	5
cis-1,3-Dichloropropene	5	5
trans-1,3-Dichloropropene	5	5
Ethylbenzene	5	5
Ethyl methacrylate	5	5
2-Hexanone	50	50
Isobutyl alcohol	100	100
Methacrylonitrile	100	100
Methylene chloride	5	5
Methyl iodide	5	5
Methyl methacrylate	5	50
4-Methyl-2-pentanone	50	50
Pentachloroethane	10	10

TABLE 2.
(Continued)

Volatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Propionitrile	100	100
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
1,1,1-Trichloroethane	5	5
1,1,2-Trichloroethane	5	5
Trichloroethene	5	5
1,2,3-Trichloropropane	5	5
Vinyl acetate	50	50
Vinyl chloride	10	10
Xylene (Total)	5	5

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight of each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[c]EQL = [EQL for low soil/sediment (see Table 2)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.
BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS
OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500- 10,000 µg/kg	100 µL
1,000- 20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

a The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

b Dilute and aliquot of the methanol extract and then take 100 µL for analysis.

TABLE 5.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromoform
Bromomethane	2-Butanone
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	2-Chloroethyl vinyl ether
Chloromethane	Dibromomethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,2-Dichloropropane
1,2-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene
1,1-Dichloroethene	1,1,1-Trichloroethane
trans-1,2-Dichloroethene	1,1,2-Trichloroethane
Iodomethane	Trichloroethene
Methylene chloride	Vinyl acetate
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

TABLE 6.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethyl vinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in µg/L.
s = Standard deviation of four recovery measurements, in µg/L.
$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 µg/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Benzene	0.93C+2.00	0.26$\bar{x}$-1.74	0.25$\bar{x}$-1.33
Bromodichloromethane	1.03C-1.58	0.15$\bar{x}$+0.59	0.20$\bar{x}$+1.13
Bromoform	1.18C-2.35	0.12$\bar{x}$+0.34	0.17$\bar{x}$+1.38
Bromomethane	1.00C	0.43$\bar{x}$	0.58$\bar{x}$
Carbon tetrachloride	1.10C-1.68	0.12$\bar{x}$+0.25	0.11$\bar{x}$+0.37
Chlorobenzene	0.98C+2.28	0.16$\bar{x}$-0.09	0.26$\bar{x}$-1.92
Chloroethane	1.18C+0.81	0.14$\bar{x}$+2.78	0.29$\bar{x}$+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62$\bar{x}$	0.84$\bar{x}$
Chloroform	0.93C+0.33	0.16$\bar{x}$+0.22	0.18$\bar{x}$+0.16
Chloromethane	1.03C-1.81	0.37$\bar{x}$+2.14	0.58$\bar{x}$+0.43
Dibromochloromethane	1.01C-0.03	0.17$\bar{x}$-0.18	0.17$\bar{x}$+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14$\bar{x}$-0.48	0.18$\bar{x}$-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,1-Dichloroethane	1.05C+0.36	0.13$\bar{x}$-0.05	0.16$\bar{x}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17$\bar{x}$-0.32	0.21$\bar{x}$-0.38
1,1-Dichloroethene	1.12C+0.61	0.17$\bar{x}$+1.06	0.43$\bar{x}$-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14$\bar{x}$+0.09	0.19$\bar{x}$+0.17
1,2-Dichloropropane[a]	1.00C	0.33$\bar{x}$	0.45$\bar{x}$
cis-1,3-Dichloropropene[a]	1.00C	0.38$\bar{x}$	0.52$\bar{x}$
trans-1,3-Dichloropropene[a]	1.00C	0.25$\bar{x}$	0.34$\bar{x}$
Ethyl benzene	0.98C+2.48	0.14$\bar{x}$+1.00	0.26$\bar{x}$-1.72
Methylene chloride	0.87C+1.88	0.15$\bar{x}$+1.07	0.32$\bar{x}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16$\bar{x}$+0.69	0.20$\bar{x}$+0.41
Tetrachloroethene	1.06C+0.60	0.13$\bar{x}$-0.18	0.16$\bar{x}$-0.45
Toluene	0.98C+2.03	0.15$\bar{x}$-0.71	0.22$\bar{x}$-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12$\bar{x}$-0.15	0.21$\bar{x}$-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14$\bar{x}$+0.02	0.18$\bar{x}$+0.00
Trichloroethene	1.04C+2.27	0.13$\bar{x}$+0.36	0.12$\bar{x}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33$\bar{x}$-1.48	0.34$\bar{x}$-0.39
Vinyl chloride	1.00C	0.48$\bar{x}$	0.65$\bar{x}$

x′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

a Estimates based upon the performance in a single laboratory.

b Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

FIGURE 1.
PURGING CHAMBER

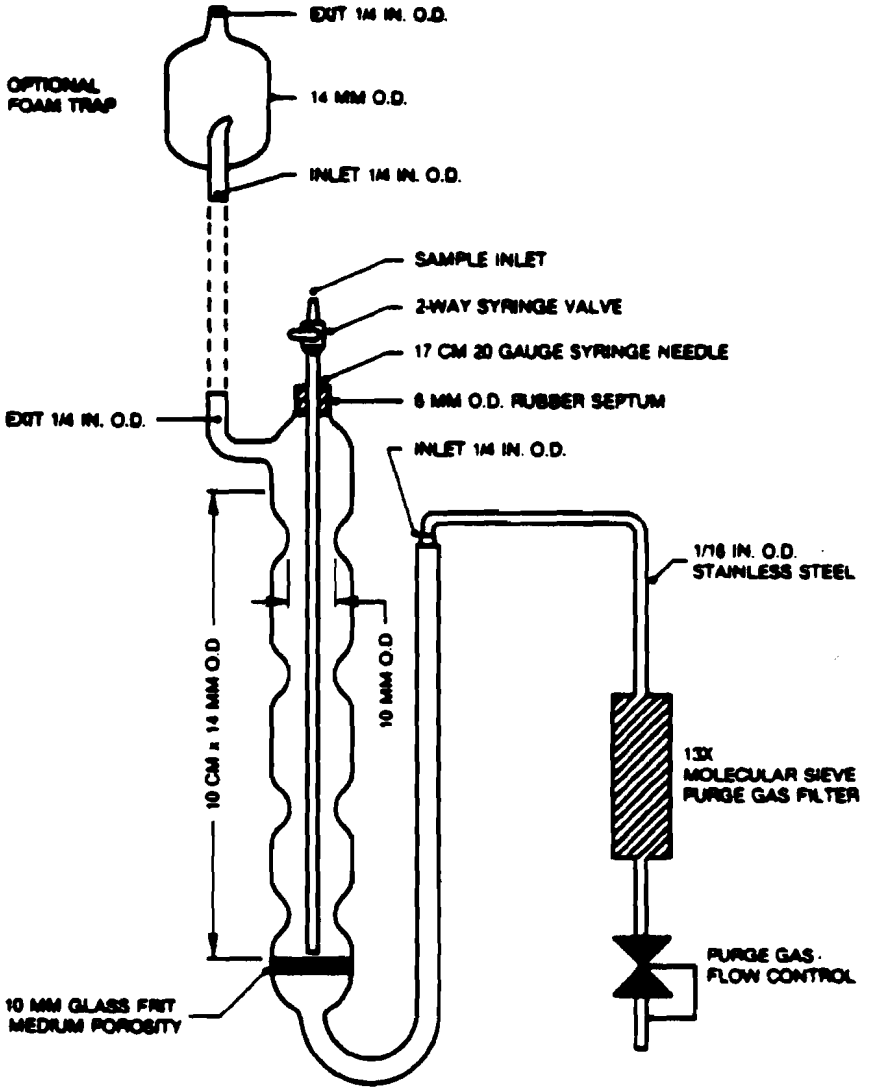


FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE
DESORB CAPABILITY FOR METHOD 8240B

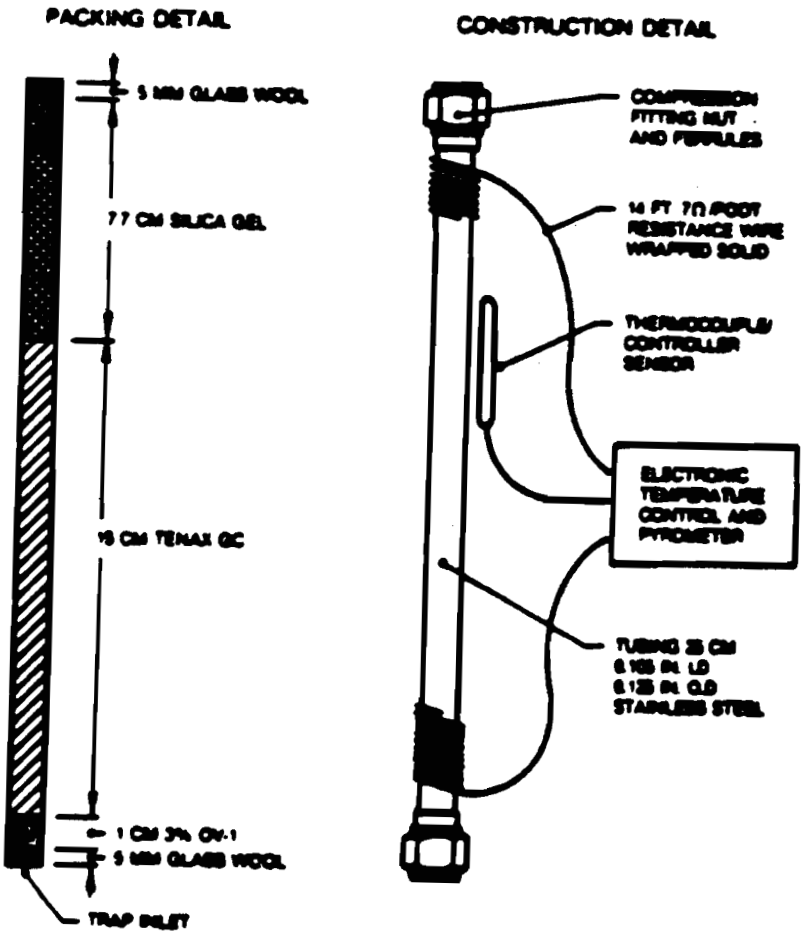


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE FOR METHOD 8240B

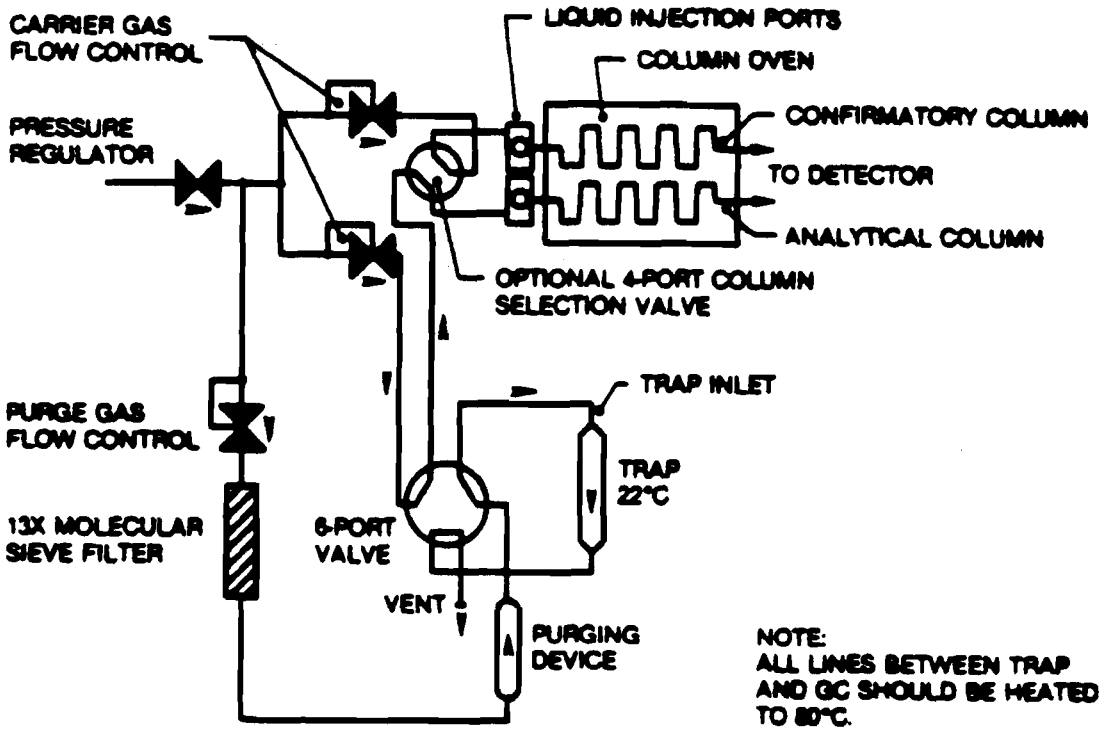


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE FOR METHOD 8240B

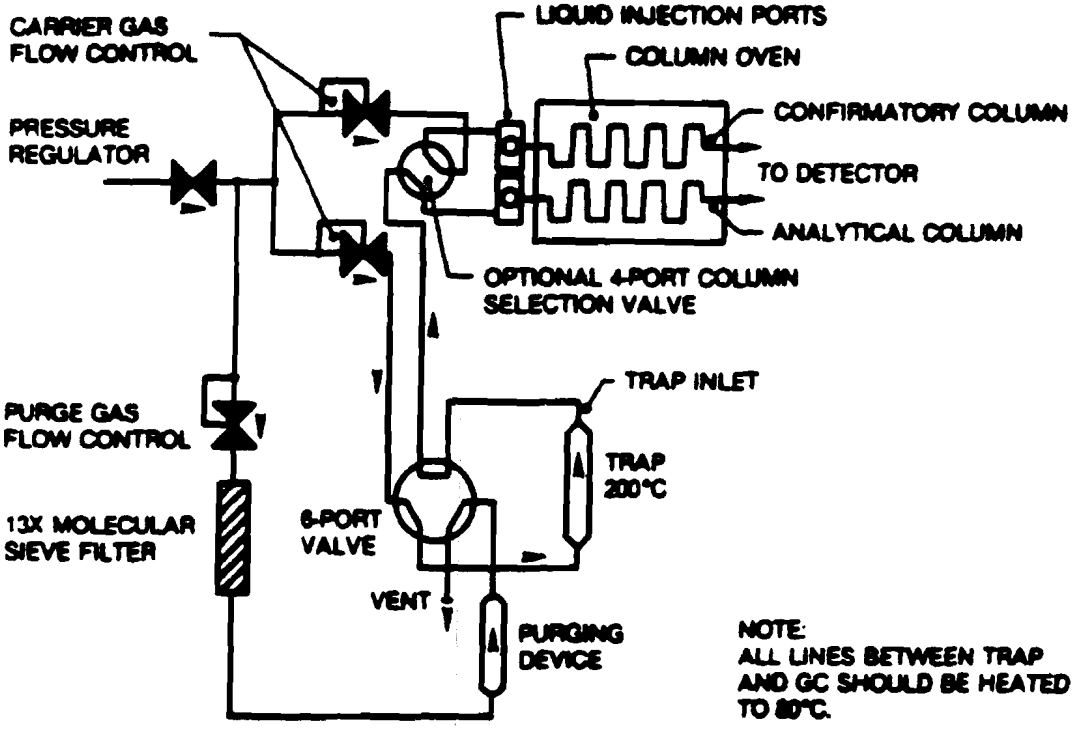
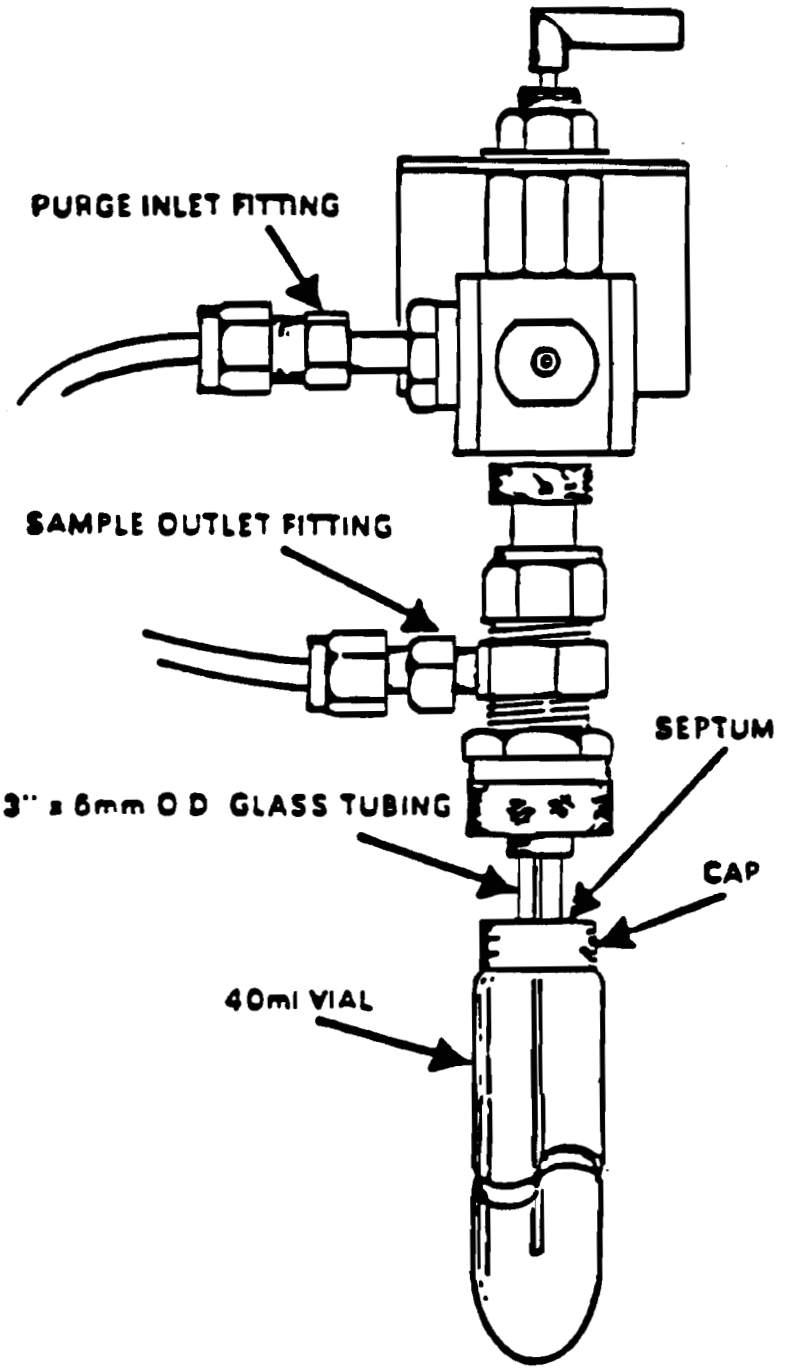
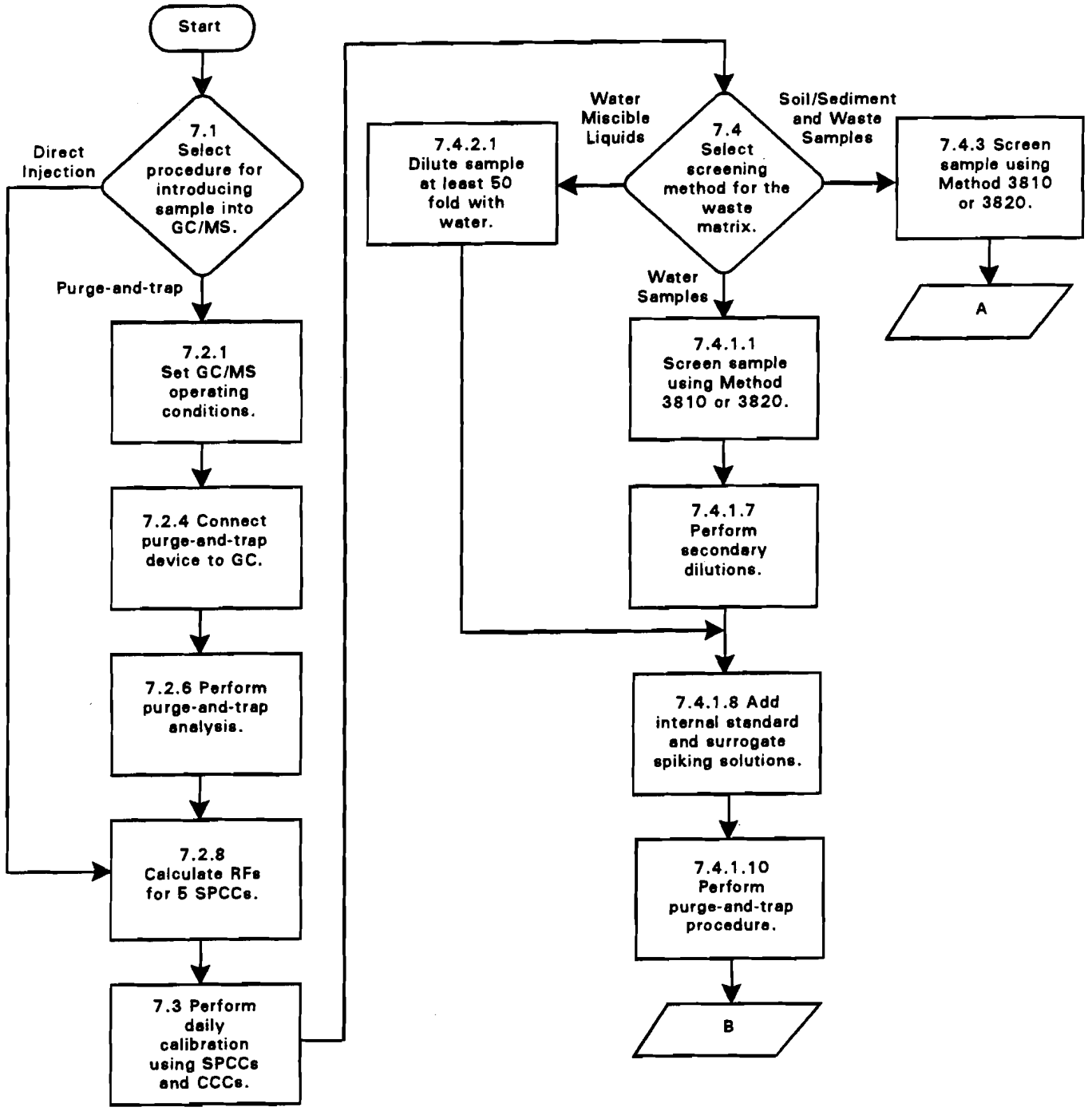
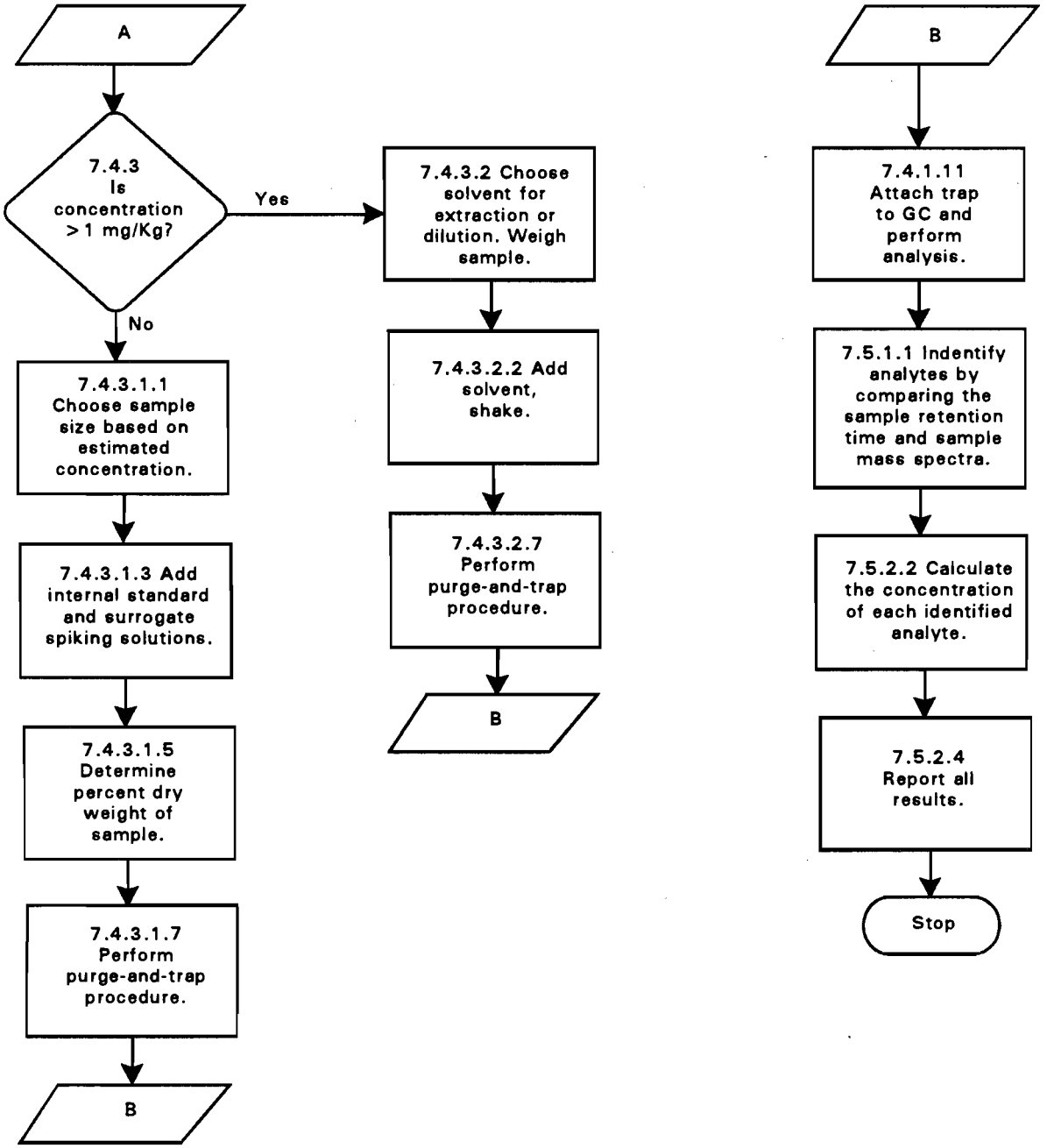


FIGURE 5.
LOW SOILS IMPINGER




Start
7.1 Select procedure for introducing sample into GC/MS.
Direct Injection
Purge-and-trap
7.2.1 Set GC/MS operating conditions.
7.2.4 Connect purge-and-trap device to GC.
7.2.6 Perform purge-and-trap analysis.
7.2.8 Calculate RFs for 5 SPCCs.
7.3 Perform daily calibration using SPCCs and CCCs.
7.4 Select screening method for the waste matrix.
Water Miscible Liquids
7.4.2.1 Dilute sample at least 50 fold with water.
Soil/Sediment and Waste Samples
7.4.3 Screen sample using Method 3810 or 3820.
A
Water Samples
7.4.1.1 Screen sample using Method 3810 or 3820.
7.4.1.7 Perform secondary dilutions.
7.4.1.8 Add internal standard and surrogate spiking solutions.
7.4.1.10 Perform purge-and-trap procedure.
B


A
7.4.3
Is
concentration
> 1 mg/Kg?
Yes
No
7.4.3.2 Choose solvent for extraction or dilution. Weigh sample.
7.4.3.2.2 Add solvent, shake.
7.4.3.2.7 Perform purge-and-trap procedure.
B
7.4.3.1.1 Choose sample size based on estimated concentration.
7.4.3.1.3 Add internal standard and surrogate spiking solutions.
7.4.3.1.5 Determine percent dry weight of sample.
7.4.3.1.7 Perform purge-and-trap procedure.
B
B
7.4.1.11 Attach trap to GC and perform analysis.
7.5.1.1 Indentify analytes by comparing the sample retention time and sample mass spectra.
7.5.2.2 Calculate the concentration of each identified analyte.
7.5.2.4 Report all results.
Stop

METHOD 8250A

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		Appropriate Preparation Techniques				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (I.S.)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
Aldrin	309-00-2	X	X	X	X	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
Anthracene	120-12-7	X	X	X	X	X
Aroclor - 1016 (PCB-1016)	12674-11-2	X	X	X	X	X
Aroclor - 1221 (PCB-1221)	11104-28-2	X	X	X	X	X
Aroclor - 1232 (PCB-1232)	11141-16-5	X	X	X	X	X
Aroclor - 1242 (PCB-1242)	53469-21-9	X	X	X	X	X
Aroclor - 1248 (PCB-1248)	12672-29-6	X	X	X	X	X
Aroclor - 1254 (PCB-1254)	11097-69-1	X	X	X	X	X
Aroclor - 1260 (PCB-1260)	11096-82-5	X	X	X	X	X
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540/ 3541	3550	3580
Chlordane (technical)	57-74-9	X	X	X	X	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
4-Chloro-3-methylphenol	59-50-7					
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (I.S.)		X	X	X	X	X
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (I.S)	3855-82-1	X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Diphenylamine	122-39-4	X	X	X	X	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540/ 3541	3550	3580
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr.)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr.)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isophorone	78-59-1	X	X	X	X	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (I.S.)	1146-65-2	X	X	X	X	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr.)	4165-60-0	X	X	X	X	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
N-Nitrosodibutylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (I.S.)	198-55-0	X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (I.S.)		X	X	X	X	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr.)	13127-88-3	DC(28)	X	X	X	X
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Pronamide	23950-58-5	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540/ 3541	3550	3580
Pyrene	129-00-0	X	X	X	X	X
Terphenyl-d_{14}(surr.)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol(surr.)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

[a] Chemical Abstract Service Registry Number.

CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
ND = Not determined.
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

1.2 Method 8250 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic packed column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected and are not being determined by Method 8080. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline,

3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The estimated quantitation limit (EQL) of Method 8250 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases.

4.1.2 Columns

4.1.2.1 For base/neutral compound detection - 2 m x 2 mm ID stainless or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport or equivalent.

4.1.2.2 For acid compound detection - 2 m x 2 mm ID glass, packed with 1% SP-1240-DA on 100/120 mesh Supelcoport or equivalent.

4.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 μL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used. GC-to-MS interfaces constructed entirely of glass or glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.1.5 Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe - 10 μL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any

concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps or crimp tops. Store at -10°C to -20°C or less and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at -10°C to -20°C or less when not being used.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.6 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Each 1 mL aliquot of calibration standard should be spiked with 10 μL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.7 Surrogate standards - The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.8 Matrix spike standards - See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of standards in all matrix spikes. Take into account all dilutions of sample extracts.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3541, 3550
Waste	3540, 3541, 3550, 3580

7.1.1 Direct injection - In very limited applications direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All basic, neutral, and acidic Priority Pollutants	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Recommended GC/MS operating conditions

Electron energy:	70 volts (nominal)
Mass range:	35-500 amu
Scan time:	1 sec/scan
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Sample volume:	1-2 µL
Carrier gas:	Helium at 30 mL/min

Conditions for base/neutral analysis (3% SP-2250-DB):

Initial column temperature and hold time:	50°C for 4 minutes
Column temperature program:	50-300°C at 8°C/min
Final column temperature hold:	300°C for 20 minutes

Conditions for acid analysis (1% SP-1240-DA):

Initial column temperature and hold time:	70°C for 2 minutes
Column temperature program:	70-200°C at 8°C/min
Final column temperature hold:	200°C for 20 minutes

7.4 Initial calibration

7.4.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50 ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20% (See Sec. 7.4.5 of Method 8080). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning.

7.4.2 The internal standards selected in Sec. 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation).

7.4.3 Analyze 1 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Calculate response factors (RFs) for each compound relative to the internal standard as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_x = Concentration of the compound being measured (ng/μL).
C_{is} = Concentration of the specific internal standard (ng/μL).

7.4.4 A system performance check must be performed to ensure that minimum average response factors, calculated as the mean of the 5 individual relative response factors, are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.4.4.1 The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RSD = relative standard deviation.
$\overline{RF}$ = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N - 1}}$$

where:

RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

7.4.4.2 If the %RSD of any CCC is 30% or greater, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.4.

7.4.5 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.7.2).

7.4.5.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Secs. 7.7.2.2 and 7.7.2.3). The use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.5 Daily GC/MS calibration

7.5.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12 hour shift.

7.5.2 A calibration standard(s) at mid-concentration containing all semivolatile analytes, including all required surrogates, must be analyzed every 12 hours during analysis. Compare the instrument response factor from the standards every 12 hours with the SPCC (Sec. 7.5.3) and CCC (Sec. 7.5.4) criteria.

7.5.3 System Performance Check Compounds (SPCCs) - A system performance check must be made during every 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column,

and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.5.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration.

Calculate the percent drift using:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins. If the CCCs are not analytes required by the permit, then all required analytes must meet the 20% drift criterion.

7.5.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last daily calibration (Sec. 7.4), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.6 GC/MS analysis

7.6.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.6.2 Spike the 1 mL extract obtained from sample preparation with 10 μL of the internal standard solution (Sec. 5.4) just prior to analysis.

7.6.3 Analyze the 1 mL extract by GC/MS using the appropriate column (as specified in Sec. 4.1.2). The recommended GC/MS operating conditions to be used are specified in Sec. 7.3.

7.6.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/μL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.6.5 Perform all qualitative and quantitative measurements as described in Sec. 7.7. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

7.7 Data interpretation

7.7.1 Qualitative analysis

7.7.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.7.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.7.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.7.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.7.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.7.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce

mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.7.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7.2 Quantitative Analysis

7.7.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion.

7.7.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (Sec. 7.4.3) and the following equation:

$$C_{ex}\ (mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times \overline{RF})}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in Sec. 7.4.3.

7.7.2.3 Alternatively, the regression line fitted to the initial calibration (Sec. 7.4.6.1) may be used for determination of the extract concentration.

7.7.2.4 Compute the concentration of the analyte in the sample using the equations in Secs. 7.7.2.4.1 and 7.7.2.4.2.

7.7.2.4.1 The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid } (\mu g/L) = \frac{(C_{ex} \times V_{ex})}{V_o}$$

where:

V_{ex} = extract volume, in mL
V_o = volume of liquid extracted, in L.

7.7.2.4.2 The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid } (\mu g/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:

V_{ex} = extract volume, in mL
W_s = sample weight, in kg.

7.7.2.5 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine

concentration. Use the nearest internal standard free of interferences.

7.7.2.6 Quantitation of multicomponent compounds (e.g. Aroclors) is beyond the scope of Method 8250A. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Sec. 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Sec. 7.4.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Sec. 7.5.3 and the CCC criteria in Sec. 7.5.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) check sample concentrate is required containing each analyte at a concentration of 100 mg/L in acetone. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 μg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of organic-free reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Sec. 7.1 with extraction of the samples.

8.5.4 Calculate the average recovery ($\bar{x}$) in μg/L, and the standard deviation of the recovery (s) in μg/L, for each analyte using the four results.

8.5.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{x}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Secs. 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Sec. 8.5.2.

8.5.6.2 Beginning with Sec. 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Sec. 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a method blank, a matrix spike, and a matrix spike/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 μg/L or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 μg/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Sec. 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 μg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Sec. 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Sec. 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Sec. 8.6, the probability that the analysis of a QC check standard will be required is high. In this case, the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 1.0 mL of the QC check sample concentrate (Sec. 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Sec. 8.6.

8.7.2 Analyze the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (P_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (P_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Sec. 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Sec. 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometry using other ionization modes must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 μg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

4. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

5. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

6. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Method Detection limit (μg/L)	Primary Ion	Secondary Ion(s)
Acenaphthene	17.8	1.9	154	153, 152
Acenaphthene-d_{10} (I.S.)	--	--	164	162, 160
Acenaphthylene	17.4	3.5	152	151, 153
Acetophenone	--	--	105	77, 51
Aldrin	24.0	1.9	66	263, 220
4-Aminobiphenyl	--	--	169	168, 170
Aniline	--	--	93	66, 65
Anthracene	22.8	1.9	178	176, 179
Aroclor-1016[b]	18-30	--	222	260, 292
Aroclor-1221[b]	15-30	30	190	224, 260
Aroclor-1232[b]	15-32	--	190	224, 260
Aroclor-1242[b]	15-32	--	222	256, 292
Aroclor-1248[b]	12-34	--	292	362, 326
Aroclor-1254[b]	22-34	36	292	362, 326
Aroclor-1260[b]	23-32	--	360	362, 394
Benzidine[a]	28.8	44	184	92, 185
Benzoic acid	--	--	122	105, 77
Benzo(a)anthracene	31.5	7.8	228	229, 226
Benzo(b)fluoranthene	34.9	4.8	252	253, 125
Benzo(k)fluoranthene	34.9	2.5	252	253, 125
Benzo(g,h,i)perylene	45.1	4.1	276	138, 277
Benzo(a)pyrene	36.4	2.5	252	253, 125
Benzyl alcohol	--	--	108	79, 77
α-BHC[a]	21.1	--	183	181, 109
β-BHC	23.4	4.2	181	183, 109
δ-BHC	23.7	3.1	183	181, 109
γ-BHC (Lindane)[a]	22.4	--	183	181, 109
Bis(2-chloroethoxy)methane	12.2	5.3	93	95, 123
Bis(2-chloroethyl) ether	8.4	5.7	93	63, 95
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77, 121
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167, 279
4-Bromophenyl phenyl ether	21.2	1.9	248	250, 141
Butyl benzyl phthalate	29.9	2.5	149	91, 206
Chlordane[b]	19-30	--	373	375, 377
4-Chloroaniline	--	--	127	129
1-Chloronaphthalene	--	--	162	127, 164
2-Chloronaphthalene	15.9	1.9	162	127, 164
4-Chloro-3-methylphenol	13.2	3.0	107	144, 142
2-Chlorophenol	5.9	3.3	128	64, 130
4-Chlorophenyl phenyl ether	19.5	4.2	204	206, 141
Chrysene	31.5	2.5	228	226, 229
Chrysene-d_{12} (I.S.)	--	--	240	120, 236
4,4′-DDD	28.6	2.8	235	237, 165

TABLE 1.
(Continued)

Compound	Retention Time (min)	Method Detection Limit (μg/L)	Primary Ion	Secondary Ion(s)
4,4′-DDT	29.3	4.7	235	237, 165
4,4′-DDE	27.2	--	246	24, 176
Dibenz(a,j)acridine	--	--	279	280, 277
Dibenz(a,h)anthracene	43.2	2.5	278	139, 279
Dibenzofuran	--	--	168	139
Di-n-butyl phthalate	24.7	2.5	149	150, 104
1,2-Dichlorobenzene	8.4	1.9	146	148, 111
1,3-Dichlorobenzene	7.4	1.9	146	148, 111
1,4-Dichlorobenzene	7.8	4.4	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	--	--	152	150, 115
3,3′-Dichlorobenzidine	32.2	16.5	252	254, 126
2,4-Dichlorophenol	9.8	2.7	162	164, 98
2,6-Dichlorophenol	--	--	162	164, 98
Dieldrin	27.2	2.5	79	263, 279
Diethyl phthalate	20.1	1.9	149	177, 150
p-Dimethylaminoazobenzene	--	--	120	225, 77
7,12-Dimethylbenz(a)anthracene	--	--	256	241, 257
α-,α-Dimethylphenethylamine	--	--	58	91, 42
2,4-Dimethylphenol	9.4	2.7	122	107, 121
Dimethyl phthalate	18.3	1.6	163	194, 164
4,6-Dinitro-2-methylphenol	16.2	24	198	51, 105
2,4-Dinitrophenol	15.9	42	184	63, 154
2,4-Dinitrotoluene	19.8	5.7	165	63, 89
2,6-Dinitrotoluene	18.7	1.9	165	63, 89
Diphenylamine	--	--	169	168, 167
1,2-Diphenylhydrazine	--	--	77	105, 182
Di-n-octyl phthalate	32.5	2.5	149	167, 43
Endosulfan I[a]	26.4	--	195	339, 341
Endosulfan II[a]	28.6	--	337	339, 341
Endosulfan sulfate	29.8	5.6	272	387, 422
Endrin[a]	27.9	--	263	82, 81
Endrin aldehyde	--	--	67	345, 250
Endrin ketone	--	--	317	67, 319
Ethyl methanesulfonate	--	--	79	109, 97
Fluoranthene	26.5	2.2	202	101, 203
Fluorene	19.5	1.9	166	165, 167
2-Fluorobiphenyl (surr.)	--	--	172	171
2-Fluorophenol (surr.)	--	--	112	64
Heptachlor	23.4	1.9	100	272, 274
Heptachlor epoxide	25.6	2.2	353	355, 351
Hexachlorobenzene	21.0	1.9	284	142, 249
Hexachlorobutadiene	11.4	0.9	225	223, 227
Hexachlorocyclopentadiene[a]	13.9	--	237	235, 272
Hexachloroethane	8.4	1.6	117	201, 199

TABLE 1.
(Continued)

Compound	Retention Time (min)	Method Detection Limit (μg/L)	Primary Ion	Secondary Ion(s)
Indeno(1,2,3-cd)pyrene	42.7	3.7	276	138, 227
Isophorone	11.9	2.2	82	95, 138
Methoxychlor	--	--	227	228
3-Methylcholanthrene	--	--	268	253, 267
Methyl methanesulfonate	--	--	80	79, 65
2-Methylnaphthalene	--	--	142	141
2-Methylphenol	--	--	108	107, 79
4-Methylphenol	--	--	108	107, 79
Naphthalene	12.1	1.6	128	129, 127
Naphthalene-d_8 (I.S.)	--	--	136	68
1-Naphthylamine	--	--	143	115, 116
2-Naphthylamine	--	--	143	115, 116
2-Nitroaniline	--	--	65	92, 138
3-Nitroaniline	--	--	138	108, 92
4-Nitroaniline	--	--	138	108, 92
Nitrobenzene	11.1	1.9	77	123, 65
Nitrobenzene-d_5 (surr.)	--	--	82	128, 54
2-Nitrophenol	6.5	3.6	139	109, 65
4-Nitrophenol	20.3	2.4	139	109, 65
N-Nitroso-di-n-butylamine	--	--	84	57, 41
N-Nitrosodimethylamine[a]	--	--	42	74, 44
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168, 167
N-Nitroso-di-n-propylamine	--	--	70	130, 42
N-Nitrosopiperidine	--	--	42	114, 55
Pentachlorobenzene	--	--	250	252, 248
Pentachloronitrobenzene	--	--	295	237, 142
Pentachlorophenol	17.5	3.6	266	264, 268
Perylene-d_{12} (I.S.)	--	--	264	260, 265
Phenacetin	--	--	108	109, 179
Phenanthrene	22.8	5.4	178	179, 176
Phenanthrene-d_{10} (I.S.)	--	--	188	94, 80
Phenol	8.0	1.5	94	65, 66
Phenol-d_6 (surr.)	--	--	99	42, 71
2-Picoline	--	--	93	66, 92
Pronamide	--	--	173	175, 145
Pyrene	27.3	1.9	202	200, 203
Terphenyl-d_{14} (surr.)	--	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	--	--	216	214, 218
2,3,4,6-Tetrachlorophenol	--	--	232	230, 131

TABLE 1.
(Continued)

Compound	Retention Time (min)	Method Detection Limit (μg/L)	Primary Ion	Secondary Ion(s)
Toxaphene[b]	25-34	--	159	231, 233
2,4,6-Tribromophenol (surr.)	--	--	330	332, 141
1,2,4-Trichlorobenzene	11.6	1.9	180	182, 145
2,4,5-Trichlorophenol	--	--	196	198, 200
2,4,6-Trichlorophenol	11.8	2.7	196	198, 200

[a]See Sec. 1.3
[b]These compounds are mixtures of various isomers.
(I.S.) = Internal Standard
(surr). = Surrogate

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

[a] EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs to be determined herein are provided for guidance and may not always be achievable.

TABLE 3.
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a]See Reference 3.

TABLE 4.
CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Benzo(a)pyrene	2,4,6-Trichlorophenol
Fluoranthene	

TABLE 5.
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-D_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethylphenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (Surr.)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr.) = surrogate

TABLE 5.
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION
(Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz-(a)anthracene
Fluoranthene	Pyrene	Di-n-octyl phthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

TABLE 6.
QC ACCEPTANCE CRITERIA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Butyl benzyl phthalate	100	23.4	D-139.9	D-152
ß-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4′-DDD	100	31.0	D-134.5	D-145
4,4′-DDE	100	32.0	19.2-119.7	4-136
4,4′-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3′-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26-155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116

TABLE 6.
QC ACCEPTANCE CRITERIA[a]
(Continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitroso-di-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a] Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{x}$-0.12	0.21$\bar{x}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{x}$-1.06	0.26$\bar{x}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{x}$-1.28	0.43$\bar{x}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{x}$-0.32	0.27$\bar{x}$-0.64
Benzo(a)anthracene	0.88C-0.60	0.15$\bar{x}$+0.93	0.26$\bar{x}$-0.21
Chloroethane	0.99C-1.53	0.14$\bar{x}$-0.13	0.17$\bar{x}$-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{x}$+0.43	0.29$\bar{x}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{x}$+1.03	0.35$\bar{x}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{x}$+0.48	0.32$\bar{x}$+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29$\bar{x}$+2.40	0.51$\bar{x}$-0.44
Butyl benzyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
ß-BHC	0.87C-0.94	0.20$\bar{x}$-0.58	0.30$\bar{x}$+1.94
δ-BHC	0.29C-1.09	0.34$\bar{x}$+0.86	0.93$\bar{x}$-0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35$\bar{x}$-0.99	0.35$\bar{x}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{x}$+1.34	0.26$\bar{x}$+2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24$\bar{x}$+0.28	0.25$\bar{x}$+1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26$\bar{x}$+0.73	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{x}$+0.66	0.16$\bar{x}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{x}$+0.52	0.13$\bar{x}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{x}$-0.94	0.30$\bar{x}$-0.46
Chrysene	0.93C-1.00	0.28$\bar{x}$+0.13	0.33$\bar{x}$-0.09
4,4′-DDD	0.56C-0.40	0.29$\bar{x}$-0.32	0.66$\bar{x}$-0.96
4,4′-DDE	0.70C-0.54	0.26$\bar{x}$-1.17	0.39$\bar{x}$-1.04
4,4′-DDT	0.79C-3.28	0.42$\bar{x}$+0.19	0.65$\bar{x}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{x}$+8.51	0.59$\bar{x}$+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{x}$+1.16	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{x}$+0.47	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{x}$+0.68	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{x}$+0.23	0.29$\bar{x}$+0.36
3,3′-Dichlorobenzidine	1.23C-12.65	0.28$\bar{x}$+7.33	0.47$\bar{x}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{x}$-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{x}$+1.44	0.52$\bar{x}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{x}$+0.19	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{x}$+1.06	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{x}$+1.26	0.19$\bar{x}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{x}$+1.19	0.37$\bar{x}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{x}$+2.47	0.63$\bar{x}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{x}$+3.91	0.73$\bar{x}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{x}$-0.73	0.28$\bar{x}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]
(Continued)

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	$0.29\bar{x}+1.46$	$0.50\bar{x}-0.44$
Isophorone	1.12C+1.41	$0.27\bar{x}+0.77$	$0.33\bar{x}+0.26$
Naphthalene	0.76C+1.58	$0.21\bar{x}-0.41$	$0.30\bar{x}-0.68$
Nitrobenzene	1.09C-3.05	$0.19\bar{x}+0.92$	$0.27\bar{x}+0.21$
N-Nitroso-di-n-propylamine	1.12C-6.22	$0.27\bar{x}+0.68$	$0.44\bar{x}+0.47$
PCB-1260	0.81C-10.86	$0.35\bar{x}+3.61$	$0.43\bar{x}+1.82$
Phenanthrene	0.87C+0.06	$0.12\bar{x}+0.57$	$0.15\bar{x}+0.25$
Pyrene	0.84C-0.16	$0.16\bar{x}+0.06$	$0.15\bar{x}+0.31$
1,2,4-Trichlorobenzene	0.94C-0.79	$0.15\bar{x}+0.85$	$0.21\bar{x}+0.39$
4-Chloro-3-methylphenol	0.84C+0.35	$0.23\bar{x}+0.75$	$0.29\bar{x}+1.31$
2-Chlorophenol	0.78C+0.29	$0.18\bar{x}+1.46$	$0.28\bar{x}+0.97$
2,4-Dichlorophenol	0.87C-0.13	$0.15\bar{x}+1.25$	$0.21\bar{x}+1.28$
2,4-Dimethylphenol	0.71C+4.41	$0.16\bar{x}+1.21$	$0.22\bar{x}+1.31$
2,4-Dinitrophenol	0.81C-18.04	$0.38\bar{x}+2.36$	$0.42\bar{x}+26.29$
2-Methyl-4,6-dinitrophenol	1.04C-28.04	$0.10\bar{x}+42.29$	$0.26\bar{x}+23.10$
2-Nitrophenol	0.07C-1.15	$0.16\bar{x}+1.94$	$0.27\bar{x}+2.60$
4-Nitrophenol	0.61C-1.22	$0.38\bar{x}+2.57$	$0.44\bar{x}+3.24$
Pentachlorophenol	0.93C+1.99	$0.24\bar{x}+3.03$	$0.30\bar{x}+4.33$
Phenol	0.43C+1.26	$0.26\bar{x}+0.73$	$0.35\bar{x}+0.58$
2,4,6-Trichlorophenol	0.91C-0.18	$0.16\bar{x}+2.22$	$0.22\bar{x}+1.81$

x′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

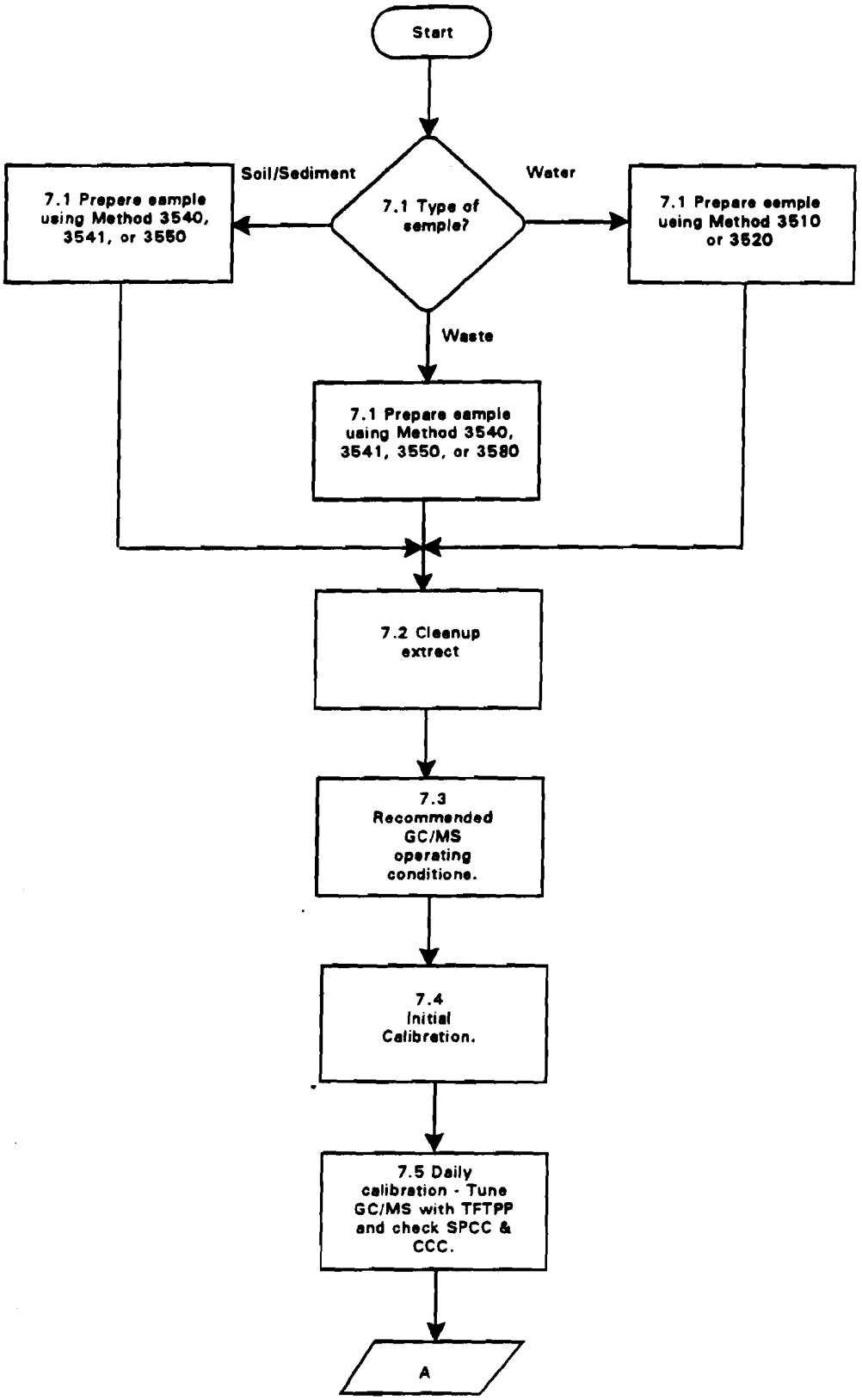
S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

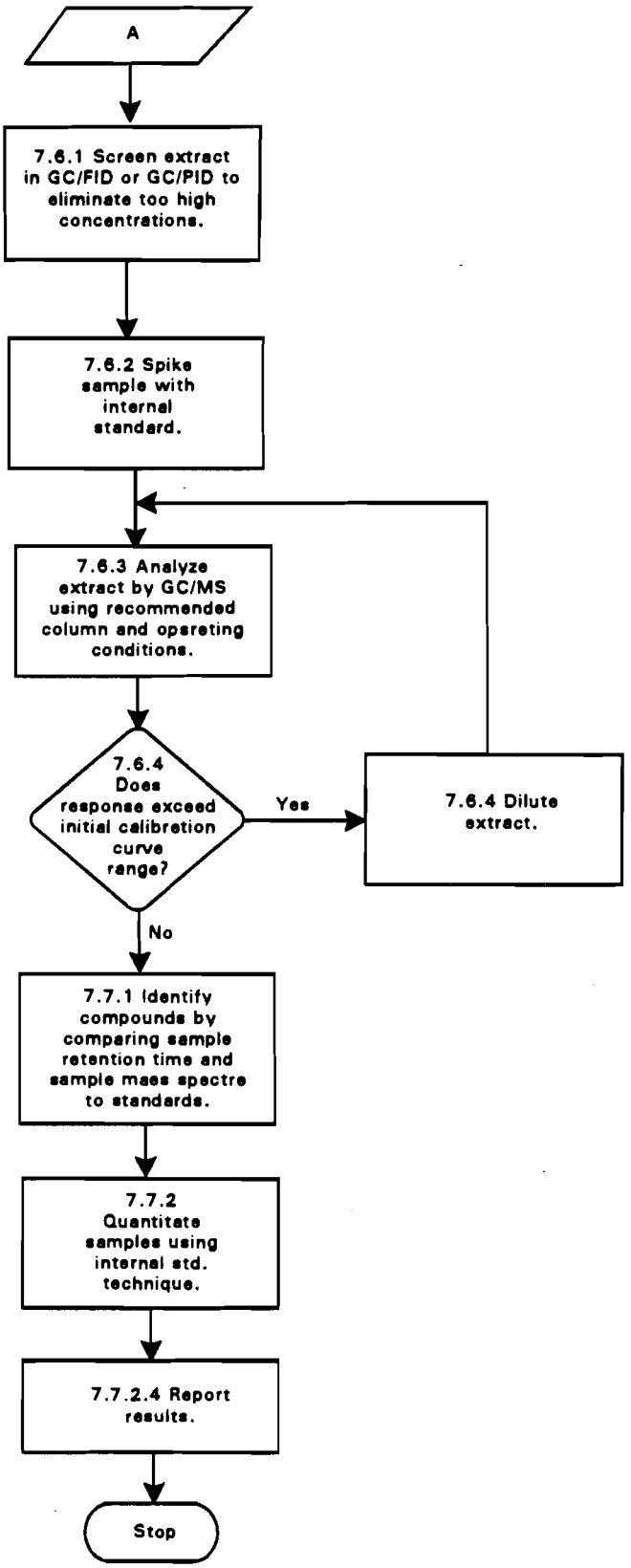
C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122


Start
7.1 Type of sample?
Soil/Sediment
Water
Waste
7.1 Prepare sample using Method 3540, 3541, or 3550
7.1 Prepare sample using Method 3510 or 3520
7.1 Prepare sample using Method 3540, 3541, 3550, or 3580
7.2 Cleanup extract
7.3 Recommended GC/MS operating conditions.
7.4 Initial Calibration.
7.5 Daily calibration - Tune GC/MS with TFTPP and check SPCC & CCC.
A


A
7.6.1 Screen extract in GC/FID or GC/PID to eliminate too high concentrations.
7.6.2 Spike sample with internal standard.
7.6.3 Analyze extract by GC/MS using recommended column and opsreting conditions.
7.6.4 Does response exceed initial calibretion curve range?
Yes
7.6.4 Dilute extract.
No
7.7.1 Identify compounds by comparing sample retention time and sample maes spectre to standards.
7.7.2 Quantitate samples using internal std. technique.
7.7.2.4 Report results.
Stop

METHOD 8260A

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Technique	
Analyte	CAS No.[b]	Purge-and-Trap	Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein (Propenal)	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	ht	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	a	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
n-Butanol	71-36-3	ht	a
2-Butanone (MEK)	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chloral hydrate	302-17-0	pp	a
Chlorobenzene	108-90-7	a	a
2-Chloro-1,3-butadiene	126-99-8	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
bis-(2-Chloroethyl) sulfide	505-60-2	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
3-Chloropropene	107-05-1	a	a
3-Chloropropionitrile	542-76-7	i	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a
1,2-Dichlorobenzene	95-50-1	a	a
1,3-Dichlorobenzene	541-73-1	a	a
1,4-Dichlorobenzene	106-46-7	a	a
cis-1,4-Dichloro-2-butene	1476-11-5	a	a
trans-1,4-Dichloro-2-butene	110-57-6	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2,3,4-Diepoxybutane	1464-53-5	a	a
Diethyl ether	60-29-7	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethyl acetate	141-78-6	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
Hexachlorobutadiene	87-68-3	a	a
Hexachloroethane	67-72-1	i	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	i	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Isopropylbenzene	98-82-8	a	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methanol	67-56-1	i	a
Methylene chloride (DCM)	75-09-2	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	a
Naphthalene	91-20-3	a	a
Nitrobenzene	98-95-3	a	a
2-Nitropropane	79-46-9	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
Pentachloroethane	76-01-7	i	a
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
ß-Propiolactone	57-57-8	pp	a
Propionitrile (ethyl cyanide)	107-12-0	ht	pc
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
1,2,4-Trichlorobenzene	120-82-1	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
o-Xylene	95-47-6	a	a
m-Xylene	108-38-3	a	a
p-Xylene	106-42-3	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
ht Method analyte only when purged at 80°C
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.
pp Poor purging efficiency resulting in high EQLs.
surr Surrogate
I.S. Internal Standard

1.2 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for lists of analytes and retention times that have been evaluated on a purge-

and-trap GC/MS system. Also, the method detection limits for 25 mL sample volumes are presented. The following analytes are also amenable to analysis by Method 8260:

Bromobenzene	1-Chlorohexane
n-Butylbenzene	2-Chlorotoluene
sec-Butylbenzene	4-Chlorotoluene
tert-Butylbenzene	Crotonaldehyde
Chloroacetonitrile	Dibromofluoromethane
1-Chlorobutane	cis-1,2-Dichloroethene
1,3-Dichloropropane	Methyl-t-butyl ether
2,2-Dichloropropane	Pentafluorobenzene
1,1-Dichloropropene	n-Propylbenzene
Fluorobenzene	1,2,3-Trichlorobenzene
p-Isopropyltoluene	1,2,4-Trimethylbenzene
Methyl acrylate	1,3,5-Trimethylbenzene

1.3 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent. Using standard quadrupole instrumentation, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8260 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 An additional method for sample introduction is direct injection. This technique has been tested for the analysis of waste oil diluted with hexadecane 1:1 (vol/vol) and may have application for the analysis of some alcohols and aldehydes in aqueous samples.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with organic-free reagent water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard with a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that replace the general requirements in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Figure 1). Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the whole purge and trap device may require dismantling and cleaning. Screening of the samples prior to purge and trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.2.1 The low purging efficiency of many analytes from a 25 mL sample often results in significant concentrations remaining in the sample purge vessel after analysis. After removal of the analyzed sample aliquot

and three rinses of the purge vessel with analyte free water, it is required that the empty vessel be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel to reduce sample to sample carryover.

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.4 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.5 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.6 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. Use of direct injection will result in the need for more frequent instrument maintenance.

3.7 If hexadecane is added to samples or petroleum samples are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semi-volatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device - aqueous samples, described in Method 5030.

4.2 Purge-and-trap device - solid samples, described in Method 5030.

4.3 Injection port liners (HP catalogue #18740-80200, or equivalent) are modified for direct injection analysis by placing a 1-cm plug of pyrex wool approximately 50-60 mm down the length of the injection port towards the oven. An 0.53 mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

Modified Injector

4.4 Gas chromatography/mass spectrometer/data system

4.4.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection or interface to purge-and-trap apparatus. The system includes all required accessories, including syringes, analytical columns, and gases. The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. For some column configurations, the column oven must be cooled to < 30°C, therefore, a subambient oven controller may be required. The capillary column should be directly coupled to the source.

4.4.1.1 Capillary precolumn interface when using cryogenic cooling - This device interfaces the purge and trap concentrator to the capillary gas chromatograph. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused silica capillary precolumn. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.4.1.1.1 During the cryofocussing step, the temperature of the fused silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.4.2 Gas chromatographic columns

4.4.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5 μm film thickness, or equivalent.

4.4.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3 μm film thickness, or equivalent.

4.4.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1 μm film thickness.

4.4.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8 μm film thickness, or equivalent.

4.4.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for p-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) is injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

4.4.3.1 The ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. In an ion trap mass spectrometer, because ion-molecule reactions with water and methanol may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.4.4 GC/MS interface - Two alternatives are used to interface the GC to the mass spectrometer.

4.4.4.1 Direct coupling by inserting the column into the mass spectrometer is generally used for 0.25-0.32 mm id columns.

4.4.4.2 A separator including an all-glass transfer line and glass enrichment device or split interface is used with an 0.53 mm column.

4.4.4.3 Any enrichment device or transfer line can be used if all of the performance specifications described in Sec. 8 (including acceptable calibration at 50 ng or less) can be achieved. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.4.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.5 Microsyringes - 10, 25, 100, 250, 500, and 1,000 µL.

4.6 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.7 Syringes - 5, 10, or 25 mL, gas-tight with shutoff valve.

4.8 Balance - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.9 Glass scintillation vials - 20 mL, with Teflon lined screw-caps or glass culture tubes with Teflon lined screw-caps.

4.10 Vials - 2 mL, for GC autosampler.

4.11 Disposable pipets - Pasteur.

4.12 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.13 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest.

5.4.1 In order to demonstrate that all interfering volatiles have been removed from the hexadecane, a direct injection blank must be analyzed.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.7.5 Prepare fresh standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 20% drift.

5.7.6 Optionally calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Preparation of Calibration Standards From a Gas Mixture

5.7.6.1.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.1.2 Wrap the pipe thread end of the Luer fitting with Teflon tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.1.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.1.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100 µL or 500 µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) **Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.**

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.1.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.1.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.1.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. **Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.**

5.7.6.1.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.1.9 Concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.1.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.1.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace for one week only.

5.9 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL in methanol. Each water sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

5.9.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L.

5.10.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/μL of BFB in methanol should be prepared.

5.11.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute BFB standard solution may be required.

5.12 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Secs. 5.7 and 5.8). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. It is EPA's intent that all target analytes for a particular analysis be included in the calibration standard(s). However, these target analytes may not include the entire List of Analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s). Calibration standards must be prepared daily.

5.13 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. It is desirable to perform a matrix spike using compounds found in samples. Some permits may require spiking specific compounds of interest, especially if they are polar and would not be represented by the above listed compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 μg/10.0 mL.

5.13.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C to -20°C in amber bottles with Teflon lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Three alternate methods are provided for sample introduction. All internal standards, surrogates, and matrix spikes (when applicable) must be added to samples before introduction.

7.1.1 Direct injection - in very limited application, (e.g., volatiles in waste oil or aqueous process wastes) direct injection of aqueous samples or samples diluted according to Method 3585 may be appropriate. Direct injection has been used for the analysis of volatiles in waste oil (diluted 1:1 with hexadecane) and for determining if the sample is ignitable (aqueous injection, Methods 1010 or 1020). Direct injection is only permitted for the determination of volatiles at the toxicity characteristic (TC) regulatory limits, at concentrations in excess of 10,000 µg/L, or for water-soluble compounds that do not purge.

7.1.2 Purge-and-trap for aqueous samples, see Method 5030 for details.

7.1.3 Purge-and-trap for solid samples, see Method 5030 for details.

7.2 Recommended Chromatographic conditions

7.2.1 General:

Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.2 Column 1 (A sample chromatogram is presented in Figure 5)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 160°C
Final temperature:	160°C, hold until all expected compounds have eluted.

7.2.3 Column 2, Cryogenic cooling (A sample chromatogram is presented in Figure 6)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 160°C
Final temperature:	160°C, hold until all expected compounds have eluted.

7.2.4 Column 2, Non-cryogenic cooling (A sample chromatogram is presented in Figure 7). It is recommended that carrier gas flow and split and make-up gases be set using performance of standards as guidance. Set the carrier gas head pressure to ≈ 10 psi and the split to ≈ 30 mL/min. Optimize the make-up gas flow for the separator (approximately 30 mL/min) by injecting BFB, and determining the optimum response when varying the make-up gas. This will require several injections of BFB. Next, make several injections of the volatile working standard with all analytes of

interest. Adjust the carrier and split to provide optimum chromatography and response. This is an especially critical adjustment for the volatile gas analytes. The head pressure should optimize between 8-12 psi and the split between 20-60 mL/min. The use of the splitter is important to minimize the effect of water on analyte response, to allow the use of a larger volume of helium during trap desorption, and to slow column flow.

Initial temperature:	45°C, hold for 2 minutes
Temperature program:	8°C/min to 200°C
Final temperature:	200°C, hold for 6 minutes.

A trap preheated to 150°C prior to trap desorption is required to provide adequate chromatography of the gas analytes.

7.2.5 Column 3 (A sample chromatogram is presented in Figure 8)

Carrier gas (He) flow rate:	4 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.6 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out (direct inj):	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.7 Direct Split Interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration - the recommended MS operating conditions

Mass range:	35-260 amu
Scan time:	0.6-2 sec/scan
Source temperature:	According to manufacturer's specifications

Ion trap only: Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2 μL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.2 Set up the purge-and-trap system as outlined in Method 5030 if purge-and-trap analysis is to be utilized. A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method. Calibration should be done using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard for purge-and-trap or aqueous direct injection, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 μL of internal standard. Then transfer the contents to a purging device or syringe. Perform purge-and-trap or direct injection as outlined in Method 5030.

7.3.2.2 To prepare a calibration standard for direct injection analysis of oil, dilute standards in hexadecane.

7.3.3 Tabulate the area response of the characteristic ions (see Table 5) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Sec. 7.6.2). The RF is calculated as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x	=	Area of the characteristic ion for the compound being measured.
A_{is}	=	Area of the characteristic ion for the specific internal standard.
C_{is}	=	Concentration of the specific internal standard.
C_x	=	Concentration of the compound being measured.

7.3.4 The average RF must be calculated and recorded for each compound using the five RF values calculated for each compound from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.3.4.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.3.4.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.4.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5 Using the RFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows:

$$\% \text{ RSD} = \frac{SD}{\overline{RF}_x} \times 100\%$$

where:

RSD	=	Relative standard deviation.
RF_x	=	mean of 5 initial RFs for a compound.
SD	=	standard deviation of the 5 initial RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{n} \frac{(RF_i - \overline{RF})^2}{n-1}}$$

where:

RF_i = RF for each of the 5 calibration levels
N = number of RF values (i.e., 5)

The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.3.5.1 If a %RSD greater than 30 percent is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is required before reattempting calibration.

7.3.6 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

7.3.6.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation. The use of calibration curves is a recommended alternative to average response factor calibration (Sec. 7.6.2.4), and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.3.7 These curves are verified each shift by purging a performance standard. Recalibration is required only if calibration and on-going performance criteria cannot be met.

7.4 GC/MS calibration verification

7.4.1 Prior to the analysis of samples, inject or purge 5-50 ng of the 4-bromofluorobenzene standard following Method 5030. The resultant mass spectra for the BFB must meet all of the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest must be checked and verified once every 12 hours during analysis with the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC and CCC.

7.4.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.4.3.1 The minimum relative response factor for volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	>0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.4.4 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs listed in Sec. 7.3.5 are used to check the validity of the initial calibration.

Calculate the percent drift using the following equation:

$$\% \text{ Drift} = (C_I - C_C)/C_I \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent drift for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift), for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 20% drift criterion.

7.4.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes

by more than 30 seconds from the last calibration check (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

7.5 GC/MS analysis

7.5.1 It is highly recommended that the extract be screened on a headspace-GC/FID (Methods 3810/8015), headspace-GC/PID/ELCD (Methods 3810/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Use of screening is particularly important when this method is used to achieve low detection levels.

7.5.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the purge-and-trap system as outlined in Method 5030 if purge-and-trap introduction will be used.

7.5.3 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3.1 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25 mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL.

7.5.4 The process of taking an aliquot destroys the validity of aqueous and soil samples for future analysis; therefore, if there is only one VOA vial, the analyst should prepare a second aliquot for analysis at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, filling one 20 mL syringe would require the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.4.1 The following procedure is appropriate for diluting aqueous purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.5.4.1.1 Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.5.4.1.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.4.1.3 Inject the proper aliquot of sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.4.1.4 Fill a 5 mL syringe with the diluted sample.

7.5.4.2 Compositing aqueous samples prior to GC/MS analysis

7.5.4.2.1 Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25 mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.

7.5.4.2.2 The samples must be cooled at 4°C during this step to minimize volatilization losses.

7.5.4.2.3 Mix well and draw out a 5 mL aliquot for analysis.

7.5.4.2.4 Follow sample introduction, purging, and desorption steps described in Method 5030.

7.5.4.2.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used unless a 25 mL sample is to be purged.

7.5.5 Add 10.0 µL of surrogate spiking solution and 10 µL of internal standard spiking solution to each sample. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of sample is equivalent to a concentration of 50 µg/kg of each surrogate standard.

7.5.5.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.6 Perform purge-and-trap or direct injection by Method 5030. If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent

water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.6.1. All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Secs. 7.6.1 and 7.6.2 for qualitative and quantitative analysis.

7.5.7 For matrix spike analysis, add 10 µL of the matrix spike solution (Sec. 5.13) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.6 Data interpretation

7.6.1 Qualitative analysis

7.6.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.6.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of

the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.6.2 Quantitative analysis

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.6.2.2 When MS response is linear and passes through the origin, calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(\overline{RF})(V_o)}$$

where:

A_x	=	Area of characteristic ion for compound being measured.
I_s	=	Amount of internal standard injected (ng).
A_{is}	=	Area of characteristic ion for the internal standard.
$\overline{RF}$	=	Mean relative response factor for compound being measured.
V_o	=	Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF})(V_i)(W_s)(D)}$$

where:

A_x, I_s, A_{is}, $\overline{RF}$, = Same as for water.

V_t	=	Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).
V_i	=	Volume of extract added (μL) for purging.
W_s	=	Weight of sample extracted or purged (g).
D	=	% dry weight of sample/100, or 1 for a wet-weight basis.

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration

obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Alternatively, the regression line fitted to the initial calibration (Sec. 7.3.6.1) may be used for determination of analyte concentration.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for general quality control procedures.

8.2 Additional required instrument QC is found in the Secs. 7.3 and 7.4:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications.

8.2.2 There must be an initial calibration of the GC/MS system

8.2.3 The GC/MS system must meet the SPCC criteria and the CCC criteria, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L or less in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.3.2 Prepare a QC reference sample to contain 20 µg/L or less of each analyte by adding 200 µL of QC reference sample concentrate to 100 mL of organic-free reagent water.

8.3.3 Four 5-mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Sec. 7.5.1.

8.3.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte using the four results.

8.3.5 Tables 7 and 8 provide single laboratory recovery and precision data obtained for the method analytes from water. Similar results from dosed water should be expected by any experienced laboratory. Compare s and $\bar{x}$ (Sec. 8.3.4) for each analyte to the single laboratory recovery and precision data. Results are comparable if the calculated standard deviation of the recovery does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater, and the mean recovery lies within the interval $\bar{x} \pm 3s$ or $\bar{x} \pm 30\%$, whichever is greater.

NOTE: The large number of analytes in Tables 7 and 8 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.3.6 When one or more of the analytes tested are not comparable to the data in Table 6 or 7, the analyst must proceed according to Sec. 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Sec. 8.3.2.

8.3.6.2 Beginning with Sec. 8.3.2, repeat the test only for those analytes that are not comparable. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Sec. 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 8.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 μg/L. Single laboratory accuracy and precision data are

presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection has been used for the analysis of waste motor oil samples using a wide-bore column. The accuracy and precision data for these compounds are presented in Table 10.

10.0 REFERENCES

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TABLE 1.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	15.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[c] Column 2' - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10°/min, program to 120°C at 5°/min, then program to 180°C at 8°/min.

[d] MDL based on a 25 mL sample volume.

TABLE 2.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.06
Chloroethane	1.45	0.02
Trichlorofluoromethane	1.77	0.07
1,1-Dichloroethene	2.33	0.05
Methylene chloride	2.66	0.09
trans-1,2-Dichloroethene	3.54	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10

TABLE 2.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (µg/L)
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25 mL sample volume.

TABLE 3.
ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

	Estimated Quantitation Limits (All Analytes in Table 1)	
	Ground water µg/L	Low Soil/Sediment[b] µg/kg
Purging 5 mL of water	5	--
Purging 25 mL of water	1	--
Soil/Sediment	-	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL is selected from the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[c]EQL = [EQL for low soil/sediment (see Table 3)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4.
BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)[a]

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

[a] Alternate tuning criteria may be used (e.g. CLP, Method 524.2, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 5.
CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	41, 40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	57, 58, 39
Allyl chloride	76	76, 41, 39, 78
Benzene	78	-
Benzyl chloride	91	91, 126, 65, 128
Bromoacetone	136	43, 136, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43, 72
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64(49*)	66(51*)
2-Chloroethanol	49	49, 44, 43, 51, 80
bis-(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50(49*)	52(51*)
Chloroprene	53	53, 88, 90, 51
3-Chloropropionitrile	54	54, 49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150

TABLE 5.(continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	75, 53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	79, 43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	55, 57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	88, 58, 43, 57
Epichlorohydrin	57	57, 49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	44, 43, 42
Ethyl methacrylate	69	69, 41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	44, 43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	43, 41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	66, 39, 65, 38
Methacrylonitrile	41	41, 67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	142, 127, 141
Methyl methacrylate	69	69, 41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77

TABLE 5.(continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
2-Nitropropane	46	-
2-Picoline	93	93, 66, 92, 78
Pentachloroethane	167	167, 130, 132, 165, 169
Propargyl alcohol	55	55, 39, 38, 53
β-Propiolactone	42	42, 43, 44
Propionitrile (ethyl cyanide)	54	54, 52, 55, 40
n-Propylamine	59	59, 41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* - characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed)

TABLE 6.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN

Analyte	Conc. Range, µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery[b]	Percent RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2

TABLE 6.
(Continued)

Analyte	Conc. Range, µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery[b]	Percent RSD
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR
VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED
WITH A NARROW-BORE CAPILLARY COLUMN

Analyte	Conc. µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery	Percent RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.7	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3
n-Propylbenzene	0.5	7	99	6.6	6.7

TABLE 7.
(Continued)

Analyte	Conc. µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery	Percent RSD
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Percent Recovery Low/High Water	Percent Recovery Low/High Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9.
QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF
HIGH-CONCENTRATION SAMPLES

Approximate Concentration Range	Volume of Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10
DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Cl_3F_3ethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation
Data are taken from Reference 9.

FIGURE 1.
PURGING DEVICE

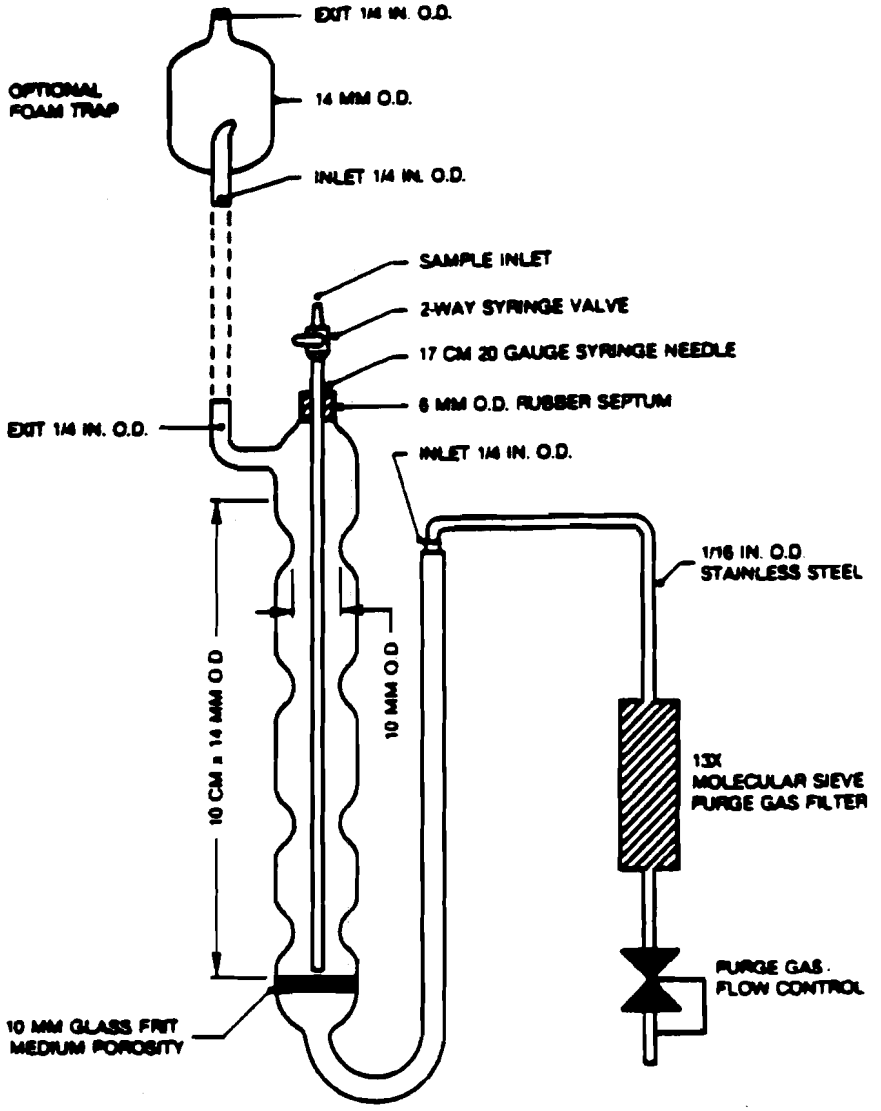


FIGURE 2.
TRAP PACKING AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

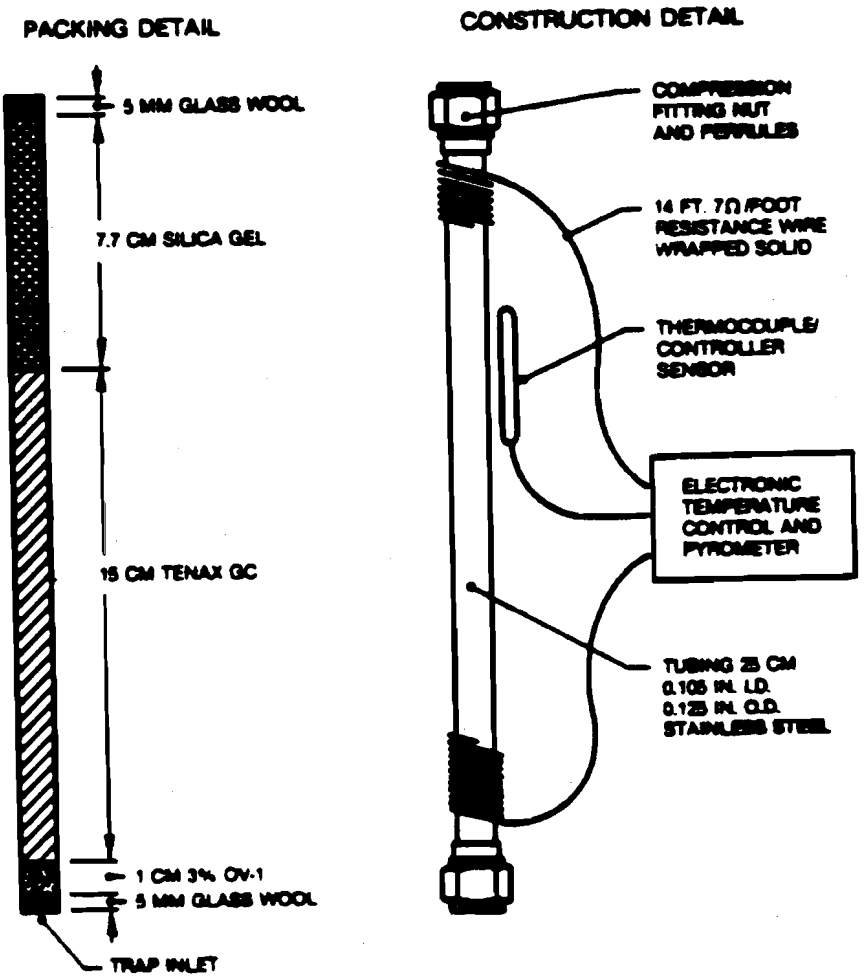


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE

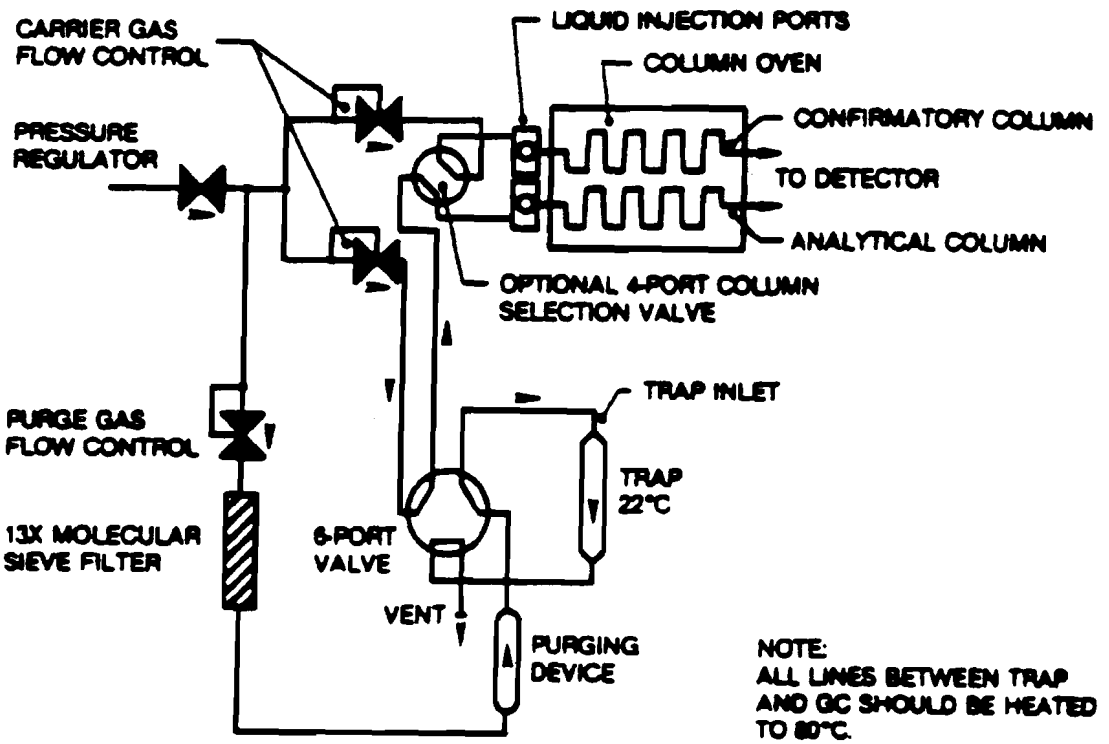


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

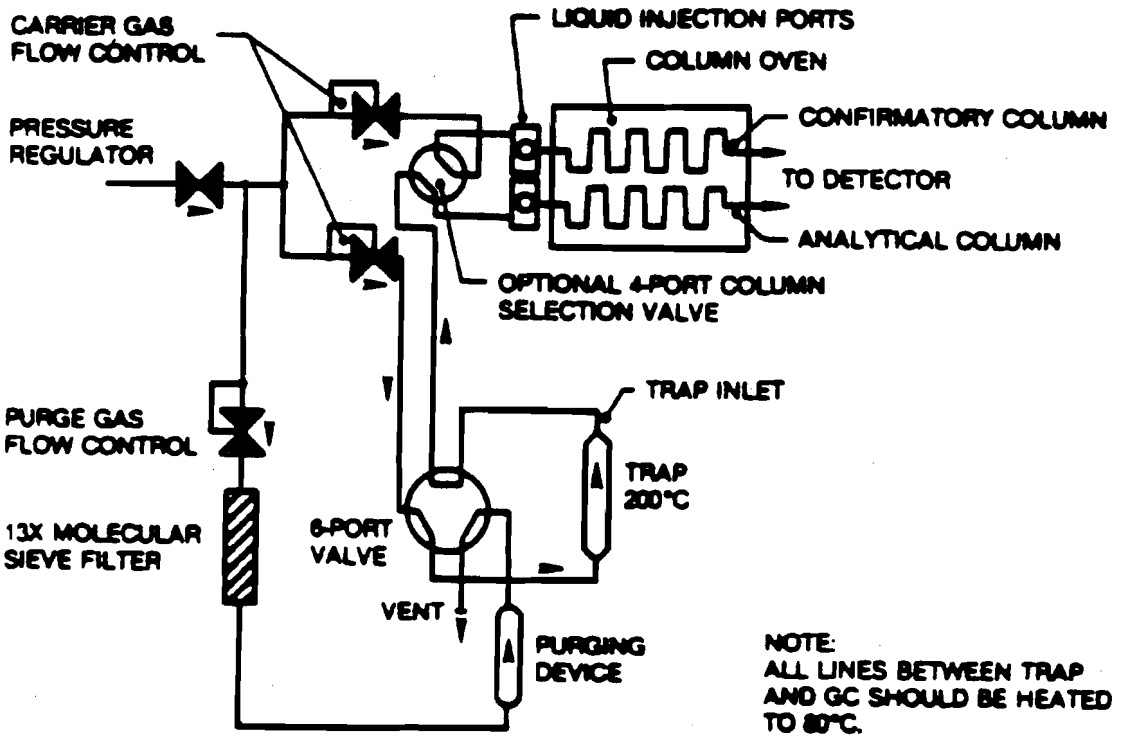


FIGURE 5.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

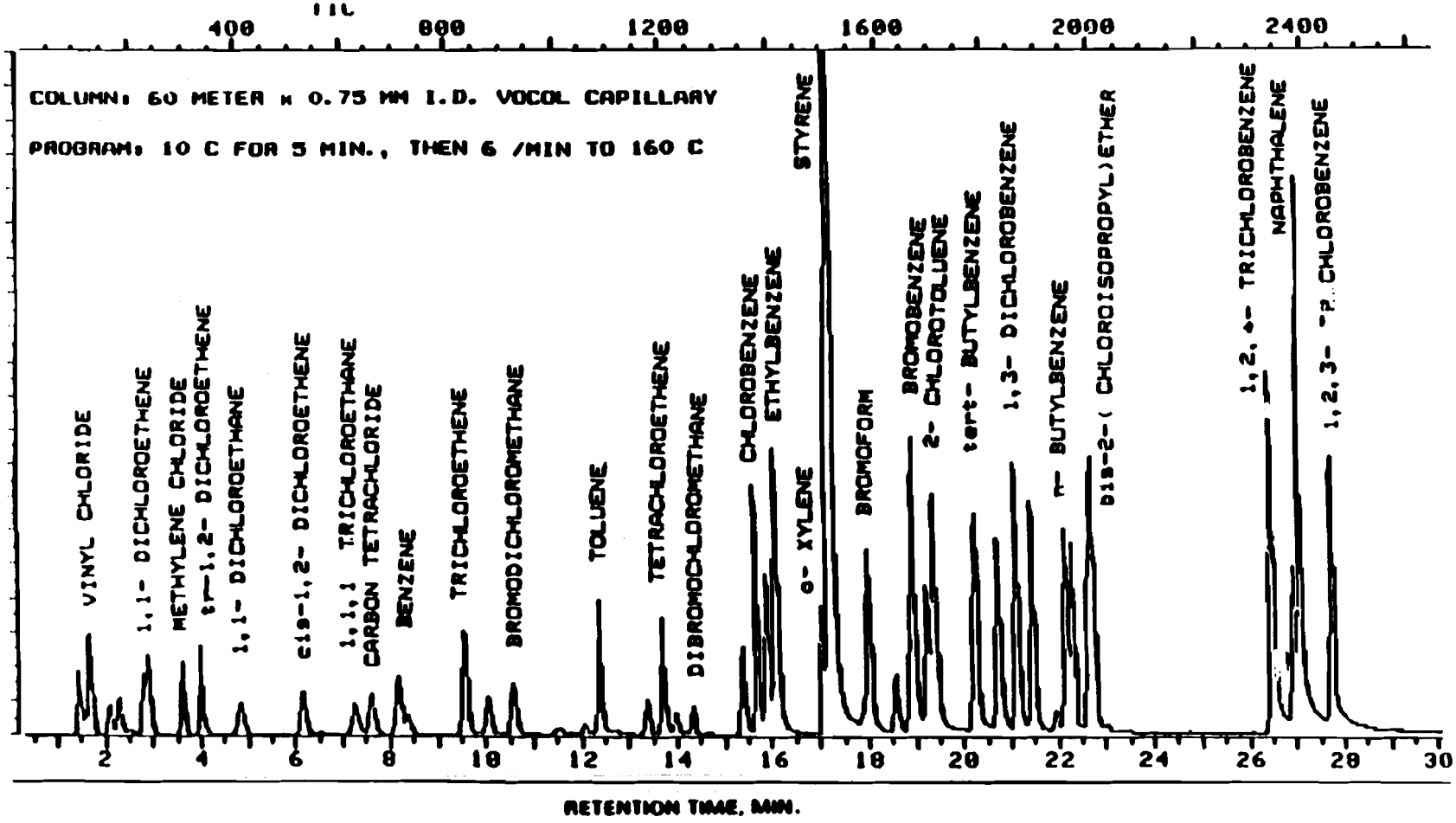


FIGURE 6.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

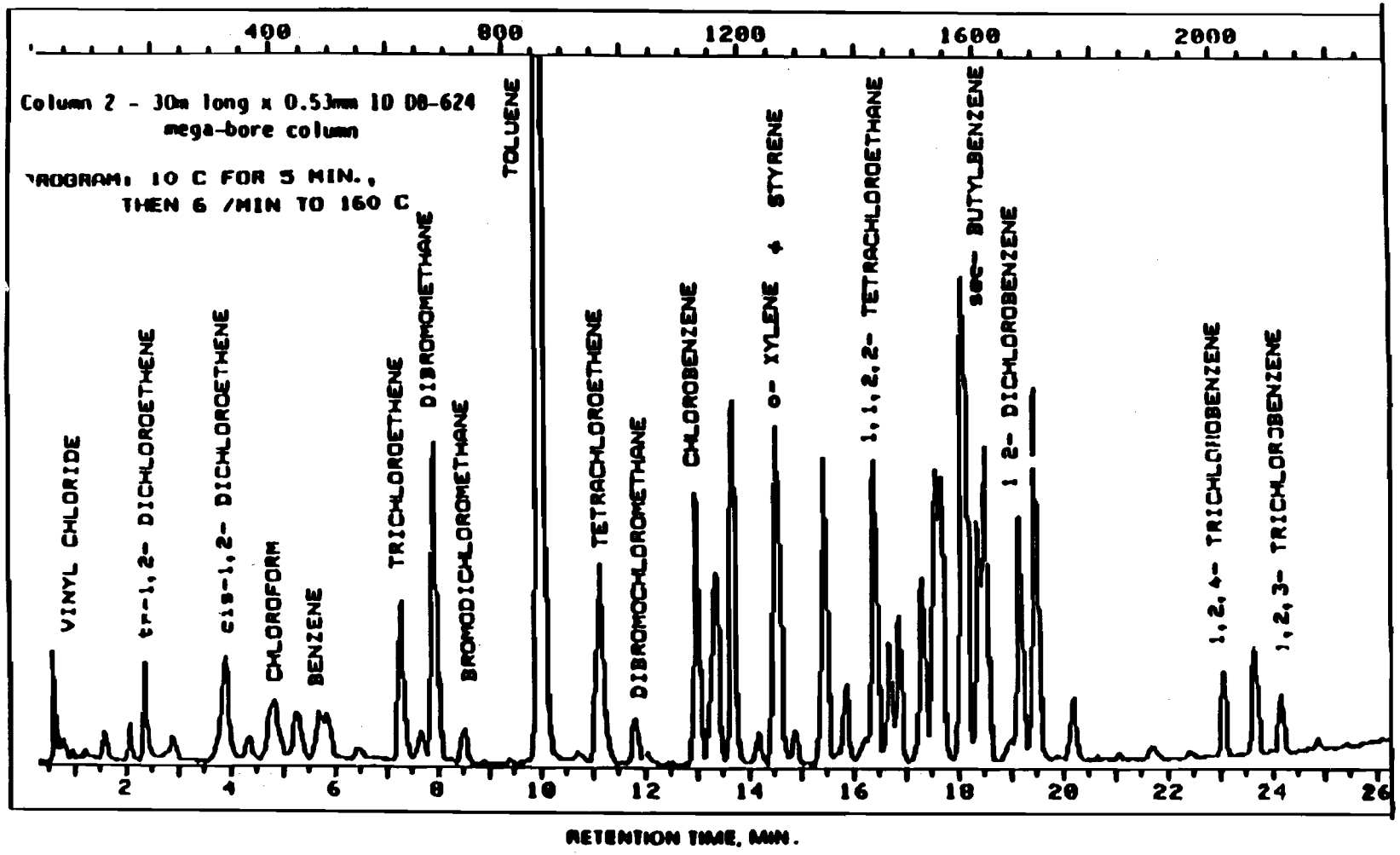


FIGURE 7.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

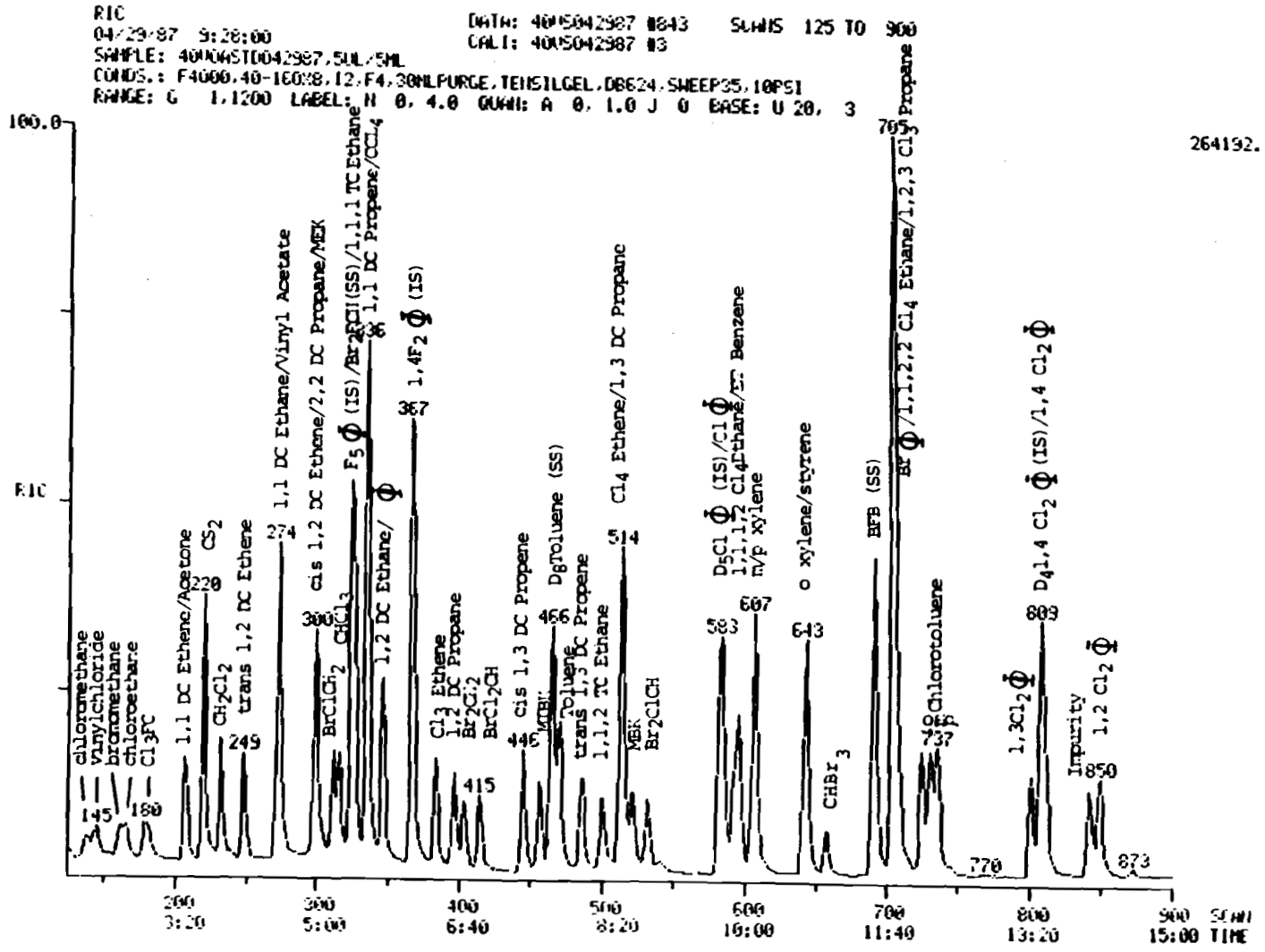
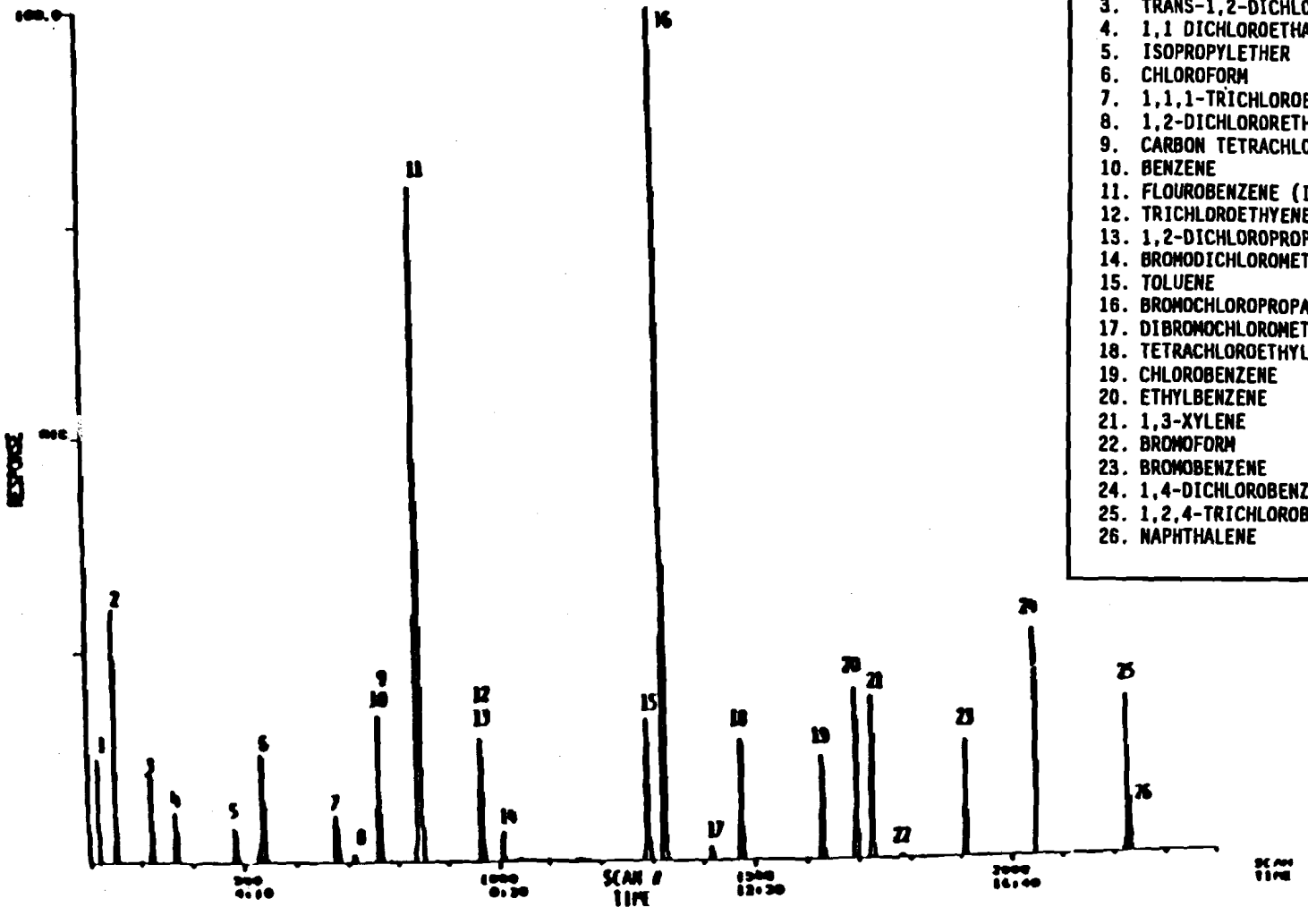


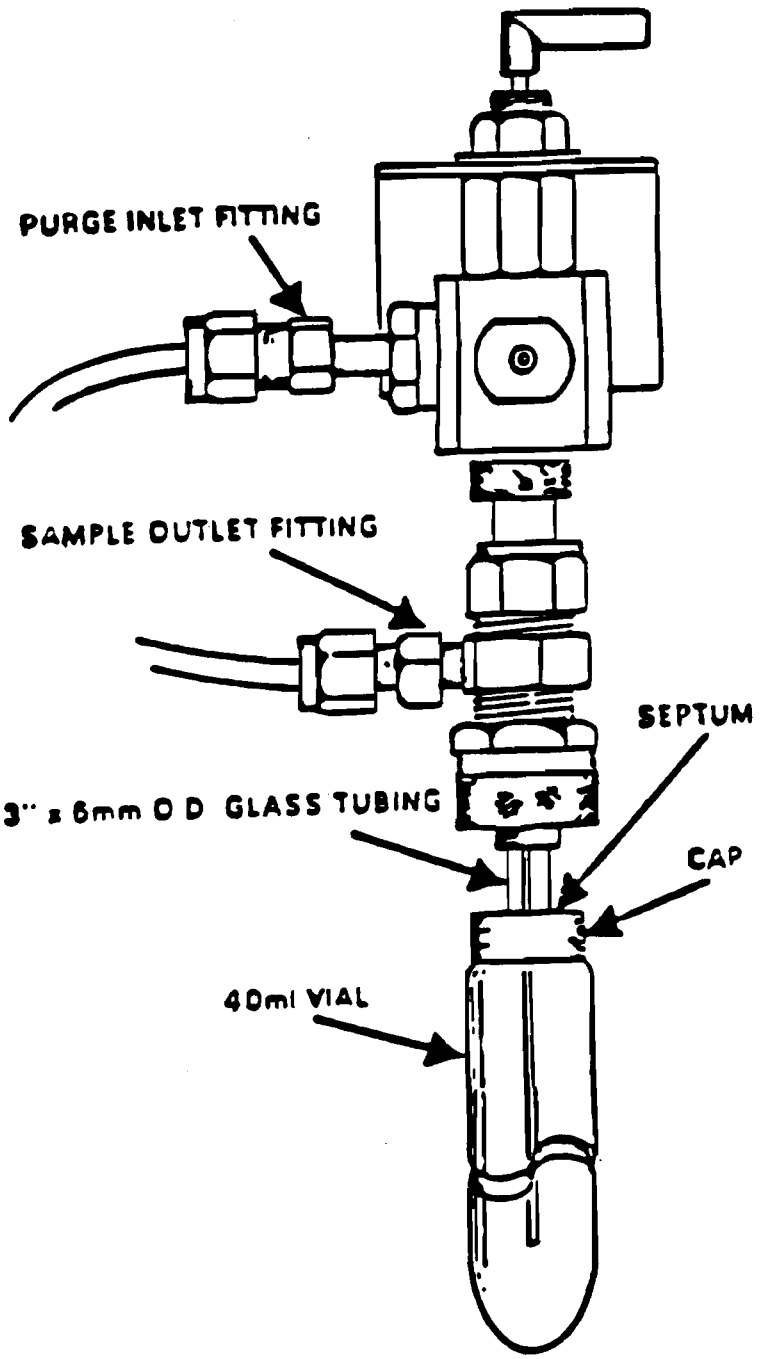
FIGURE 8.
GAS CHROMATOGRAM OF TEST MIXTURE

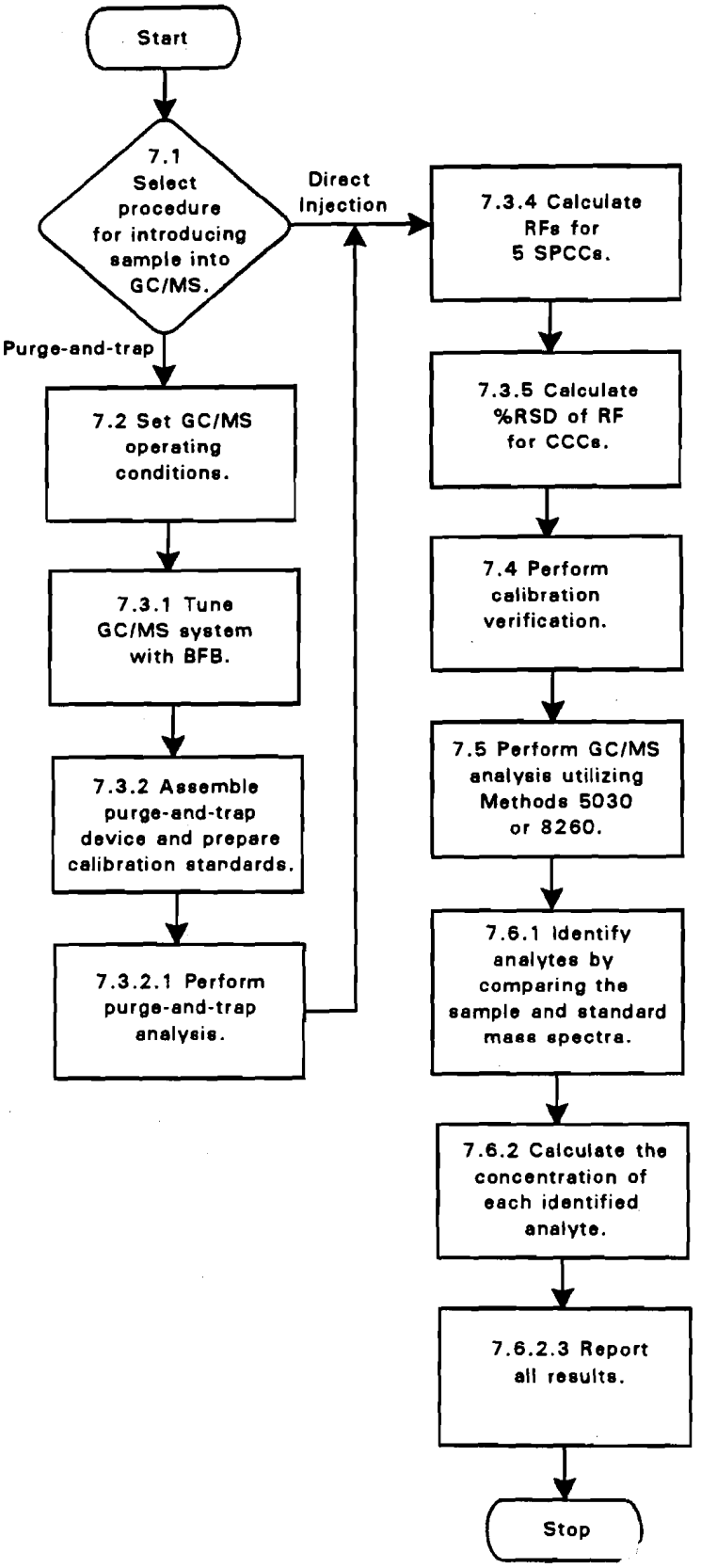


0.5 g/L PER COMPOUND

1. 1,1-DICHLOROETHYLENE
2. METHYLENE CHLORIDE
3. TRANS-1,2-DICHLOROETHYLENE
4. 1,1 DICHLOROETHANE
5. ISOPROPYLETHER
6. CHLOROFORM
7. 1,1,1-TRICHLOROETHANE
8. 1,2-DICHLORORETHYLENE
9. CARBON TETRACHLORIDE
10. BENZENE
11. FLOUROBENZENE (INT. STD.)
12. TRICHLOROETHYENE
13. 1,2-DICHLOROPROPANE
14. BROMODICHLOROMETHANE
15. TOLUENE
16. BROMOCHLOROPROPANE INT. STD.)
17. DIBROMOCHLOROMETHANE
18. TETRACHLOROETHYLENE
19. CHLOROBENZENE
20. ETHYLBENZENE
21. 1,3-XYLENE
22. BROMOFORM
23. BROMOBENZENE
24. 1,4-DICHLOROBENZENE
25. 1,2,4-TRICHLOROBENZENE
26. NAPHTHALENE

FIGURE 9.
LOW SOILS IMPINGER




Start
7.1 Select procedure for introducing sample into GC/MS.
Direct Injection
Purge-and-trap
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.2.1 Perform purge-and-trap analysis.
7.3.4 Calculate RFs for 5 SPCCs.
7.3.5 Calculate %RSD of RF for CCCs.
7.4 Perform calibration verification.
7.5 Perform GC/MS analysis utilizing Methods 5030 or 8260.
7.6.1 Identify analytes by comparing the sample and standard mass spectra.
7.6.2 Calculate the concentration of each identified analyte.
7.6.2.3 Report all results.
Stop

METHOD 8270B

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		Appropriate Preparation Techniques				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (I.S.)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor - 1016	12674-11-2	X	X	X	X	X
Aroclor - 1221	11104-28-2	X	X	X	X	X
Aroclor - 1232	11141-16-5	X	X	X	X	X
Aroclor - 1242	53469-21-9	X	X	X	X	X
Aroclor - 1248	12672-29-6	X	X	X	X	X
Aroclor - 1254	11097-69-1	X	X	X	X	X
Aroclor - 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540/ 3541	3550	3580
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
2-sec-Butyl-4,6-dinitrophenol	88-85-7	X	ND	ND	ND	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (I.S.)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4′-DDD	72-54-8	X	X	X	X	X
4,4′-DDE	72-55-9	X	X	X	X	X
4,4′-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC,OE(42)	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540/ 3541	3550	3580
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (I.S)		X	X	X	X	X
3,3′-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,OS(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3′-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3′-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540/ 3541	3550	3580
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Ethyl parathion	56-38-2	X	X	ND	ND	ND
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr.)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr.)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540/ 3541	3550	3580
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
2-Methyl-5-nitroaniline	99-55-8	X	X	ND	ND	ND
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
2-Methylpyridine	109-06-8	X	X	ND	ND	ND
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (I.S.)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr.)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	ND	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodibutylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	ND	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540/ 3541	3550	3580
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (I.S.)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (I.S.)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr.)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	60-41-3	AW,OS(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d_{14}(surr.)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr.)		X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540/ 3541	3550	3580
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
0,0,0-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

a Chemical Abstract Service Registry Number.

AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

1.2 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol,

4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and for their qualitative and quantitative analysis by mass spectrometry.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 μm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 μL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.1.6 Guard column (optional) (J&W Deactivated Fused Silica, 0.25 mm ID x 6 m, or equivalent) between the injection port and the analytical column joined with column joiners (Hewlett Packard No. 5062-3556, or equivalent).

4.2 Syringe - 10 μL.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

4.4 Balance - Analytical, 0.0001 g.

4.5 Bottles - glass with Teflon-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at -10°C to -20°C or less and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met. Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at -10°C to -20°C or less when not being used.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at -10°C to -20°C or less when not being used.

5.6 Calibration standards - A minimum of five calibration standards should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Each 1 mL aliquot of calibration standard should

be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C or less, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.7 Surrogate standards - The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.8 Matrix spike standards - See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all matrix spikes. Take into account all dilutions of sample extracts.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - Pesticide quality or equivalent

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3541, 3550
Waste	3540, 3541, 3550, 3580

7.1.1 Direct injection - In very limited applications direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a] Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration - The recommended GC/MS operating conditions:

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene has eluted
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Sample volume:	1-2 μL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec

(Split injection is allowed if the sensitivity of the mass spectrometer is sufficient).

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50 ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. (See Sec. 8.3.1 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column. The use of a guard column (Sec. 4.1.6) between the injection port and the analytical column may help prolong analytical column performance.

7.3.2 The internal standards selected in Sec. 5.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation).

7.3.3 Analyze 1 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x	=	Area of the characteristic ion for the compound being measured.
A_{is}	=	Area of the characteristic ion for the specific internal standard.
C_{is}	=	Concentration of the specific internal standard (ng/μL).
C_x	=	Concentration of the compound being measured (ng/μL).

7.3.4 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine;hexachlorocyclopentadiene;2,4-dinitro-phenol; and 4-nitrophenol. The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.1 The percent relative standard deviation (%RSD) should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RSD	=	relative standard deviation.
$\overline{RF}$	=	mean of 5 initial RFs for a compound.
SD	=	standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N - 1}}$$

where:

RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

7.3.4.2 If the %RSD of any CCC is 30% or greater, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with section 7.3.

7.3.5 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.5.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Sec. 7.6.2.2 and 7.6.2.3). The use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.4 Daily GC/MS calibration

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12 hour shift.

7.4.2 A calibration standard(s) at mid-concentration containing all semivolatile analytes, including all required surrogates, must be analyzed every 12 hours during analysis. Compare the instrument response factor from the standards every 12 hours with the SPCC (Sec. 7.4.3) and CCC (Sec. 7.4.4) criteria.

7.4.3 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour shift. For each SPCC compound in the daily calibration a minimum response factor of 0.050 must be obtained. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column,

and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration.

Calculate the percent drift using:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins. If the CCCs are not analytes required by the permit, then all required analytes must meet the 20% drift criterion.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last calibration check (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration check standard, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1 mL extract obtained from sample preparation with 10 μL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1 mL extract by GC/MS using a 30 m x 0.25 mm (or 0.32 mm) silicone-coated fused-silica capillary column. The volume to be injected should ideally contain 100 ng of base/neutral and 200 ng of acid

surrogates (for a 1 μL injection). The recommended GC/MS operating conditions to be used are specified in Sec. 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/μL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Sec. 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

7.6 Data interpretation

7.6.1 Qualitative analysis

7.6.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.6.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.6.2 Quantitative analysis

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion.

7.6.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.4.5.2) and the following equation:.

$$C_{ex}\ (mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times \overline{RF})}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in Sec. 7.4.3.

7.6.2.3 Alternatively, the regression line fitted to the initial calibration (Sec. 7.3.5.1) may be used for determination of the extract concentration.

7.6.2.4 Compute the concentration of the analyte in the sample using the equations in Secs. 7.6.2.4.1 and 7.6.2.4.2.

7.6.2.4.1 The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid } (\mu g/L) = \frac{(C_{ex} \times V_{ex})}{V_o}$$

where:

V_{ex} = extract volume, in mL
V_o = volume of liquid extracted, in L.

7.6.2.4.2 The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid } (\mu g/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:

V_{ex} = extract volume, in mL
W_s = sample weight, in kg.

7.6.2.5 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae

given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.6 Quantitation of multicomponent compounds (e.g. Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8081.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample (Sec. 8.5.1) must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following sections

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Secs. 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Sec. 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Sec. 7.4.3 and the CCC criteria in Sec. 7.4.4, each 12 hours.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) reference sample concentrate is required containing each base/neutral analyte at a concentration of 100 mg/L and each acid analyte at a concentration of 200 mg/L in acetone or methanol. (See Sec. 5.5.1 of Method 3500 for minimum requirements.) The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Using a pipet, prepare QC reference samples at a concentration of 100 µg/L by adding 1.00 mL of QC reference sample concentrate to each of four 1-L aliquots of water.

8.5.3 Analyze the well-mixed QC reference samples according to the method beginning in Sec. 7.1 with extraction of the samples.

8.5.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte of interest using the four results.

8.5.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{x}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Sec. 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Sec. 8.5.2.

8.5.6.2 Beginning with Sec. 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Sec. 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a method blank, a matrix spike, and a replicate for each analytical batch (up to a maximum of 20

samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of matrix spiked samples. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be at 100 µg/L or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger. For other matrices, recommended spiking concentration is 20 times the EQL.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g. maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L. For other matrices, recommended spiking concentration is 20 times the EQL.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Sec. 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Sec. 8.7.

8.7 If any analyte in a sample fails the acceptance criteria for recovery in Sec. 8.6, a QC reference sample containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference sample will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Sec. 8.6, the probability that the analysis of a QC reference sample will be required is high. In this case, the QC reference sample should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 1.0 mL of the QC reference sample concentrate (Sec. 8.5.1 or 8.6.2) to 1 L of water. The QC reference sample needs only to contain the analytes that failed criteria in the test in Sec. 8.6.

8.7.2 Analyze the QC reference sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Sec. 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Sec. 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 The following procedure should be performed to determine acceptable accuracy and precision limits for surrogate standards.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory-established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance-based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Sec. 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially

independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 9.

9.3 Method performance data (using Method 3541 Automated Soxhlet extraction) are presented in Table 10. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hr prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 11 and were taken from Reference 9.

10.0 REFERENCES

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4. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

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9. Lopez-Avila, V. (W. Beckert, Project Officer); "Development of a Soxtec Extraction Procedure for Extraction of Organic Compounds from Soils and Sediments"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Las Vegas, NV, October 1991; EPA 600/X-91/140.

TABLE 1.
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d_4 (I.S.)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,88,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	62,44,45,74
Thiophenol (Benzenethiol)	7.42	110	110,66,109,84
Methyl methanesulfonate	7.48	80	80,79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	54,98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	102,42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,108,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	110,79,95,109,140
Ethyl methanesulfonate	9.62	79	79,109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d_8 (I.S.)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	99,155,127,81,109
Diethyl sulfate	11.37	139	139,45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	107,108,77,79,90
Hexachloropropene	12.45	213	213,211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272
N-Nitrosopyrrolidine	12.65	100	100,41,42,68,69
Acetophenone	12.67	105	71,105,51,120
4-Methylphenol	12.82	107	107,108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	106,107,77,51,79
3-Methylphenol	12.93	107	107,108,77,79,90

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,114,55,56,41
1,4-Phenylenediamine	13.62	108	108,80,53,54,52
1-Chloronaphthalene	13.65[a]	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	106,141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	104,76,50,148
o-Anisidine	15.00	108	80,108,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d_{10} (I.S.)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	162,164,126,98,63
4-Chloroaniline	15.50	127	127,129,65,92
Isosafrole	15.60	162	162,131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	121,122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	158,104,102,76,50,130
p-Cresidine	16.45	122	122,94,137,77,93
Dichlorovos	16.48	109	109,185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	120,135,134,91,77
N-Nitrosodibutylamine	16.73	84	84,57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	110,81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	110,81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	162,162,104,77,103,135
Hexamethyl phosphoramide	17.33	135	135,44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	92,127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	216,214,179,108,143,218
1-Naphthylamine	18.20	143	143,115,89,63
1-Acetyl-2-thiourea	18.22	118	43,118,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	174,145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	196,198,97,132,99
Hexachlorobenzene	18.65	284	142,249

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Nicotine	18.70	84	84,133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,152,79,106,94
Thionazine	19.35	107	96,107,97,143,79,68
4-Nitroaniline	19.37	138	138,65,108,92,80,39
Phenanthrene-d_{10}(i.s.)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	168,75,50,76,92,122
Mevinphos	19.90	127	127,192,109,67,164
Naled	20.03	109	109,145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	168,76,50,75,92,122
Diallate (cis or trans)	20.57	86	86,234,43,70
1,2-Dinitrobenzene	20.58	168	168,50,63,74
Diallate (trans or cis)	20.78	86	86,234,43,70
Pentachlorobenzene	21.35	250	250,252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	168,79,52,138,153,77
Pentachloronitrobenzene	21.72	237	237,142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	174,101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	232,131,230,166,234,168
Dihydrosaffrole	22.42	135	135,64,77
Demeton-O	22.72	88	88,89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	75,74,213,120,91,63
Dicrotophos	23.82	127	127,67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	306,43,264,41,290
Bromoxynil	23.90	277	277,279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	127,192,67,97,109
Phorate	24.10	75	75,121,97,93,260
Sulfallate	24.23	188	188,88,72,60,44
Demeton-S	24.30	88	88,60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	87,93,125,143,229
Phenobarbital	24.70	204	204,117,232,146,161
Carbofuran	24.90	164	164,149,131,122
Octamethyl pyrophosphoramide	24.95	135	135,44,199,286,153,243
4-Aminobiphenyl	25.08	169	169,168,170,115
Dioxathion	25.25	97	97,125,270,153
Terbufos	25.35	231	231,57,97,153,103
α,α-Dimethylphenylamine	25.43	58	58,91,65,134,42
Pronamide	25.48	173	173,175,145,109,147
Aminoazobenzene	25.72	197	92,197,120,65,77
Dichlone	25.77	191	191,163,226,228,135,193

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Dinoseb	25.83	211	211,163,147,117,240
Disulfoton	25.83	88	88,97,89,142,186
Fluchloralin	25.88	306	306,63,326,328,264,65
Mexacarbate	26.02	165	165,150,134,164,222
4,4′-Oxydianiline	26.08	200	200,108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	199,152,141,169,151
Phosphamidon	26.85	127	127,264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	231,185,41,193,266
Methyl parathion	27.03	109	109,125,263,79,93
Carbaryl	27.17	144	144,115,116,201
Dimethylaminoazobenzene	27.50	225	225,120,77,105,148,42
Propylthiouracil	27.68	170	170,142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d_{12} (I.S.)	27.88	240	120,236
3,3′-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	173,125,127,93,158
Kepone	28.18	272	272,274,237,178,143,270
Fenthion	28.37	278	278,125,109,169,153
Parathion	28.40	109	109,97,291,139,155
Anilazine	28.47	239	239,241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3′-Dimethylbenzidine	28.55	212	212,106,196,180
Carbophenothion	28.58	157	157,97,121,342,159,199
5-Nitroacenaphthene	28.73	199	199,152,169,141,115
Methapyrilene	28.77	97	97,50,191,71
Isodrin	28.95	193	193,66,195,263,265,147
Captan	29.47	79	79,149,77,119,117
Chlorfenvinphos	29.53	267	267,269,323,325,295
Crotoxyphos	29.73	127	127,105,193,166
Phosmet	30.03	160	160,77,93,317,76
EPN	30.11	157	157,169,185,141,323
Tetrachlorvinphos	30.27	329	109,329,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	223,167,195
Barban	30.83	222	222,51,87,224,257,153
Aramite	30.92	185	185,191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	283,285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	251,139,253,111,141
Fensulfothion	31.87	293	293,97,308,125,292
Ethion	32.08	231	231,97,153,125,121
Diethylstilbestrol	32.15	268	268,145,107,239,121,159
Famphur	32.67	218	218,125,93,109,217

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Tri-p-tolyl phosphate[b]	32.75	368	368,367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d_{12} (I.S.)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	256,241,239,120
5,5-Diphenylhydantoin	33.40	180	180,104,252,223,209
Captafol	33.47	79	79,77,80,107
Dinocap	33.47	69	69,41,39
Methoxychlor	33.55	227	227,228,152,114,274,212
2-Acetylaminofluorene	33.58	181	181,180,223,152
4,4′-Methylenebis(2-chloroaniline)	34.38	231	231,266,268,140,195
3,3′-Dimethoxybenzidine	34.47	244	244,201,229
3-Methylcholanthrene	35.07	268	268,252,253,126,134,113
Phosalone	35.23	182	182,184,367,121,379
Azinphos-methyl	35.25	160	160,132,93,104,105
Leptophos	35.28	171	171,377,375,77,155,379
Mirex	35.43	272	272,237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,201,119,217,219,199
Dibenz(a,j)acridine	36.40	279	279,280,277,250
Mestranol	36.48	277	277,310,174,147,242
Coumaphos	37.08	362	362,226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	302,151,150,300
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	162,135,105,77
Hexachlorophene	47.98	196	196,198,209,211,406,408
Aldrin	--	66	263,220
Aroclor-1016	--	222	260,292
Aroclor-1221	--	190	224,260
Aroclor-1232	--	190	224,260
Aroclor-1242	--	222	256,292
Aroclor-1248	--	292	362,326
Aroclor-1254	--	292	362,326
Aroclor-1260	--	360	362,394
α-BHC	--	183	181,109
β-BHC	--	181	183,109
δ-BHC	--	183	181,109
γ-BHC (Lindane)	--	183	181,109
4,4′-DDD	--	235	237,165
4,4′-DDE	--	246	248,176
4,4′-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
Endosulfan I	--	195	339,341
Endosulfan II	--	337	339,341

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Endosulfan sulfate	--	272	387,422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d_5 (surr.)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d_6 (surr.)	--	99	42,71
Terphenyl-d_{14} (surr.)	--	244	122,212
2,4,6-Tribromophenol (surr.)	--	330	332,141
Toxaphene	--	159	231,233

I.S. = internal standard.
surr. = surrogate.
[a]Estimated retention times.
[b]Substitute for the non-specific mixture, tricresyl phosphate.

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

Semivolatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3′-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3′-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3′-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodibutylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
Toluene diisocyanate	100	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
0,0,0-Triethyl phosphorothioate	NT	ND

a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.
b EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. These EQLs are based on a 30 g sample and gel permeation chromatography cleanup.
ND = Not determined.
NA = Not applicable.
NT = Not tested.

Other Matrices	Factor[c]
High-concentration soil and sludges by sonicator	7.5
Non-water miscible waste	75

[c]EQL = (EQL for Low Soil/Sediment given above in Table 2) X (Factor).

TABLE 3.
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a] See Reference 3.

[b] Alternate tuning criteria may be used (e.g., CLP, Method 525, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 4.
CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5.
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethylphenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodibutylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr.)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr.) = surrogate

TABLE 5.
(Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluor-anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluor-anthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl-phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	7,12-Dimethylbenz-(a)anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd) pyrene
Pentachlorophenol		3-Methylchol-anthrene
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

TABLE 6.
QC ACCEPTANCE CRITERIA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4′-DDD	100	31.0	D-134.5	D-145
4,4′-DDE	100	32.0	19.2-119.7	4-136
4,4′-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3′-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116

TABLE 6.
(Continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Compound	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Acenaphthene	0.96C+0.19	$0.15\bar{x}-0.12$	$0.21\bar{x}-0.67$
Acenaphthylene	0.89C+0.74	$0.24\bar{x}-1.06$	$0.26\bar{x}-0.54$
Aldrin	0.78C+1.66	$0.27\bar{x}-1.28$	$0.43\bar{x}+1.13$
Anthracene	0.80C+0.68	$0.21\bar{x}-0.32$	$0.27\bar{x}-0.64$
Benz(a)anthracene	0.88C-0.60	$0.15\bar{x}+0.93$	$0.26\bar{x}-0.21$
Chloroethane	0.99C-1.53	$0.14\bar{x}-0.13$	$0.17\bar{x}-0.28$
Benzo(b)fluoranthene	0.93C-1.80	$0.22\bar{x}+0.43$	$0.29\bar{x}+0.96$
Benzo(k)fluoranthene	0.87C-1.56	$0.19\bar{x}+1.03$	$0.35\bar{x}+0.40$
Benzo(a)pyrene	0.90C-0.13	$0.22\bar{x}+0.48$	$0.32\bar{x}+1.35$
Benzo(ghi)perylene	0.98C-0.86	$0.29\bar{x}+2.40$	$0.51\bar{x}-0.44$
Benzyl butyl phthalate	0.66C-1.68	$0.18\bar{x}+0.94$	$0.53\bar{x}+0.92$
β-BHC	0.87C-0.94	$0.20\bar{x}-0.58$	$0.30\bar{x}+1.94$
δ-BHC	0.29C-1.09	$0.34\bar{x}+0.86$	$0.93\bar{x}-0.17$
Bis(2-chloroethyl) ether	0.86C-1.54	$0.35\bar{x}-0.99$	$0.35\bar{x}+0.10$
Bis(2-chloroethoxy)methane	1.12C-5.04	$0.16\bar{x}+1.34$	$0.26\bar{x}+2.01$
Bis(2-chloroisopropyl) ether	1.03C-2.31	$0.24\bar{x}+0.28$	$0.25\bar{x}+1.04$
Bis(2-ethylhexyl) phthalate	0.84C-1.18	$0.26\bar{x}+0.73$	$0.36\bar{x}+0.67$
4-Bromophenyl phenyl ether	0.91C-1.34	$0.13\bar{x}+0.66$	$0.16\bar{x}+0.66$
2-Chloronaphthalene	0.89C+0.01	$0.07\bar{x}+0.52$	$0.13\bar{x}+0.34$
4-Chlorophenyl phenyl ether	0.91C+0.53	$0.20\bar{x}-0.94$	$0.30\bar{x}-0.46$
Chrysene	0.93C-1.00	$0.28\bar{x}+0.13$	$0.33\bar{x}-0.09$
4,4′-DDD	0.56C-0.40	$0.29\bar{x}-0.32$	$0.66\bar{x}-0.96$
4,4′-DDE	0.70C-0.54	$0.26\bar{x}-1.17$	$0.39\bar{x}-1.04$
4,4′-DDT	0.79C-3.28	$0.42\bar{x}+0.19$	$0.65\bar{x}-0.58$
Dibenzo(a,h)anthracene	0.88C+4.72	$0.30\bar{x}+8.51$	$0.59\bar{x}+0.25$
Di-n-butyl phthalate	0.59C+0.71	$0.13\bar{x}+1.16$	$0.39\bar{x}+0.60$
1,2-Dichlorobenzene	0.80C+0.28	$0.20\bar{x}+0.47$	$0.24\bar{x}+0.39$
1,3-Dichlorobenzene	0.86C-0.70	$0.25\bar{x}+0.68$	$0.41\bar{x}+0.11$
1,4-Dichlorobenzene	0.73C-1.47	$0.24\bar{x}+0.23$	$0.29\bar{x}+0.36$
3,3′-Dichlorobenzidine	1.23C-12.65	$0.28\bar{x}+7.33$	$0.47\bar{x}+3.45$
Dieldrin	0.82C-0.16	$0.20\bar{x}-0.16$	$0.26\bar{x}-0.07$
Diethyl phthalate	0.43C+1.00	$0.28\bar{x}+1.44$	$0.52\bar{x}+0.22$
Dimethyl phthalate	0.20C+1.03	$0.54\bar{x}+0.19$	$1.05\bar{x}-0.92$
2,4-Dinitrotoluene	0.92C-4.81	$0.12\bar{x}+1.06$	$0.21\bar{x}+1.50$
2,6-Dinitrotoluene	1.06C-3.60	$0.14\bar{x}+1.26$	$0.19\bar{x}+0.35$
Di-n-octyl phthalate	0.76C-0.79	$0.21\bar{x}+1.19$	$0.37\bar{x}+1.19$
Endosulfan sulfate	0.39C+0.41	$0.12\bar{x}+2.47$	$0.63\bar{x}-1.03$
Endrin aldehyde	0.76C-3.86	$0.18\bar{x}+3.91$	$0.73\bar{x}-0.62$
Fluoranthene	0.81C+1.10	$0.22\bar{x}-0.73$	$0.28\bar{x}-0.60$

TABLE 7.
(Continued)

Compound	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{x}$+1.46	0.50$\bar{x}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{x}$+0.77	0.33$\bar{x}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{x}$-0.41	0.30$\bar{x}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{x}$+0.92	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{x}$+0.68	0.44$\bar{x}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{x}$+3.61	0.43$\bar{x}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{x}$+0.57	0.15$\bar{x}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{x}$+0.06	0.15$\bar{x}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{x}$+0.85	0.21$\bar{x}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{x}$+0.75	0.29$\bar{x}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{x}$+1.46	0.28$\bar{x}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{x}$+1.25	0.21$\bar{x}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{x}$+1.21	0.22$\bar{x}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{x}$+2.36	0.42$\bar{x}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{x}$+42.29	0.26$\bar{x}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{x}$+1.94	0.27$\bar{x}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{x}$+2.57	0.44$\bar{x}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{x}$+3.03	0.30$\bar{x}$+4.33
Phenol	0.43C+1.26	0.26$\bar{x}$+0.73	0.35$\bar{x}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{x}$+2.22	0.22$\bar{x}$+1.81

x′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in μg/L.

S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

TABLE 9.
EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

COMPOUND	PERCENT RECOVERY ON DAY 0		PERCENT RECOVERY ON DAY 7	
	AVG.	RSD	AVG.	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
2-sec-Butyl-4,6-dinitrophenol	99	3	97	6
Ethyl parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
2-Methyl-5-nitroaniline	99	10	93	4
2-Methylpyridine	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data from Reference 8.

TABLE 10.
AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR THE TARGET COMPOUNDS FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION WITH HEXANE-ACETONE (1:1)[a]

	Clay Soil		Topsoil	
Compound name	Average percent recovery	Percent RSD	Average percent recovery	Percent RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, compounds 23, 27, and 28 at 1500 ng/g, compound 3 at 2000 ng/g, and compounds 1 and 2 at 5000 ng/g.

TABLE 11.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound name	Average percent recovery	Percent RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0

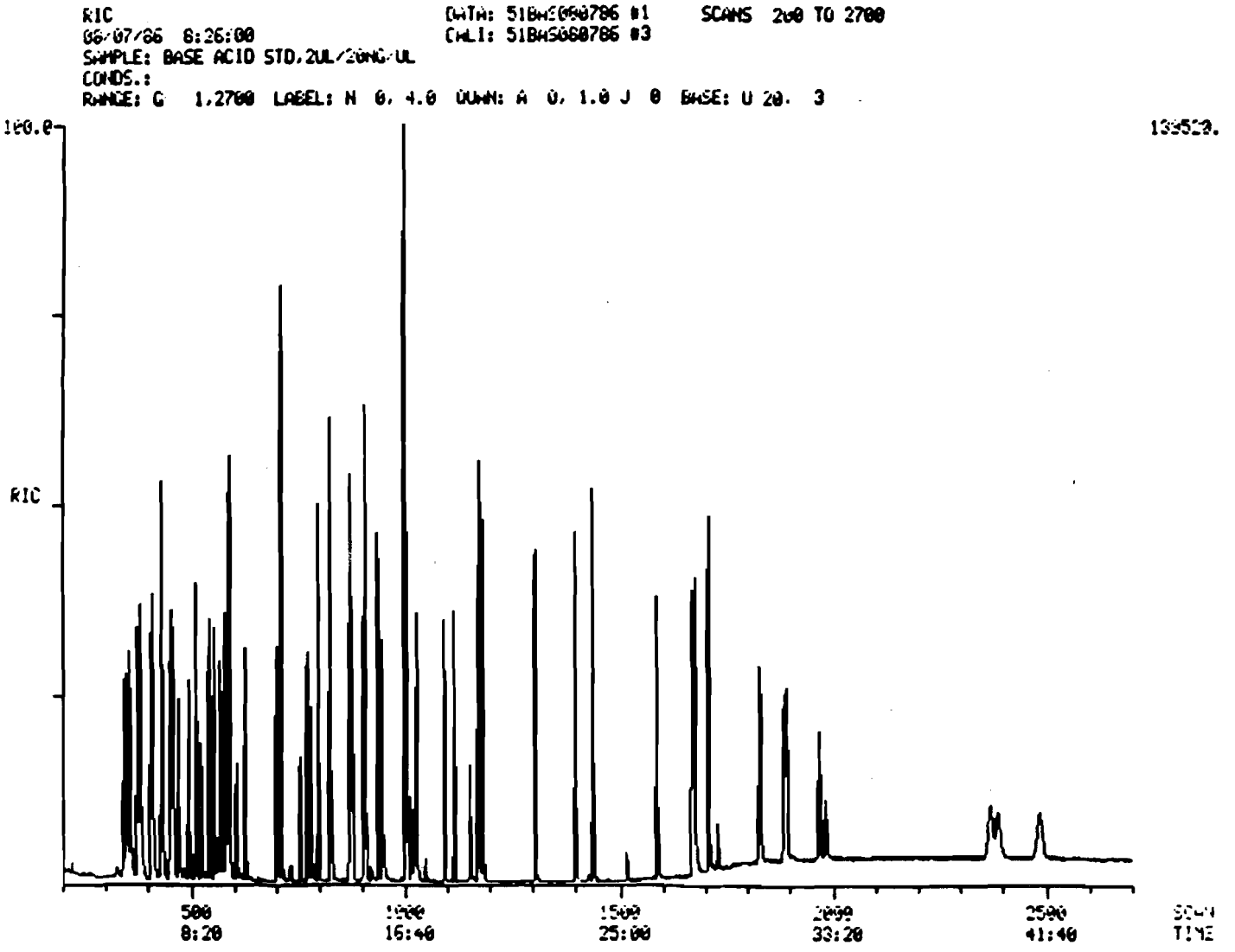
Table 11. (Continued)

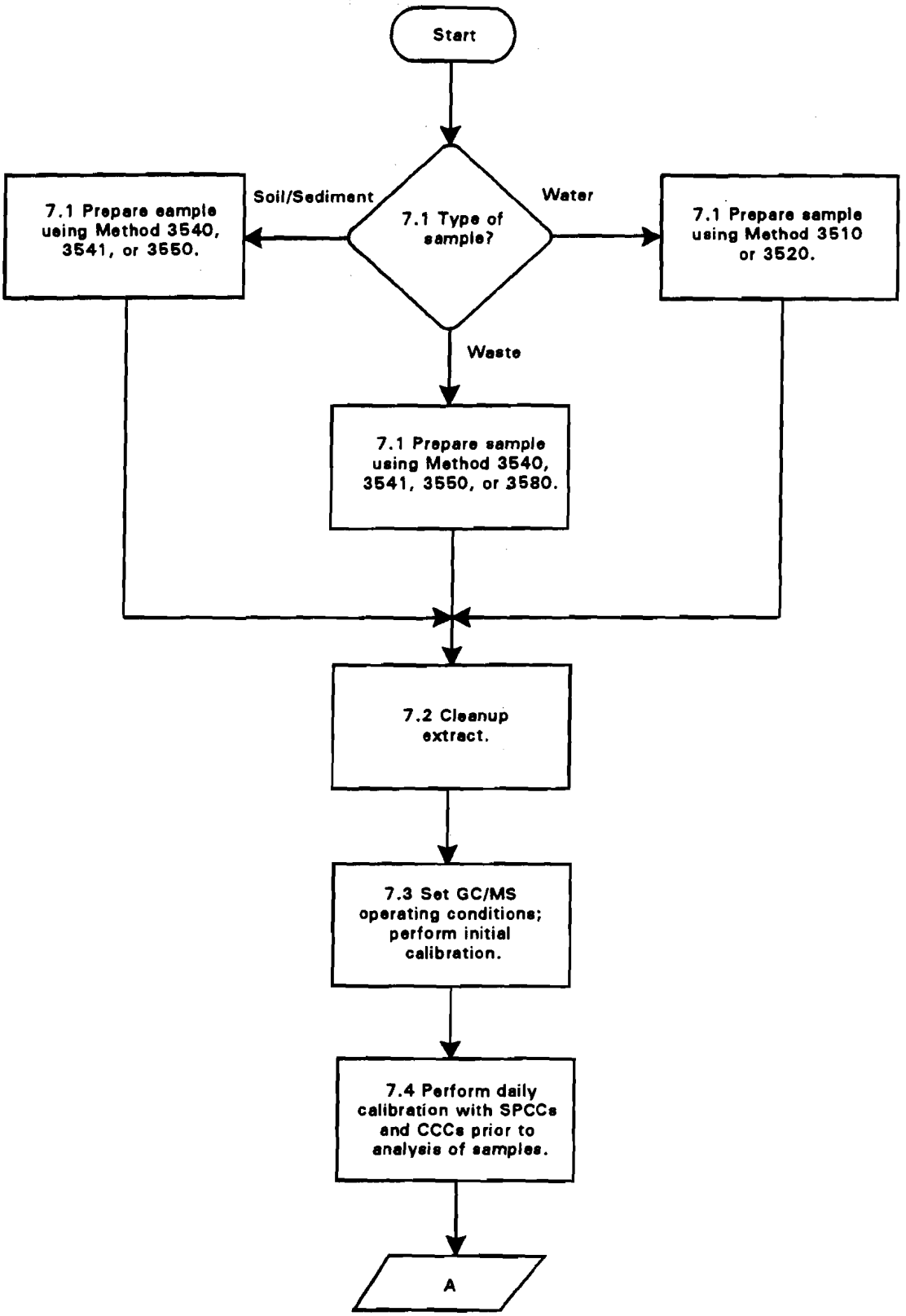
Compound name	Average percent recovery	Percent RSD
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

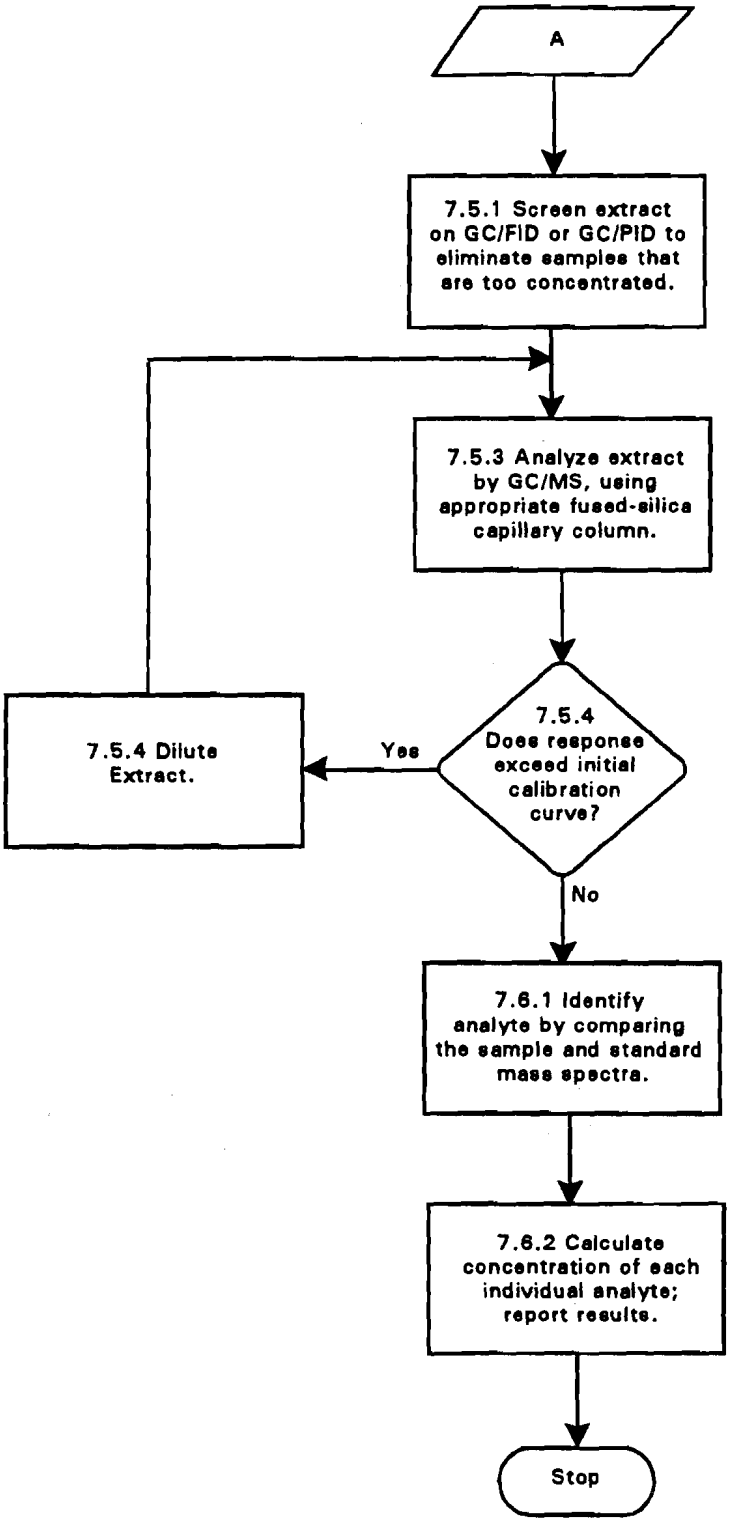
[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 9.

FIGURE 1.
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD




Start
7.1 Type of sample?
Soil/Sediment
Water
Waste
7.1 Prepare sample using Method 3540, 3541, or 3550.
7.1 Prepare sample using Method 3510 or 3520.
7.1 Prepare sample using Method 3540, 3541, 3550, or 3580.
7.2 Cleanup extract.
7.3 Set GC/MS operating conditions; perform initial calibration.
7.4 Perform daily calibration with SPCCs and CCCs prior to analysis of samples.
A


A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate samples that are too concentrated.
7.5.3 Analyze extract by GC/MS, using appropriate fused-silica capillary column.
7.5.4 Does response exceed initial calibration curve?
Yes
7.5.4 Dilute Extract.
No
7.6.1 Identify analyte by comparing the sample and standard mass spectra.
7.6.2 Calculate concentration of each individual analyte; report results.
Stop

METHOD 8280

THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

1.0 SCOPE AND APPLICATION

1.1 This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, ~~reactor residues~~, soil and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent human exposure to them ~~the analyst must take necessary precautions to prevent exposure to himself, or to others, of~~ materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. A laboratory planning to use these compounds should prepare a disposal plan. ~~to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450).~~ Additional safety instructions are outlined in Appendix B.

2.0 SUMMARY OF THE METHOD

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

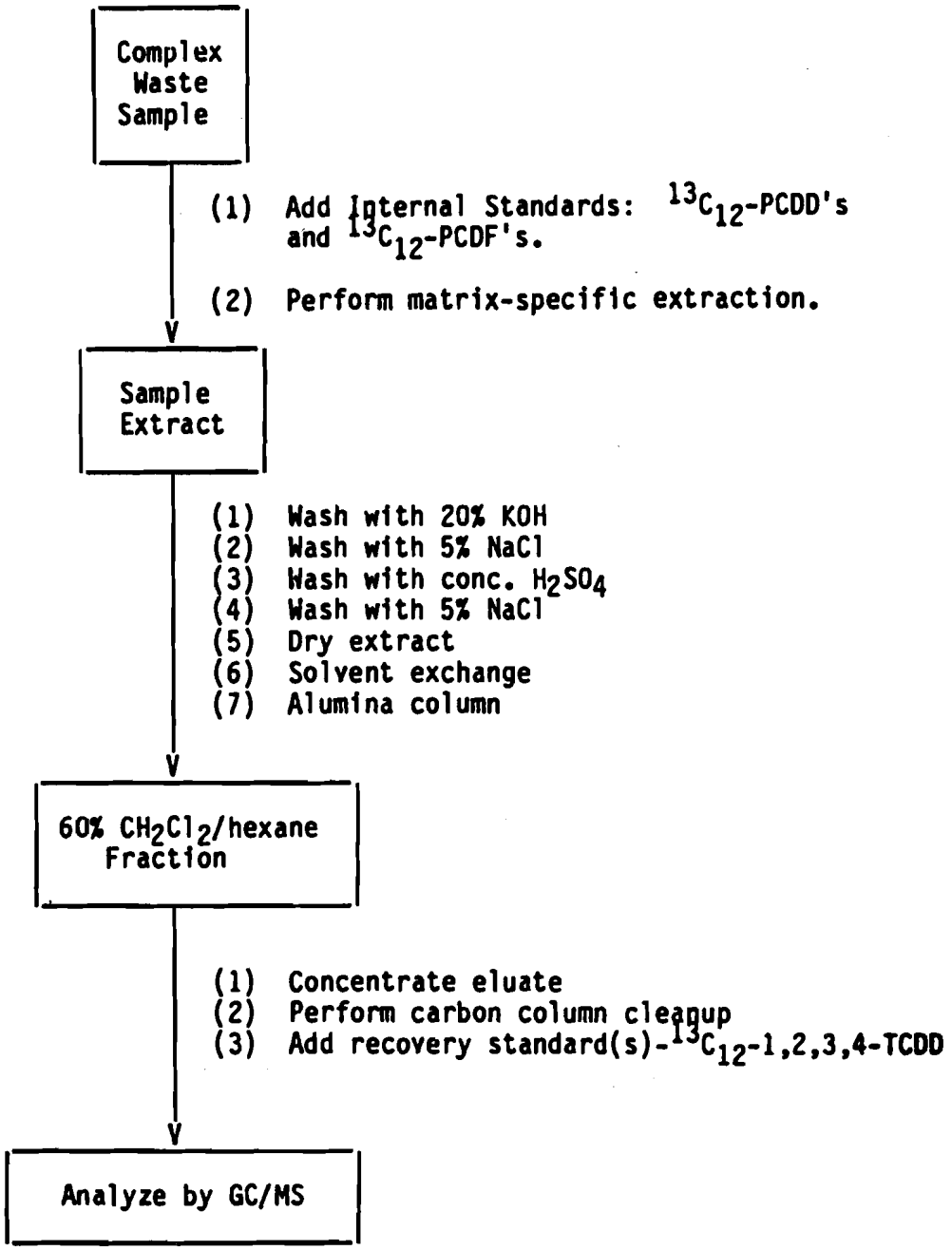


Figure 1. Method 8280 flow chart for sample extraction and cleanup as used for the analysis of PCDD's and PCDF's in complex waste samples.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 6-3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit (Section 11.6) stated in Table 8.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers.

3.5 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling:

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottom.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.3 Gas chromatograph/mass spectrometer data system:

4.3.1 **Gas chromatograph:** An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, three columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 2,3,7,8-TCDD, 1,2,3,4,7 PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50-m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) DB-5 (30-m x 0.25-mm I.D.; 0.25-um film thickness) programmed 170° for 10 minutes, then 170°-320° at 8°/minute, hold at 320°C for 20 minutes; (c) 30-m SP-2250 programmed 70°-320° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) can also provide acceptable separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged, and may provide better separation from certain classes of interferents. Data presented in Figure 2 and Tables 1 to 8 of this Method were obtained using a DB-5 column with temperature programming described in (b) above. However, any capillary column which provides separation of 2,3,7,8-TCDD from all other TCDD isomers equivalent to that specified in Section 6.3 may be used; this separation must be demonstrated and documented using the performance test mixture described in Paragraph 6.3.

4.3.3 **Mass spectrometer:** A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms per m/z. The use of systems not capable of monitoring 11 ions simultaneously will require the analyst to make multiple injections.

4.3.4 **GC/MS interface:** Any GC-to-MS interface that gives an acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (see Paragraphs 6.1.-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.3.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot

is defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance, in any SICP, between specified time or scan number limits.

4.4 Pipets-Disposable, Pasteur, 150-mm long x 5-mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.4.1 Pipet, disposable, serological 10-mL (American Scientific Products No. P4644-10, or equivalent) for preparation of the carbon column specified in Paragraph 4.19.

4.5 Amber glass bottle (500-mL, Teflon-lined screw-cap).

4.6 Reacti-vial 2-mL, amber glass (Pierce Chemical Company). These should be silanized prior to use.

4.7 500-mL Erlenmeyer flask (American Scientific Products Cat. No. f4295 500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125-mL and 2-L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500-mL Kuderna-Danish fitted with a 10-mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300-mm x 10.5-mm glass chromatographic column fitted with Teflon stopcock.

4.13 15-mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen blowdown apparatus (N-Evap (reg. trademark) Analytical Evaporator Model 111, Organomation Associates Inc., Northborough, Massachusetts or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials 2.0-mL (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No. 54, or equivalent). Glass fiber filters or glass wool plugs are also recommended.

4.18 Solvent reservoir (125-mL) Kontes: (special order item) 12.5-cm diameter, compatible with gravity carbon column.

4.19 Carbon column (gravity flow): Prepare carbon/silica gel packing material by mixing 5 percent (by weight) active carbon AX-21 (Anderson Development Co., Adrain, Michigan), pre-washed with methanol and dried in vacuo at 110°C and 95 percent (by weight) Silica gel (Type 60, EM reagent 70 to 230 mesh, CMS No. 393-066) followed by activation of the mixture at 130° for 6 hr. Prepare a 10-mL disposable serological pipet by cutting off each end to achieve a 4-in. column. Fire polish both ends; flare if desired. Insert a glass-wool plug at one end and pack with 1 g of the carbon/silica gel mixture. Cap the packing with a glass-wool plug. (Attach reservoir to column for addition of solvents).

Option: Carbon column (HPLC): A silanized glass HPLC column (10 mm x 7 cm), or equivalent, which contains 1 g of a packing prepared by mixing 5 percent (by weight) active carbon AX-21, (Anderson Development Co., Adrian, Michigan), washed with methanol and dried in vacuo at 110°C, and 95 percent (by weight) 10 um silica (Spherisorb S10W from Phase Separations, Inc., Norwalk, Connecticut). The mixture must then be stirred and sieved through a 38-um screen (U.S. Sieve Designation 400-mesh, American Scientific Products, No. S1212-400, or equivalent) to remove any clumps.[1]

4.20 HPLC pump with loop valve (1.0 mL) injector to be used in the optional carbon column cleanup procedure.

4.21 Dean-Stark trap, 5- or 10-mL with T joints, (Fisher Scientific Company, No. 09-146-5, or equivalent) condenser and 125-mL flask.

4.22 Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915; or equivalent.).

4.23 Roto-evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10; or equivalent.

5.0 REAGENTS

5.1 Potassium hydroxide (ASC): 20 percent (w/v) in distilled water.

5.2 Sulfuric acid (ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tridecane, isooctane, toluene, cyclohexane. Distilled in glass or highest available purity.

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions (50 ppm) are stored in the dark at 4°C, and checked frequently for signs of degradation or evaporation, especially just prior to the preparation of working standards.

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1 The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade): Extracted by manual shaking with several portions of hexane and dried at 100°C.

5.8 Sodium chloride - (analytical reagent), 5 percent (w/v) in distilled water.

6.0 CALIBRATION

6.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, routine calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/mL (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraphs 6.3 and 6.6 is demonstrated and documented.

6.2 Initial calibration:

6.2.1 Prepare multi-level calibration standards[2] keeping one of the recovery standards and the internal standard at fixed concentrations (500 ng/mL). Additional internal standards ($^{13}C_{12}$-OCDD 1,000 ng/mL) are recommended when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Each calibration standard should contain the following compounds:

2,3,7,8-TCDD,		
1,2,3,7,8-PeCDD	or any available	2,3,7,8,X-PeCDD isomer,
1,2,3,4,7,8-HxCDD	or any available	2,3,7,8,X,Y-HxCDD isomer,
1,2,3,4,6,7,8-HpCDD	or any available	2,3,7,8,X,Y,Z-HpCDD isomer,
2,3,7,8-TCDF		
1,2,3,7,8,PeCDF	or any available	2,3,7,8,X-PeCDF isomer,
1,2,3,4,7,8-HxCDF	or any available	2,3,7,8,X,Y,HxCDF isomer,
1,2,3,4,6,7,8-HpCDF	or any available	2,3,7,8,X,Y,Z-HpCDF isomer,

OCDD, OCDF, $^{13}C_{12}$-2,3,7,8-TCDD, $_{13}C_{12}$-1,2,3,4-TCDD and $_{13}C_{12}$-OCDD.

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2 $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper quantification requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution.

Recommended concentration levels for standard analytes are 200, 500, 1,000, 2,000, and 5,000 ng/mL. These values may be adjusted in order to insure that the analyte concentration falls within the calibration range. Two uL injections of calibration standards should be made. However, some GC/MS instruments may require the use of a 1-uL injection volume; if this injection volume is used then all injections of standards, sample extracts and blank extracts must also be made at this injection volume. Calculation of relative response factors is described in Paragraph 11.1.2. Standards must be analyzed using the same solvent as used in the final sample extract. A wider calibration range is useful for higher level samples provided it can be described within the linear range of the method, and the identification criteria defined in Paragraph 10.4 are met. All standards must be stored in an isolated refrigerator at 4°C and protected from light. Calibration standard solutions must be replaced routinely after six months.

6.3 Establish operating parameters for the GC/MS system; the instrument should be tuned to meet the isotopic ratio criteria listed in Table 3 for PCDD's and PCDF's. Once tuning and mass calibration procedures have been completed, a column performance check mixture[3] containing the isomers listed below should be injected into the GC/MS system:

TCDD	1,3,6,8; 1,2,8,9; 2,3,7,8; 1,2,3,4; 1,2,3,7; 1,2,3,9
PeCDD	1,2,4,6,8; 1,2,3,8,9
HxCDD	1,2,3,4,6,9; 1,2,3,4,6,7
HpCDD	1,2,3,4,6,7,8; 1,2,3,4,6,7,9
OCDD	1,2,3,4,6,7,8,9
TCDF	1,3,6,8; 1,2,8,9
PeCDF	1,3,4,6,8; 1,2,3,8,9
HxCDF	1,2,3,4,6,8; 1,2,3,4,8;9
HpCDF	1,2,3,4,6,7,8; 1,2,3,4,7,8,9
OCDF	1,2,3,4,6,7,8,9

Because of the known overlap between the late-eluting tetra-isomers and the early-eluting penta-isomers under certain column conditions, it may be necessary to perform two injections to define the TCDD/TCDF and PeCDD/PeCDF elution windows, respectively. Use of this performance check mixture will enable the following parameters to be checked: (a) the retention windows for each of the homologues, (b) the GC resolution of 2,3,7,8-TCDD and 1,2,3,4-TCDD, and (c) the relative ion abundance criteria listed for PCDD's and PCDF's in Table 3. GC column performance should be checked daily for resolution and peak shape using this check mixture.

The chromatographic peak separation between 2,3,7,8-TCDD and 1,2,3,4-TCDD must be resolved with a valley of $\leq$25 percent, where

Valley Percent = (x/y) (100)

x = ~~measured as in Figure 2~~ height of the valley between 2,3,7,8-TCDD and 1,2,3,4-TCDD using the column performance check mixture

y = the peak height of 2,3,7,8-TCDD

3 Performance check mixtures are available from Brehm Laboratory, Wright State University, Dayton, Ohio.

It is the responsibility of the laboratory to verify the conditions suitable for maximum resolution of 2,3,7,8-TCDD from all other TCDD isomers. The peak representing 2,3,7,8-TCDD should be labeled and identified as such on all chromatograms.

6.4 Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard.

6.5 From injections of the 5 calibration standards, calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described in Paragraph 11.1.2. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

6.6 For each analyte calculate the mean relative response factor (RRF), the standard deviation, and the percent relative standard deviation from triplicate determinations of relative response factors for each calibration standard solution.

6.7 The percent relative standard deviations (based on triplicate analysis) of the relative response factors for each calibration standard solution should not exceed 15 percent. If this condition is not satisfied, remedial action should be taken.

6.8 The Laboratory must not proceed with analysis of samples before determining and documenting acceptable calibration with the criteria specified in Paragraphs 6.3 and 6.7.

6.9 <u>Routine calibration:</u>

6.9.1 Inject a 2-uL aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of a 12 hr period. If the contractor laboratory operates during consecutive 12-hr periods (shifts), analysis of the performance check solution at the beginning of each 12-hr period and at the end of the final 12-hr period is sufficient.

Determine and document acceptable column performance as described in Paragraph 6.3.

6.9.2 Inject a 2-uL aliquot of the calibration standard solution at 500 ng/mL at the beginning of a 12-hr period. Determine and document acceptable calibration as specified in Paragraph 6.3, i.e., SIM sensitivity and relative ion abundance criteria. The measured RRF's of

all analytes must be within ±30 percent of the mean values established by initial analyses of the calibration standard solutions.

7.0 QUALITY CONTROL

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

7.2 A laboratory "method blank" must be run along with each analytical batch (20 or fewer samples). A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a sample. The method blank is also dosed with the internal standards. For water samples, one liter of deionized and/or distilled water should be used as the method blank. Mineral oil may be used as the method blank for other matrices.

7.3 The laboratory will be expected to analyze performance evaluation samples as provided by the EPA on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and acceptable performance must be demonstrated before sample analyses can resume.

7.4 Samples may be split with other participating labs on a periodic basis to ensure interlaboratory consistency. At least one sample per set of 20~~24~~ must be run in duplicate to determine intralaboratory precision.

7.5 Field duplicates (individual samples taken from the same location at the same time) should be analyzed periodically to determine the total precision (field and lab).

7.6 Where appropriate, "field blanks" will be provided to monitor for possible cross-contamination of samples in the field. The typical "field blank" will consist of uncontaminated soil (background soil taken off-site).

7.7 GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hr period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

7.8 Before using any cleanup procedure, the analyst must process a series of calibration standards (Paragraph 6.2) through the procedure to validate elution patterns and the absence of interferents from reagents. Both alumina column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

NOTE: This fraction is intended to contain a high level of interferents and analysis near the method detection limit may not be possible.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing, other potential sources of contamination which may absorb the target analytes.

8.2 All samples must be stored at 4°C, extracted within 30 days and completely analyzed within 45 days of collection.

9.0 EXTRACTION AND CLEANUP PROCEDURES

9.1 Internal standard addition. Use a sample aliquot of 1 g to 1,000 mL (typical sample size requirements for each type of matrix are provided in Paragraph 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and any other material which is to be used as an internal standard, (Paragraph 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give a concentration of 500 ng/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 uL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, assuming 100% recovery. Adoption of different calibration solution sets (as needed to achieve different quantification limits for different congeners) will require a change in the fortification level. Individual concentration levels for each homologous series must be specified.

9.2 Extraction

9.2.1 Sludge/fuel oil. Extract aqueous sludge samples by refluxing a sample (e.g. 2 g) with 50 mL of toluene (benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100-mL round bottom flask. Rinse the filter with 10 mL of toluene, combine the extract and rinsate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.4.

9.2.2 Still bottom. Extract still bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (benzene) in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50-mL round bottom flask. Rinse the beaker and filter with 10 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.2.4.

9.2.3 Fly ash. Extract fly ash samples by placing a sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with 100 mL of toluene (benzene) and extract for 16 hr using a three cycle/hour schedule. Cool and filter the toluene extract through a glass fiber filter paper into a 500-mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with Step 9.2.4.

9.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5-mL aliquots of hexane and add the rinses to the funnel. Shake 2 min with 50 mL of 5% NaCl solution, discard the aqueous layer and proceed with Step 9.3.

9.2.5 Soil. Extract soil samples by placing the sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether, in that order, to the flask. Shake on a wrist-action shaker for two hr. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Paragraph 9.2.5 through a glass funnel fitted with a glass fiber filter and filled with anhydrous sodium sulfate into a 500-mL Kuderna-Danish (KD) concentrator fitted with a 10-mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional 50-mL aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional 5-mL portions of petroleum ether.

9.2.5.2 Add a Teflon or PFTE boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 min.

9.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 min.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two 1-mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125-mL separatory funnel. Rinse the KD with two additional 5-mL portions of hexane, combine. Proceed with Step 9.3.

9.2.6 Aqueous samples: Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume.

Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Step 9.2.6.1.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 sec to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.2.6.1 and 9.2.6.2. Proceed with Paragraph 9.2.6.3.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Paragraph 9.3.

9.3 In a 250-mL Separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 min.

Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times). Strong base (KOH) is known to degrade certain PCDD/PCDF's, contact time must be minimized.

9.4 Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard aqueous layer (bottom).

NOTE: Care should be taken due to the heat of neutralization and hydration.

9.5 Partition the solvent (15 mL hexane) against 40 mL of concentrated sulfuric acid. Shake for 2 min. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

9.6 Partition the extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate into a 50-mL round bottom flask, wash the separatory funnel with two 15-mL portions of hexane, pour through the funnel, and combine the hexane extracts. Concentrate the hexane solution to near dryness with a rotary evaporator (35°C water bath), making sure all traces of toluene are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted).

9.7 Pack a gravity column (glass 300-mm x 10.5-mm), fitted with a Teflon stopcock, in the following manner:

Insert a glass-wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4-g layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored in a sealed desiccator. Add a 4-g layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present discard the column. Do not tap a wetted column.

9.8 Dissolve the residue from Step 9.6 in 2 mL of hexane and apply the hexane solution to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. Check by GC/MS analysis that no PCDD's or PCDF's are eluted in this fraction. See Paragraph 9.9.1.

9.8.2 Elute the PCDD's and PCDF's from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15-mL) concentrator tube.

9.9 Carbon column cleanup:

Prepare a carbon column as described in Paragraph 4.18.

9.9.1 Using a carefully regulated stream of nitrogen (Paragraph 4.15), concentrate the 8 percent fraction from the alumina column (Paragraph 9.8.1) to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDD's and PCDF's. Concentrate the 60 percent fraction (Paragraph 9.8.2) to about 2 to 3 mL. Rinse the carbon with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of cyclohexane/methylene chloride (50:50 v/v) and 5 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine (this fraction may be used as a check on column efficiency). Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 mL toluene.

NOTE: Be sure no carbon fines are present in the eluant.

9.9.2 Alternate carbon column cleanup. Proceed as in Section 9.9.1 to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to an HPLC injector loop (1 mL). The injector loop is connected to the optional column described in Paragraph 4.18. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column. Elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is then discarded and 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0-mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2. The final volume should be 100 uL for soil samples and 500 uL for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial (Paragraph 4.16). Add to this sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 uL aliquot of extract and 4 uL of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 uL) of the sample into the GC/MS instrument.

10.0 GC/MS ANALYSIS

10.1 When toluene is employed as the final solvent use of a bonded phase column from Paragraph 4.3.2 is recommended. Solvent exchange into tridecane is required for other liquid phases or nonbonded columns (CP-Sil-88).

NOTE: Chromatographic conditions must be adjusted to account for solvent boiling points.

10.2 Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD (see Section 11). Add the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring, using all of the ions listed in Table 2. It is recommended that the GC/MS run be divided into five selected ion monitoring sections, namely: (1) 243, 257,, 304, 306, 320, 322, 332, 334, 340, 356, 376 (TCDD's, TCDF's, $^{13}C_{12}$-labeled internal and recovery standards, PeCDD's, PeCDF's, HxCDE); (2) 277, 293, 306, 332, 338, 340, 342, 354, 356, 358, 410 (peCDD's, PeCDF's, HpCDE); (3) 311, 327, 340, 356, 372, 374, 376, 388, 390, 392, 446, (HxCDD's, HxCDF's, OCDE); (4) 345, 361, 374, 390, 406, 408, 410, 422, 424, 426, 480 (HpCDD's, HpCDF's, NCDE) and (5) 379, 395, 408, 424, 442, 444, 458, 460, 470, 472, 514 (OCDD, OCDF, $^{13}C_{12}$-OCDD, DCDE). Cycle time not to exceed 1 sec/descriptor. It is recommended that selected ion monitoring section 1 should be applied during the GC run to encompass the retention window (determined in Paragraph 6.3) of the first- and last-eluting tetra-chlorinated isomers. If a response is observed at m/z 340 or 356, then the GC/MS analysis must be repeated; selected ion monitoring section 2 should then be applied to encompass the retention window of the first- and last-eluting penta-chlorinated isomers. HxCDE, HpCDE, OCDE, NCDE, DCDE, are abbreviations for hexa-, hepta-, octa-, nona-, and decachlorinated diphenyl ether, respectively.

10.4 <u>Identification criteria for PCDD's and PCDF's:</u>

10.4.1 All of the characteristic ions, i.e. quantitation ion, confirmation ions, listed in Table 2 for each class of PCDD and PCDF, must be present in the reconstructed ion chromatogram. It is desirable that the M - COCl ion be monitored as an additional requirement. Detection limits will be based on quantitation ions within the molecules in cluster.

10.4.2 The maximum intensity of each of the specified characteristic ions must coincide within 2 scans or 2 sec.

10.4.3 The relative intensity of the selected, isotopic ions within the molecular ion cluster of a homologous series of PCDD's of PCDF's must lie within the range specified in Table 3.

10.4.4 The GC peaks assigned to a given homologous series must have retention times within the window established for that series by the column performance solution.

10.5 Quantitate the PCDD and PCDF peaks from the response relative to the appropriate internal standard. Recovery of each internal standard) vs. the recovery standard must be greater than 40 percent. It is recommended that samples with recoveries of less than 40 percent or greater than 120 percent be re-extracted and re-analyzed.

NOTE: These criteria are used to assess method performance; when properly applied, isotope dilution techniques are independent of internal standard recovery.

In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

11.0 CALCULATIONS

NOTE: The relative response factors of a given congener within any homologous series are known to be different. However, for purposes of these calculations, it will be assumed that every congener within a given series has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, a 2,3,7,8-substituted isomer that is commercially available was chosen as representative of each series. All relative response factor calculations for a given homologous series are based on that compound.

11.1 Determine the concentration of individual isomers of tetra-, penta, and hexa-CDD/CDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.1 Determine the concentration of individual isomers of hepta-CDD/CDF and the concentration of OCDD and OCDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-OCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 472) of the internal standard, $^{13}C_{12}$-OCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 472 of $^{13}C_{12}$-OCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.2 Relative response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

C_{is} = concentration of the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD)

C_s = concentration of the compound of interest.

11.1.3 The concentrations of unknown isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer.

The concentrations of unknown isomers of HxCDD shall be calculated using the mean RRF determined for 1,2,3,4,7,8-HxCDD or any available 2,3,7,8,-X,Y-HXCDD isomer.

The concentrations of unknown isomers of HpCDD shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer.

The concentrations of unknown isomers of TCDF shall be calculated using the mean RRF determined for 2,3,7,8-TCDF.

The concentrations of unknown isomers of PeCDF shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer.

The concentrations of unknown isomers of HxCDF shall be calculated using the mean RRF determined for 1,2,4,7,8-HxCDF or any available 2,3,7,8-X,Y-HxCDF isomer.

The concentrations of unknown isomers of HpCDF shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer.

The concentration of the octa-CDD and octa-CDF shall be calculated using the mean RRF determined for each.

Mean relative response factors for selected PCDD's and PCDF's are given in Table 4.

11.1.4 Calculate the percent recovery, R_{is}, for each internal standard in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_r \times Q_{is}} = 100\%$$

where:

A_{rs} = Area of quantitation ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

where:

C_{rs} = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.1.5 Calculation of total concentration of all isomers within each homologous series of PCDD's and PCDF's.

Total concentration of PCDD's or PCDF's = Sum of the concentrations of the individual PCDD or PCDF isomers

11.4 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.5 Accuracy and Precision. Table 5 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 6 lists recovery data for the same analyses. Table 2 shows the linear range and variation of response factors for selected analyte standards. Table 8 provides the method detection limits as measured in specific sample matrices.

11.6 Method Detection Limit. The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The procedure used to determine the MDL values reported in Table 8 was obtained from Appendix A of EPA Test Methods manual, EPA-600/4-82-057 July 1982, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater."

11.7 Maximum Holding Time (MHT). Is that time at which a 10 percent change in the analyte concentration (C_{t10}) occurs and the precision of the method of measurement allows the 10 percent change to be statistically different from the 0 percent change (C_{t0}) at the 90 percent confidence level. When the precision of the method is not sufficient to statistically discriminate a 10 percent change in the concentration from 0 percent change, then the maximum holding time is that time where the percent change in the analyte concentration (C_{tn}) is statistically different than the concentration at 0 percent change (C_{t0}) and greater than 10 percent change at the 90 percent confidence level.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

Analyte	50-m CP-Sil-88	30-m DB-5	3--m SP-2250
2,3,7,8-TCDF	25.2	17.8	26.7
2,3,7,8-TCDD	23.6	17.4	26.7
1,2,3,4-TCDD	24.1	17.3	26.5
1,2,3,4,7-PeCDD	30.0	20.1	28.1
1,2,3,4,7,8-HxCDD	39.5	22.1	30.6
1,2,3,4,6,7,8-HpCDD	57.0	24.1	33.7
OCDD	NM	25.6	NM

*Retention time in min, using temperature programs shown below.

NM = not measured.

Temperature Programs:

CP-Sil-88	60°C-190°C at 20°/min; 190°-240° at 5°/min.
DB-5 30 m x 0.25 mm Thin film (0.25 um)	170°, 10 min; then at 8°/min to 320°C, hold at 320°C 20 min (until OCDD elutes).
SP-2250	70°-320° at 10°/minute.

Column Manufacturers

CP-Sil-88	Chrompack, Incorporated, Bridgewater, New Jersey
DB-5,	J and W Scientific, Incorporated, Rancho Cordova, California
SP-2250	Supelco, Incorporated, Bellefonte, Pennsylvania

TABLE 2. IONS SPECIFIED[a] FOR SELECTED ION MONITORING FOR PCDD'S AND PCDF'S

	Quantitation ion	Confirmation ions	M-COCl
PCDD's			
$^{13}C_{12}$-Tetra	334	332	---
Tetra	322	320	257
Penta	356	354;358	293
Hexa	390	388;392	327
Hepta	424	422;426	361
Octa	460	458	395
$^{13}C_{12}$-Octa	472	470	
PCDF's			
Tetra	306	304	243
Penta	340	338;342	277
Hexa	374	372;376	311
Hepta	408	406;410	345
Octa	444	442	379

[a]Ions at m/z 376 (HxCDE), 410 (HpCDE), 446 (OCDE), 480 (NCDE) and 514 (DCDE) are also included in the scan monitoring sections (1) to (5), respectively. See Paragraph 10.3.

TABLE 3. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDD'S AND PCDF'S

	Selected ions (m/z)	Relative intensity
PCDD's		
Tetra	320/322	0.65-0.89
Penta	358/356	0.55-0.75
Hexa	392/390	0.69-0.93
Hepta	426/424	0.83-1.12
Octa	458/460	0.75-1.01
PCDF's		
Tetra	304/306	0.65-0.89
Penta	342/340	0.55-0.75
Hexa	376/374	0.69-0.93
Hepta	410/408	0.83-1.12
Octa	442/444	0.75-1.01

TABLE 4. MEAN RELATIVE RESPONSE FACTORS OF CALIBRATION STANDARDS

Analyte	RRF[a]	RSD% (n = 5)	Quantitation ion (m/z)
2,3,7,8-TCDD	1.13	3.9	322
1,2,3,7,8-PeCDD	0.70	10.1	356
1,2,3,4,7,8-HxCDD	0.51	6.6	390
1,2,3,4,6,7,8-HpCDD[b]	1.08	6.6	424
OCDD[b]	1.30	7.2	460
2,3,7,8-TCDF	1.70	8.0	306
1,2,3,7,8-PeCDF	1.25	8.7	340
1,2,3,4,7,8-HxCDF	0.84	9.4	374
1,2,3,4,6,7,8-HpCDF[b]	1.19	3.8	444
OCDF[b]	1.57	8.6	408
$^{13}C_{12}$-2,3,7,8-TCDD	1.00	-	334
$^{13}C_{12}$-1,2,3,4-TCDD	0.75	4.6	334
$^{13}C_{12}$-OCDD	1.00	-	472

[a]The RRF value is the mean of the five determinations made. Nominal weights injected were 0.2, 0.5, 1.0, 2.0 and 5.0 ng.

[b]RRF values for these analytes were determined relative to $^{13}C_{12}$-OCDD. All other RRF's were determined relative to $^{13}C_{12}$-2,3,7,8-TCDD.

Instrument Conditions/Tune - GC/MS system was tuned as specified in Paragraph 6.3. RRF data was acquired under SIM control, as specified in Paragraph 10.3.

GC Program - The GC column temperature was programmed as specified in Paragraph 4.3.2(b).

TABLE 5. PRECISION DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[b]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom	487	487	4	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	fly ash	38.5	38.5	4	7.9
	still bottom	ND	2500	4	-
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	19.1	2	-
	still bottom	227	2727	2	-
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	58.4	2	-
	still bottom	ND	2500	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	16.0	4	3.5
	still bottom	422	2920	2	-
1,2,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	2.6	3	23
	still bottom	ND	2500	2	-
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-

TABLE 5 (Continued)

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	25.8	2	6.9
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	-
	soil	ND	25.0	4	-
	sludge[c]	8760	8780	4	-
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	7.4	3	7.6
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom[3]	25600	28100	2	-
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	24.2	4	13.5
	still bottom	ND	2500	2	-

TABLE 5. (Continued)

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
OCDF	clay	ND	-	-	-
	soil	ND	-	-	-
	sludge	192	317	4	3.3
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only. (Carbon column not used.)

[b]ND - not detected at concentration injected (final volume 0.1 mL or greater).

[c]Estimated concentration out of calibration range of standards.

TABLE 6. RECOVERY DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	-	-
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	-	-
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	615	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[d]	8780	125	-
	fly ash	ND	-	-
	still bottom	ND	-	-
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25600	2500	-

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	-	-
	soil	ND	-	-
	sludge	192	125	86.8
	fly ash	ND	-	-
	still bottom	ND	-	-

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator: resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[b]Final volume of concentrate 0.1 mL or greater, ND means below quantification limit, 2 or more samples analyzed.

[c]Amount of analyte added to sample, 2 or more samples analyzed.

[d]Estimated concentration out of calibration range of standards.

TABLE 7. LINEAR RANGE AND VARIATIOIN OF RESPONSE FACTORS

Analyte	Linear range tested (pg)	n[b]	Mean RF	%RSD
1,2,7,8-TCDF[a]	50-6000	8	1.634	12.0
2,3,7,8-TCDD[a]	50-7000	7	0.721	11.9
2,3,7,8-TCDF	300-4000	5	2.208	7.9

[a]Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

[b]Each value of n represents a different concentration level.

TABLE 8. METHOD DETECTION LIMITS OF $^{13}C_{12}$ - LABELED PCDD'S and PCDF'S

IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly-Ash[b]	Industrial Sludge[c]	Still-Bottom[d]	Fuel Oil[d]	Fuel Oil/Sawdust[b]
2,3,7,8-TCDD	0.44	0.17	0.07	0.82	1.81	0.75	0.13
1,2,3,7,8-PeCDD	1.27	0.70	0.25	1.34	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	2.21	1.25	0.55	2.30	6.21	5.02	0.36
1,2,3,4,6,7,8-HpCDD	2.77	1.87	1.41	4.65	4.59	8.14	0.51
OCDD	3.93	2.35	2.27	6.44	10.1	23.2	1.48
2,3,7,8-TCDF	0.63	0.11	0.06	0.46	0.26	0.48	0.40
1,2,3,7,8-PeCDF	1.64	0.33	0.16	0.92	1.61	0.80	0.43
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	2.17	2.27	2.09	2.22

[a]Sample size 1,000 mL.
[b]Sample size 10 g.
[c]Sample size 2 g.
[d]Sample size 1 g.
Note: The final sample-extract volume was 100 uL for all samples.

Matrix types used in MDL Study:

- Reagent water: distilled, deionized laboratory water.
- Missouri soil: soil blended to form a homogeneous sample.
- Fly-ash: alkaline ash recovered from the electrostatic precipitator of a coal-burning power plant.
- Industrial sludge: sludge from cooling tower which received creosotic and pentachlorophenolic wastewaters. Sample was ca. 70 percent water, mixed with oil and sludge.
- Still-bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.
- Fuel oil: wood-preservative solution from the modified Thermal Process tanks. Sample was an oily liquid (>90 percent oil) containing no water.
- Fuel oil/Sawdust: sawdust was obtained as a very fine powder from the local lumber yard. Fuel oil (described above) was mixed at the 4 percent (w/w) level.

Procedure used for the Determination of Method Detection Limits was obtained from "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" Appendix A, EPA-600/4-82-057, July 1982. Using this procedure, the method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero.

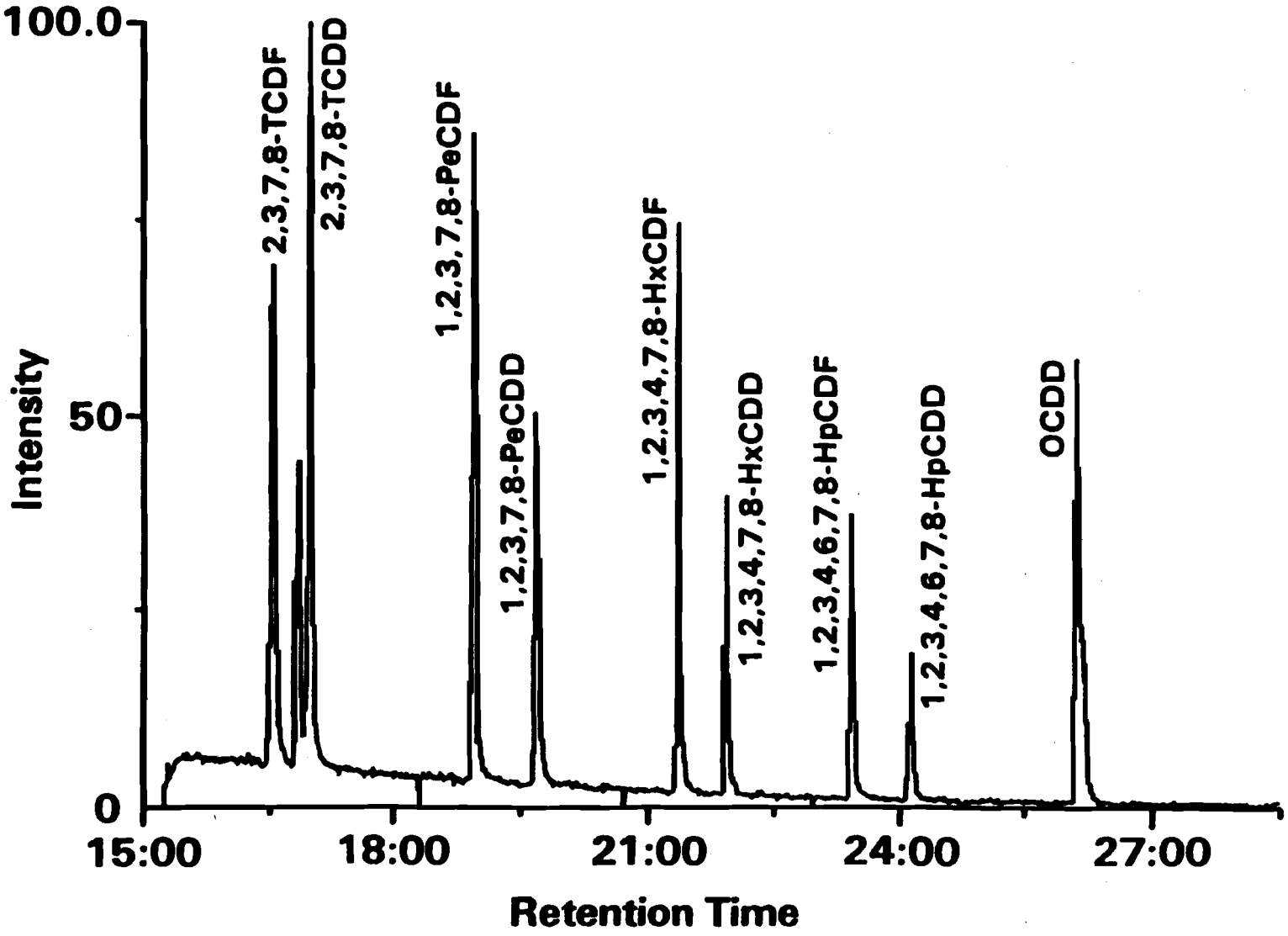
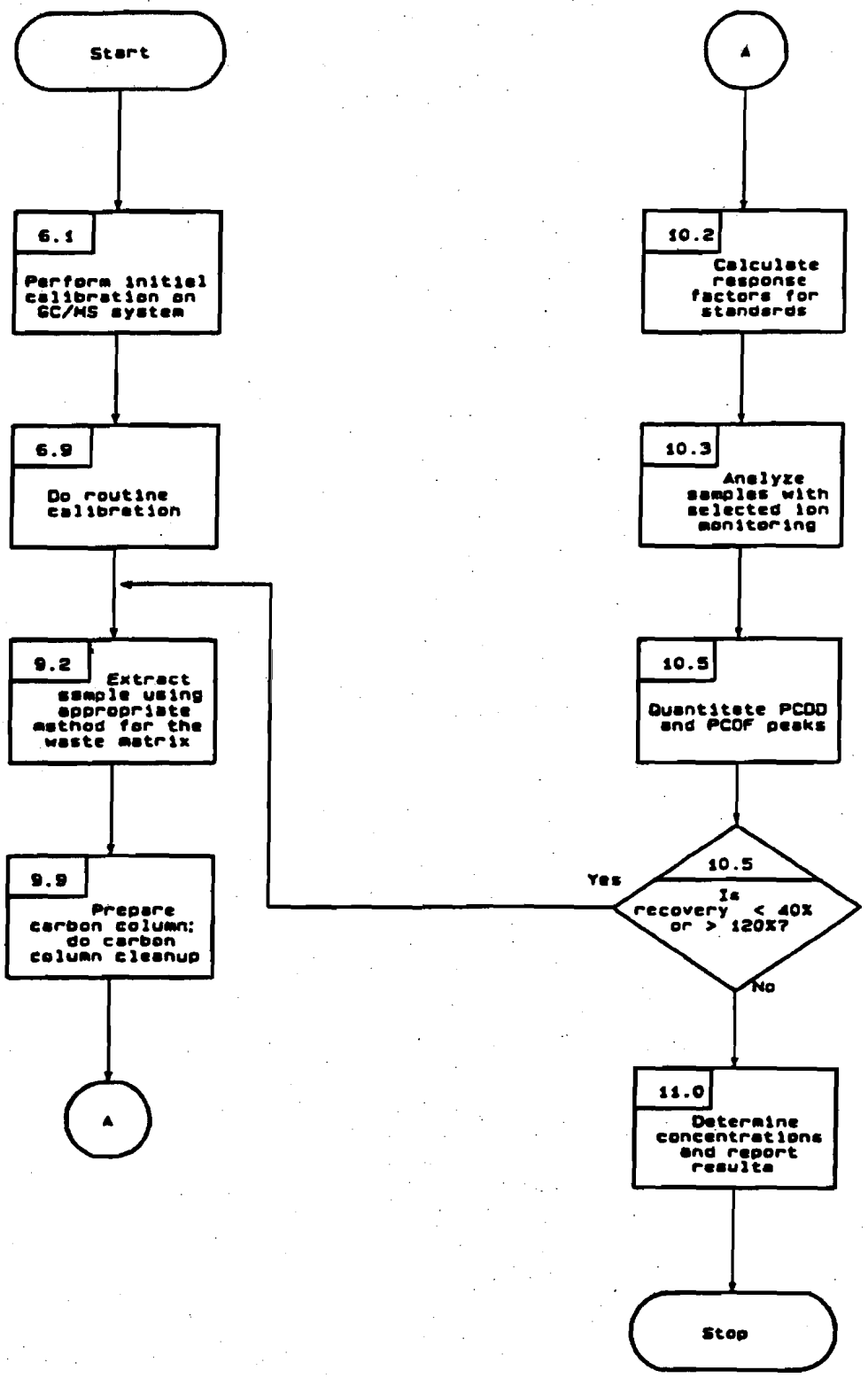


Figure 2. Mass Chromatogram of Selected PCDD and PCDF Congeners.


Start
6.1
Perform initial calibration on GC/MS system
6.9
Do routine calibration
9.2
Extract sample using appropriate method for the waste matrix
9.9
Prepare carbon column; do carbon column cleanup
A
A
10.2
Calculate response factors for standards
10.3
Analyze samples with selected ion monitoring
10.5
Quantitate PCDD and PCDF peaks
10.5
Is recovery < 40% or > 120%?
Yes
No
11.0
Determine concentrations and report results
Stop

APPENDIX A

SIGNAL-TO-NOISE DETERMINATION METHODS

MANUAL DETERMINATION

This method corresponds to a manual determination of the S/N from a GC/MS signal, based on the measurement of its peak height relative to the baseline noise. The procedure is composed of four steps as outlined below. (Refer to Figure 1 for the following discussion).

1. Estimate the peak-to-peak noise (N) by tracing the two lines (E_1 and E_2) defining the noise envelope. The lines should pass through the estimated statistical mean of the positive and the negative peak excursions as shown in Figure 1. In addition, the signal offset (0) should be set high enough such that negative-going noise (except for spurious negative spikes) is recorded.

2. Draw the line (C) corresponding to the mean noise between the segments defining the noise envelope.

3. Measure the height of the GC/MS signal (S) at the apex of the peak relative to the mean noise C. For noisy GC/MS signals, the average peak height should be measured from the estimated mean apex signal D between E_3 and E_4.

4. Compute the S/N.

This method of S/N measurement is a conventional, accepted method of noise measurement in analytical chemistry.

INTERACTIVE COMPUTER GRAPHICAL METHOD

This method calls for the measurement of the GC/MS peak area using the computer data system and Eq. 1:

$$S/N = \frac{A/t}{\frac{A_l/2t + A_r/2t}{2}}$$

where t is the elution time window (time interval, t_2-t_2, at the base of the peak used to measure the peak area A). (Refer to Figure 2, for the following discussion).

A_l and A_r correspond to the areas of the noise level in a region to the left (A_l) and to the right (A_r) of the GC peak of interest.

The procedure to determine the S/N is as follows:

1. Estimate the average negative peak excursions of the noise (i.e., the low segment-E_2-of the noise envelope). Line E_2 should pass through the estimated statistical mean of the negative-going noise excursions. As stated earlier, it is important to have the signal offset (0) set high enough such that negative-going noise is recorded.

2. Using the cross-hairs of the video display terminal, measure the peak area (A) above a baseline corresponding to the mean negative noise value (E_2) and between the time t_1 and t_2 where the GC/MS peak intersects the baseline, E_2. Make note of the time width $t=t_2-t_1$.

3. Following a similar procedure as described above, measure the area of the noise in a region to the left (A_l) and to the right (A_r) of the GC/MS signal using a time window twice the size of t, that is, 2 x t.

The analyst must sound judgement in regard to the proper selection of interference-free regions in the measurement of A_l and A_r. It is not recommended to perform these noise measurements (A_l and A_r) in remote regions exceeding ten time widths (10t).

4. Compute the S/N using Eq. 1.

NOTE: If the noise does not occupy at least 10 percent of the vertical axis (i.e., the noise envelope cannot be defined accurately), then it is necessary to amplify the vertical axis so that the noise occupies 20 percent of the terminal display (see Figure 3).

FIGURE CAPTIONS

Figure 1. Manual determination of S/N.
The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E_1 and E_2, and between the apex average noise extremes, E_3 and E_4, at the apex of the signal. Note, it is imperative that the instrument's interface amplifier electronic's zero offset be set high enough such that negative-going baseline noise is recorded.

Figure 2. Interactive determination of S/N.
The peak area (A) is measured above the baseline average negative noise E_2 and between times t_1 and t_2. The noise is obtained from the areas A_1 and A_r measured to the left and to the right of the peak of interest using time windows T_1 and T_r (T_1=T_r=2t).

Figure 3. Interactive determination of S/N.
A) Area measurements without amplification of the vertical axis. Note that the noise cannot be determined accurately by visual means. B) Area measurements after amplification (10X) of the vertical axis so that the noise level occupies approximately 20 percent of the display, thus enabling a better visual estimation of the baseline noise, E_1, E_2, and C.

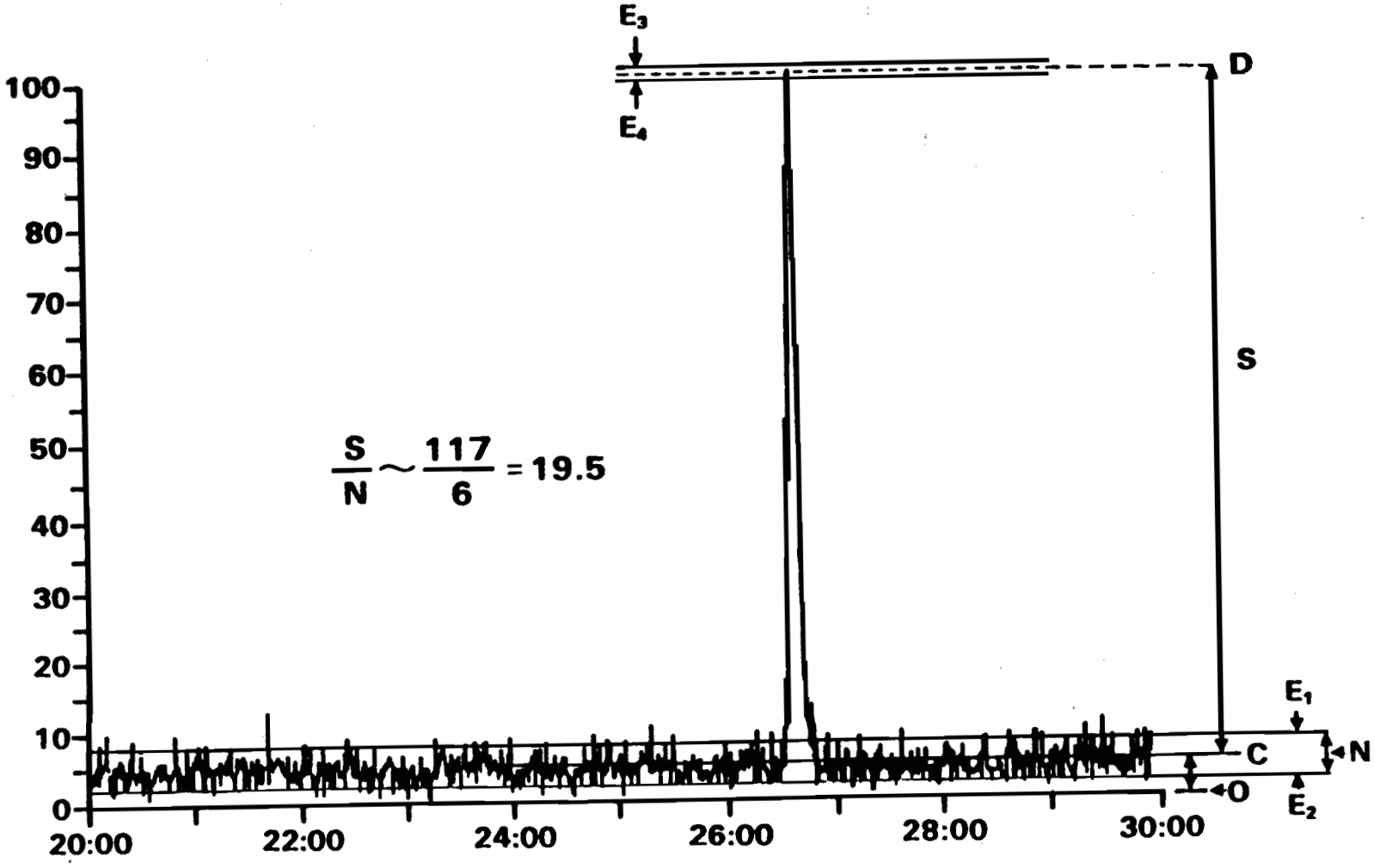


Figure 1. Manual Determination of S/N.

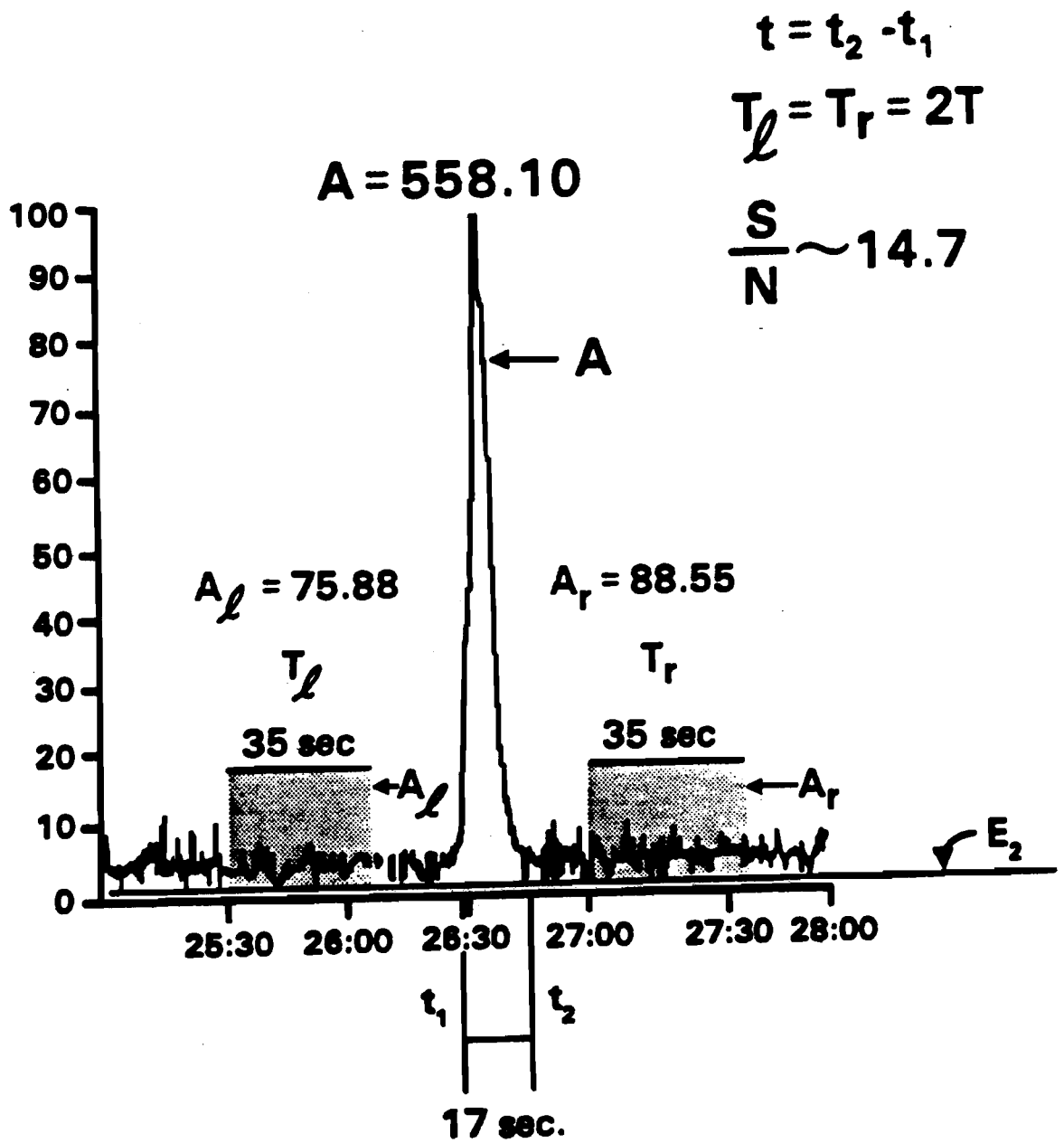


Figure 2. Interactive Determination of S/N.

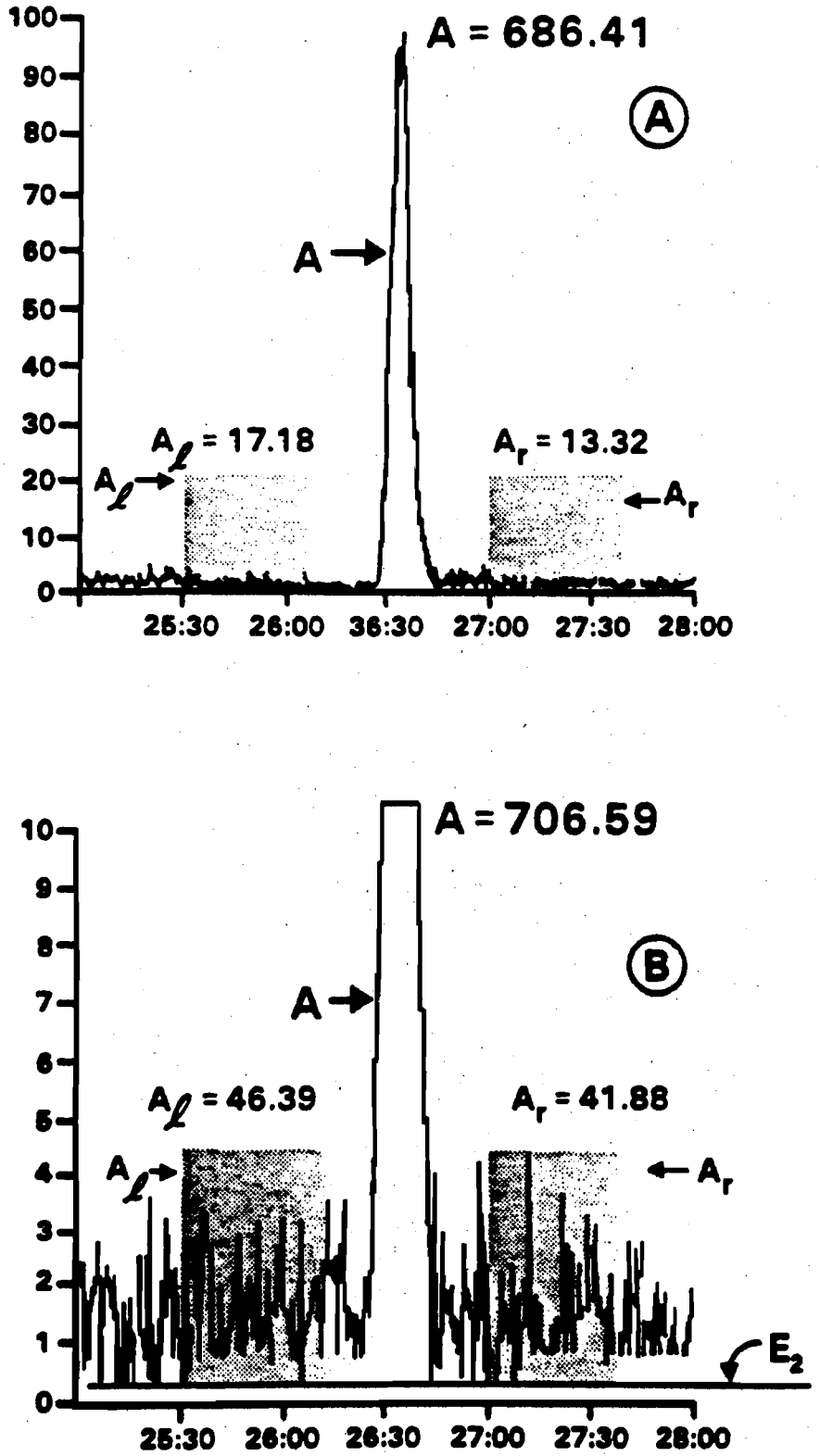


Figure 3. Interactive Determination of S/N.

APPENDIX B

RECOMMENDED SAFETY AND HANDLING PROCEDURES FOR PCDD'S/PCDF'S

1. The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001 perent to 0.14 percent. The physical properties of the 135 other tetra- through octa-chlorinated PCDD/PCDF have not been well established, although it is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer. On the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personel entering these laboratories should wear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves are also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are processed, removal of these from sample contaners, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing, and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-aproved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than 50 ng/m^2, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500 ng/m^2. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scurbbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgeable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY _____

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

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Date September 1986

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY _____

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

Revision 0
Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-2

LAB NAME _____ ANALYST(s) _____ CASE No. _____

SAMPLE No. _____ TYPE OF SAMPLE _____ CONTRACT No. _____

SAMPLE SIZE _____ % MOISTURE _____ FINAL EXTRACT VOLUME _____

EXTRACTION METHOD _____ ALIQUOT USED FOR ANALYSIS _____

CLEAN UP OPTION _____

CONCENTRATION FACTOR _____ DILUTION FACTOR _____

DATE EXTRACTED _____ DATA ANALYZED _____

VOLUME $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____ TO SAMPLE VOLUME _____

VOLUME INJECTED _____ Wt $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____

Wt $^{13}C_{12}$-2,3,7,8-TCDD ADDED _____ $^{13}C_{12}$-2,3,7,8-TCDD % RECOVERY _____

Wt $^{13}C_{12}$-2,3,7,8-OCDD ADDED _____ $^{13}C^{12}$-OCDD % RECOVERY _____

$^{13}C_{12}$-2,3,7,8-TCDD RRF _____ $^{13}C_{12}$-OCDD RRF _____

$^{13}C_{12}$-2,3,7,8-TCDD

AREA 332 _____ AREA 334 _____ RATIO 332/334 _____

$^{13}C_{12}$-OCDD AREA 470 _____ AREA 472 _____ RATIO 470/472 _____

RT 2,3,7,8-TCDD (Standard) _____ RT 2,3,7,8-TCDD (Sample) _____

$^{13}C_{12}$-2,3,7,8-TCDD - $^{13}C_{12}$-1,2,3,4-TCDD Percent Valley _____

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Date September 1986

DIOXIN INITIAL CALIBRATION STANDARD DATA SUMMARY

FORM 8280-3

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s) _____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD _____ or $^{13}C_{12}$-1,2,3,4-TCDD _____

CALIBRATION STANDARD	RRF 1	RRF 2	RRF 3	RRF 4	RRF 5	MEAN	%RSD
TCDD							
PeCDD							
HxCDD							
HpCDD							
OCDD							
TCDF							
PeCDF							
HxCDF							
HpCDF							
OCDF							

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FORM 8280-3 (Continued)

CONCENTRATIONS IN PG/UL

	1	2	3	4	5
TCDD					
PeCDD					
HxCDD					
HpCDD					
OCDD					
TCDF					
PeCDF					
HxCDF					
HpCDF					
OCDF					

DIOXIN CONTINUING CALIBRATION SUMMARY

FORM 8280-4

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s) _____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD _____ or $^{13}C_{12}$-1,2,3,4-TCDD _____

COMPOUND	$\overline{RRF}$	RRF	%D
TCDD			
PeCDD			
HxCDD			
HpCDD			
OCDD			
TCDF			
PeCDF			
HxCDF			
HpCDF			
OCDF			

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Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-A

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

TCDD REQUIRED 320/322 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 322	AREA 320	AREA 257	320/ 322	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD _____

TCDF REQUIRED 304/306 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 306	AREA 304	AREA 243	304/ 306	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD _____

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Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-B

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

PeCDD REQUIRED 320/322 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 356	AREA 358	AREA 354	AREA 293	358/ 356	CONFIRM AS PeCDD Y/N	CONC.

TOTAL PeCDD _____

PeCDF REQUIRED 342/340 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 340	AREA 342	AREA 338	AREA 277	342/ 340	CONFIRM AS PeCDF Y/N	CONC.

TOTAL PeCDF _____

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DIOXIN RAW SAMPLE DATA FORM 8280-5-C

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No._____ SAMPLE No._____

HxCDD REQUIRED 392/390 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 390	AREA 392	AREA 388	AREA 327	392/ 390	CONFIRM AS HxCDD Y/N	CONC.

TOTAL HxCDD _____

HxCDF REQUIRED 376/374 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 376	AREA 374	AREA 372	AREA 311	376/ 374	CONFIRM AS HxCDF Y/N	CONC.

TOTAL HxCDF _____

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Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-D

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No._____ SAMPLE No._____

HpCDD REQUIRED 426/444 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 424	AREA 426	AREA 422	AREA 361	426/ 424	CONFIRM AS HpCDD Y/N	CONC.

TOTAL HpCDD _____

HpCDF REQUIRED 410/408 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 408	AREA 410	AREA 406	AREA 345	410/ 408	CONFIRM AS HpCDF Y/N	CONC.

TOTAL HpCDF _____

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DIOXIN RAW SAMPLE DATA FORM 8280-5-E

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No. _____ SAMPLE No. _____

OCDD REQUIRED 458/460 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 460	AREA 458	AREA 395	458/460	CONFIRM AS OCDD Y/N	CONC.

TOTAL OCDD _____

OCDF REQUIRED 442/444 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 444	AREA 442	AREA 379	442/444	CONFIRM AS OCDF Y/N	CONC.

TOTAL OCDF _____

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Date September 1986

DIOXIN SYSTEM PERFORMANCE CHECK ANALYSIS FORM 8280-6

LAB NAME _____ CASE No. _____

BEGINNING DATE _____ TIME _____ CONTRACT No. _____

ENDING DATE _____ TIME _____ ANALYST(s) _____

PC SOLUTION IDENTIFIER _____

ISOTOPIC RATIO CRITERIA MEASUREMENT

PCDD's	IONS RATIOED	RATIO AT BEGINNING OF 12 HOUR PERIOD	RATIO AT END OF 12 HOUR PERIOD	ACCEPTABLE WINDOW
Tetra	320/322			0.65-0.89
Penta	358/356			0.55-0.75
Hexa	392/390			0.69-0.93
Hepta	426/424			0.83-1.12
Octa	458/460			0.75-1.01

PCDF's				
Tetra	304/306			0.65-0.89
Penta	342-340			0.55-0.75
Hexa	376-374			0.69-0.93
Hepta	410/408			0.83-1.12
Octa	442/444			0.75-1.01

Ratios out of criteria

	Beginning	End
PCDD	_____ out of _____	_____ out of _____
PCDF	_____ out of _____	_____ out of _____

NOTE: One form is required for each 12 hour period samples are analyzed.

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ERRATA FOR METHOD 8280

In Section **1.1**, **delete** the following text:

"reactor residues" with no replacement.

In Section **1.5**, **replace** the following text:

"the analyst must take necessary precautions to prevent exposure to himself, or to others, of"

with:

"the analyst must take necessary precautions to prevent human exposure from" and

delete the following text:

"to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH 548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450)."

In Section **6.3**, **replace** the following text:

"x = measured as in Figure 2"

with:

"x = height of the valley between 2,3,7,8-TCDD and 1,2,3,4-TCDD, using the column performance check mixture."

In Section **6.9.2**, **replace** "a 2-hr period" with "a 12 hr period".

In Section **7.4**, **replace** "24" with "20".

METHOD 8290

POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs)BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. The following compounds can be determined by this method:

Compound Name	CAS No[a]
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	40321-76-4
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	57653-85-7
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	39227-28-6
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	35822-39-4
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	72918-21-9
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	70648-26-9
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	55673-89-7
1,2,3,4,6,7,8,9-Octachlorodibenzofuran (OCDF)	39001-02-0

[a] Chemical Abstract Service Registry Number

1.2 The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits (MCLs), and other pertinent information. Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within the scope of this method that are greater than ten times the upper MCLs must be analyzed by a protocol designed for such concentration levels, e.g., Method 8280. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is described.

1.3 The sensitivity of this method is dependent upon the level of interferences within a given matrix. The calibration range of the method for a 1 L water sample is 10 to 2000 ppq for TCDD/TCDF and PeCDD/PeCDF, and 1.0 to 200 ppt for a 10 g soil, sediment, fly ash, or tissue sample for the same analytes (Table 1). Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL. The actual limits of detection and quantitation will differ from the lower MCL, depending on the complexity of the matrix.

1.4 This method is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Sec. 11 of this method discusses safety procedures.

2.0 SUMMARY OF METHOD

2.1 This procedure uses matrix specific extraction, analyte specific cleanup, and HRGC/HRMS analysis techniques.

2.2 If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is presented at the end of this method.

2.3 A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still bottom, fuel oil, chemical reactor residue, fish tissue, or human adipose tissue is spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs listed in Column 1 of Table 2. The sample is then extracted according to a matrix specific extraction procedure. Aqueous samples that are judged to contain 1 percent or more solids, and solid samples that show an aqueous phase, are filtered, the solid phase (including the filter) and the aqueous phase extracted separately, and the extracts combined before extract cleanup. The extraction procedures are:

a) Toluene: Soxhlet extraction for soil, sediment, fly ash, and paper pulp samples;

b) Methylene chloride: liquid-liquid extraction for water samples;

c) Toluene: Dean-Stark extraction for fuel oil, and aqueous sludge samples;

d) Toluene extraction for still bottom samples;

e) Hexane/methylene chloride: Soxhlet extraction or methylene chloride: Soxhlet extraction for fish tissue samples; and

f) Methylene chloride extraction for human adipose tissue samples.

g) As an option, all solid samples (wet or dry) may be extracted with toluene using a Soxhlet/Dean Stark extraction system.

The decision for the selection of an extraction procedure for chemical reactor residue samples is based on the appearance (consistency, viscosity) of the samples. Generally, they can be handled according to the procedure used for still bottom (or chemical sludge) samples.

2.4 The extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the extracts are cleaned up by column chromatography on alumina, silica gel, and activated carbon.

2.4.1 The extracts from adipose tissue samples are treated with silica gel impregnated with sulfuric acid before chromatography on acidic silica gel, neutral alumina, and activated carbon.

2.4.2 Fish tissue and paper pulp extracts are subjected to an acid wash treatment only, prior to chromatography on alumina and activated carbon.

2.5 The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 10 to 50 μL (depending on the matrix) of a nonane solution containing 50 pg/μL of the recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD (Table 2). The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of the hexa-, hepta- and octachlorinated PCDD/PCDF congeners.

2.6 Two μL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.7 The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners (Table 3), for which a ^{13}C-labeled standard is available in the sample fortification and recovery standard solutions (Table 2), is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region. The remaining six 2,3,7,8-substituted congeners (i.e., 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other PCDD/PCDF congeners are identified when their relative retention times fall within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Identification also is based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios.

2.8 Quantitation of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points)

calibration curve for each homologue, during which each calibration solution is analyzed once.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data (see references 1 and 2.) All of these materials must be demonstrated to be free from interferants under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves.

3.2 The use of high purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

3.3 Interferants coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans, that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Sec. 8.1.1.3. While cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

3.4 A high-resolution capillary column (60 m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity (Sec. 8.1.1). In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent).

4.0 APPARATUS AND MATERIALS

4.1 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS) - The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns.

4.1.1 GC Injection Port - The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On column 1 μL injections can be used on the 60 m DB-5 column. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2 μL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2 μL). One μL injections are allowed; however, laboratories must remain

consistent throughout the analyses by using the same injection volume at all times.

4.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Interface - The GC/MS interface components should withstand 350°C. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules are recommended.

4.1.3 Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

4.1.4 Data System - A dedicated data system is employed to control the rapid multiple-ion monitoring process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitations may be reported based upon computer generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass spectral peak profiles (Sec. 8.1.2.3) and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should permit the measurement of noise on the base line.

> NOTE: The detector ADC zero setting must allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power. In Figure 2, the effect of different zero settings on the measured resolving power is shown.

4.2 GC Columns

4.2.1 In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, use of the 60 m DB-5 fused silica capillary column is recommended. Minimum acceptance criteria must be demonstrated and documented (Sec. 8.2.2). At the beginning of each 12 hour period (after mass resolution and GC resolution are demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended column are shown in Sec. 7.6.

4.2.2 Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 GC column alone. In order to determine the proper concentrations of the individual 2,3,7,8-substituted congeners, the sample extract must be reanalyzed on another GC column that resolves the isomers.

4.2.3 30 m DB-225 fused silica capillary column, (J&W Scientific) or equivalent.

4.3 Miscellaneous Equipment and Materials - The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

4.3.1 Nitrogen evaporation apparatus with variable flow rate.

4.3.2 Balances capable of accurately weighing to 0.01 g and 0.0001 g.

4.3.3 Centrifuge.

4.3.4 Water bath, equipped with concentric ring covers and capable of being temperature controlled within ± 2°C.

4.3.5 Stainless steel or glass container large enough to hold contents of one pint sample containers.

4.3.6 Glove box.

4.3.7 Drying oven.

4.3.8 Stainless steel spoons and spatulas.

4.3.9 Laboratory hoods.

4.3.10 Pipets, disposable, Pasteur, 150 mm long x 5 mm ID.

4.3.11 Pipets, disposable, serological, 10 mL, for the preparation of the carbon columns specified in Sec. 7.5.3.

4.3.12 Reaction vial, 2 mL, silanized amber glass (Reacti-vial, or equivalent).

4.3.13 Stainless steel meat grinder with a 3 to 5 mm hole size inner plate.

4.3.14 Separatory funnels, 125 mL and 2000 mL.

4.3.15 Kuderna-Danish concentrator, 500 mL, fitted with 10 mL concentrator tube and three ball Snyder column.

4.3.16 Teflon™ or carborundum (silicon carbide) boiling chips (or equivalent), washed with hexane before use.

NOTE: Teflon™ boiling chips may float in methylene chloride, may not work in the presence of any water phase, and may be penetrated by nonpolar organic compounds.

4.3.17 Chromatographic columns, glass, 300 mm x 10.5 mm, fitted with Teflon™ stopcock.

4.3.18 Adapters for concentrator tubes.

4.3.19 Glass fiber filters, 0.70 μm, Whatman GFF, or equivalent.

4.3.20 Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125 mL flask.

4.3.21 Continuous liquid-liquid extractor.

4.3.22 All glass Soxhlet apparatus, 500 mL flask.

4.3.23 Soxhlet/Dean Stark extractor (optional), all glass, 500 mL flask.

4.3.24 Glass funnels, sized to hold 170 mL of liquid.

4.3.25 Desiccator.

4.3.26 Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

4.3.27 Rotary evaporator with a temperature controlled water bath.

4.3.28 High speed tissue homogenizer, equipped with an EN-8 probe, or equivalent.

4.3.29 Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.

4.3.30 Extraction jars, glass, 250 mL, with teflon lined screw cap.

4.3.31 Volumetric flasks, Class A - 10 mL to 1000 mL.

4.3.32 Glass vials, 1 dram (or metric equivalent).

NOTE: Reuse of glassware should be minimized to avoid the risk of contamination. All glassware that is reused must be scrupulously cleaned as soon as possible after use, according to the following procedure: Rinse glassware with the last solvent used in it. Wash with hot detergent water, then rinse with copious amounts of tap water and several portions of organic-free reagent water. Rinse with high purity acetone

and hexane and store it inverted or capped with solvent rinsed aluminum foil in a clean environment.

5.0 REAGENTS AND STANDARD SOLUTIONS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Column Chromatography Reagents

5.2.1 Alumina, neutral, 80/200 mesh (Super 1, Woelm®, or equivalent). Store in a sealed container at room temperature, in a desiccator, over self-indicating silica gel.

5.2.2 Alumina, acidic AG4, (Bio Rad Laboratories catalog #132-1240, or equivalent). Soxhlet extract with methylene chloride for 24 hours if blanks show contamination, and activate by heating in a foil covered glass container for 24 hours at 190°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.3 Silica gel, high purity grade, type 60, 70-230 mesh; Soxhlet extract with methylene chloride for 24 hours if blanks show contamination, and activate by heating in a foil covered glass container for 24 hours at 190°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.4 Silica gel impregnated with sodium hydroxide. Add one part (by weight) of 1 M NaOH solution to two parts (by weight) silica gel (extracted and activated) in a screw cap bottle and mix with a glass rod until free of lumps. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.5 Silica gel impregnated with 40 percent (by weight) sulfuric acid. Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw capped glass bottle. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.6 Celite 545® (Supelco), or equivalent.

5.2.7 Active carbon AX-21 (Anderson Development Co., Adrian, MI), or equivalent, prewashed with methanol and dried in vacuo at 110°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.3 Reagents

5.3.1 Sulfuric acid, H_2SO_4, concentrated, ACS grade, specific gravity 1.84.

5.3.2 Potassium hydroxide, KOH, ACS grade, 20 percent (w/v) in organic-free reagent water.

5.3.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in organic-free reagent water.

5.3.4 Potassium carbonate, K_2CO_3, anhydrous, analytical reagent.

5.4 Desiccating agent

5.4.1 Sodium sulfate (powder, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Solvents

5.5.1 Methylene chloride, CH_2Cl_2. High purity, distilled in glass or highest available purity.

5.5.2 Hexane, C_6H_{14}. High purity, distilled in glass or highest available purity.

5.5.3 Methanol, CH_3OH. High purity, distilled in glass or highest available purity.

5.5.4 Nonane, C_9H_{20}. High purity, distilled in glass or highest available purity.

5.5.5 Toluene, $C_6H_5CH_3$. High purity, distilled in glass or highest available purity.

5.5.6 Cyclohexane, C_6H_{12}. High purity, distilled in glass or highest available purity.

5.5.7 Acetone, CH_3COCH_3. High purity, distilled in glass or highest available purity.

5.6 High-Resolution Concentration Calibration Solutions (Table 5) - Five nonane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (1.0 pg/μL) and the highest values for the octachlorinated congeners (1000 pg/μL).

5.6.1 Depending on the availability of materials, these high-resolution concentration calibration solutions may be obtained from the Environmental Monitoring Systems Laboratory, U.S. EPA, Cincinnati, Ohio. However, additional secondary standards must be obtained from commercial sources, and solutions should be prepared in the analyst's laboratory. It is the responsibility of the laboratory to ascertain that the calibration solutions received (or prepared) are indeed at the appropriate concentrations before they are used to analyze samples.

5.6.2 Store the concentration calibration solutions in 1 mL minivials at room temperature in the dark.

5.7 GC Column Performance Check Solution - This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The $^{13}C_{12}$-2,3,7,8-TCDD is also present. The laboratory is required to use nonane as the solvent and adjust the volume so that the final concentration does not exceed 100 pg/μL per congener. Table 7 summarizes the qualitative composition (minimum requirement) of this performance evaluation solution.

5.8 Sample Fortification Solution - This nonane solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note that $^{13}C_{12}$-OCDF is not present in the solution.)

5.9 Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at a nominal concentration of 50 pg/μL per compound. 10 to 50 μL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

5.10 Matrix Spike Fortification Solution - Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes listed in Table 5 at concentrations corresponding to the HRCC 3.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Sample Collection

6.2.1 Sample collection personnel should, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the laboratory. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly not homogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula before removal of a sample portion for analysis.

6.2.2 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Sampling equipment must be free of potential sources of contamination.

6.3 Grinding or Blending of Fish Samples - If not otherwise specified by the U.S. EPA, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3 to 5 mm

hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the U.S. EPA. If so requested, the above whole fish requirement is superseded.

6.4 Storage and Holding Times - All samples, except fish and adipose tissue samples, must be stored at 4°C in the dark, extracted within 30 days and completely analyzed within 45 days of extraction. Fish and adipose tissue samples must be stored at -20°C in the dark, extracted within 30 days and completely analyzed within 45 days of collection. Whenever samples are analyzed after the holding time expiration date, the results should be considered to be minimum concentrations and should be identified as such.

NOTE: The holding times listed in Sec. 6.4 are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in Sec. 6.4 may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.

6.5 Phase Separation - This is a guideline for phase separation for very wet (>25 percent water) soil, sediment and paper pulp samples. Place a 50 g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipet, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent dry weight determination, extraction). Return the remaining solid portion to the original sample bottle (empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil, sediment and paper pulp method. Take note of, and report, the estimated volume of liquid before disposing of the liquid as a liquid waste.

6.6 Soil, Sediment, or Paper Sludge (Pulp) Percent Dry Weight Determination - The percent dry weight of soil, sediment or paper pulp samples showing detectable levels (see note below) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined according to the following procedure. Weigh a 10 g portion of the soil or sediment sample (± 0.5 g) to three significant figures. Dry it to constant weight at 110°C in an adequately ventilated oven. Allow the sample to cool in a desiccator. Weigh the dried solid to three significant figures. Calculate and report the percent dry weight. Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste.

NOTE: Until detection limits have been established (Sec. 1.3), the lower MCLs (Table 1) may be used to estimate the minimum detectable levels.

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

CAUTION: Finely divided soils and sediments contaminated with PCDDs/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing PCDDs/PCDFs

(including 2,3,7,8-TCDD). Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

6.7 Lipid Content Determination

6.7.1 Fish Tissue - To determine the lipid content of fish tissue, concentrate 125 mL of the fish tissue extract (Sec. 7.2.2), in a tared 200 mL round bottom flask, on a rotary evaporator until a constant weight (W) is achieved.

$$\text{Percent lipid} = \frac{100\ (W)}{10}$$

Dispose of the lipid residue as a hazardous waste if the results of the analysis indicate the presence of PCDDs or PCDFs.

6.7.2 Adipose Tissue - Details for the determination of the adipose tissue lipid content are provided in Sec. 7.3.3.

7.0 PROCEDURE

7.1 Internal standard addition

7.1.1 Use a portion of 1 g to 1000 g (± 5 percent) of the sample to be analyzed. Typical sample size requirements for different matrices are given in Sec. 7.4 and in Table 1. Transfer the sample portion to a tared flask and determine its weight.

7.1.2 Except for adipose tissue, add an appropriate quantity of the sample fortification mixture (Sec. 5.8) to the sample. All samples should be spiked with 100 µL of the sample fortification mixture to give internal standard concentrations as indicated in Table 1. As an example, for $^{13}C_{12}$-2,3,7,8-TCDD, a 10 g soil sample requires the addition of 1000 pg of $^{13}C_{12}$-2,3,7,8-TCDD to give the required 100 ppt fortification level. The fish tissue sample (20 g) must be spiked with 200 µL of the internal standard solution, because half of the extract will be used to determine the lipid content (Sec. 6.7.1).

7.1.2.1 For the fortification of soil, sediment, fly ash, water, fish tissue, paper pulp and wet sludge samples, mix the sample fortification solution with 1.0 mL acetone.

7.1.2.2 Do not dilute the nonane solution for the other matrices.

7.1.2.3 The fortification of adipose tissue is carried out at the time of homogenization (Sec. 7.3.2.3).

7.2 Extraction and Purification of Fish and Paper Pulp Samples

7.2.1 Add 60 g anhydrous sodium sulfate to a 20 g portion of a homogeneous fish sample (Sec. 6.3) and mix thoroughly with a stainless

steel spatula. After breaking up any lumps, place the fish/sodium sulfate mixture in the Soxhlet apparatus on top of a glass wool plug. Add 250 mL methylene chloride or hexane/methylene chloride (1:1) to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour. Follow the same procedure for the partially dewatered paper pulp sample (using a 10 g sample, 30 g of anhydrous sodium sulfate and 200 mL of toluene).

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.2.2 Transfer the fish extract from Sec. 7.2.1 to a 250 mL volumetric flask and fill to the mark with methylene chloride. Mix well, then remove 125 mL for the determination of the lipid content (Sec. 6.7.1). Transfer the remaining 125 mL of the extract, plus two 15 mL hexane/methylene chloride rinses of the volumetric flask, to a KD apparatus equipped with a Snyder column. Quantitatively transfer all of the paper pulp extract to a KD apparatus equipped with a Snyder column.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

7.2.3 Add a Teflon™, or equivalent, boiling chip. Concentrate the extract in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

7.2.4 Add 50 mL hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 5 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

NOTE: The methylene chloride must have been completely removed before proceeding with the next step.

7.2.5 Remove and invert the Snyder column and rinse it into the KD apparatus with two 1 mL portions of hexane. Decant the contents of the KD apparatus and concentrator tube into a 125 mL separatory funnel. Rinse the KD apparatus with two additional 5 mL portions of hexane and add the rinses to the funnel. Proceed with the cleanup according to the instructions starting in Sec. 7.5.1.1, but omit the procedures described in Secs. 7.5.1.2 and 7.5.1.3.

7.3 Extraction and Purification of Human Adipose Tissue

7.3.1 Human adipose tissue samples must be stored at a temperature of -20°C or lower from the time of collection until the time of analysis. The use of chlorinated materials during the collection of the samples must be avoided. Samples are handled with stainless steel forceps, spatulas, or scissors. All sample bottles (glass) are cleaned as specified in the note at the end of Sec. 4.3. Teflon™ lined caps should be used.

NOTE: The specified storage temperature of -20°C is the maximum storage temperature permissible for adipose tissue samples. Lower storage temperatures are recommended.

7.3.2 Adipose Tissue Extraction

7.3.2.1 Weigh, to the nearest 0.01 g, a 10 g portion of a frozen adipose tissue sample into a culture tube (2.2 x 15 cm).

NOTE: The sample size may be smaller, depending on availability. In such a situation, the analyst is required to adjust the volume of the internal standard solution added to the sample to meet the fortification level stipulated in Table 1.

7.3.2.2 Allow the adipose tissue specimen to reach room temperature (up to 2 hours).

7.3.2.3 Add 10 mL methylene chloride and 100 µL of the sample fortification solution. Homogenize the mixture for approximately 1 minute with a tissue homogenizer.

7.3.2.4 Allow the mixture to separate, then remove the methylene chloride extract from the residual solid material with a disposable pipet. Percolate the methylene chloride through a filter funnel containing a clean glass wool plug and 10 g anhydrous sodium sulfate. Collect the dried extract in a graduated 100 mL volumetric flask.

7.3.2.5 Add a second 10 mL portion of methylene chloride to the sample and homogenize for 1 minute. Decant the solvent, dry it, and transfer it to the 100 mL volumetric flask (Sec. 7.3.2.4).

7.3.2.6 Rinse the culture tube with at least two additional portions of methylene chloride (10 mL each), and transfer the entire contents to the filter funnel containing the anhydrous sodium sulfate. Rinse the filter funnel and the anhydrous sodium sulfate contents with additional methylene chloride (20 to 40 mL) into the 100 mL flask. Discard the sodium sulfate.

7.3.2.7 Adjust the volume to the 100 mL mark with methylene chloride.

7.3.3 Adipose Tissue Lipid Content Determination

7.3.3.1 Preweigh a clean 1 dram (or metric equivalent) glass vial to the nearest 0.0001 g on an analytical balance tared to zero.

7.3.3.2 Accurately transfer 1.0 mL of the final extract (100 mL) from Sec. 7.3.2.7 to the vial. Reduce the volume of the extract on a water bath (50-60°C) by a gentle stream of purified

nitrogen until an oily residue remains. Nitrogen blowdown is continued until a constant weight is achieved.

NOTE: When the sample size of the adipose tissue is smaller than 10 g, then the analyst may use a larger portion (up to 10 percent) of the extract defined in Sec. 7.3.2.7 for the lipid determination.

7.3.3.3 Accurately weigh the vial with the residue to the nearest 0.0001 g and calculate the weight of the lipid present in the vial based on the difference of the weights.

7.3.3.4 Calculate the percent lipid content of the original sample to the nearest 0.1 percent as shown below:

$$\text{Lipid content, LC (\%)} = \frac{W_{lr} \times V_{ext}}{W_{at} \times V_{al}} \times 100$$

where:

W_{lr} = weight of the lipid residue to the nearest 0.0001 g calculated from Sec. 7.3.3.3,

V_{ext} = total volume (100 mL) of the extract in mL from Sec. 7.3.2.7,

W_{at} = weight of the original adipose tissue sample to the nearest 0.01 g from Sec. 7.3.2.1, and

V_{al} = volume of the aliquot of the final extract in mL used for the quantitative measure of the lipid residue (1.0 mL) from Sec. 7.3.3.2.

7.3.3.5 Record the lipid residue measured in Sec. 7.3.3.3 and the percent lipid content from Sec. 7.3.3.4.

7.3.4 Adipose Tissue Extract Concentration

7.3.4.1 Quantitatively transfer the remaining extract from Sec. 7.3.3.2 (99.0 mL) to a 500 mL Erlenmeyer flask. Rinse the volumetric flask with 20 to 30 mL of additional methylene chloride to ensure quantitative transfer.

7.3.4.2 Concentrate the extract on a rotary evaporator and a water bath at 40°C until an oily residue remains.

7.3.5 Adipose Tissue Extract Cleanup

7.3.5.1 Add 200 mL hexane to the lipid residue in the 500 mL Erlenmeyer flask and swirl the flask to dissolve the residue.

7.3.5.2 Slowly add, with stirring, 100 g of 40 percent (w/w) sulfuric acid-impregnated silica gel. Stir with a magnetic stirrer for two hours at room temperature.

7.3.5.3 Allow the solid phase to settle, and decant the liquid through a filter funnel containing 10 g anhydrous sodium sulfate on a glass wool plug, into another 500 mL Erlenmeyer flask.

7.3.5.4 Rinse the solid phase with two 50 mL portions of hexane. Stir each rinse for 15 minutes, decant, and dry as described under Sec. 7.3.5.3. Combine the hexane extracts from Sec. 7.3.5.3 with the rinses.

7.3.5.5 Rinse the sodium sulfate in the filter funnel with an additional 25 mL hexane and combine this rinse with the hexane extracts from Sec. 7.3.5.4.

7.3.5.6 Prepare an acidic silica column as follows: Pack a 2 cm x 10 cm chromatographic column with a glass wool plug, add approximately 20 mL hexane, add 1 g silica gel and allow to settle, then add 4 g of 40 percent (w/w) sulfuric acid-impregnated silica gel and allow to settle. Elute the excess hexane from the column until the solvent level reaches the top of the chromatographic packing. Verify that the column does not have any air bubbles and channels.

7.3.5.7 Quantitatively transfer the hexane extract from the Erlenmeyer flask (Secs. 7.3.5.3 through 7.3.5.5) to the silica gel column reservoir. Allow the hexane extract to percolate through the column and collect the eluate in a 500 mL KD apparatus.

7.3.5.8 Complete the elution by percolating 50 mL hexane through the column into the KD apparatus. Concentrate the eluate on a steam bath to approximately 5 mL. Use nitrogen blowdown to bring the final volume to about 100 μL.

NOTE: If the silica gel impregnated with 40 percent sulfuric acid is highly discolored throughout the length of the adsorbent bed, the cleaning procedure must be repeated beginning with Sec. 7.3.5.1.

7.3.5.9 The extract is ready for the column cleanups described in Secs. 7.5.2 through 7.5.3.6.

7.4 Extraction and Purification of Environmental and Waste Samples

7.4.1 Sludge/Wet Fuel Oil

7.4.1.1 Extract aqueous sludge or wet fuel oil samples by refluxing a sample (e.g., 2 g) with 50 mL toluene in a 125 mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water is removed.

NOTE: If the sludge or fuel oil sample dissolves in toluene, treat it according to the instructions in Sec. 7.4.2 below. If the labeled sludge sample originates from pulp (paper mills), treat it according to the instructions starting in Sec. 7.2, but without the addition of sodium sulfate.

7.4.1.2 Cool the sample, filter the toluene extract through a glass fiber filter, or equivalent, into a 100 mL round bottom flask.

7.4.1.3 Rinse the filter with 10 mL toluene and combine the extract with the rinse.

7.4.1.4 Concentrate the combined solutions to near dryness on a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Sec. 7.4.4.

7.4.2 Still Bottom/Oil

7.4.2.1 Extract still bottom or oil samples by mixing a sample portion (e.g., 1.0 g) with 10 mL toluene in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50 mL round bottom flask. Rinse the beaker and filter with 10 mL toluene.

7.4.2.2 Concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Sec. 7.4.4.

7.4.3 Fly Ash

NOTE: Because of the tendency of fly ash to "fly", all handling steps should be performed in a hood in order to minimize contamination.

7.4.3.1 Weigh about 10 g fly ash to two decimal places and transfer to an extraction jar. Add 100 µL sample fortification solution (Sec. 5.8), diluted to 1 mL with acetone, to the sample. Add 150 mL of 1 M HCl to the fly ash sample. Seal the jar with the Teflon™ lined screw cap and shake for 3 hours at room temperature.

7.4.3.2 Rinse a glass fiber filter with toluene, and filter the sample through the filter paper, placed in a Buchner funnel, into a 1 L flask. Wash the fly ash cake with approximately 500 mL organic-free reagent water and dry the filter cake overnight at room temperature in a desiccator.

7.4.3.3 Add 10 g anhydrous powdered sodium sulfate, mix thoroughly, let sit in a closed container for one hour, mix again, let sit for another hour, and mix again.

7.4.3.4 Place the sample and the filter paper into an extraction thimble, and extract in a Soxhlet extraction apparatus

charged with 200 mL toluene for 16 hours using a five cycle/hour schedule.

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.4.3.5 Cool and filter the toluene extract through a glass fiber filter into a 500 mL round bottom flask. Rinse the filter with 10 mL toluene. Add the rinse to the extract and concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Sec. 7.4.4.

7.4.4 Transfer the concentrate to a 125 mL separatory funnel using 15 mL hexane. Rinse the flask with two 5 mL portions of hexane and add the rinses to the funnel. Shake the combined solutions in the separatory funnel for two minutes with 50 mL of 5 percent sodium chloride solution, discard the aqueous layer, and proceed with Sec. 7.5.

7.4.5 Aqueous samples

7.4.5.1 Allow the sample to come to ambient temperature, then mark the water meniscus on the side of the 1 L sample bottle for later determination of the exact sample volume. Add the required acetone diluted sample fortification solution (Sec. 5.8).

7.4.5.2 When the sample is judged to contain 1 percent or more solids, the sample must be filtered through a glass fiber filter that has been rinsed with toluene. If the suspended solids content is too great to filter through the 0.45 µm filter, centrifuge the sample, decant, and then filter the aqueous phase.

NOTE: Paper mill effluent samples normally contain 0.02%-0.2% solids, and would not require filtration. However, for optimum analytical results, all paper mill effluent samples should be filtered, the isolated solids and filtrate extracted separately, and the extracts recombined.

7.4.5.3 Combine the solids from the centrifuge bottle(s) with the particulates on the filter and with the filter itself and proceed with the Soxhlet extraction as specified in Secs. 7.4.6.1 through 7.4.6.4. Remove and invert the Snyder column and rinse it down into the KD apparatus with two 1 mL portions of hexane.

7.4.5.4 Pour the aqueous filtrate into a 2 L separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting.

7.4.5.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface

between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation (e.g., glass stirring rod).

7.4.5.6 Collect the methylene chloride into a KD apparatus (mounted with a 10 mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g anhydrous sodium sulfate.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

7.4.5.7 Repeat the extraction twice with fresh 60 mL portions of methylene chloride. After the third extraction, rinse the sodium sulfate with an additional 30 mL methylene chloride to ensure quantitative transfer. Combine all extracts and the rinse in the KD apparatus.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered when using a separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor. Repeat the rinse of the sample bottle with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL methylene chloride to the distilling flask, add sufficient organic-free reagent water (Sec. 5.1) to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Secs. 7.4.5.6 and 7.4.5.8 through 7.4.5.10. Proceed with Sec. 7.4.5.11.

7.4.5.8 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid is 5 mL. Remove the KD apparatus and allow it to drain and cool for at least 10 minutes.

7.4.5.9 Remove the Snyder column, add 50 mL hexane, add the concentrate obtained from the Soxhlet extraction of the suspended solids (Sec. 7.4.5.3), if applicable, re-attach the Snyder column, and concentrate to approximately 5 mL. Add a new boiling chip to the KD apparatus before proceeding with the second concentration step.

7.4.5.10 Rinse the flask and the lower joint with two 5 mL portions of hexane and combine the rinses with the extract to give a final volume of about 15 mL.

7.4.5.11 Determine the original sample volume by filling the sample bottle to the mark with water and transferring the water to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Sec. 7.5.

7.4.6 Soil/Sediment

7.4.6.1 Add 10 g anhydrous powdered sodium sulfate to the sample portion (e.g., 10 g) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass wool plug (the use of an extraction thimble is optional).

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.4.6.2 Add 200 to 250 mL toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour.

NOTE: If the dried sample is not of free flowing consistency, more sodium sulfate must be added.

7.4.6.3 Cool and filter the extract through a glass fiber filter into a 500 mL round bottom flask for evaporation of the toluene. Rinse the filter with 10 mL of toluene, and concentrate the combined fractions to near dryness on a rotary evaporator at 50°C. Remove the flask from the water bath and allow to cool for 5 minutes.

7.4.6.4 Transfer the residue to a 125 mL separatory funnel, using 15 mL of hexane. Rinse the flask with two additional portions of hexane, and add the rinses to the funnel. Proceed with Sec. 7.5.

7.5 Cleanup

7.5.1 Partition

7.5.1.1 Partition the hexane extract against 40 mL of concentrated sulfuric acid. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

7.5.1.2 Omit this step for the fish sample extract. Partition the extract against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

7.5.1.3 Omit this step for the fish sample extract. Partition the extract against 40 mL of 20 percent (w/v) aqueous

potassium hydroxide (KOH). Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform a maximum of four base washings). Strong base (KOH) is known to degrade certain PCDDs/PCDFs, so contact time must be minimized.

7.5.1.4 Partition the extract against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the extract by pouring it through a filter funnel containing anhydrous sodium sulfate on a glass wool plug, and collect it in a 50 mL round bottom flask. Rinse the funnel with the sodium sulfate with two 15 mL portions of hexane, add the rinses to the 50 mL flask, and concentrate the hexane solution to near dryness on a rotary evaporator (35°C water bath), making sure all traces of toluene (when applicable) are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted.)

7.5.2 Silica/Alumina Column Cleanup

7.5.2.1 Pack a gravity column (glass, 30 cm x 10.5 mm), fitted with a Teflon™ stopcock, with silica gel as follows: Insert a glass wool plug into the bottom of the column. Place 1 g silica gel in the column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 4 g sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed. Elute with 10 mL hexane and close the stopcock just before exposure of the top layer of silica gel to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap the wetted column.

7.5.2.2 Pack a gravity column (glass, 300 mm x 10.5 mm), fitted with a Teflon™ stopcock, with alumina as follows: Insert a glass wool plug into the bottom of the column. Add a 4 g layer of sodium sulfate. Add a 4 g layer of Woelm® Super 1 neutral alumina. Tap the top of the column gently. Woelm® Super 1 neutral alumina need not be activated or cleaned before use, but it should be stored in a sealed desiccator. Add a 4 g layer of anhydrous sodium sulfate to cover the alumina. Elute with 10 mL hexane and close the stopcock just before exposure of the sodium sulfate layer to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap a wetted column.

<u>NOTE</u>: Optionally, acidic alumina (Sec. 5.2.2) can be used in place of neutral alumina.

7.5.2.3 Dissolve the residue from Sec. 7.5.1.4 in 2 mL hexane and apply the hexane solution to the top of the silica gel column. Rinse the flask with enough hexane (3-4 mL) to complete the quantitative transfer of the sample to the surface of the silica gel.

7.5.2.4 Elute the silica gel column with 90 mL of hexane, concentrate the eluate on a rotary evaporator (35°C water bath) to approximately 1 mL, and apply the concentrate to the top of the alumina column (Sec. 7.5.2.2). Rinse the rotary evaporator flask twice with 2 mL of hexane, and add the rinses to the top of the alumina column.

7.5.2.5 Add 20 mL hexane to the alumina column and elute until the hexane level is just below the top of the sodium sulfate. Do not discard the eluted hexane, but collect it in a separate flask and store it for later use, as it may be useful in determining where the labeled analytes are being lost if recoveries are not satisfactory.

7.5.2.6 Add 15 mL of 60 percent methylene chloride in hexane (v/v) to the alumina column and collect the eluate in a conical shaped (15 mL) concentration tube. With a carefully regulated stream of nitrogen, concentrate the 60 percent methylene chloride/hexane fraction to about 2 mL.

7.5.3 Carbon Column Cleanup

7.5.3.1 Prepare an AX-21/Celite 545® column as follows: Thoroughly mix 5.40 g active carbon AX-21 and 62.0 g Celite 545® to produce an 8 percent (w/w) mixture. Activate the mixture at 130°C for 6 hours and store it in a desiccator.

7.5.3.2 Cut off both ends of a 10 mL disposable serological pipet to give a 10 cm long column. Fire polish both ends and flare, if desired. Insert a glass wool plug at one end, then pack the column with enough Celite 545® to form a 1 cm plug, add 1 g of the AX-21/Celite 545® mixture, top with additional Celite 545® (enough for a 1 cm plug), and cap the packing with another glass wool plug.

NOTE: Each new batch of AX-21/Celite 545® must be checked as follows: Add 50 µL of the continuing calibration solution to 950 µL hexane. Take this solution through the carbon column cleanup step, concentrate to 50 µL and analyze. If the recovery of any of the analytes is <80 percent, discard this batch of AX-21/Celite 545®.

7.5.3.3 Rinse the AX-21/Celite 545® column with 5 mL of toluene, followed by 2 mL of 75:20:5 (v/v) methylene chloride/methanol/toluene, 1 mL of 1:1 (v/v) cyclohexane/methylene chloride, and 5 mL hexane. The flow rate should be less than 0.5 mL/min. Discard the rinses. While the column is still wet with hexane, add the sample concentrate (Sec. 7.5.2.6) to the top of the column. Rinse the concentrator tube (which contained the sample concentrate) twice with 1 mL hexane, and add the rinses to the top of the column.

7.5.3.4 Elute the column sequentially with two 2 mL portions of hexane, 2 mL cyclohexane/methylene chloride (50:50,

v/v), and 2 mL methylene chloride/methanol/toluene (75:20:5, v/v). Combine these eluates; this combined fraction may be used as a check on column efficiency.

7.5.3.5 Turn the column upside down and elute the PCDD/PCDF fraction with 20 mL toluene. Verify that no carbon fines are present in the eluate. If carbon fines are present in the eluate, filter the eluate through a glass fiber filter (0.45 µm) and rinse the filter with 2 mL toluene. Add the rinse to the eluate.

7.5.3.6 Concentrate the toluene fraction to about 1 mL on a rotary evaporator by using a water bath at 50°C. Carefully transfer the concentrate into a 1 mL minivial and, again at elevated temperature (50°C), reduce the volume to about 100 µL using a stream of nitrogen and a sand bath. Rinse the rotary evaporator flask three times with 300 µL of a solution of 1 percent toluene in methylene chloride, and add the rinses to the concentrate. Add 10 µL of the nonane recovery standard solution (Sec. 5.9) for soil, sediment, water, fish, paper pulp and adipose tissue samples, or 50 µL of the recovery standard solution for sludge, still bottom and fly ash samples. Store the sample at room temperature in the dark.

7.6 Chromatographic/Mass Spectrometric Conditions and Data Acquisition Parameters

7.6.1 Gas Chromatograph

Column coating: DB-5
Film thickness: 0.25 µm
Column dimension: 60 m x 0.32 mm
Injector temperature: 270°C
Splitless valve time: 45 s
Interface temperature: Function of the final temperature
Temperature program:

Stage	Init. Temp. (°C)	Init. Hold Time (min)	Temp. Ramp (°C/min)	Final Temp. (°C)	Final Hold Time (min)
1	200	2	5	220	16
2			5	235	7
3			5	330	5

Total time: 60 min

7.6.2 Mass Spectrometer

7.6.2.1 The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less (Sec. 7.6.3.1). At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that with the

exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection (Table 6) of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

NOTE: At the option of the analyst, the tetra- and pentachlorinated dioxins and furans can be combined into a single descriptor.

7.6.2.2 The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 6. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).

7.6.3 Data Acquisition

7.6.3.1 The total cycle time for data acquisition must be $\leq$ 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

7.6.3.2 Acquire SIM data for all the ions listed in the five descriptors of Table 6.

7.7 Calibration

7.7.1 Initial Calibration - Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (Sec. 7.7.3) does not meet the required criteria listed in Sec. 7.7.2.

7.7.1.1 All five high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

7.7.1.2 Tune the instrument with PFK as described in Sec. 7.6.2.2.

7.7.1.3 Inject 2 μL of the GC column performance check solution (Sec. 5.7) and acquire SIM mass spectral data as described

earlier in Sec. 7.6.2. The total cycle time must be $\leq$ 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criterion listed in Sec. 8.2.1 was met.

7.7.1.4 By using the same GC (Sec. 7.6.1) and MS (Sec. 7.6.2) conditions that produced acceptable results with the column performance check solution, analyze a 2 μL portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameters.

7.7.1.4.1 The ratio of integrated ion current for the ions appearing in Table 8 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series) for all unlabeled calibration standards in Table 5.

7.7.1.4.2 The ratio of integrated ion current for the ions belonging to the carbon-labeled internal and recovery standards (Table 5) must be within the control limits stipulated in Table 8.

NOTE: Secs. 7.7.1.4.1 and 7.7.1.4.2 require that 17 ion ratios from Sec. 7.7.1.4.1 and 11 ion ratios from Sec. 7.7.1.4.2 be within the specified control limits simultaneously in one run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

7.7.1.4.3 For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Measurement of S/N is required for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question.

7.7.1.4.4 Referring to Table 9, calculate the 17 relative response factors (RF) for unlabeled target analytes [RF(n); n = 1 to 17] relative to their appropriate internal standards (Table 5) and the nine RFs for the labeled $^{13}C_{12}$ internal standards [RF(m); m = 18 to 26)] relative to the two recovery standards (Table 5) according to the following formulae:

$$RF_n = \frac{A_x \times Q_{is}}{Q_x \times A_{is}} \qquad RF_m = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs}}$$

where:

A_x = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled recovery standards,

Q_{is} = quantity of the internal standard injected (pg),

Q_{rs} = quantity of the recovery standard injected (pg), and

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RF_n and RF_m are dimensionless quantities; the units used to express Q_{is}, Q_{rs} and Q_x must be the same.

7.7.1.4.5 Calculate the $\overline{RF}$ and their respective percent relative standard deviations (%RSD) for the five calibration solutions:

$$\overline{RF}_n = 1/5 \sum_{j=1}^{5} RF_{n(j)}$$

Where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17; Table 9), and j is the injection number (or calibration solution number; j = 1 to 5).

7.7.1.4.6 The relative response factors to be used for the determination of the concentration of total isomers in a homologous series (Table 9) are calculated as follows:

7.7.1.4.6.1 For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean $\overline{RF}$ used will be the same as the mean $\overline{RF}$ determined in Sec. 7.7.1.4.5.

NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}C_{12}$-OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}C_{12}$-OCDF with $[M]^+$ of OCDD). Therefore, the $\overline{RF}$ for OCDF is calculated relative to $^{13}C_{12}$-OCDD.

7.7.1.4.6.2 For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the mean $\overline{RF}$ used for those homologous series will be the mean of the RFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\overline{RF}_k = \frac{1}{t} \sum_{n=1}^{t} RF_n$$

where:

k = 27 to 30 (Table 9), with 27 = PeCDF; 28 = HxCDF; 29 = HxCDD; and 30 = HpCDF,

t = total number of 2,3,7,8-substituted isomers present in the calibration solutions (Table 5) for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologous series are different. However, this analytical protocol will make the assumption that the HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

7.7.1.4.7 Relative response factors [$\overline{RF}_m$] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$RF_m = \frac{A_{is}^{m} \times Q_{rs}}{Q_{is}^{m} \times A_{rs}}$$

$$\overline{RF}_m = 1/5 \sum_{j=1}^{5} RF_{m(j)},$$

where:

m	=	18 to 26 (congener type) and j = 1 to 5 (injection number),
A_{is}^{m}	=	sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for a given internal standard (m = 18 to 26),
A_{rs}	=	sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the appropriate recovery standard (see Table 5, footnotes),
Q_{rs}, Q_{is}^{m}	=	quantities of, respectively, the recovery standard (rs) and a particular internal standard (is = m) injected (pg),
RF_m	=	relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from one injection, and
$\overline{RF}_m$	=	calculated mean relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from the five initial calibration injections (j).

7.7.2 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed.

7.7.2.1 The percent relative standard deviations for the mean response factors [RF_n and RF_m] from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 30 percent.

7.7.2.2 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be $\geq$ 10.

7.7.2.3 The ion abundance ratios (Table 8) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Sec. 7.7.2.1 is met, the analyte-specific RF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RFs will be used for all calculations until the routine calibration criteria (Sec. 7.7.4) are no longer met. At such time, new mean RFs will be calculated from a new set of injections of the calibration solutions.

7.7.3 Routine Calibration (Continuing Calibration Check) - Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hour shift.

7.7.3.1 Inject 2 μL of the concentration calibration solution HRCC-3 standard (Table 5). By using the same HRGC/HRMS conditions as used in Secs. 7.6.1 and 7.6.2, determine and document an acceptable calibration as provided in Sec. 7.7.4.

7.7.4 Criteria for Acceptable Routine Calibration - The following criteria must be met before further analysis is performed.

7.7.4.1 The measured RFs [RF_n for the unlabeled standards] obtained during the routine calibration runs must be within $\pm$ 20 percent of the mean values established during the initial calibration (Sec. 7.7.1.4.5).

7.7.4.2 The measured RFs [RF_m for the labeled standards] obtained during the routine calibration runs must be within $\pm$ 30 percent of the mean values established during the initial calibration (Sec. 7.7.1.4.7).

7.7.4.3 The ion abundance ratios (Table 8) must be within the allowed control limits.

7.7.4.4 If either one of the criteria in Secs. 7.7.4.1 and 7.7.4.2 is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire routine calibration process (Sec. 7.7.1) must be reviewed. It is realized that it may not always be possible to achieve all RF criteria. For example, it has occurred that the RF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however, the RF values for the corresponding unlabeled compounds were routinely within the criteria established in the method. In these cases, 24 of the 26 RF parameters have met the QC criteria, and the data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event.

In these situations, the analyst must assess the effect on overall data quality as required for the data quality objectives and decide on appropriate action. Corrective action would be in order, for example, if the compounds for which the RF criteria were not met included both the unlabeled and the corresponding internal standard compounds. If the ion abundance ratio criterion (Sec. 7.7.4.3) is not satisfied, refer to the note in Sec. 7.7.1.4.2 for resolution.

NOTE: An initial calibration must be carried out whenever the HRCC-3, the sample fortification, or the recovery standard solution is replaced by a new solution from a different lot.

7.8 Analysis

7.8.1 Remove the sample or blank extract (from Sec. 7.5.3.6) from storage. With a stream of dry, purified nitrogen, reduce the extract volume to 10 µL to 50 µL.

NOTE: A final volume of 20 µL or more should be used whenever possible. A 10 µL final volume is difficult to handle, and injection of 2 µL out of 10 µL leaves little sample for confirmations and repeat injections, and for archiving.

7.8.2 Inject a 2 µL aliquot of the extract into the GC, operated under the conditions that have been established to produce acceptable results with the performance check solution (Secs. 7.6.1 and 7.6.2).

7.8.3 Acquire SIM data according to Secs. 7.6.2 and 7.6.3. Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (Secs. 7.7.1.4.4 through 7.7.1.4.7). Ions characteristic of polychlorinated diphenyl ethers are included in the descriptors listed in Table 6.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined (Sec. 8.2.1.3). Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run (see Sec. 8.2.2 for the proper level of reference compound to be metered into the ion chamber.) The analyst may be required to monitor a PFK ion, not as a lock-mass, but as a regular ion, in order to meet this requirement. It is recommended to examine the lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements [Tondeur et al., 1984, 1987]. Report any discrepancies in the case narrative.

7.8.4 Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

7.8.4.1 Retention Times

7.8.4.1.1 For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Tables 2 and 3), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 6) must be within -1 to +3 seconds of the isotopically labeled standard.

7.8.4.1.2 For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of six congeners; Table 3), the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the daily routine calibration results.

7.8.4.1.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution (Sec. 8.1.3).

7.8.4.1.4 The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach maximum simultaneously (± 2 seconds).

7.8.4.1.5 The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously (± 2 seconds).

<u>NOTE</u>: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF (Sec. 8.1.3) in the SICPs of the daily performance checks. Should either one compound be missing, the analyst is required to take corrective action as it may indicate a potential problem with the ability to detect all the PCDDs/PCDFs.

7.8.4.2 Ion Abundance Ratios

7.8.4.2.1 The integrated ion currents for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series

to which the peak is assigned. See Secs. 7.7.1.4.1 and 7.7.1.4.2 and Table 8 for details.

7.8.4.3 Signal-to-Noise Ratio

7.8.4.3.1 All ion current intensities must be $\geq$ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers. Figure 6 describes the procedure to be followed for the determination of the S/N.

7.8.4.4 Polychlorinated Diphenyl Ether Interferences

7.8.4.4.1 In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N $\geq$ 2.5 is detected at the same retention time ($\pm$ 2 seconds) in the corresponding polychlorinated diphenyl ether (PCDPE, Table 6) channel.

7.9 Calculations

7.9.1 For gas chromatographic peaks that have met the criteria outlined in Secs. 7.8.4.1.1 through 7.8.4.3.1, calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RF}_n}$$

where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 6) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight, in g, of the sample (solid or organic liquid), or volume in mL of an aqueous sample, and

$\overline{RF}_n$ = calculated mean relative response factor for the analyte [$\overline{RF}_n$ with n = 1 to 17; Sec. 7.7.1.4.5].

If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs, $\overline{RF}_n$ is the value calculated using the equation in Sec. 7.7.1.4.5. However, if it is a non-2,3,7,8-substituted congener, the $\overline{RF}(k)$ value is

the one calculated using the equation in Sec. 7.7.1.4.6.2. [RF_k k = 27 to 30].

7.9.2 Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal standard percent recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RF}_m} \times 100$$

where:

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (see Table 5, footnotes),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RF}_m$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5, footnotes) recovery standard. This represents the mean obtained in Sec. 7.7.1.4.7 [$\overline{RF}_m$ with m = 18 to 26].

NOTE: For human adipose tissue, adjust the percent recoveries by adding 1 percent to the calculated value to compensate for the 1 percent of the extract diverted for the lipid determination.

7.9.3 If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limits (MCL) listed in Table 1 (e.g., 200 pg/µL for TCDD in soil), the linear range of response versus concentration may have been exceeded, and a second analysis of the sample (using a one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation (Secs. 7.1 to 7.9.3). For the other congeners (including OCDD), however, report the measured concentration and indicate that the value exceeds the MCL.

7.9.3.1 If a smaller sample size would not be representative of the entire sample, one of the following options is recommended:

(1) Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a

higher concentration of internal standard. Prior to GC/MS analysis, dilute the sample so that it has a concentration of internal standard equivalent to that present in the calibration standard. Then, analyze the diluted extract.

(2) Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Immediately following extraction, transfer the sample to a volumetric flask and dilute to known volume. Remove an appropriate aliquot and proceed with cleanup and analysis.

(3) Use the original analysis data to quantitate the internal standard recoveries. Respike the original extract (note that no additional cleanup is necessary) with 100 times the usual quantity of internal standards. Dilute the re-spiked extract by a factor of 100. Reanalyze the diluted sample using the internal standard recoveries calculated from the initial analysis to correct the results for losses during isolation and cleanup.

7.9.4 The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report. If an isomer is not detected, use zero (0) in this calculation.

7.9.5 Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

7.9.5.1 Samples giving a response for both quantitation ions (Tables 6 and 9) that is less than 2.5 times the background level.

7.9.5.1.1 Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e., S/N < 2.5). The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions (Table 6) of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard),

multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Use the formula:

$$\text{EDL (specific 2,3,7,8-subst. PCDD/PCDF)} = \frac{2.5 \times H_x \times Q_{is}}{H_{is} \times W \times \overline{RF}_n}$$

where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

H_x = sum of the height of the noise level for each quantitation ion (Table 6) for the unlabeled PCDDs/PCDFs, measured as shown in Figure 6.

H_{is} = sum of the height of the noise level for each quantitation ion (Table 6) for the labeled internal standard, measured as shown in Figure 6.

W, $\overline{RF}_n$, and Q_{is} retain the same meanings as defined in Sec. 7.9.1.

7.9.5.2 Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions (Tables 6 and 9).

7.9.5.2.1 When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in Sec. 7.8.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Sec. 7.9.1, except that A_x in Sec. 7.9.1 should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

7.9.6 The relative percent difference (RPD) of any duplicate sample results are calculated as follows:

$$RPD = \frac{| S_1 - S_2 |}{(S_1 + S_2) / 2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

7.9.7 The 2,3,7,8-TCDD toxicity equivalents (TE) of PCDDs and PCDFs present in the sample are calculated, if requested by the data user, according to the method recommended by the Chlorinated Dioxins Workgroup

(CDWG) of the EPA and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs (Table 3) and to OCDD and OCDF, as shown in Table 10. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 10. The exclusion of other homologous series such as mono-, di-, and tri- chlorinated dibenzodioxins and dibenzofurans does not mean that they are non-toxic. However, their toxicity, as known at this time, is much lower than the toxicity of the compounds listed in Table 10. The above procedure for calculating the 2,3,7,8-TCDD toxicity equivalents is not claimed by the CDWG to be based on a thoroughly established scientific foundation. The procedure, rather, represents a "consensus recommendation on science policy". Since the procedure may be changed in the future, reporting requirements for PCDD and PCDF data would still include the reporting of the analyte concentrations of the PCDD/PCDF congener as calculated in Secs. 7.9.1 and 7.9.4.

7.9.7.1 Two GC Column TEF Determination

7.9.7.1.1 The concentration of 2,3,7,8-TCDD (see note below), is calculated from the analysis of the sample extract on the 60 m DB-5 fused silica capillary column. The experimental conditions remain the same as the conditions described previously in Sec. 7.8, and the calculations are performed as outlined in Sec. 7.9. The chromatographic separation between the 2,3,7,8-TCDD and its close eluters (1,2,3,7/1,2,3,8-TCDD and 1,2,3,9-TCDD) must be equal or less than 25 percent valley.

7.9.7.1.2 The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30 m DB-225 fused silica capillary column. However, the GC/MS conditions must be altered so that: (1) only the first three descriptors (i.e., tetra-, penta-, and hexachlorinated congeners) of Table 6 are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$-1,2,3,7,8-PeCDD. The concentration calculations are performed as outlined in Sec. 7.9. The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF) must be equal or less than 25 percent valley.

<u>NOTE</u>: The confirmation and quantitation of 2,3,7,8-TCDD (Sec. 7.9.7.1.1) may be accomplished on the SP-2330 GC column instead of the DB-5 column, provided the criteria listed in Sec. 8.2.1 are met and the requirements described in Sec. 8.3.2 are followed.

7.9.7.1.3 For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria listed in Secs. 7.8.4.2 and 7.8.4.3, respectively. In addition, the retention time identification criterion described in Sec. 7.8.4.1.1 applies here for congeners for which a carbon-labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described in Table 11 and the results from the routine calibration run on the SP-2330 column.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 System Performance Criteria - System performance criteria are presented below. The laboratory may use the recommended GC column described in Sec. 4.2. It must be documented that all applicable system performance criteria (specified in Secs. 8.2.1 and 8.2.2) were met before analysis of any sample is performed. Sec. 7.6.1 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 3 provides a typical 12-hour analysis sequence, whereby the response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hour period of operation. A GC column performance check is only required at the beginning of each 12-hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

8.2.1 GC Column Performance

8.2.1.1 Inject 2 μL (Sec. 4.1.1) of the column performance check solution (Sec. 5.7) and acquire selected ion monitoring (SIM) data as described in Sec. 7.6.2 within a total cycle time of $\leq$ 1 second (Sec. 7.6.3.1).

8.2.1.2 The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of $\leq$ 25 percent (Figure 4), where:

$$\text{Valley percent} = (x/y)\ (100)$$

x = measured as in Figure 4 from the 2,3,7,8-closest TCDD eluting isomer, and
y = the peak height of 2,3,7,8-TCDD.

It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used to determine the eight homologue retention time windows that are used for qualitative (Sec. 7.8.4.1) and quantitative purposes. All peaks (that includes $^{13}C_{12}$-2,3,7,8-TCDD) should be labeled and identified on the chromatograms. Furthermore, all first eluters of a homologous series should be labeled with the letter F, and all last eluters of a homologous series should be labeled with the letter L (Figure 4 shows an example of peak labeling for TCDD isomers). Any individual selected ion current profile (SICP) (for the tetras, this would be the SICP for m/z 322 and m/z 304) or the reconstructed homologue ion current (for the tetras, this would correspond to m/z 320 + m/z 322 + m/z 304 + m/z 306) constitutes an acceptable form of data presentation. An SICP for the labeled compounds (e.g., m/z 334 for labeled TCDD) is also required.

8.2.1.3 The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds. Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column. A laboratory with a GC/MS system that is not capable of detecting both congeners (1,2,8,9-TCDD and 1,3,4,6,8-PeCDF) within one analysis must take corrective action. If the recommended column is not used, then the first and last eluting isomer of each homologue must be determined experimentally on the column which is used, and the appropriate isomers must then be used for window definition and switching times.

8.2.2 Mass Spectrometer Performance

8.2.2.1 The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed (Sec. 7.8). Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. However, it is recommended that a check of the static resolution be made and documented before and after each analysis. Corrective action must be implemented whenever the resolving power does not meet the requirement.

8.2.2.2 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in downtime for source cleaning.

8.2.2.3 Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 5) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

8.3 Quality Control Samples

8.3.1 Performance Evaluation Samples - Included among the samples in all batches may be samples (blind or double blind) containing known amounts of unlabeled 2,3,7,8-substituted PCDDs/PCDFs or other PCDD/PCDF congeners.

8.3.2 Performance Check Solutions

8.3.2.1 At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3; see Table 5) shall be analyzed

to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended). If the required criteria are not met, remedial action must be taken before any samples are analyzed.

8.3.2.2 To validate positive sample data, the routine or continuing calibration (HRCC-3; Table 5) and the mass resolution check must be performed also at the end of each 12-hour period during which samples are analyzed. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

8.3.2.2.1 If the laboratory operates only during one period (shift) each day of 12 hours or less, the GC performance check solution must be analyzed only once (at the beginning of the period) to validate the data acquired during the period. However, the mass resolution and continuing calibration checks must be performed at the beginning as well as at the end of the period.

8.3.2.2.2 If the laboratory operates during consecutive 12-hour periods (shifts), analysis of the GC performance check solution must be performed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

8.3.2.3 Results of at least one analysis of the GC column performance check solution and of two mass resolution and continuing calibration checks must be reported with the sample data collected during a 12 hour period.

8.3.2.4 Deviations from criteria specified for the GC performance check or for the mass resolution check invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed.

If the routine calibration run fails at the beginning of a 12 hour shift, the instructions in Sec. 7.7.4.4 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than 25 percent RPD for the 17 unlabeled compounds and 35 percent RPD for the 9 labeled reference compounds, use the mean $\overline{RF}$s from the two daily routine calibration runs to compute the analyte concentrations, instead of the $\overline{RF}$s obtained from the initial calibration. A new initial calibration (new $\overline{RF}$s) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent or 35 percent, respectively. Failure to perform a new initial calibration immediately following the analysis of the samples will automatically require reanalysis of all

positive sample extracts analyzed before the failed end-of-shift continuing calibration check.

8.3.3 The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-CIN. However, if not available from the EMSL-CIN, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDDs/PCDFs, which are not obtained from the EMSL-CIN, must be verified by comparison with the EPA standard solutions that are available from the EMSL-CIN.

8.3.4 Field Blanks - Each batch of samples usually contains a field blank sample of uncontaminated soil, sediment or water that is to be fortified before analysis according to Sec. 8.3.4.1. In addition to this field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment.

8.3.4.1 Fortified Field Blank

8.3.4.1.1 Weigh a 10 g portion or use 1 L (for aqueous samples) of the specified field blank sample and add 100 µL of the solution containing the nine internal standards (Table 2) diluted with 1.0 mL acetone (Sec. 7.1).

8.3.4.1.2 Extract by using the procedures beginning in Secs. 7.4.5 or 7.4.6, as applicable, add 10 µL of the recovery standard solution (Sec. 7.5.3.6) and analyze a 2 µL aliquot of the concentrated extract.

8.3.4.1.3 Calculate the concentration (Sec. 7.9.1) of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards (Sec. 7.9.2).

8.3.4.1.4 Extract and analyze a new simulated fortified field blank whenever new lots of solvents or reagents are used for sample extraction or for column chromatographic procedures.

8.3.4.2 Rinsate Sample

8.3.4.2.1 The rinsate sample must be fortified like a regular sample.

8.3.4.2.2 Take a 100 mL (± 0.5 mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100 µL of the solution containing the nine internal standards (Table 2).

8.3.4.2.3 Using a KD apparatus, concentrate to approximately 5 mL.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the rinsate.

8.3.4.2.4 Transfer the 5 mL concentrate from the KD concentrator tube in 1 mL portions to a 1 mL minivial, reducing the volume in the minivial as necessary with a gentle stream of dry nitrogen.

8.3.4.2.5 Rinse the KD concentrator tube with two 0.5 mL portions of hexane and transfer the rinses to the 1 mL minivial. Blow down with dry nitrogen as necessary.

8.3.4.2.6 Just before analysis, add 10 µL recovery standard solution (Table 2) and reduce the volume to its final volume, as necessary (Sec. 7.8.1). No column chromatography is required.

8.3.4.2.7 Analyze an aliquot following the same procedures used to analyze samples.

8.3.4.2.8 Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds in µg/L of rinsate solvent.

8.3.5 Duplicate Analyses

8.3.5.1 In each batch of samples, locate the sample specified for duplicate analysis, and analyze a second 10 g soil or sediment sample portion or 1 L water sample, or an appropriate amount of the type of matrix under consideration.

8.3.5.1.1 The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean). Report all results.

8.3.5.1.2 Recommended actions to help locate problems:

8.3.5.1.2.1 Verify satisfactory instrument performance (Secs. 8.2 and 8.3).

8.3.5.1.2.2 If possible, verify that no error was made while weighing the sample portions.

8.3.5.1.2.3 Review the analytical procedures with the performing laboratory personnel.

8.3.6 Matrix Spike and Matrix Spike Duplicate

8.3.6.1 Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").

8.3.6.2 Add an appropriate volume of the matrix spike fortification solution (Sec. 5.10) and of the sample fortification solution (Sec. 5.8), adjusting the fortification level as specified in Table 1 under IS Spiking Levels.

8.3.6.3 Analyze the MS and MSD samples as described in Sec. 7.

8.3.6.4 The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

8.4 Percent Recovery of the Internal Standards - For each sample, method blank and rinsate, calculate the percent recovery (Sec. 7.9.2). The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

NOTE: A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data.

8.5 Identification Criteria

8.5.1 If either one of the identification criteria appearing in Secs. 7.8.4.1.1 through 7.8.4.1.4 is not met for an homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit (Sec. 7.9.5)

8.5.2 If the first initial identification criteria (Secs. 7.8.4.1.1 through 7.8.4.1.4) are met, but the criteria appearing in Secs. 7.8.4.1.5 and 7.8.4.2.1 are not met, that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form, and the sample should be rerun or the extract reanalyzed.

8.6 Unused portions of samples and sample extracts should be preserved for six months after sample receipt to allow further analyses.

8.7 Reuse of glassware is to be minimized to avoid the risk of contamination.

9.0 METHOD PERFORMANCE

9.1 Data are currently not available.

10.0 REFERENCES

1. "Control of Interferences in the Analysis of Human Adipose Tissue for 2,3,7,8-Tetrachlorodibenzo-p-dioxin". D. G. Patterson, J.S. Holler, D.F. Grote, L.R. Alexander, C.R. Lapeza, R.C. O'Connor and J.A. Liddle. Environ. Toxicol. Chem. 5, 355-360 (1986).

2. "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry". Y. Tondeur and W.F. Beckert. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

3. "Carcinogens - Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.

4. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

5. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety (3rd Edition, 1979.)

6. "Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated Dibenzo-p-dioxins in Environmental Samples." Y. Tondeur, W.J. Niederhut, S.R. Missler, and J.E. Campana, Mass Spectrom. 14, 449-456 (1987).

7. USEPA National Dioxin Study - Phase II, "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", EPA-Duluth, October 26, 1987.

11.0 SAFETY

11.1 The following safety practices are excerpts from EPA Method 613, Sec. 4 (July 1982 version) and amended for use in conjunction with this method. The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should wear masks fitted with charcoal filters to prevent inhalation of dust.

11.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be made available to all personnel involved in the chemical analysis of samples suspected to contain PCDDs and/or PCDFs. Additional references to laboratory safety are given in references 3, 4 and 5.

11.3 Each laboratory must develop a strict safety program for the handling of PCDDs and PCDFs. The laboratory practices listed below are recommended.

11.3.1 Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood.

11.3.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols.

11.3.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps, or equivalent). Using this analytical method, analyze the irradiated liquid wastes and dispose of the solutions when 2,3,7,8-TCDD and -TCDF congeners can no longer be detected.

11.4 The following precautions were issued by Dow Chemical U.S.A. (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory and amended for use in conjunction with this method.

11.4.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2,3,7,8-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Many techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

11.4.1.1 Protective Equipment: Throw away plastic gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work. However, PVC gloves should not be used.

11.4.1.2 Training: Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

11.4.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

11.4.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic backed absorbent paper on benchtops.

11.4.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

11.4.1.6 Disposal of Hazardous Wastes: Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin containing wastes.

11.4.1.7 Decontamination: Personnel - apply a mild soap with plenty of scrubbing action. Glassware, tools and surfaces - Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with a detergent and water. Dish water may be disposed to the sewer after percolation through a charcoal bed filter. It is prudent to minimize solvent wastes because they require special disposal through commercial services that are expensive.

11.4.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Hazardous Wastes". Laboratory coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through one full cycle before being used again for other clothing.

11.4.1.9 Wipe Tests: A useful method for determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, extract the filter paper and analyze the extract.

NOTE: A procedure for the collection, handling, analysis, and reporting requirements of wipe tests performed within the laboratory is described in Attachment A. The results and decision making processes are based on the presence of 2,3,7,8-substituted PCDDs/PCDFs.

11.4.1.10 Inhalation: Any procedure that may generate airborne contamination must be carried out with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no significant inhalation hazards except in case of an accident.

11.4.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

Attachment A

PROCEDURES FOR THE COLLECTION, HANDLING, ANALYSIS, AND REPORTING OF WIPE TESTS PERFORMED WITHIN THE LABORATORY

This procedure is designed for the periodic evaluation of potential contamination by 2,3,7,8-substituted PCDD/PCDF congeners of the working areas inside the laboratory.

A.1 Perform the wipe tests on surface areas of two inches by one foot with glass fiber paper saturated with distilled in glass acetone using a pair of clean stainless steel forceps. Use one wiper for each of the designated areas. Combine the wipers to one composite sample in an extraction jar containing 200 mL distilled in glass acetone. Place an equal number of unused wipers in 200 mL acetone and use this as a control. Add 100 μL of the sample fortification solution to each jar containing used or unused wipers (Sec. 5.8).

A.1.1 Close the jar containing the wipers and the acetone and extract for 20 minutes using a wrist action shaker. Transfer the extract into a KD apparatus fitted with a concentration tube and a three ball Snyder column. Add two Teflon™ or Carborundum™ boiling chips and concentrate the extract to an apparent volume of 1.0 mL on a steam bath. Rinse the Snyder column and the KD assembly with two 1 mL portions of hexane into the concentrator tube, and concentrate its contents to near dryness with a gentle stream of nitrogen. Add 1.0 mL hexane to the concentrator tube and swirl the solvent on the walls.

A.1.2 Prepare a neutral alumina column as described in Sec. 7.5.2.2 and follow the steps outlined in Secs. 7.5.2.3 through 7.5.2.5.

A.1.3 Add 10 μL of the recovery standard solution as described in Sec. 7.5.3.6.

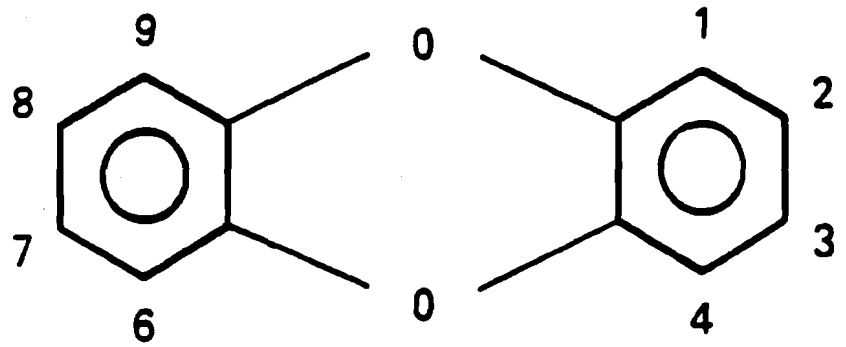
A.2 Concentrate the contents of the vial to a final volume of 10 μL (either in a minivial or in a capillary tube). Inject 2 μL of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDDs/PCDFs as specified in the analytical method in Sec. 7.8. Perform calculations according to Sec. 7.9.

A.3 Report the presence of 2,3,7,8-substituted PCDDs and PCDFs as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 10 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 3 pg of 2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is 10 x 5 = 50 pg/WTE and the positive response for the blank would be 3 x 5 = 15 pg). Also, report the recoveries of the internal standards during the simplified cleanup procedure.

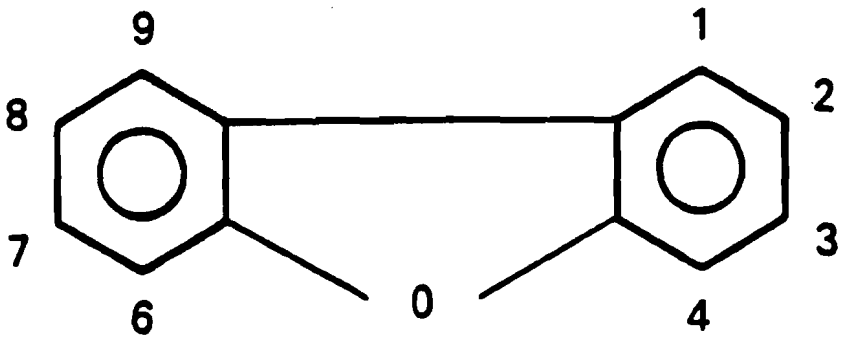
A.4 At a minimum, wipe tests should be performed when there is evidence of contamination in the method blanks.

A.5 An upper limit of 25 pg per TCDD isomer and per wipe test experiment is allowed (use multiplication factors listed in footnote (a) from Table 1 for other congeners). This value corresponds to 2½ times the lower calibration limit of the analytical method. Steps to correct the contamination must be taken whenever these levels are exceeded. To that effect, first vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high efficiency particulate absorbent (HEPA) filter and then wash with a detergent. A new set of wipes should be analyzed before anyone is allowed to work in the dioxin area of the laboratory after corrective action has been taken.

Figure 1.



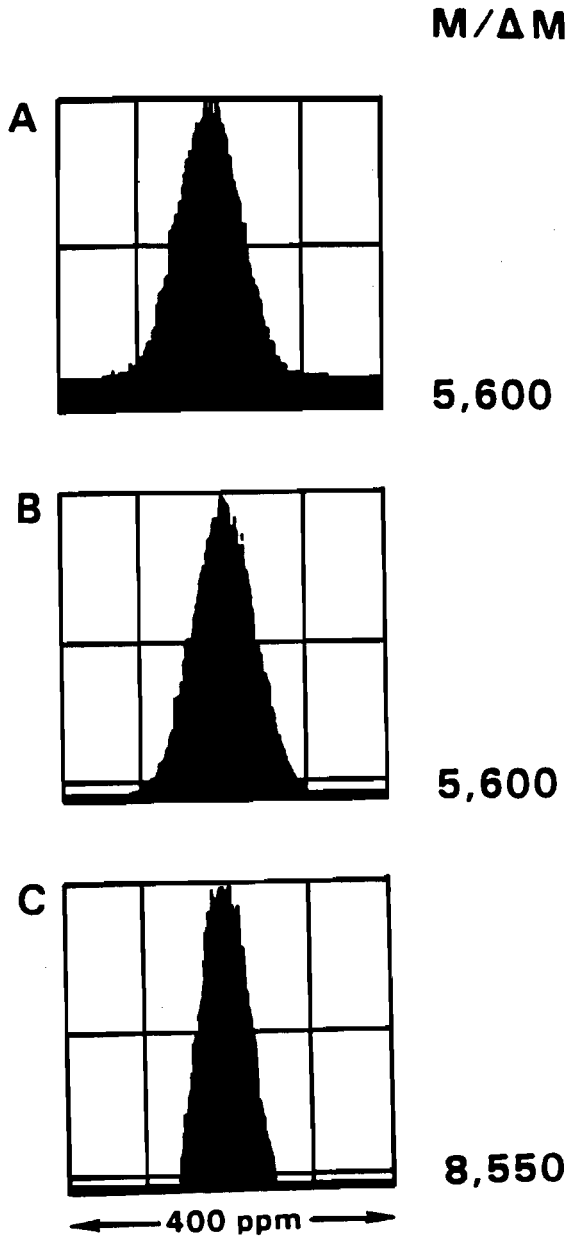
Dibenzodioxin



Dibenzofuran

General structures of dibenzo-p-dioxin and dibenzofuran.

Figure 2.



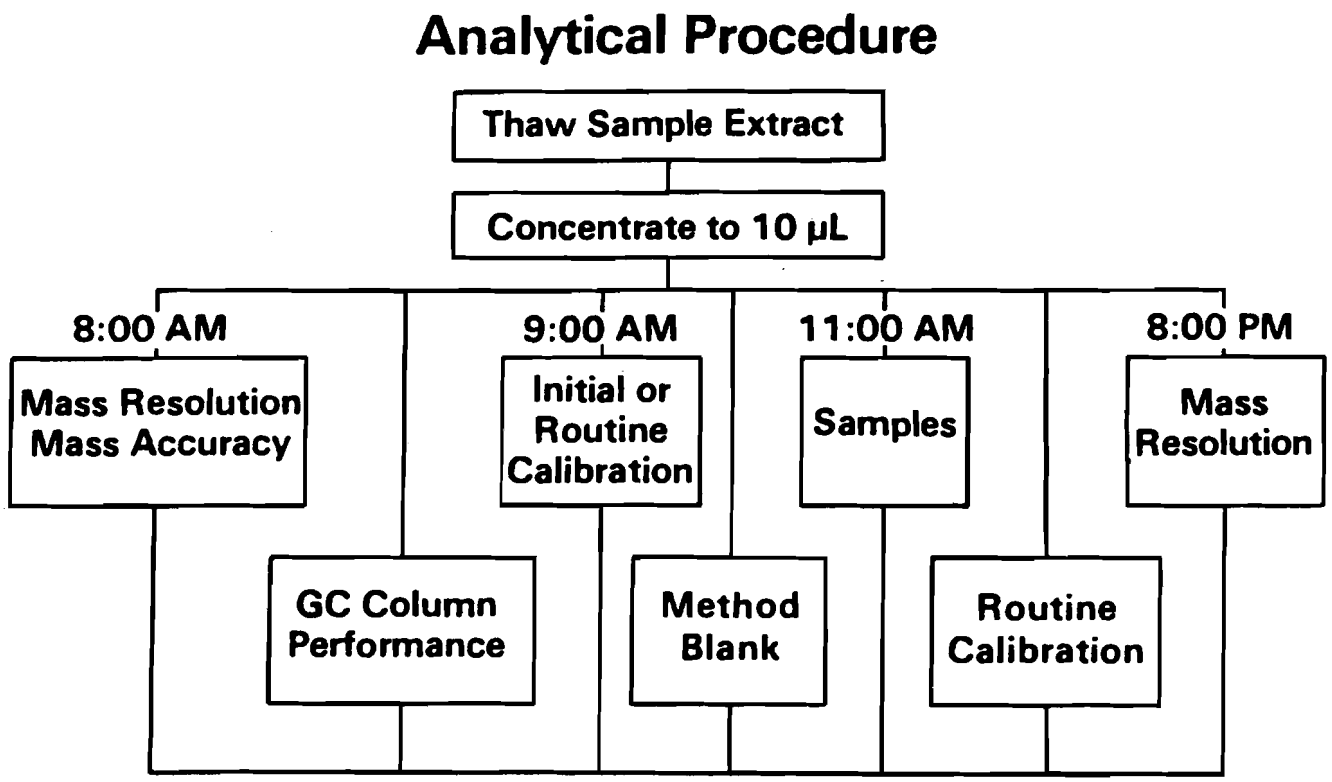
Peak profile displays demonstrating the effect of the detector zero on the measured resolving power. In this example, the true resolving power is 5,600.

A) The zero was set too high; no effect is observed upon the measurement of the resolving power.

B) The zero was adjusted properly.

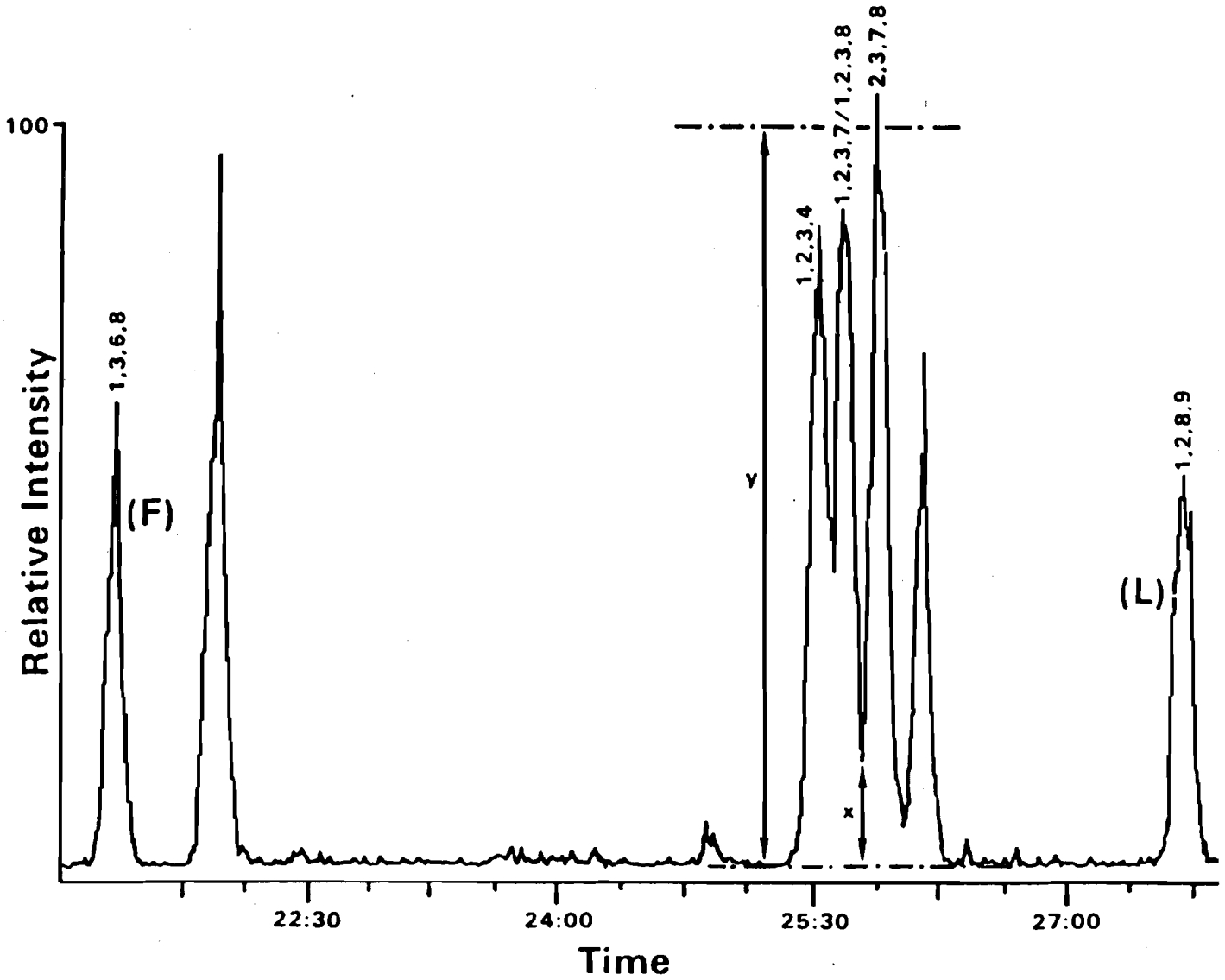
C) The zero was set too low; this results in overestimating the actual resolving power because the peak-to-peak noise cannot be measured accurately.

Figure 3.



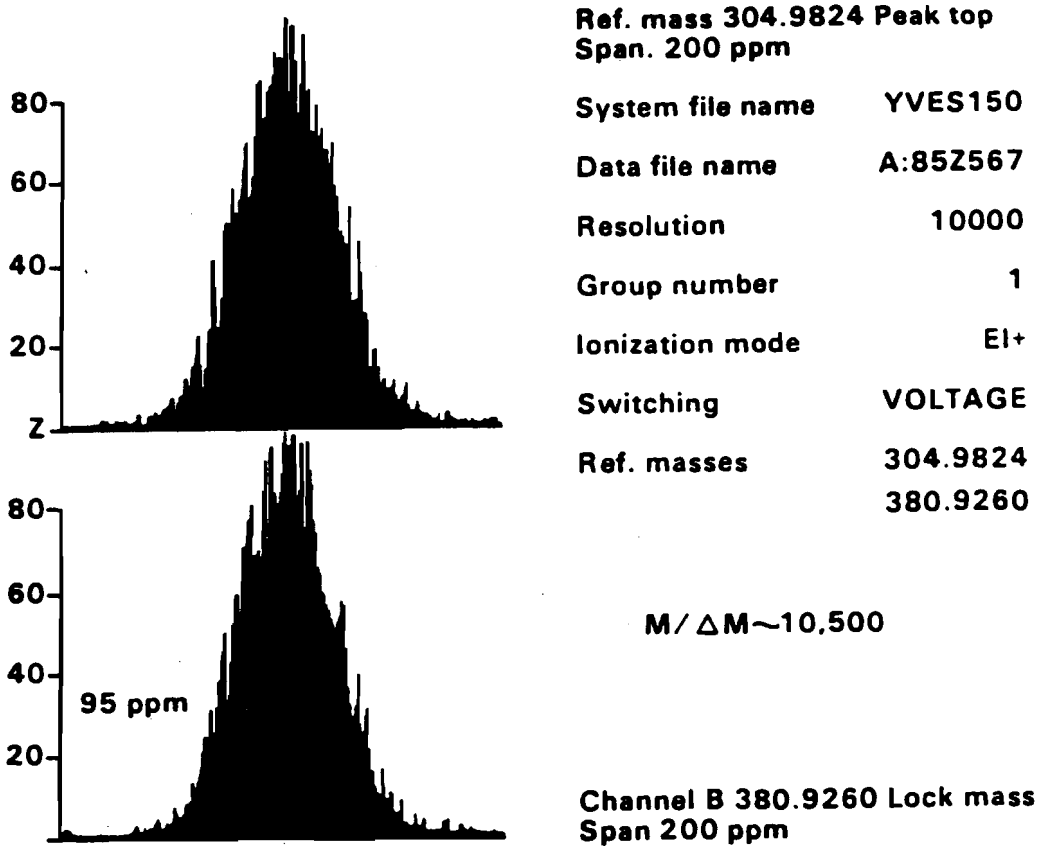
Typical 12 hour analysis sequence of events.

Figure 4.



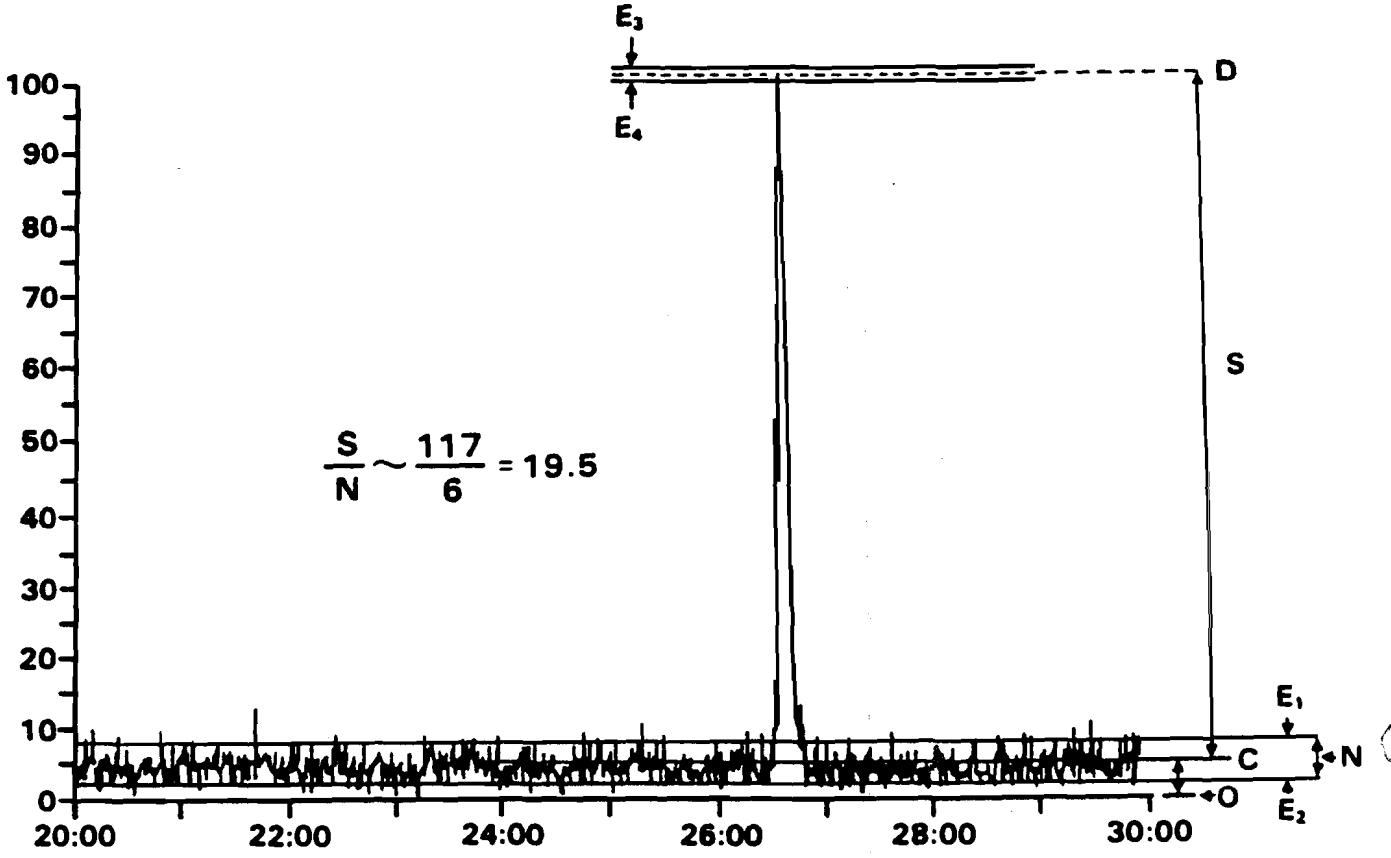
Selected ion current profile for m/z 322 (TCDDs) produced by MS analysis of the GC performance check solution on a 60 m DB-5 fused silica capillary column under the conditions listed in Sec. 7.6.

Figure 5.



Peak profiles representing two PFK reference ions at m/z 305 and 381. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power M/△M of 10,500 (10 percent valley definition).

Figure 6.



Manual determination of S/N.

The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE: It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

Table 1.

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (Parts per Trillion)

	Water	Soil Sediment Paper Pulp[b]	Fly Ash	Fish Tissue[c]	Human Adipose Tissue	Sludges, Fuel Oil	Still-Bottom
Lower MCL[a]	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL[a]	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	20	10	2	1
IS Spiking Levels (ppt)	1	100	100	100	100	500	1000
Final Extr. Vol. (μL)[d]	10-50	10-50	50	10-50	10-50	50	50

a For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

b Sample dewatered according to Sec. 6.5.

c One half of the extract from the 20 g sample is used for determination of lipid content (Sec. 7.2.2).

d See Sec. 7.8.1, Note.

NOTE: Chemical reactor residues are treated as still bottoms if their appearances so suggest.

Table 2.

Composition of the Sample Fortification and Recovery Standard Solutions[a]

Analyte	Sample Fortification Solution Concentration (pg/μL; Solvent: Nonane)	Recovery Standard Solution Concentration (pg/μL; Solvent: Nonane)
$^{13}C_{12}$-2,3,7,8-TCDD	10	--
$^{13}C_{12}$-2,3,7,8-TCDF	10	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	10	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	10	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	--	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25	--
$^{13}C_{12}$-OCDD	50	--

(a) These solutions should be made freshly every day because of the possibility of adsorptive losses to glassware. If these solutions are to be kept for more than one day, then the sample fortification solution concentrations should be increased ten fold, and the recovery standard solution concentrations should be doubled. Corresponding adjustments of the spiking volumes must then be made.

Table 3.

The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

(*) The 13C-labeled analogue is used as an internal standard.

(+) The 13C-labeled analogue is used as a recovery standard.

Table 4.

Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	---	4	---
2	10	---	16	---
3	14	---	28	---
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

Table 5.

High-Resolution Concentration Calibration Solutions

Compound	HRCC	Concentration (pg/μL, in Nonane) 5	4	3	2	1
Unlabeled Analytes						
2,3,7,8-TCDD		200	50	10	2.5	1
2,3,7,8-TCDF		200	50	10	2.5	1
1,2,3,7,8-PeCDD		500	125	25	6.25	2.5
1,2,3,7,8-PeCDF		500	125	25	6.25	2.5
2,3,4,7,8-PeCDF		500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDD		500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDD		500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDD		500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDF		500	125	25	6.25	2.5
2,3,4,6,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDD		500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDF		500	125	25	6.25	2.5
1,2,3,4,7,8,9-HpCDF		500	125	25	6.25	2.5
OCDD		1,000	250	50	12.5	5
OCDF		1,000	250	50	12.5	5
Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD		50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF		50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD		50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF		50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD		125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF		125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD		125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF		125	125	125	125	125
$^{13}C_{12}$-OCDD		250	250	250	250	250
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD[a]		50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[b]		125	125	125	125	125

[a] Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.

[b] Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF and OCDD internal standards.

Table 6.

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK

Table 6.
Continued

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7780	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9728]	LOCK	$C_{10}F_{17}$	PFK

[a] The following nuclidic masses were used:

H	=	1.007825	O	=	15.994915
C	=	12.000000	^{35}Cl	=	34.968853
^{13}C	=	13.003355	^{37}Cl	=	36.965903
F	=	18.9984			

S = internal/recovery standard

Table 7.

PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and Used for Defining the Homologous GC Retention Time Windows on a 60 m DB-5 Column

No. of Chlorine Atoms	PCDD Positional Isomer		PCDF Positional Isomer	
	First Eluter	Last Eluter	First Eluter	Last Eluter
4[a]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/ 1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,4,6,7,9/ 1,2,4,6,8,9	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8		1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9

[a] In addition to these two TCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present as a check of column resolution.

Table 8.

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Control Limits upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF (IS).

[b] Used only for ^{13}C-HpCDF (IS).

Table 9.

Relative Response Factor [RF (number)] Attributions

Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and total HpCDDs)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	$^{13}C_{12}$-2,3,7,8-TCDD
19	$^{13}C_{12}$-2,3,7,8-TCDF
20	$^{13}C_{12}$-1,2,3,7,8-PeCDD
21	$^{13}C_{12}$-1,2,3,7,8-PeCDF
22	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
23	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
24	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
25	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
26	$^{13}C_{12}$-OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

Table 10.

2,3,7,8-TCDD Toxicity Equivalency Factors (TEFs) for the Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF[a]
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

[a] Taken from "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxin and -Dibenzofurans (CDDs and CDFs) and 1989 Update", (EPA/625/3-89/016, March 1989).

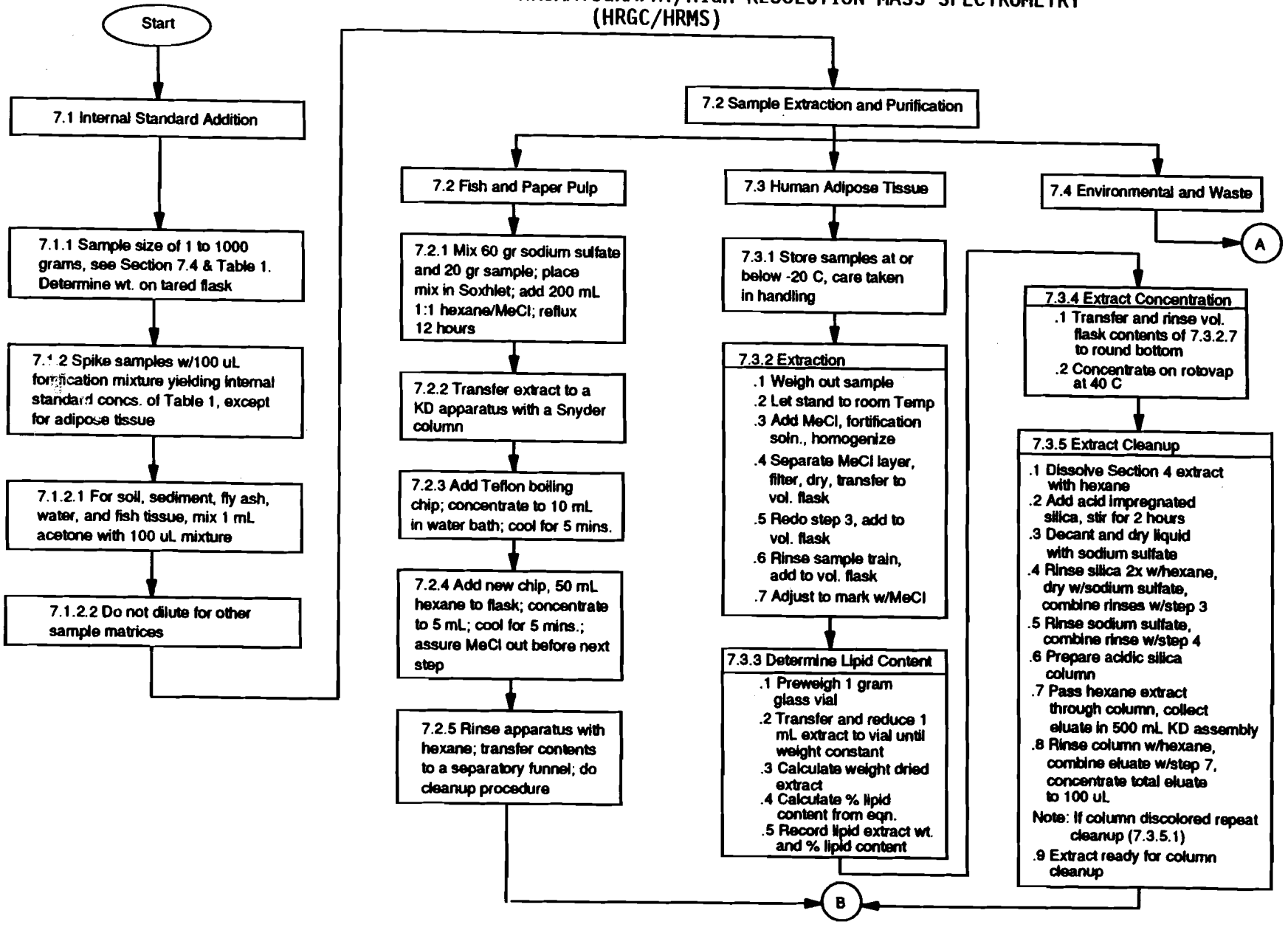
Table 11.

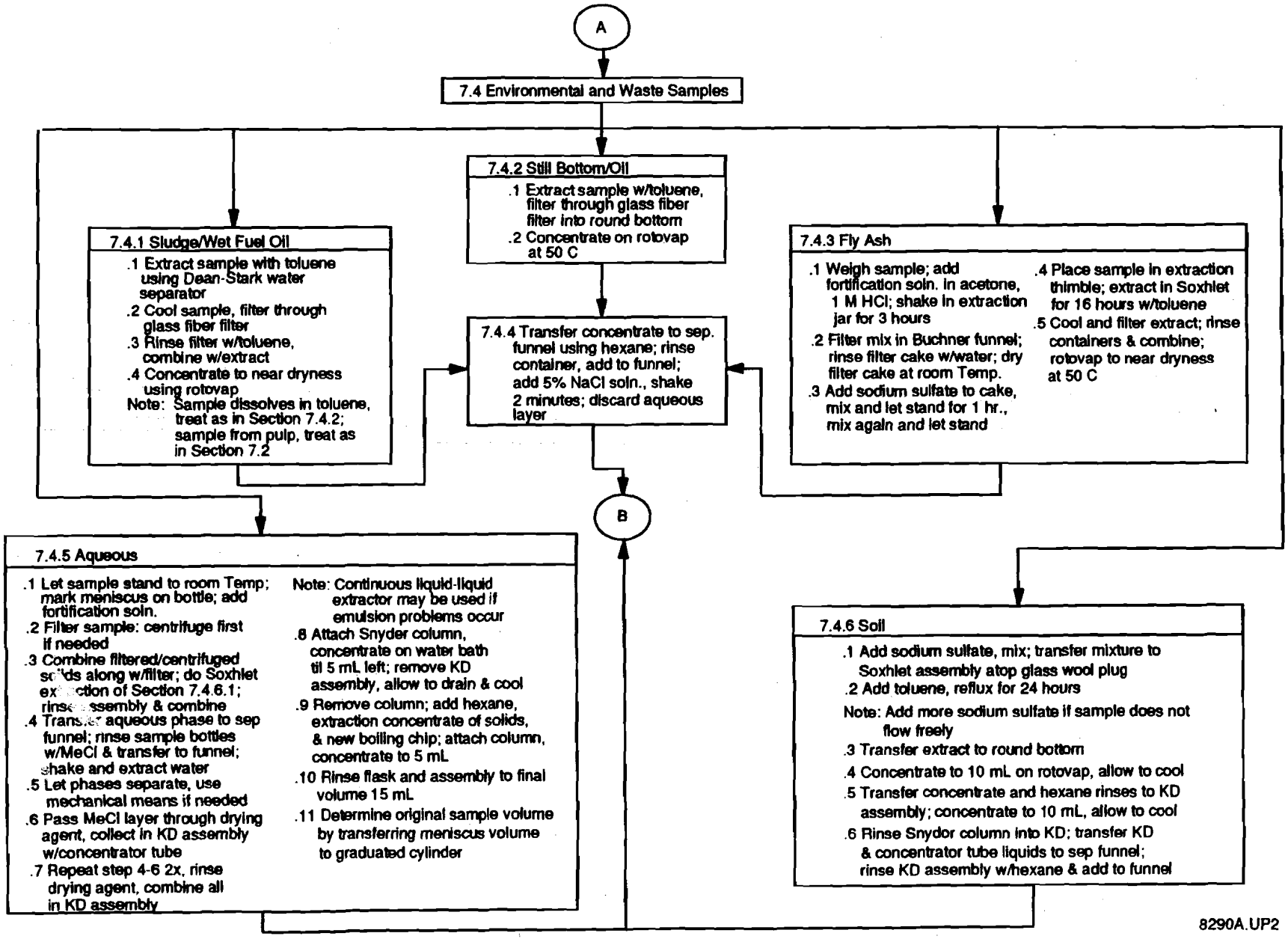
Analyte Relative Retention Time Reference Attributions

Analyte	Analyte RRT Reference[a]
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF

[a] The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to $^{13}C_{12}$-1,2,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF.

METHOD 8290
POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)




A
7.4 Environmental and Waste Samples
7.4.1 Sludge/Wet Fuel Oil
.1 Extract sample with toluene using Dean-Stark water separator
.2 Cool sample, filter through glass fiber filter
.3 Rinse filter w/toluene, combine w/extract
.4 Concentrate to near dryness using rotovap
Note: Sample dissolves in toluene, treat as in Section 7.4.2; sample from pulp, treat as in Section 7.2
7.4.2 Still Bottom/Oil
.1 Extract sample w/toluene, filter through glass fiber filter into round bottom
.2 Concentrate on rotovap at 50 C
7.4.3 Fly Ash
.1 Weigh sample; add fortification soln. in acetone, 1 M HCl; shake in extraction jar for 3 hours
.2 Filter mix in Buchner funnel; rinse filter cake w/water; dry filter cake at room Temp.
.3 Add sodium sulfate to cake, mix and let stand for 1 hr., mix again and let stand
.4 Place sample in extraction thimble; extract in Soxhlet for 16 hours w/toluene
.5 Cool and filter extract; rinse containers & combine; rotovap to near dryness at 50 C
7.4.4 Transfer concentrate to sep. funnel using hexane; rinse container, add to funnel; add 5% NaCl soln., shake 2 minutes; discard aqueous layer
B
7.4.5 Aqueous
.1 Let sample stand to room Temp; mark meniscus on bottle; add fortification soln.
.2 Filter sample: centrifuge first if needed
.3 Combine filtered/centrifuged solids along w/filter; do Soxhlet extraction of Section 7.4.6.1; rinse assembly & combine
.4 Transfer aqueous phase to sep funnel; rinse sample bottles w/MeCl & transfer to funnel; shake and extract water
.5 Let phases separate, use mechanical means if needed
.6 Pass MeCl layer through drying agent, collect in KD assembly w/concentrator tube
.7 Repeat step 4-6 2x, rinse drying agent, combine all in KD assembly
Note: Continuous liquid-liquid extractor may be used if emulsion problems occur
.8 Attach Snyder column, concentrate on water bath til 5 mL left; remove KD assembly, allow to drain & cool
.9 Remove column; add hexane, extraction concentrate of solids, & new boiling chip; attach column, concentrate to 5 mL
.10 Rinse flask and assembly to final volume 15 mL
.11 Determine original sample volume by transferring meniscus volume to graduated cylinder
7.4.6 Soil
.1 Add sodium sulfate, mix; transfer mixture to Soxhlet assembly atop glass wool plug
.2 Add toluene, reflux for 24 hours
Note: Add more sodium sulfate if sample does not flow freely
.3 Transfer extract to round bottom
.4 Concentrate to 10 mL on rotovap, allow to cool
.5 Transfer concentrate and hexane rinses to KD assembly; concentrate to 10 mL, allow to cool
.6 Rinse Snydor column into KD; transfer KD & concentrator tube liquids to sep funnel; rinse KD assembly w/hexane & add to funnel

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B

7.5 Cleanup

7.5.1 Partition

.1 Partition extract w/ concentrated sulfuric acid; shake, discard acid layer; repeat acid wash till no color present or done 4x

.2 OMIT FOR FISH SAMPLES. Partition extract w/NaCl soln.; shake, discard aqueous layer

.3 OMIT FOR FISH SAMPLES. Partition extract w/KOH soln.; shake, discard base layer; repeat base wash till no color obtained in wash or done 4x

.4 Partition extract w/NaCl soln.; shake, discard aqueous layer. Dry extract w/sodium sulfate into round bottom flask; rinse sodium sulfate w/hexane; concentrate hexane soln. in rotovap

7.5.2 Silica/Alumina Column

.1 Pack a gravity column w/silica gel; fill w/hexane, elute to top of bed; check for channeling

.2 Pack a gravity column w/alumina; fill w/hexane, elute to top of bed, check for channeling

Note: Acidic alumina may be used instead of neutral alumina.

.3 Dissolve residue of Section 7.5.1.4 in hexane; transfer soln. to top of silica column

.4 Elute silica column w/hexane directly onto alumina column

.5 Add hexane to alumina column; elute to top of sodium sulfate in collect and save eluted hexane

.6 Add MeCl/hexane soln. to alumina column; collect eluate in concentrator tube

7.5.3 Carbon Column

.1 Prepare AX-21/Celite 545 column; activate mixture at 130 C for 6 hours; store in dessicator

.2 Pack a 10 mL serological pipet w/prepared AX-21/Celite 545 mix

Note: Each batch of AX-21/Celite 545 must be checked for % recovery of analytes.

.3 Concentrate MeCl/hexane fraction of Section 7.5.2.6 to 2 mL w/nitrogen; rinse column w/several solns.; add sample concentrate and rinses to top of column

.4 Elute column sequentially w/cyclohexane/MeCl; MeCl/methanol/toluene; combine eluates

.5 Turn column upside down, elute PCDD/PCDF fraction w/toluene; filter if carbon fines present

.6 Concentrate toluene fraction on rotovap; further concentrate to 100 uL in minivial using nitrogen at 50 C; rinse flask 3x w/1% toluene in MeCl; add tridecane recovery std.; store room temp. in the dark

C

C

7.6 Chromatographic, Mass Spectrometric, and Data Acquisition Parameters

7.6.1 Gas Chromatograph

Select correct dimensions and parameters of column, and set-up chromatographic conditions.

7.6.2 Mass Spectrometer

.1 Operate mass spectrometer in selected ion monitoring (SIM) mode; monitor ions of five SIM descriptors
.2 Tune mass spectrometer based on ions of SIM descriptors

7.6.3 Data Aquisition

.1 Total cycle time of < or = 1 second
.2 Acquire SIM data for ions of 5 descriptors

7.7 Calibration

7.7.1 Initial Calibration

Required before any sample analysis, and if routine calibration does not meet criteria
.1 All 5 calibration solns. must be used for initial calibration
.2 Tune mass spectrometer w/PFK as described in Section 7.7.3
.3 Inject 2 uL of GC column performance check soln. and acquire SIM data; assure Section 8.1.2 criteria are met
.4 Analyze each of 5 calibration standards using the same conditions, with the following MS operating parameters:
.1 Ratio of integrated ion current for Table 8 ions within control limits
.2 Ratio of integrated ion current for carbon labeled internal and recovery standards within control limits
Note: Control limits must be achieved in one run for all ions.
.3 Signal to noise (S/N) ratio for each target analyte and labeled std. selected ion current profiles (SICP) and GC signals > 2.5

7.7.1.4
.4 Calculate relative response factors (RRF) for unlabeled and labeled target analytes relative to internal stds. (Table 5)
.5 Calculate average and relative standard deviation for the 5 calibration solutions
.6 RRF's for concentration determination of total isomers in a homologous series are calculated as:
.1 Congeners in a homologous series w/one isomer, mean RRF used is same as Section 7.7.1.4.5
Note: Calibration solns. do not contain labeled OCDF; therefore, RRF OCDF relative to labeled OCDD
.2 Calculation for mean RRF for congeners in a homologous series w/more than one isomer
Note: Isomers in homologous series w/o 2,3,7,8 substitution pattern alloted same response factor as other 2,3, 7, 8 isomers in series
.7 Calculation of RRF's used to determine % recoveries of nine internal standards

7.7.2 Criteria for Acceptable Calibration

Criteria listed must be met before analysis
.1 The % RSD for unlabeled stds. must be within +/- 20%; for labeled, +/- 30%
.2 S/N ratio for GC signals > = 2.5
.3 Table 8 isotopic ratios within limits
Note: When criteria for acceptable calibration are met, mean RRF's used for calculations until routine calibration criteria are not met

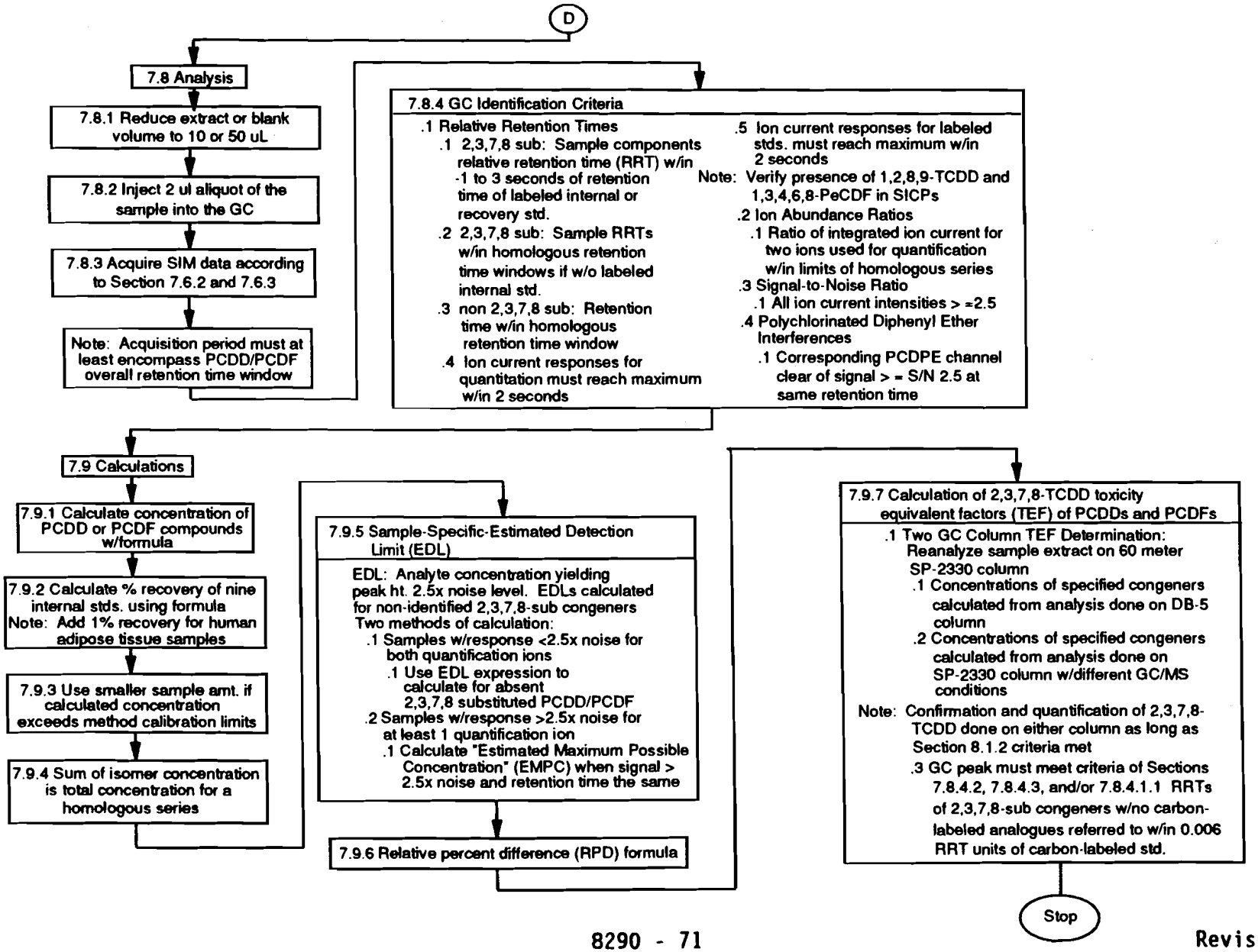
7.7.3 Routine Calibration

Performed at 12 hour periods after successful resolution checks
.1 Inject 2 uL calibration soln. HRCC-3; use same HRGC/HRMS conditions of Sections 7.6.1 and 7.6.2; document an acceptable calibration

7.7.4 Criteria for Acceptable Routine Calibration

.1 Measured unlabeled RRFs must be w/in +/- 20% of initial calibration values
.2 Measured labeled RRFs must be w/in +/- 30% of initial calibration values
.3 Table 8 ion abundance ratios must be w/in limits
.4 Review routine calibration process if criteria of steps 1 and 2 are not satisfied
Note: An initial calibration must be done when new HRCC-3, sample fortification, or recovery std. soln. from another lot is used

D


D
7.8 Analysis
7.8.1 Reduce extract or blank volume to 10 or 50 uL
7.8.2 Inject 2 ul aliquot of the sample into the GC
7.8.3 Acquire SIM data according to Section 7.6.2 and 7.6.3
Note: Acquisition period must at least encompass PCDD/PCDF overall retention time window
7.8.4 GC Identification Criteria
.1 Relative Retention Times
.1 2,3,7,8 sub: Sample components relative retention time (RRT) w/in -1 to 3 seconds of retention time of labeled internal or recovery std.
.2 2,3,7,8 sub: Sample RRTs w/in homologous retention time windows if w/o labeled internal std.
.3 non 2,3,7,8 sub: Retention time w/in homologous retention time window
.4 Ion current responses for quantitation must reach maximum w/in 2 seconds
.5 Ion current responses for labeled stds. must reach maximum w/in 2 seconds
Note: Verify presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF in SICPs
.2 Ion Abundance Ratios
.1 Ratio of integrated ion current for two ions used for quantification w/in limits of homologous series
.3 Signal-to-Noise Ratio
.1 All ion current intensities > =2.5
.4 Polychlorinated Diphenyl Ether Interferences
.1 Corresponding PCDPE channel clear of signal > = S/N 2.5 at same retention time
7.9 Calculations
7.9.1 Calculate concentration of PCDD or PCDF compounds w/formula
7.9.2 Calculate % recovery of nine internal stds. using formula
Note: Add 1% recovery for human adipose tissue samples
7.9.3 Use smaller sample amt. if calculated concentration exceeds method calibration limits
7.9.4 Sum of isomer concentration is total concentration for a homologous series
7.9.5 Sample-Specific-Estimated Detection Limit (EDL)
EDL: Analyte concentration yielding peak ht. 2.5x noise level. EDLs calculated for non-identified 2,3,7,8-sub congeners
Two methods of calculation:
.1 Samples w/response <2.5x noise for both quantification ions
.1 Use EDL expression to calculate for absent 2,3,7,8 substituted PCDD/PCDF
.2 Samples w/response >2.5x noise for at least 1 quantification ion
.1 Calculate "Estimated Maximum Possible Concentration" (EMPC) when signal > 2.5x noise and retention time the same
7.9.6 Relative percent difference (RPD) formula
7.9.7 Calculation of 2,3,7,8-TCDD toxicity equivalent factors (TEF) of PCDDs and PCDFs
.1 Two GC Column TEF Determination: Reanalyze sample extract on 60 meter SP-2330 column
.1 Concentrations of specified congeners calculated from analysis done on DB-5 column
.2 Concentrations of specified congeners calculated from analysis done on SP-2330 column w/different GC/MS conditions
Note: Confirmation and quantification of 2,3,7,8-TCDD done on either column as long as Section 8.1.2 criteria met
.3 GC peak must meet criteria of Sections 7.8.4.2, 7.8.4.3, and/or 7.8.4.1.1 RRTs of 2,3,7,8-sub congeners w/no carbon-labeled analogues referred to w/in 0.006 RRT units of carbon-labeled std.
Stop

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC METHODS

The following methods are included in this section:

Method 8310:	Polynuclear Aromatic Hydrocarbons
Method 8315:	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)
Appendix A:	Recrystallization of 2,4-Dinitrophenylhydrazine (DNPH)
Method 8316:	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
Method 8318:	N-Methylcarbamates by High Performance Liquid Chromatography (HPLC)
Method 8321:	Solvent Extractable Non-Volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TSP/MS) or Ultraviolet (UV) Detection
Method 8330:	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
Method 8331:	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)

METHOD 8310

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8310 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in ground water and wastes. Specifically, Method 8310 is used to detect the following substances:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(ghi)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

1.2 Use of Method 8310 presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds listed above, he must develop independent protocols for the verification of identity.

1.3 The method detection limits for each compound in reagent water are listed in Table 1. Table 2 lists the practical quantitation limit (PQL) for other matrices. The sensitivity of this method usually depends on the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 for the liquid chromatographic approach represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

2.1 Method 8310 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. A 5- to 25-uL aliquot of the extract is injected into an HPLC, and compounds in the effluent are detected by ultraviolet (UV) and fluorescence detectors.

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

TABLE 1. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF PAHs[a]

Compound	Retention time (min)	Column capacity factor (k')	Method Detection limit (ug/L) UV	Method Detection limit (ug/L) Fluorescence
Naphthalene	16.6	12.2	1.8	
Acenaphthylene	18.5	13.7	2.3	
Acenaphthene	20.5	15.2	1.8	
Fluorene	21.2	15.8	0.21	
Phenanthrene	22.1	16.6		0.64
Anthracene	23.4	17.6		0.66
Fluoranthrene	24.5	18.5		0.21
Pyrene	25.4	19.1		0.27
Benzo(a)anthracene	28.5	21.6		0.013
Chrysene	29.3	22.2		0.15
Benzo(b)fluoranthene	31.6	24.0		0.018
Benzo(k)fluoranthene	32.9	25.1		0.017
Benzo(a)pyrene	33.9	25.9		0.023
Dibenzo(a,h)anthracene	35.7	27.4		0.030
Benzo(ghi)perylene	36.3	27.8		0.076
Indeno(1,2,3-cd)pyrene	37.4	28.7		0.043

[a] HPLC conditions: Reverse phase HC-ODS Sil-X, 5 micron particle size, in a 250-mm x 2.6-mm I.D. stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method Detection Limit (Table 1) X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source. Although a general cleanup technique is provided as part of this method, individual samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 The chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Kuderna-Danish (K-D) apparatus:

4.1.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.1.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.1.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.1.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.4 Syringe: 5-mL.

4.5 High pressure syringes.

4.6 HPLC apparatus:

4.6.1 **Gradient pumping system:** Constant flow.

4.6.2 **Reverse phase column:** HC-ODS Sil-X, 5-micron particle size diameter, in a 250-mm x 2.6-mm I.D. stainless steel column (Perkin Elmer No. 089-0716 or equivalent).

4.6.3 **Detectors:** Fluorescence and/or UV detectors may be used.

4.6.3.1 Fluorescence detector: For excitation at 280-nm and emission greater than 389-nm cutoff (Corning 3-75 or equivalent). Fluorometers should have dispersive optics for excitation and can utilize either filter or dispersive optics at the emission detector.

4.6.3.2 UV detector: 254-nm, coupled to the fluorescence detector.

4.6.4 **Strip-chart recorder:** compatible with detectors. A data system for measuring peak areas and retention times is recommended.

4.7 Volumetric flasks: 10-, 50-, and 100-mL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Acetonitrile: HPLC quality, distilled in glass.

5.3 Stock standard solutions:

5.3.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in acetonitrile and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with acetonitrile. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. Calibration standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each analyte as described in Paragraph 5.4.

5.5.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with acetonitrile.

5.5.3 Analyze each calibration standard according to Section 7.0.

5.6 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., decafluorobiphenyl or other PAHs not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for HPLC analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and must be analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.1.2 Prior to HPLC analysis, the extraction solvent must be exchanged to acetonitrile. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to 95-100°C. Momentarily remove the Snyder column, add 4 mL of acetonitrile, a new boiling chip, and attach a two-ball micro-Snyder column. Concentrate the extract using 1 mL of acetonitrile to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of acetonitrile. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with HPLC analysis if further cleanup is not required.

7.2 HPLC conditions (Recommended):

7.2.1 Using the column described in Paragraph 4.6.2: Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

7.3 Calibration:

7.3.1 Refer to Method 8000 for proper calibration procedures. The procedure of internal or external standard calibration may be used. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.2 Assemble the necessary HPLC apparatus and establish operating parameters equivalent to those indicated in Section 7.2.1. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

7.3.3 Before using any cleanup procedure, the analyst should process a series of calibration standards through the procedure to confirm elution patterns and the absence of interferences from the reagents.

7.4 HPLC analysis:

7.4.1 Table 1 summarizes the estimate retention times of PAHs determinable by this method. Figure 1 is an example of the separation achievable using the conditions given in Paragraph 7.2.1.

Column: HC-ODS SIL-X
Mobile Phase: 40% to 100% Acetonitrile in Water
Detector: Fluorescence

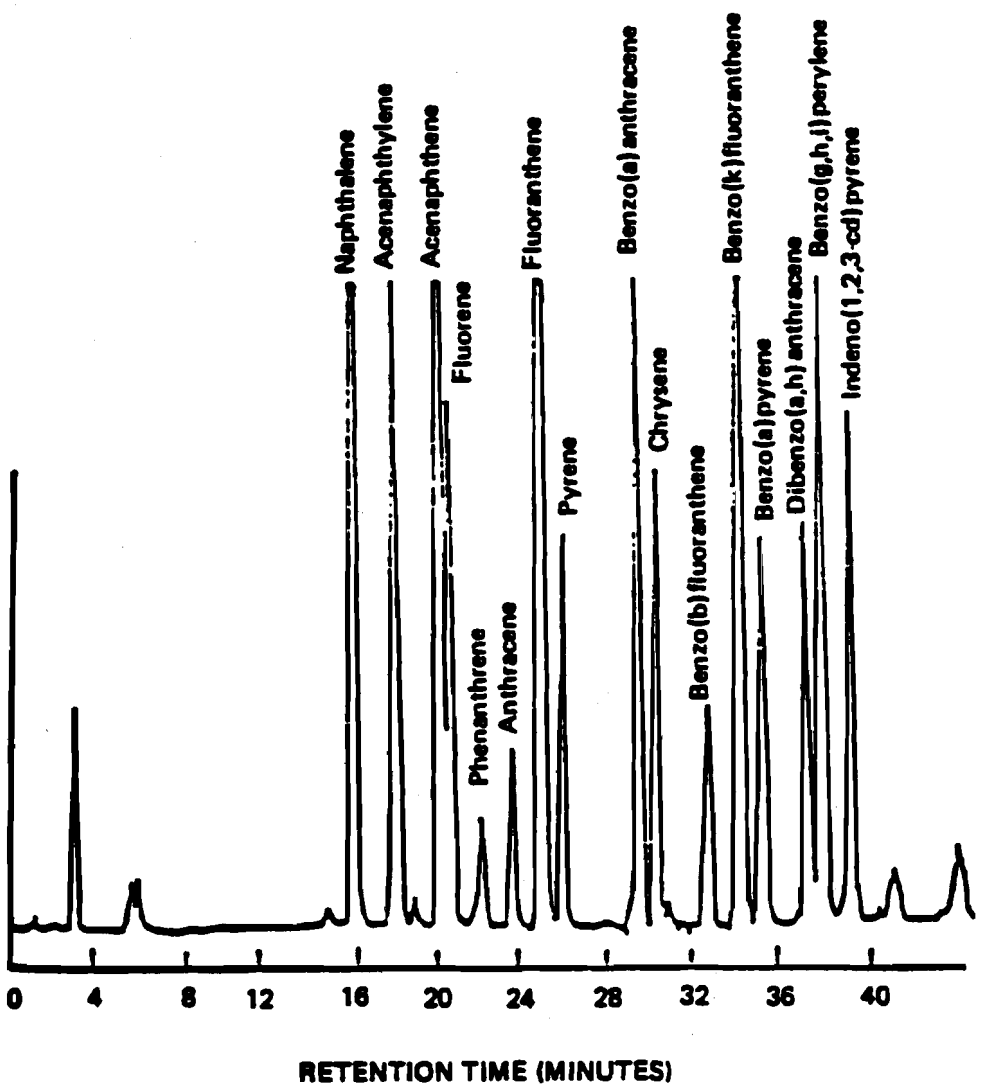


Figure 1. Liquid chromatogram of polynuclear aromatics.

7.4.2 If internal standard calibration is to be performed, add 10 uL of internal standard to the sample prior to injection. Inject 2-5 uL of the sample extract with a high-pressure syringe or sample injection loop. Record the volume injected to the nearest 0.1 uL, and the resulting peak size, in area units or peak heights. Re-equilibrate the HPLC column at the initial gradient conditions for at least 10 min between injections.

7.4.3 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.4 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.5 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

7.5 Cleanup:

7.5.1 Cleanup of the acetonitrile extract takes place using Method 3630 (Silica Gel Cleanup). Specific instructions for cleanup of the extract for PAHs is given in Section 7.1 of Method 3630.

7.5.2 Following cleanup, analyze the samples using HPLC as described in Section 7.4.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method used. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to validate the HPLC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

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4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

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6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

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TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Indeno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

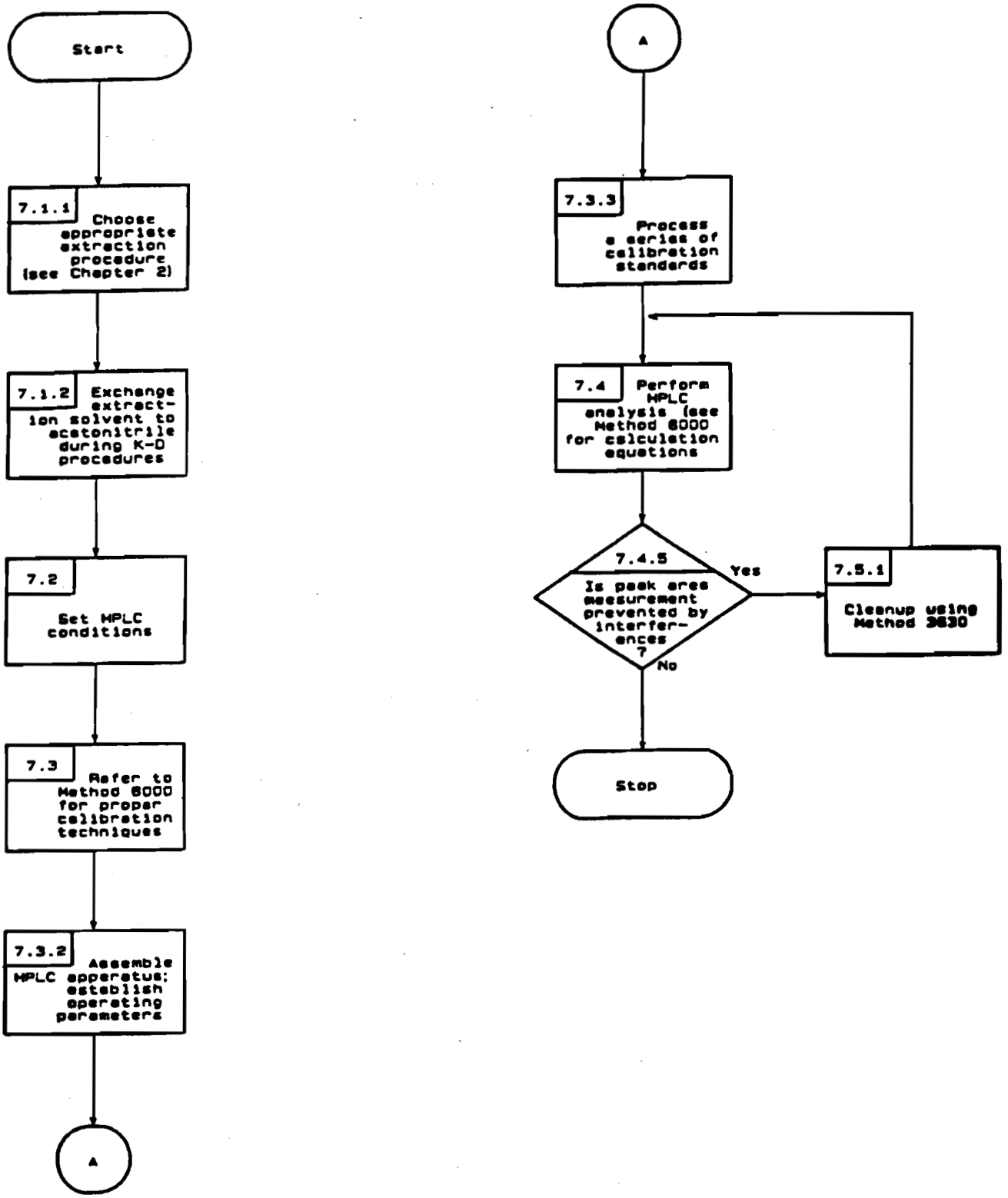
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to acetonitrile during K-D procedures
7.2 Set HPLC conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Assemble HPLC apparatus; establish operating parameters
A
A
7.3.3 Process a series of calibration standards
7.4 Perform HPLC analysis (see Method 8000 for calculation equations
7.4.5 Is peak area measurement prevented by interferences ?
Yes
No
7.5.1 Cleanup using Method 3630
Stop

METHOD 8315

DETERMINATION OF CARBONYL COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of free carbonyl compounds in various matrices by derivatization with 2,4-dinitrophenylhydrazine (DNPH). The method utilizes high performance liquid chromatography (HPLC) with ultraviolet/visible (UV/vis) detection to identify and quantitate the target analytes using two different sets of conditions: Option 1 and Option 2. Option 1 has been shown to perform well for one set of target analytes for aqueous samples, soil or waste samples, and stack samples collected by Method 0011. Option 2 has been shown to work well for another set of target analytes in indoor air samples collected by Method 0100. The two sets of target analytes overlap for some compounds. Refer to the Analysis Option listed in the following table to determine which analytes may be analyzed by which option. The following compounds may be determined by this method:

Compound Name	CAS No.[a]	Analysis Option[b]
Acetaldehyde	75-07-0	1,2
Acetone	67-64-1	2
Acrolein	107-02-8	2
Benzaldehyde	100-52-7	2
Butanal (butyraldehyde)	123-72-8	1,2
Crotonaldehyde	123-73-9	1,2
Cyclohexanone	108-94-1	1
Decanal	112-31-2	1
2,5-Dimethylbenzaldehyde	5779-94-2	2
Formaldehyde	50-00-0	1,2
Heptanal	111-71-7	1
Hexanal (hexaldehyde)	66-25-1	1,2
Isovaleraldehyde	590-86-3	2
Nonanal	124-19-6	1
Octanal	124-13-0	1
Pentanal (valeraldehyde)	110-62-3	1,2
Propanal (propionaldehyde)	123-38-6	1,2
m-Tolualdehyde	620-23-5	2
o-Tolualdehyde	529-20-4	2
p-Tolualdehyde	104-87-0	2

[a] Chemical Abstract Services Registry Number.

[b] This list of target analytes contains an overlapping list of compounds that have been evaluated using modifications of the

analysis. Refer to the respective option number when choosing the appropriate analysis technique for a particular compound.

1.2 The Option 1 method detection limits (MDL) are listed in Tables 1 and 2. The sensitivity data for sampling and analysis using Method 0100 (Option 2) are given in Table 3. The MDL for a specific sample may differ from that listed, depending upon the nature of interferences in the sample matrix and the amount of sample used in the procedure.

1.3 The extraction procedure for solid samples is similar to that specified in Method 1311. Thus, a single sample may be extracted to measure the analytes included in the scope of other appropriate methods. The analyst is allowed the flexibility to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these analytes.

1.4 When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results for the target analytes, using the extract produced by this method.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Sec. 7.0.

2.0 SUMMARY OF METHOD

2.1 Liquid and Solid Samples (Option 1)

2.1.1 For wastes comprised of solids, or for aqueous wastes containing significant amounts of solid material, the aqueous phase, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solids in the waste is reduced. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatiles. Following extraction, the aqueous extract is separated from the solid phase by filtration employing 0.6 to 0.8 μm glass fiber filter.

2.1.2 If compatible (i.e., multiple phases will not form on combination), the initial aqueous phase of the waste is added to the aqueous extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.1.3 A measured volume of aqueous sample (approx. 100 mL) or an appropriate amount of solids extract (approx. 25 g), is buffered to pH 3 and derivatized with 2,4-dinitrophenylhydrazine (DNPH), using either the liquid-solid or a liquid-liquid extraction option. If the liquid-solid

option is used, the derivative is extracted using solid sorbent cartridges, followed by elution with ethanol. If the liquid-liquid option is used, the derivative is extracted from the sample with three (3) portions of methylene chloride. The methylene chloride extracts are concentrated using the Kuderna-Danish (K-D) procedure and exchanged with acetonitrile prior to HPLC analysis. Liquid chromatographic conditions are described which permit the separation and measurement of various carbonyl compounds in the extract by absorbance detection at 360 nm.

2.1.4 If formaldehyde is the only analyte of interest, the aqueous sample or solids extract should be buffered to pH 5.0 to minimize artifact formaldehyde formation.

2.2 Stack Gas Samples Collected by Method 0011 (Option 1) - The entire sample returned to the laboratory is extracted with methylene chloride and the methylene chloride extract is brought up to a known volume. An aliquot of the methylene chloride extract is solvent exchanged and concentrated or diluted as necessary. Liquid chromatographic conditions are described that permit the separation and measurement of various carbonyl compounds in the extract by absorbance detection at 360 nm.

2.3 Indoor Air Samples by Method 0100 (Option 2) - The sample cartridges are returned to the laboratory and backflushed with acetonitrile into a 5 mL volumetric flask. The eluate is brought up to volume with more acetonitrile. Two (2) aliquots of the acetonitrile extract are pipetted into two (2) sample vials having Teflon-lined septa. Liquid chromatographic conditions are described that permit the separation and measurement of the various carbonyl compounds in the extract by absorbance detection at 360 nm.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Sec. 8.5.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. It should then be drained, dried, and heated in a laboratory oven at 130°C for several hours before use. Solvent rinses with acetonitrile may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

<u>NOTE</u>: Do not use acetone or methanol. These solvents react with DNPH to form interfering compounds.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.1.3 Polyethylene gloves must be worn when handling the silica gel cartridges to reduce the possibility of contamination.

3.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem due to its widespread occurrence in the environment. The DNPH reagent in Option 2 must be purified by multiple recrystallizations in UV-grade acetonitrile. Recrystallization is accomplished, at 40-60°C, by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV-grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined prior to the analysis of the samples and should be less than 25 mg/L. Refer to Appendix A for the recrystallization procedure.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. Although the HPLC conditions described allow for a resolution of the specific compounds covered by this method, other matrix components may interfere. If interferences occur in subsequent samples, modification of the mobile phase or some additional cleanup may be necessary.

3.4 In Option 1, acetaldehyde is generated during the derivatization step if ethanol is present in the sample. This background will impair the measurement of acetaldehyde at levels below 0.5 ppm (500 ppb).

3.5 For Option 2, at the stated two column analysis conditions, the identification and quantitation of butyraldehyde may be difficult due to coelution with isobutyraldehyde and methyl ethyl ketone. Precautions should be taken and adjustment of the analysis conditions should be done, if necessary, to avoid potential problems.

4.0 APPARATUS AND MATERIALS

4.1 High performance liquid chromatograph (modular)

4.1.1 Pumping system - Gradient, with constant flow control capable of 1.50 mL/min.

4.1.2 High pressure injection valve with 20 μL loop.

4.1.3 Column - 250 mm x 4.6 mm ID, 5 μm particle size, C18 (Zorbax or equivalent).

4.1.4 Absorbance detector - 360 nm.

4.1.5 Strip-chart recorder compatible with detector - Use of a data system for measuring peak areas and retention times is recommended.

4.1.6 Helium - for degassing mobile phase solvents. (Options 1 and 2)

4.1.7 Mobile Phase Reservoirs and Suction Filtration Apparatus - For holding and filtering HPLC mobile phase. Filtering system should be all glass and Teflon and use a 0.22 µm polyester membrane filter. (Option 2)

4.1.8 Syringes - for HPLC injection loop loading, with capacity at least four times the loop volume.

4.2 Apparatus and Materials for Option 1

4.2.1 Reaction vessel - 250 mL Florence flask.

4.2.2 Separatory funnel - 250 mL, with Teflon stopcock.

4.2.3 Kuderna-Danish (K-D) apparatus.

4.2.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.2.4 Boiling chips - Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

4.2.5 pH meter - Capable of measuring to the nearest 0.01 units.

4.2.6 Glass fiber filter paper - 1.2 µm pore size (Fisher Grade G4 or equivalent).

4.2.7 Solid sorbent cartridges - Packed with 2 g C18 (Baker or equivalent).

4.2.8 Vacuum manifold - Capable of simultaneous extraction of up to 12 samples (Supelco or equivalent).

4.2.9 Sample reservoirs - 60 mL capacity (Supelco or equivalent).

4.2.10 Pipet - Capable of accurately delivering 0.10 mL solution (Pipetman or equivalent).

4.2.11 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used under a hood.

4.2.12 Sample shaker - Controlled temperature incubator (± 2°C) with orbital shaking (Lab-Line Orbit Environ-Shaker Model 3527 or equivalent).

4.2.13 Syringes - 5 mL, 500 µL, 100 µL, (Luer-Lok or equivalent).

4.2.14 Syringe Filters - 0.45 µm filtration disks (Gelman Acrodisc 4438 or equivalent).

4.3 Apparatus and Materials for Option 2

4.3.1 Syringes - 10 mL, with Luer-Lok type adapter, used to backflush the sample cartridges by gravity feed.

4.3.2 Syringe Rack - made of an aluminum plate with adjustable legs on all four corners. Circular holes of a diameter slightly larger than the diameter of the 10 mL syringes are drilled through the plate to allow batch processing of cartridges for cleaning, coating, and sample elution. A plate (0.16 x 36 x 53 cm) with 45 holes in a 5x9 matrix is recommended. See Figure 2 in Method 0100.

4.4 Volumetric Flasks - 5 mL, 10 mL, and 250 or 500 mL.

4.5 Vials - 10 or 25 mL, glass with Teflon-lined screw caps or crimp tops.

4.6 Balance - Analytical, capable of accurately weighing to 0.0001 g.

4.7 Glass Funnels

4.8 Polyethylene Gloves - used to handle silica gel cartridges.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - Water in which an interferant is not observed at the method detection limit for the compounds of interest.

5.3 Formalin - Solution of formaldehyde (CH_2O) in organic-free reagent water, nominally 37.6 percent (w/w). Exact concentration will be determined for the stock solution in Sec. 5.7.1.1.

5.4 Aldehydes and ketones - analytical grade, used for preparation of DNPH derivative standards of target analytes other than formaldehyde. Refer to the target analyte list.

5.5 Option 1 Reagents

5.5.1 Methylene chloride, CH_2Cl_2 - HPLC grade or equivalent.

5.5.2 Acetonitrile, CH_3CN - HPLC grade or equivalent.

5.5.3 Sodium hydroxide solutions, NaOH, 1.0 N and 5 N.

5.5.4 Sodium chloride, NaCl, saturated solution - Prepare by dissolving an excess of the reagent grade solid in organic-free reagent water.

5.5.5 Sodium sulfite solution, Na_2SO_3, 0.1 M.

5.5.6 Sodium sulfate, Na_2SO_4 - granular, anhydrous.

5.5.7 Citric Acid, $C_8H_8O_7$, 1.0 M solution.

5.5.8 Sodium Citrate, $C_6H_5Na_3O_7.2H_2O$, 1.0 M trisodium salt dihydrate solution.

5.5.9 Acetic acid (glacial), CH_3CO_2H.

5.5.10 Sodium acetate, CH_3CO_2Na.

5.5.11 Hydrochloric Acid, HCl, 0.1 N.

5.5.12 Citrate buffer, 1 M, pH 3 - Prepare by adding 80 mL of 1 M citric acid solution to 20 mL of 1 M sodium citrate solution. Mix thoroughly. Adjust pH with NaOH or HCl as needed.

5.5.13 pH 5.0 Acetate buffer (5M) - Formaldehyde analysis only. Prepared by adding 40 mL 5M acetic acid solution to 60 mL 5M sodium acetate solution. Mix thoroughly. Adjust pH with NaOH or HCl as needed.

5.5.14 2,4-Dinitrophenylhydrazine, $2,4\text{-}(O_2N)_2C_6H_3]NHNH_2$, (DNPH), 70% in organic-free reagent water (w/w).

5.5.14.1 DNPH (3.00 mg/mL) - Dissolve 428.7 mg of 70% (w/w) DNPH solution in 100 mL acetonitrile.

5.5.15 Extraction fluid for Option 1 - Dilute 64.3 mL of 1.0 N NaOH and 5.7 mL glacial acetic acid to 900 mL with organic-free reagent water.

Dilute to 1 liter with organic-free reagent water. The pH should be 4.93 ± 0.02.

5.6 Option 2 Reagents

5.6.1 Acetonitrile, CH_3CN - UV grade.

5.6.2 2,4-Dinitrophenylhydrazine, $C_6H_6N_4O_4$, (DNPH) - recrystallize at least twice with UV grade acetonitrile using the procedure in Appendix A.

5.7 Stock Standard Solutions for Option 1

5.7.1 Stock formaldehyde (approximately 1000 mg/L) - Prepare by diluting an appropriate amount of the certified or standardized formaldehyde (approximately 265 µL) to 100 mL with organic-free reagent water. If a certified formaldehyde solution is not available or there is any question regarding the quality of a certified solution, the solution may be standardized using the procedure in Sec. 5.7.1.1.

5.7.1.1 Standardization of formaldehyde stock solution - Transfer a 25 mL aliquot of a 0.1 M Na_2SO_3 solution to a beaker and record the pH. Add a 25.0 mL aliquot of the formaldehyde stock solution (Sec. 5.18.1) and record the pH. Titrate this mixture back to the original pH using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

$$\text{Concentration (mg/L)} = \frac{(30.03)(\text{N HCl})(\text{mL HCl})}{25.0 \text{ mL}}$$

where:

N HCl	=	Normality of HCl solution used (in milli-equivalents/mL) (1 mmole of HCl = 1 milli-equivalent of HCl)
mL HCl	=	mL of standardized HCl solution used
30.03	=	Molecular of weight of formaldehyde (in mg/mmole)

5.7.2 Stock aldehyde(s) and ketone(s) - Prepare by adding an appropriate amount of the pure material to 90 mL of acetonitrile and dilute to 100 mL, to give a final concentration of 1000 mg/L.

5.8 Stock Standard Solutions for Option 2

5.8.1 Preparation of the DNPH Derivatives for HPLC analysis

5.8.1.1 To a portion of the recrystallized DNPH, add sufficient 2N HCl to obtain an approximately saturated solution. Add to this solution the target analyte in molar excess of the DNPH. Filter the DNPH derivative precipitate, wash it with 2N HCl, wash it again with water, and allow it to dry in air.

5.8.1.2 Check the purity of the DNPH derivative by melting point determination or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in acetonitrile. Repeat the purity check and recrystallization as necessary until 99% purity is achieved.

5.8.2 Preparation of DNPH Derivative Standards and Calibration Standards for HPLC analysis

5.8.2.1 Stock Standard Solutions - Prepare individual stock standard solutions for each of the target analyte DNPH derivatives by dissolving accurately weighed amounts in acetonitrile. Individual stock solutions of approximately 100 mg/L may be prepared by dissolving 0.010 g of the solid derivative in 100 mL of acetonitrile.

5.8.2.2 Secondary Dilution Standard(s) - Using the individual stock standard solutions, prepare secondary dilution standards in acetonitrile containing the DNPH derivatives from the target analytes mixed together. Solutions of 100 µg/L may be prepared by placing 100 µL of a 100 mg/L solution in a 100 mL volumetric flask and diluting to the mark with acetonitrile.

5.8.2.3 Calibration Standards - Prepare a working calibration standard mix from the secondary dilution standard, using the mixture of DNPH derivatives at concentrations of 0.5-2.0 µg/L (which spans the concentration of interest for most indoor air work). The concentration of the DNPH derivative in the standard mix solutions may need to be adjusted to reflect relative concentration distribution in a real sample.

5.9 Standard Storage - Store all standard solutions at 4°C in a glass vial with a Teflon-lined cap, with minimum headspace, and in the dark. They should be stable for about 6 weeks. All standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10 Calibration Standards

5.10.1 Prepare calibration solutions at a minimum of 5 concentrations for each analyte of interest in organic-free reagent water (or acetonitrile for Option 2) from the stock standard solution. The lowest concentration of each analyte should be at, or just above, the MDLs listed in Tables 1 or 2. The other concentrations of the calibration curve should correspond to the expected range of concentrations found in real samples.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

6.2 Samples must be refrigerated at 4°C. Aqueous samples must be derivatized and extracted within 3 days of sample collection. The holding times of leachates of solid samples should be kept at a minimum. All derivatized sample extracts should be analyzed within 3 days after preparation.

6.3 Samples collected by Methods 0011 or 0100 must be refrigerated at 4°C. It is recommended that samples be extracted and analyzed within 30 days of collection.

7.0 PROCEDURE

7.1 Extraction of Solid Samples (Option 1)

7.1.1 All solid samples should be made as homogeneous as possible by stirring and removal of sticks, rocks, and other extraneous material. When the sample is not dry, determine the dry weight of the sample, using a representative aliquot. If particle size reduction is necessary, proceed as per Method 1311.

7.1.1.1 Determination of dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data are desired or required, a portion of sample for dry weight determination should be weighed out at the same time as the portion used for analytical determination.

<u>WARNING</u>: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

7.1.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.1.2 Measure 25 g of solid into a 500 mL bottle with a Teflon lined screw cap or crimp top, and add 500 mL of extraction fluid (Sec. 5.5.15). Extract the solid by rotating the bottle at approximately 30 rpm for 18 hours. Filter the extract through glass fiber filter paper and store in sealed bottles at 4°C. Each mL of extract represents 0.050 g solid. Smaller quantities of solid sample may be used with

correspondingly reduced volumes of extraction fluid maintaining the 1:20 mass to volume ratio.

7.2 Cleanup and Separation (Option 1)

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various sample types. If particular samples demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of formaldehyde from a spiked sample is greater than 85%. Recovery may be lower for samples which form emulsions.

7.2.2 If the sample is not clear, or the complexity is unknown, the entire sample should be centrifuged at 2500 rpm for 10 minutes. Decant the supernatant liquid from the centrifuge bottle, and filter through glass fiber filter paper into a container which can be tightly sealed.

7.3 Derivatization (Option 1)

7.3.1 For aqueous samples, measure an aliquot of sample which is appropriate to the anticipated analyte concentration range (nominally 100 mL). Quantitatively transfer the sample aliquot to the reaction vessel (Sec. 4.2).

7.3.2 For solid samples, 1 to 10 mL of extract (Sec. 7.1) will usually be required. The amount used for a particular sample must be determined through preliminary experiments.

NOTE: In cases where the selected sample or extract volume is less than 100 mL, the total volume of the aqueous layer should be adjusted to 100 mL with organic-free reagent water. Record original sample volume prior to dilution.

7.3.3 Derivatization and extraction of the target analytes may be accomplished using the liquid-solid (Sec. 7.3.4) or liquid-liquid (Sec. 7.3.5) procedures.

7.3.4 Liquid-Solid Derivatization and Extraction

7.3.4.1 For analytes other than formaldehyde, add 4 mL of citrate buffer and adjust the pH to 3.0 $\pm$ 0.1 with 6M HCl or 6M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker (Sec. 4.2.12) for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.4.2 If formaldehyde is the only analyte of interest, add 4 mL acetate buffer and adjust pH to 5.0 $\pm$ 0.1 with 6M HCl or 6M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker (Sec. 4.2.12) for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.4.3 Assemble the vacuum manifold and connect to a water aspirator or vacuum pump. Attach a 2 g sorbent cartridge to the vacuum manifold. Condition each cartridge by passing 10 mL dilute citrate buffer (10 mL of 1 M citrate buffer dissolved in 250 mL of organic-free reagent water) through each sorbent cartridge.

7.3.4.4 Remove the reaction vessel from the shaker immediately at the end of the one hour reaction period and add 10 mL saturated NaCl solution to the vessel.

7.3.4.5 Quantitatively transfer the reaction solution to the sorbent cartridge and apply a vacuum so that the solution is drawn through the cartridge at a rate of 3 to 5 mL/min. Continue applying the vacuum for about 1 minute after the liquid sample has passed through the cartridge.

7.3.4.6 While maintaining the vacuum conditions described in Sec. 7.3.4.4, elute each cartridge train with approximately 9 mL of acetonitrile directly into a 10 mL volumetric flask. Dilute the solution to volume with acetonitrile, mix thoroughly, and place in a tightly sealed vial until analyzed.

NOTE: Because this method uses an excess of DNPH, the cartridges will remain a yellow color after completion of Sec. 7.3.4.5. The presence of this color is not indicative of the loss of the analyte derivatives.

7.3.5 Liquid-Liquid Derivatization and Extraction

7.3.5.1 For analytes other than formaldehyde, add 4 mL of citrate buffer and adjust the pH to 3.0 ± 0.1 with 6M HCl or 6M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.5.2 If formaldehyde is the only analyte of interest, add 4 mL acetate buffer and adjust pH to 5.0 ± 0.1 with 6M HCl or 6M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.5.3 Serially extract the solution with three 20 mL portions of methylene chloride using a 250 mL separatory funnel. If an emulsion forms upon extraction, remove the entire emulsion and centrifuge at 2000 rpm for 10 minutes. Separate the layers and proceed with the next extraction. Combine the methylene chloride layers in a 125 mL Erlenmeyer flask containing 5.0 grams of anhydrous sodium sulfate. Swirl contents to complete the extract drying process.

7.3.5.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Pour the extract into the evaporator flask being careful to minimize transfer of sodium sulfate granules. Wash the Erlenmeyer flask with 30 mL of methylene chloride and add wash to the evaporator flask to complete quantitative transfer.

7.3.5.5 Add one to two clean boiling chips to the evaporative flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.5.6 Prior to liquid chromatographic analysis, the extract solvent must be exchanged to acetonitrile. The analyst must ensure quantitative transfer of the extract concentrate. The exchange is performed as follows:

7.3.5.6.1 Remove the three-ball Snyder column and evaporator flask. Add 5 mL of acetonitrile , a new glass bead or boiling chip, and attach the micro-Snyder column to the concentrator tube. Concentrate the extract using 1 mL of acetonitrile to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches less than 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.5.6.2 Remove the Snyder column and rinse the flask and its lower joint with 1-2 mL of acetonitrile and add to concentrator tube. Quantitatively transfer the sample to a 10 mL volumetric flask using a 5 mL syringe with an attached Acrodisc 0.45 μm filter cassette. Adjust the extract volume to 10 mL. Stopper the flask and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two (2) days, it should be transferred to a vial with a Teflon lined screw cap or crimp top. Proceed with HPLC chromatographic analysis if further cleanup is not required.

7.4 Extraction of Samples from Methods 0011 and 0100 (Options 1 and 2)

7.4.1 Stack gas samples collected by Method 0011 (Option 1)

7.4.1.1 Measure the volume of the aqueous phase of the sample prior to extraction (for moisture determination in case the volume was not measured in the field). Pour the sample into a separatory funnel and drain the methylene chloride into a volumetric flask.

7.4.1.2 Extract the aqueous solution with two or three aliquots of methylene chloride. Add the methylene chloride extracts to the volumetric flask.

7.4.1.3 Fill the volumetric flask to the line with methylene chloride. Mix well and remove an aliquot.

7.4.1.4 If high concentrations of formaldehyde are present, the extract can be diluted with mobile phase, otherwise the extract solvent must be exchanged as described in Sec. 7.3.5.5. If low concentrations of formaldehyde are present, the sample should be concentrated during the solvent exchange procedure.

7.4.1.5 Store the sample at 4°C. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap, or a crimp top with a Teflon-lined septum. Proceed with HPLC chromatographic analysis if further cleanup is not required.

7.4.2 Ambient air samples collected by Method 0100 (Option 2)

7.4.2.1 The samples will be received by the laboratory in a friction-top can containing 2 to 5 cm of granular charcoal, and should be stored in this can, in a refrigerator, until analysis. Alternatively, the samples may also be stored alone in their individual glass containers. The time between sampling and analysis should not exceed 30 days.

7.4.2.2 Remove the sample cartridge from the labeled culture tube. Connect the sample cartridge (outlet or long end during sampling) to a clean syringe.

<u>NOTE</u>: The liquid flow during desorption should be in the opposite direction from the air flow during sample collection (i.e, backflush the cartridge).

7.4.2.3 Place the cartridge/syringe in the syringe rack.

7.4.2.4 Backflush the cartridge (gravity feed) by passing 6 mL of acetonitrile from the syringe through the cartridge to a graduated test tube, or to a 5 mL volumetric flask.

NOTE: A dry cartridge has an acetonitrile holdup volume slightly greater than 1 mL. The eluate flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe Luer-Lok tip. If this happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.

7.4.2.5 Dilute to the 5 mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials having Teflon-lined septa.

7.4.2.6 Store the sample at 4°C. Proceed with HPLC chromatographic analysis of the first aliquot if further cleanup is not required. Store the second aliquot in the refrigerator until the results of the analysis of the first aliquot are complete and validated. The second aliquot can be used for confirmatory analysis, if necessary.

7.5 Chromatographic Conditions (Recommended):

7.5.1 Option 1 - For aqueous samples, soil or waste samples, and stack gas samples collected by Method 0011.

Column:	C18, 4.6 mm x 250 mm ID, 5 µm particle size
Mobile Phase Gradient:	70%/30% acetonitrile/water (v/v), hold for 20 min. 70%/30% acetonitrile/water to 100% acetonitrile in 15 min. 100% acetonitrile for 15 min.
Flow Rate:	1.2 mL/min
Detector:	Ultraviolet, operated at 360 nm
Injection Volume:	20 µL

7.5.2 Option 2 - For ambient air samples collected by Method 0100.

Column:	Two HPLC columns, 4.6 mm x 250 mm ID, (Zorbax ODS, or equivalent) in series
Mobile Phase Gradient:	60%/40% CH_3CN/H_2O, hold for 0 min. 60%/40% to 75%/25% CH_3CN/H_2O, linearly in 30 min. 75%/25% to 100%/0% CH_3CN/H_2O, linearly in 20 min. 100% CH_3CN for 5 minutes. 100%/0% to 60%/40% CH_3CN/H_2O, linearly in 1 min. 60%/40% CH_3CN/H_2O for 15 minutes.
Detector:	Ultraviolet, operated at 360 nm
Flow Rate:	1.0 mL/min
Sample Injection volume:	25 µL (suggested)

NOTE: For Options 1 and 2, analysts are advised to adjust their HPLC systems to optimize chromatographic conditions for their particular analytical needs. The separation of acrolein, acetone, and propionaldehyde should be a minimum criterion of the optimization in Option 2.

7.5.3 Filter and degas the mobile phase to remove dissolved gasses, using the following procedure:

7.5.3.1 Filter each solvent (water and acetonitrile) through a 0.22 μm polyester membrane filter, in an all glass and Teflon suction filtration apparatus.

7.5.3.2 Degas each filtered solution by purging with helium for 10-15 minutes (100 mL/min) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (350 kPa) or 15-30 cm of 0.25 mm ID Teflon tubing should be placed after the detector to eliminate further mobile phase outgassing.

7.5.3.3 Place the mobile phase components in their respective HPLC solvent reservoirs, and program the gradient system according to the conditions listed in Sec. 7.5.2. Allow the system to pump for 20-30 minutes at a flow rate of 1.0 mL/min with the initial solvent mixture ratio (60%/40% CH_3CN/H_2O). Display the detector output on a strip chart recorder or similar output device to establish a stable baseline.

7.6 Calibration

7.6.1 Establish liquid chromatographic operating conditions to produce a retention time similar to that indicated in Table 1 for the liquid-solid derivatization and extraction or in Table 2 for liquid-liquid derivatization and extraction. For determination of retention time windows, see Sec. 7.5 of Method 8000. Suggested chromatographic conditions are provided in Sec. 7.5.

7.6.2 Process each calibration standard solution through derivatization and extraction, using the same procedure employed for sample processing (Secs. 7.3.4 or 7.3.5).

7.6.3 Analyze a solvent blank to ensure that the system is clean and interference free.

NOTE: The samples and standards must be allowed to come to ambient temperature before analysis.

7.6.4 Analyze each processed calibration standard using the chromatographic conditions listed in Sec. 7.5, and tabulate peak area against calibration solution concentration in μg/L.

7.6.5 Tabulate the peak area along with standard concentration injected to determine the response factor (RF) for the analyte at each concentration (see Sec. 7.8.1 for equations). The percent relative standard deviation (%RSD) of the mean RF of the calibration standards should be no greater than ± 20 percent or a system check will have to be performed. If a calibration check after the system check does not meet the criteria, a recalibration will have to be performed. If the recalibration does not meet the established criteria, new calibration standards must be made.

7.6.6 The working calibration curve must be verified each day, before and after analyses are performed, by analyzing one or more calibration standards. The response obtained should fall within ± 15 percent of the initially established response or a system check will have to be performed. If a calibration check after the system check does not meet the criteria, the system must be recalibrated.

7.6.7 After 10 sample runs, or less, one of the calibration standards must be reanalyzed to ensure that the DNPH derivative response factors remain within ±15% of the original calibration response factors.

7.7 Sample Analysis

7.7.1 Analyze samples by HPLC, using conditions established in Sec. 7.5. For analytes to be analyzed by Option 1, Tables 1 and 2 list the retention times and MDLs that were obtained under these conditions. For Option 2 analytes, refer to Figure 3 for the sample chromatogram.

7.7.2 If the peak area exceeds the linear range of the calibration curve, a smaller sample injection volume should be used. Alternatively, the final solution may be diluted with acetonitrile and reanalyzed.

7.7.3 After elution of the target analytes, calculate the concentration of analytes found in the samples using the equations found in Sec. 7.8 or the specific sampling method used.

7.7.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required.

7.8 Calculations

7.8.1 Calculate each response factor, mean response factor, and percent relative standard deviation as follows:

$$RF_i = \frac{\text{Concentration of standard injected, } \mu g/L}{\text{Area of signal}}$$

$$\text{Mean RF} = \overline{RF} = \frac{\Sigma RF_i}{N}$$

$$\%RSD = \frac{\sqrt{\Sigma\,(RF_i - \overline{RF})^2\,/N-1}}{\overline{RF}} \times 100\%$$

where:

$\overline{RF}$	=	Mean response factor or mean of the response factors using the 5 calibration concentrations.
RF_i	=	Response factor for calibration standard i (i = 1-5).
%RSD	=	Percent relative standard deviation of the response factors.
N	=	Number of calibration standards.

7.8.2 Calculate the analyte concentrations in liquid samples as follows:

Concentration of aldehydes in $\mu g/L = (\overline{RF})(\text{Area of signal})(100/V_s)$

where:

$\overline{RF}$	=	Mean response factor for a particular analyte.
V_s	=	Number of mL of sample (unitless).

7.8.3 Calculate the analyte concentration in solid samples as follows:

Concentration of aldehydes in $\mu g/g = (\overline{RF})(\text{Area of signal})(20/\ V_{ex})$

where:

$\overline{RF}$	=	Mean response factor for a particular analyte.
V_{ex}	=	Number of mL extraction fluid aliquot (unitless).

7.8.4 Calculate the concentration of formaldehyde in stack gas samples (Method 0011) as follows: (Option 1)

7.8.4.1 Calculation of Total Formaldehyde: To determine the total formaldehyde in mg, use the following equation:

$$\text{Total mg formaldehyde} = C_d \times V \times DF \times \frac{[\text{g/mole formaldehyde}]}{[\text{g/mole DNPH derivative}]} \times 10^{-3}\ \text{mg}/\mu\text{g}$$

where:

C_d	=	measured concentration of DNPH-formaldehyde derivative, mg/L
V	=	organic extract volume, mL
DF	=	dilution factor

7.8.4.2 Formaldehyde concentration in stack gas: Determine the formaldehyde concentration in the stack gas using the following equation:

$$C_f = K\ [\text{total formaldehyde, mg}]\ /\ V_{m(std)}$$

where:

K	=	35.31 ft^3/m^3, if $V_{m(std)}$ is expressed in English units
	=	1.00 m^3/m^3, if $V_{m(std)}$ is expressed in metric units
$V_{m(std)}$	=	volume of gas sample as measured by dry gas meter, corrected to standard conditions, dscm (dscf)

7.8.5 Calculation of the Concentration of Formaldehyde and Other Carbonyls from Indoor Air Sampling by Method 0100. (Option 2)

7.8.5.1 The concentration of target analyte "a" in air at standard conditions (25°C and 101.3 kPa), $Conc_{astd}$ in ng/L, may be calculated using the following equation:

$$Conc_a = \frac{(Area_a)(\overline{RF})(Vol_a)(MW_a)(1000\ \text{ng}/\mu\text{g})}{(MW_d)(V_{TotStd})(1000\ \text{mL/L})} \times DF$$

where:

$Area_a$	=	Area of the sample peak for analyte "a"
$\overline{RF}$	=	Mean response factor for analyte "a" from the calibration in μg/L. (See Sec. 7.8.1)
Vol_a	=	Total volume of the sample cartridge eluate (mL)
MW_a	=	Molecular weight of analyte "a" in g/mole
MW_d	=	Molecular weight of the DNPH derivative of analyte "a" in g/mole

V_{TotStd}	=	Total volume of air sampled converted to standard conditions in liters (L). (To calculate the concentration at sampling conditions use V_{tot}.)(See Sec. 9.1.3 of Method 0100)
DF	=	Dilution Factor for the sample cartridge eluate, if any. If there is no dilution, DF = 1

7.8.5.2 The target analyte "a" concentration at standard conditions may be converted to parts per billion by volume, $Conc_a$ in ppbv, using the following equation:

$$Conc_a \text{ in ppbv} = \frac{(Conc_a)(22.4)}{(MW_a)}$$

where:

$Conc_a$	=	Concentration of analyte "a" in ng/L
22.4	=	Ideal gas law volume (22.4 nL of gas = 1 nmole at standard conditions)
MW_a	=	Molecular weight of analyte "a" in g/mole (or ng/nmole)

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Refer to Table 4 for QC acceptance limits derived from the interlaboratory method validation study on Method 8315.

9.0 METHOD PERFORMANCE

9.1 The MDLs for Option 1 listed in Table 1 were obtained using organic-free reagent water and liquid-solid extraction. The MDLs for Option 1 listed in Table 2 were obtained using organic-free reagent water and methylene chloride extraction. Results reported in Tables 1 and 2 were achieved using fortified reagent water volumes of 100 mL. Lower detection limits may be obtained using larger sample volumes.

9.1.1 Option 1 of this method has been tested for linearity of recovery from spiked organic-free reagent water and has been demonstrated to be applicable over the range 50-1000 μg/L .

9.1.2 To generate the MDL and precision and accuracy data reported in this section, analytes were segregated into two spiking groups, A and B. Representative chromatograms using liquid-solid and liquid-liquid extraction are presented in Figures 1 (a and b) and 2 (a and b), respectively.

9.2 The Sensitivity of Option 2 sampling (Method 0100) and analysis is listed in Table 3.

9.3 Method 8315, Option 1, was tested by 12 laboratories using reagent water and ground waters spiked at six concentration levels over the range 30-2200 µg/L. Method accuracy and precision were found to be directly related to the concentration of the analyte and independent of the sample matrix. Mean recovery weighted linear regression equations, calculated as a function of spike concentration, as well as overall and single-analyst precision regression equations, calculated as functions of mean recovery, are presented in Table 5. These equations can be used to estimate mean recovery and precision at any concentration value within the range tested.

10.0 REFERENCES

1. "OSHA Safety and Health Standards, General Industry", (29CRF1910). Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

11.0 SAFETY

11.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

11.2 Formaldehyde has been tentatively classified as a known or suspected, human or mammalian carcinogen.

TABLE 1.

OPTION 1 - METHOD DETECTION LIMITS[a] USING LIQUID-SOLID EXTRACTION

Analyte	Retention Time (minutes)	MDL (μg/L)[a]
Formaldehyde	5.3	6.2
Acetaldehyde	7.4	43.7[b]
Propanal	11.7	11.0
Crotonaldehyde	16.1	5.9
Butanal	18.1	6.3
Cyclohexanone	27.6	5.8
Pentanal	28.4	15.3
Hexanal	34.1	10.7
Heptanal	35.0	10.0
Octanal	40.1	6.9
Nonanal	40.4	13.6
Decanal	44.1	4.4

[a] The method detection limit (MDL) is defined as the minimum concentration that can be measured with 99% confidence that the value is above background level. With the exception of acetaldehyde, all reported MDLs are based upon analyses of 6 to 8 replicate blanks spiked at 25 μg/L. The MDL was computed as follows:

$$MDL = t_{(N-1,\ 0.01)}(\text{Std. Dev.})$$

where:

$t_{(N-1,\ 0.01)}$ = The upper first percentile point of the t-distribution with n-1 degrees of freedom.

Std. Dev. = Standard deviation, calculated using n-1 degrees of freedom.

[b] The reported MDL is based upon analyses of 3 replicate, fortified blanks at 250 μg/L.

TABLE 2.

OPTION 1 - METHOD DETECTION LIMITS[a] USING LIQUID-LIQUID EXTRACTION

Analyte	Retention Time (minutes)	MDL (µg/L)[a]
Formaldehyde	5.3	23.2
Acetaldehyde	7.4	110.2[b]
Propanal	11.7	8.4
Crotonaldehyde	16.1	5.9
Butanal	18.1	7.8
Cyclohexanone	27.6	6.9
Pentanal	28.4	13.4
Hexanal	34.1	12.4
Heptanal	35.0	6.6
Octanal	40.1	9.9
Nonanal	40.4	7.4
Decanal	44.1	13.1

[a] The method detection limit (MDL) is defined as the minimum concentration that can be measured with 99% confidence that the value is above background level. With the exception of acetaldehyde, all reported MDLs are based upon analyses of 6 to 8 replicate blanks spiked at 25 µg/L. The MDL was computed as follows:

$$MDL = t_{(N-1,\ 0.01)}(\text{Std. Dev.})$$

where:

$t_{(N-1,\ 0.01)}$ = The upper first percentile point of the t-distribution with n-1 degrees of freedom.

Std. Dev. = Standard deviation, calculated using n-1 degrees of freedom.

[b] The reported MDL is based upon analyses of 3 replicate, fortified blanks at 250 µg/L.

TABLE 3.

OPTION 2 - SENSITIVITY (ppb, v/v) OF SAMPLING AND ANALYSIS FOR CARBONYL COMPOUNDS IN AMBIENT AIR USING AN ADSORBENT CARTRIDGE FOLLOWED BY GRADIENT HPLC[a]

	Sample Volume (L)[b]									
Compound	10	20	30	40	50	100	200	300	400	500
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03
Acetone	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.11	0.05	0.04	0.03	0.02
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.12	0.06	0.04	0.03	0.02
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.12	0.06	0.04	0.03	0.02
2,5-Dimethyl-benzaldehyde	0.97	0.49	0.32	0.24	0.19	0.10	0.05	0.03	0.02	0.02
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03
Hexanal	1.09	0.55	0.36	0.27	0.22	0.11	0.05	0.04	0.03	0.02
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
m-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
o-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
p-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02

[a] The ppb values are measured at 1 atm and 25°C. The sample cartridge is eluted with 5 mL acetonitrile and 25 μL is injected into the HPLC. The maximum sampling flow through a DNPH-coated Sep-Pak is about 1.5 L/minute.

[b] A sample volume of 1000 L was also analyzed. The results show a sensitivity of 0.01 ppb for all the target analytes.

TABLE 4.

PERFORMANCE-BASED QC ACCEPTANCE LIMITS CALCULATED USING THE COLLABORATIVE STUDY DATA

Analyte	Spike Concentration[a]	X[b]	S_R[c]	Acceptance Limits, %[d]
Formaldehyde	160	154	30.5	39-153
Propanal	160	148	22.4	50-134
Crotonaldehyde	160	160	34.8	35-165
Butanal	160	151	22.7	52-137
Cyclohexanone	160	169	39.2	32-179
Hexanal	160	151	34.6	30-159
Octanal	160	145	40.1	15-166
Decanal	160	153	40.0	21-171

[a] Spike concentration, µg/L.
[b] Mean recovery calculated using the reagent water, mean recovery, linear regression equation, µg/L.
[c] Overall standard deviation calculated using the reagent water, overall standard deviation linear regression equation, µg/L.
[d] Acceptance limits calculated as $(X \pm 3s_R)100$/spike concentration.

TABLE 5.

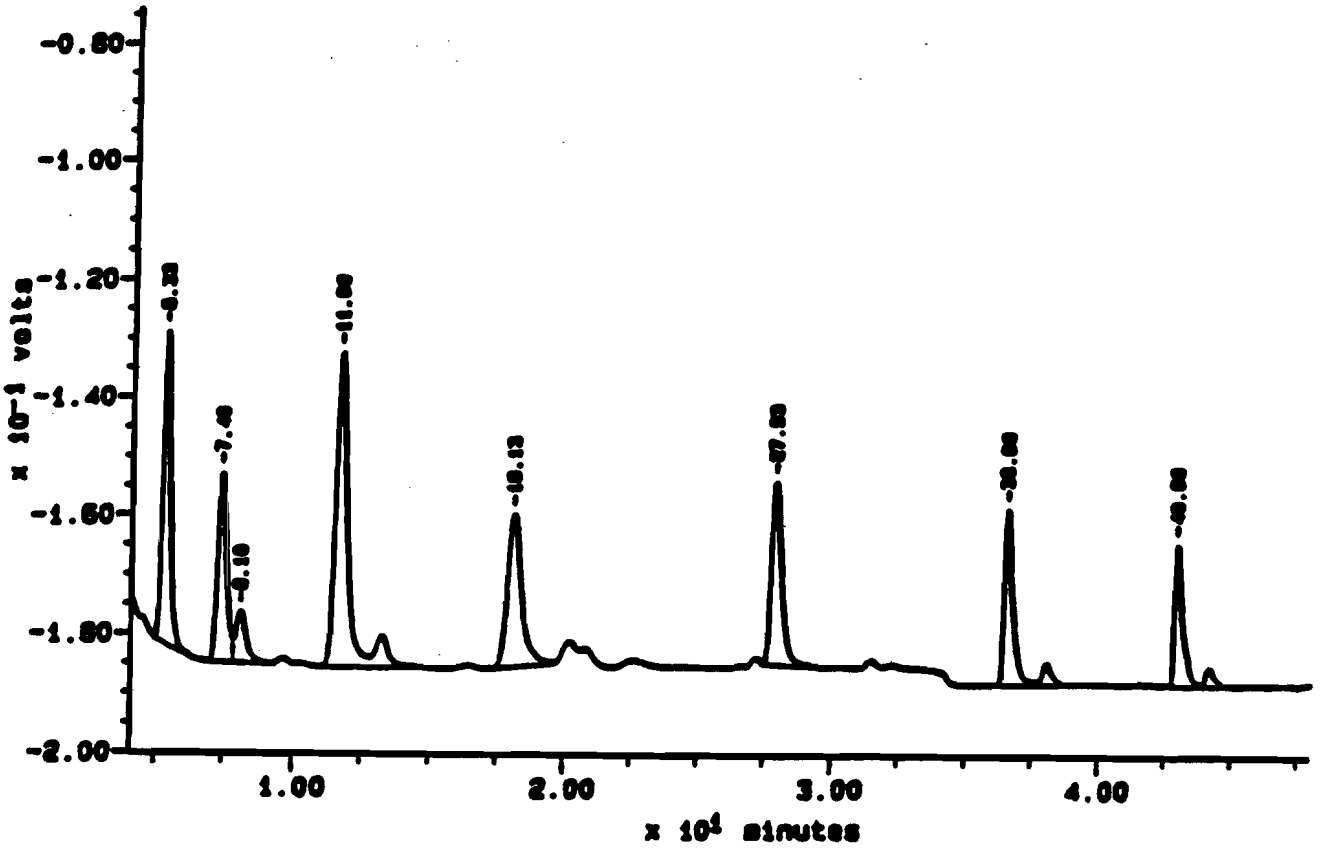
WEIGHTED LINEAR REGRESSION EQUATIONS FOR MEAN RECOVERY AND PRECISION (μg/L)

Analyte	Applicable Conc. Range		Reagent Water	Ground Water
Formaldehyde	39.2-2450	X	0.909C + 8.79	0.870C +14.84
		s_R	0.185X + 1.98[a]	0.177X + 13.85
		s_r	0.093X + 5.79	0.108X + 6.24
Propanal	31.9-2000	X	0.858C + 10.49	0.892C + 22.22
		s_R	0.140X + 1.63	0.180X + 12.37
		s_r	0.056X + 2.76	0.146X + 2.08[a]
Crotonaldehyde	32.4-2030	X	0.975C + 4.36	0.971C + 2.94
		s_R	0.185X + 5.15	0.157X + 6.09
		s_r	0.096X + 1.85	0.119X - 2.27
Butanal	35.4-2220	X	0.902C + 6.65	0.925C + 12.71
		s_R	0.149X + 0.21	0.140X + 6.89
		s_r	0.086X - 0.71	0.108X - 1.63[a]
Cyclohexanone	31.6-1970	X	0.962C + 14.97	0.946C + 28.95
		s_R	0.204X + 4.73[a]	0.345X + 5.02
		s_r	0.187X + 3.46	0.123X + 7.64
Hexanal	34.1-2130	X	0.844C + 15.81	0.926C + 9.16
		s_R	0.169X + 9.07	0.132X + 8.31
		s_r	0.098X + 0.37[a]	0.074X - 0.40[a]
Octanal	32.9-2050	X	0.856C + 7.88	0.914C + 13.09
		s_R	0.200X + 11.17	0.097X + 12.41
		s_r	0.092X + 1.71[a]	0.039X + 1.14
Decanal	33.2-2080	X	0.883C + 12.00	0.908C + 6.46
		s_R	0.225X + 5.52	0.153X + 2.23
		s_r	0.088X + 2.28[a]	0.052X + 0.37

[a] Variance is not constant over concentration range.
X Mean recovery, μg/L, exclusive of outliers.
s_R Overall standard deviation, μg/L, exclusive of outliers.
s_r Single-analyst standard deviation, μg/L, exclusive of outliers.

FIGURE 1a.

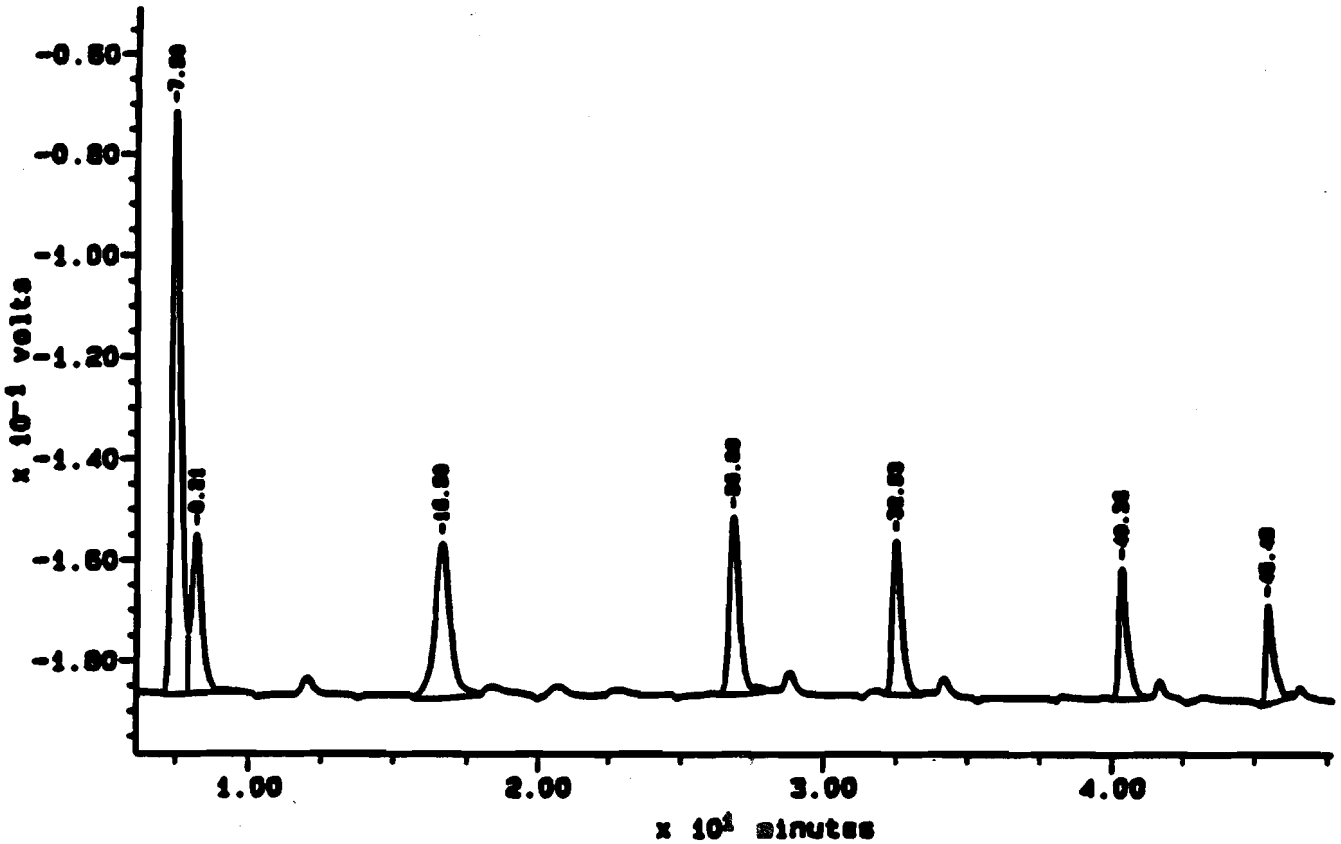
OPTION 2 - LIQUID-SOLID PROCEDURAL STANDARD OF GROUP A ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
5.33	Formaldehyde
11.68	Propanal
18.13	Butanal
27.93	Cyclohexanone
36.60	Heptanal
42.99	Nonanal

FIGURE 1b.

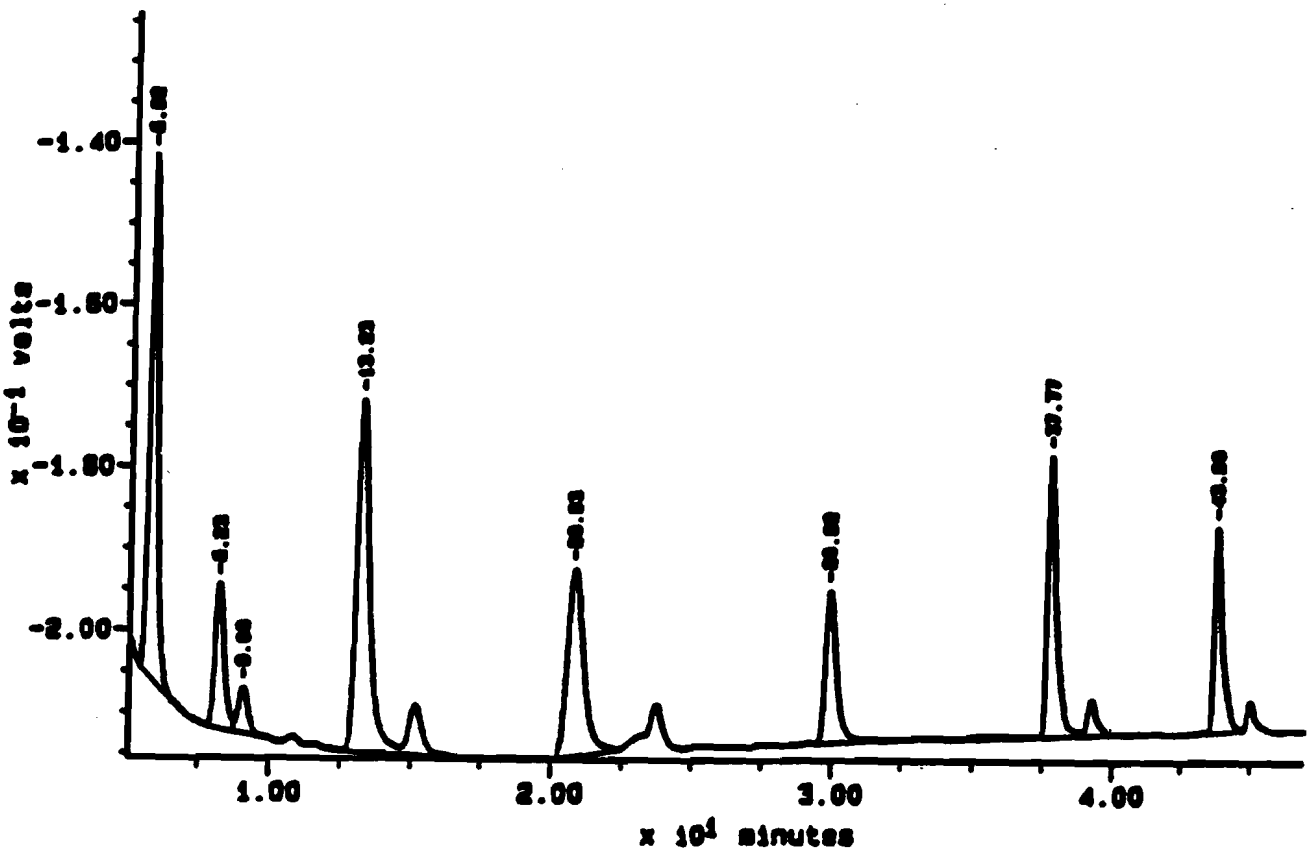
OPTION 1 - LIQUID-SOLID PROCEDURAL STANDARD OF GROUP B ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
7.50	Acetaldehyde
16.68	Crotonaldehyde
26.88	Pentanal
32.53	Hexanal
40.36	Octanal
45.49	Decanal

FIGURE 2a.

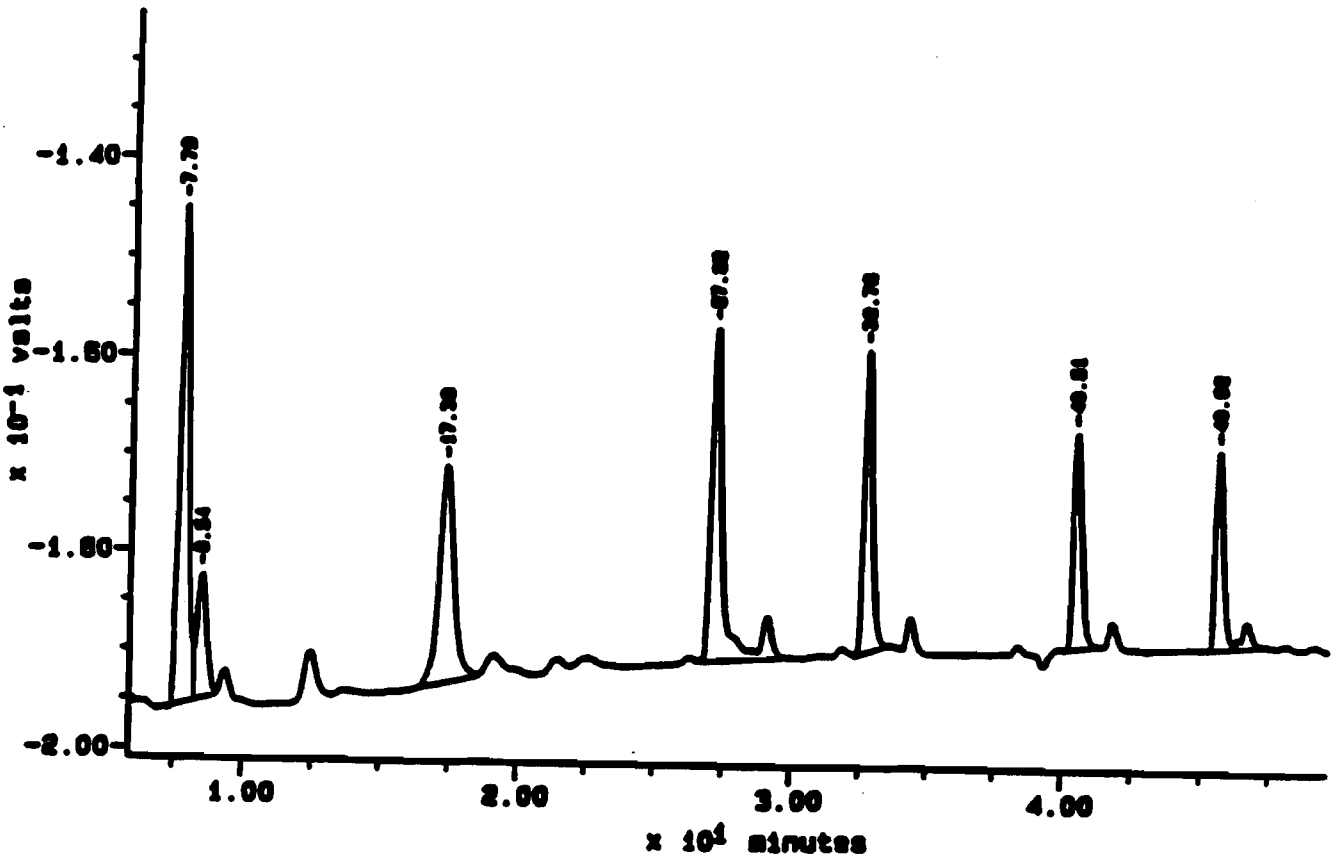
OPTION 1 - LIQUID-LIQUID PROCEDURAL STANDARD OF GROUP A ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
5.82	Formaldehyde
13.23	Propanal
20.83	Butanal
29.95	Cyclohexanone
37.77	Heptanal
43.80	Nonanal

FIGURE 2b.

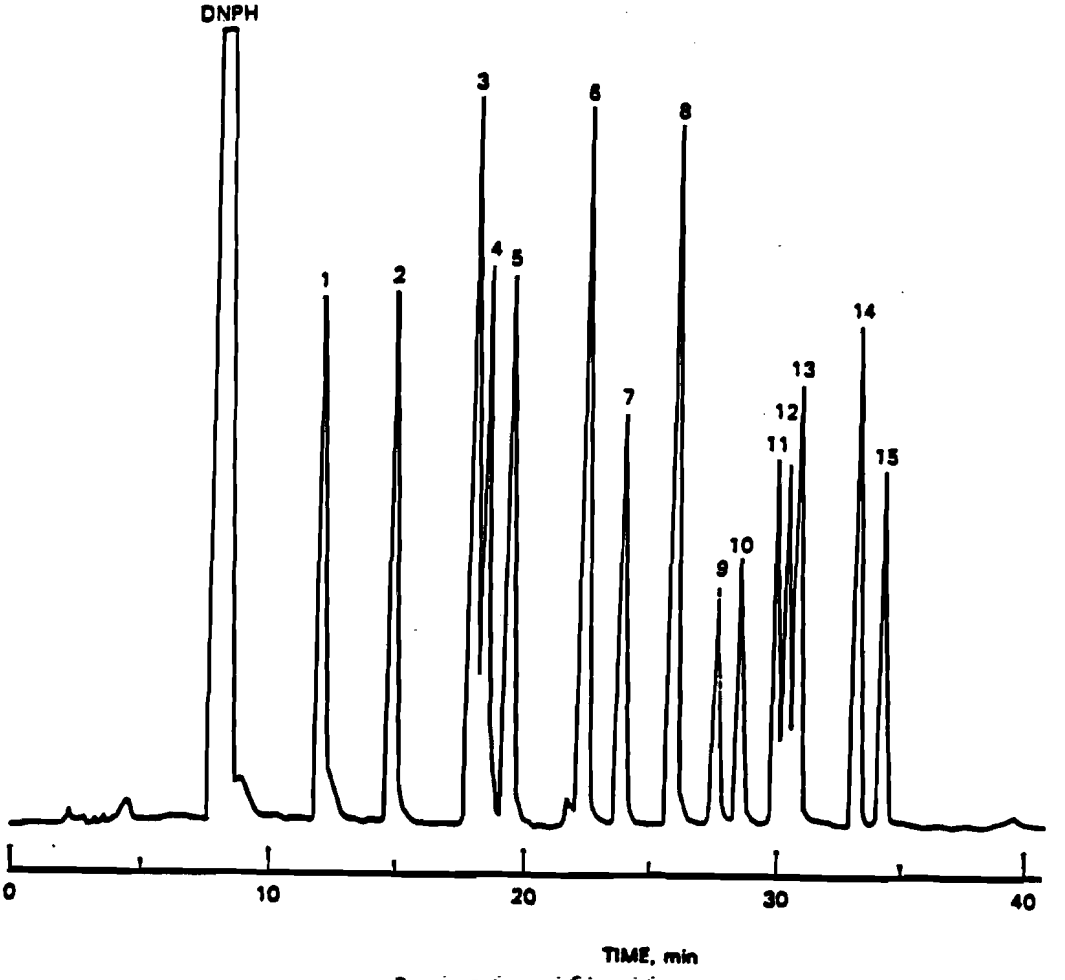
OPTION 1 - LIQUID-LIQUID PROCEDURAL STANDARD OF GROUP B ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
7.79	Acetaldehyde
17.38	Crotonaldehyde
27.22	Pentanal
32.76	Hexanal
40.51	Octanal
45.62	Decanal

FIGURE 3.

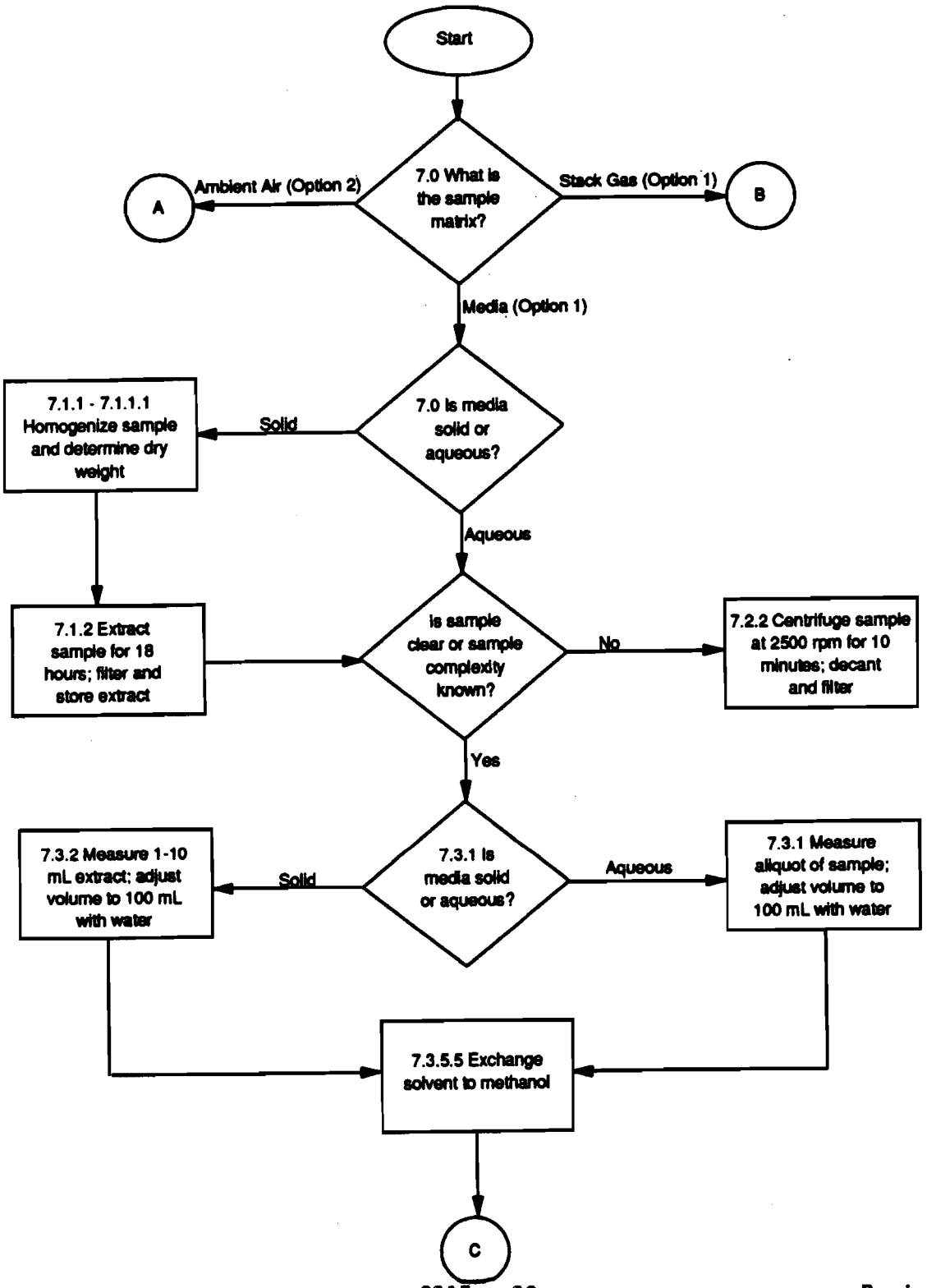
OPTION 2 - CHROMATOGRAPHIC SEPARATION OF THE DNPH DERIVATIVES OF 15 CARBONYL COMPOUNDS

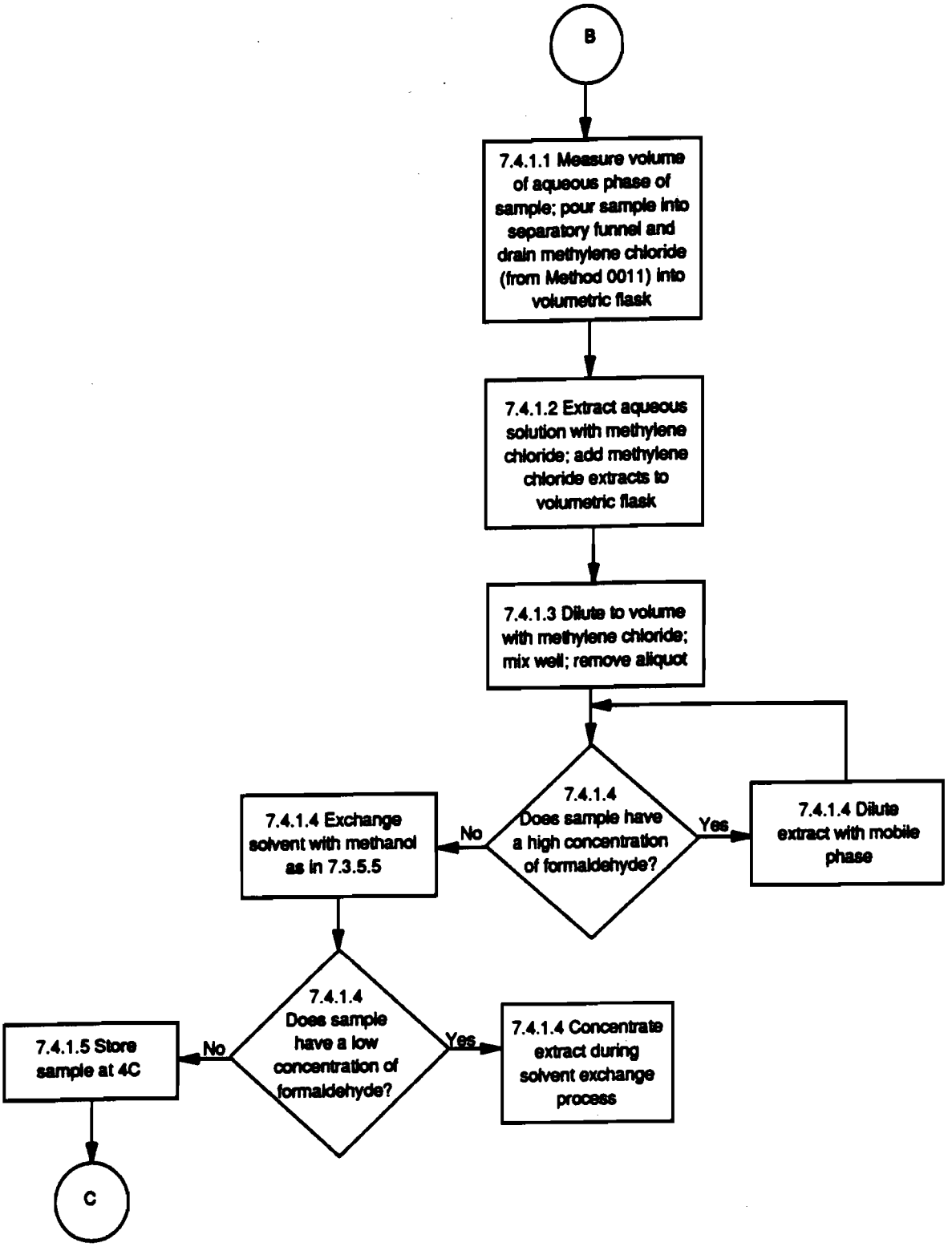


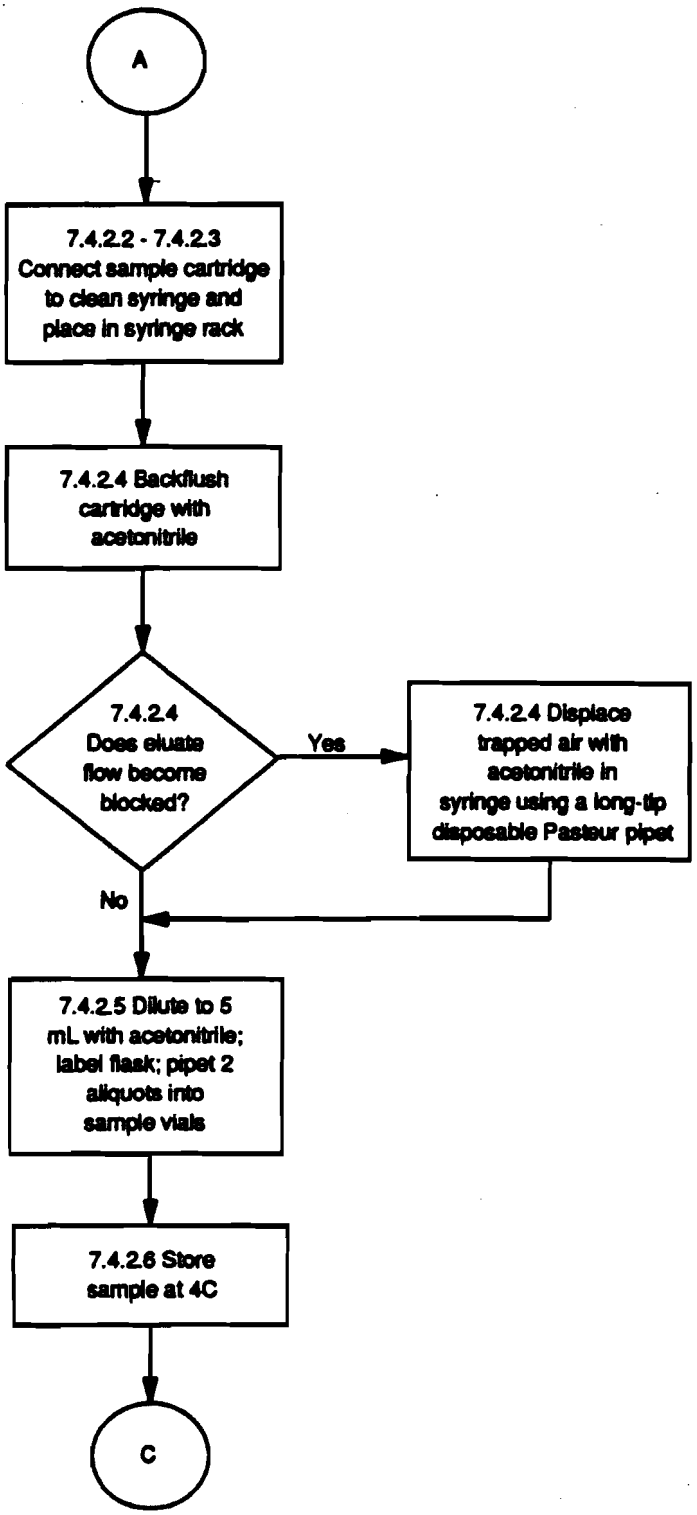
Peak Identification

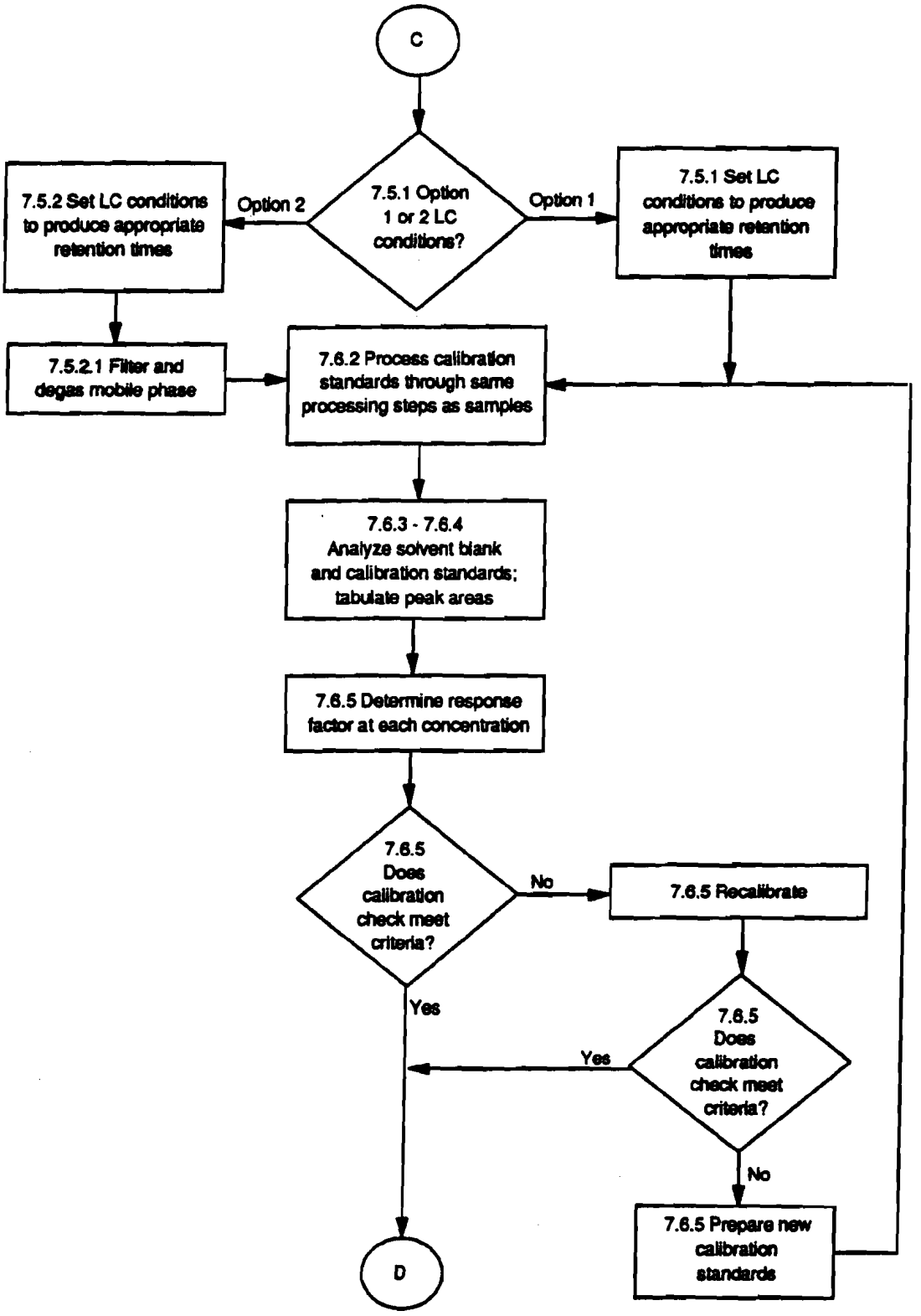
Number	Compound	Concentration(ng/ L)
1	Formaldehyde	1.140
2	Acetaldehyde	1.000
3	Acrolein	1.000
4	Acetone	1.000
5	Propanal	1.000
6	Crotonaldehyde	1.000
7	Butanal	0.905
8	Benzaldehyde	1.000
9	Isovaleraldehyde	0.450
10	Pentanal	0.485
11	o-Tolualdehyde	0.515
12	m-Tolualdehyde	0.505
13	p-Tolualdehyde	0.510
14	Hexanal	1.000
15	2,4-Dimethylbenzaldehyde	0.510

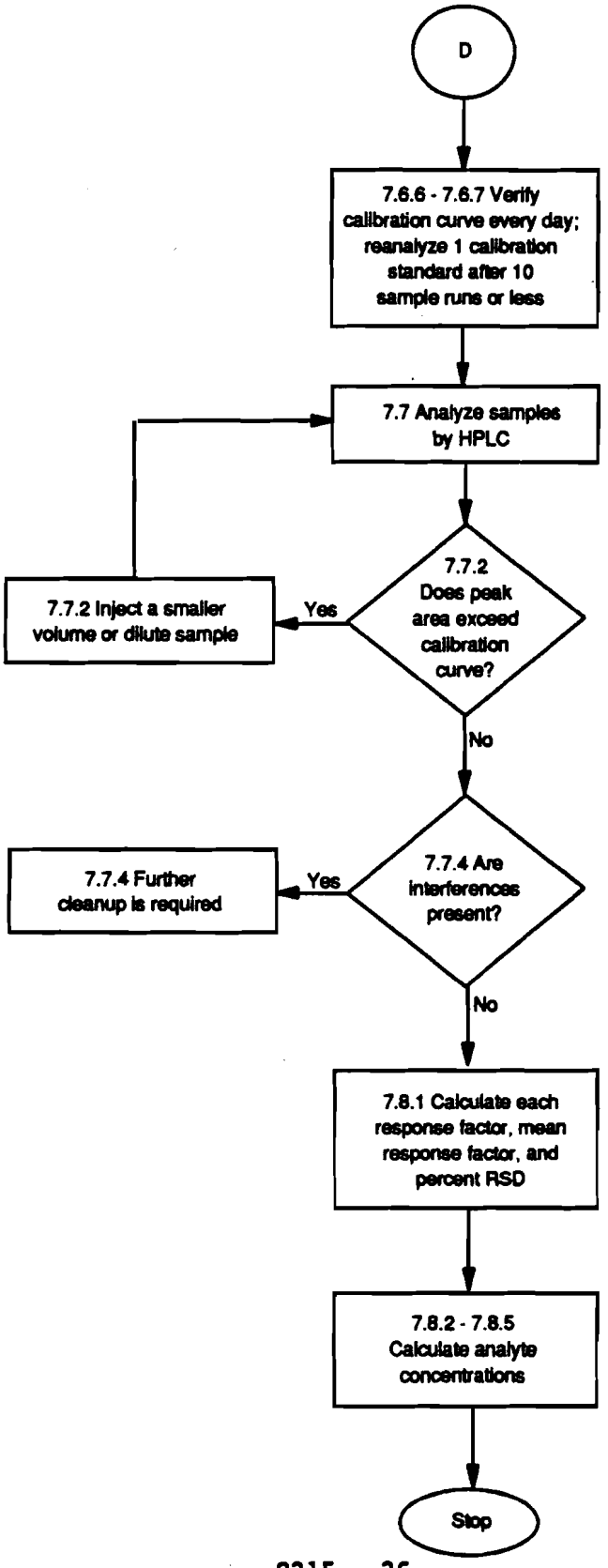
DETERMINATION OF CARBONYL COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)




B
7.4.1.1 Measure volume of aqueous phase of sample; pour sample into separatory funnel and drain methylene chloride (from Method 0011) into volumetric flask
7.4.1.2 Extract aqueous solution with methylene chloride; add methylene chloride extracts to volumetric flask
7.4.1.3 Dilute to volume with methylene chloride; mix well; remove aliquot
7.4.1.4 Does sample have a high concentration of formaldehyde?
Yes
7.4.1.4 Dilute extract with mobile phase
No
7.4.1.4 Exchange solvent with methanol as in 7.3.5.5
7.4.1.4 Does sample have a low concentration of formaldehyde?
Yes
7.4.1.4 Concentrate extract during solvent exchange process
No
7.4.1.5 Store sample at 4C
C


A
7.4.2.2 - 7.4.2.3 Connect sample cartridge to clean syringe and place in syringe rack
7.4.2.4 Backflush cartridge with acetonitrile
7.4.2.4 Does eluate flow become blocked?
Yes
7.4.2.4 Displace trapped air with acetonitrile in syringe using a long-tip disposable Pasteur pipet
No
7.4.2.5 Dilute to 5 mL with acetonitrile; label flask; pipet 2 aliquots into sample vials
7.4.2.6 Store sample at 4C
C


C
7.5.1 Option 1 or 2 LC conditions?
Option 2
Option 1
7.5.2 Set LC conditions to produce appropriate retention times
7.5.1 Set LC conditions to produce appropriate retention times
7.5.2.1 Filter and degas mobile phase
7.6.2 Process calibration standards through same processing steps as samples
7.6.3 - 7.6.4 Analyze solvent blank and calibration standards; tabulate peak areas
7.6.5 Determine response factor at each concentration
7.6.5 Does calibration check meet criteria?
No
7.6.5 Recalibrate
Yes
7.6.5 Does calibration check meet criteria?
Yes
No
7.6.5 Prepare new calibration standards
D


D
7.6.6 - 7.6.7 Verify calibration curve every day; reanalyze 1 calibration standard after 10 sample runs or less
7.7 Analyze samples by HPLC
7.7.2 Does peak area exceed calibration curve?
Yes
7.7.2 Inject a smaller volume or dilute sample
No
7.7.4 Are interferences present?
Yes
7.7.4 Further cleanup is required
No
7.8.1 Calculate each response factor, mean response factor, and percent RSD
7.8.2 - 7.8.5 Calculate analyte concentrations
Stop

APPENDIX A

RECRYSTALLIZATION OF 2,4-DINITROPHENYLHYDRAZINE (DNPH)

NOTE: This procedure should be performed under a properly ventilated hood. Inhalation of acetonitrile can result in nose and throat irritation (brief exposure at 500 ppm) or more serious effects at higher concentration and/or longer exposures.

A.1 Prepare a saturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately 1 hour.

A.2 After 1 hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40 to 60°C. Maintain this temperature range until 95% of the solvent has evaporated, leaving crystals.

A.3 Decant the solution to waste and rinse the remaining crystals twice with three times their apparent volume of acetonitrile.

A.4 Transfer the crystals to a clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let the crystals grow slowly at 40 to 60°C until 95% of the solvent has evaporated. Repeat the rinsing process as in Sec. A.3.

A.5 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze with HPLC as in Sec. 7.0 for Option 2. An acceptable impurity level is less than 0.025 ng/µL of formaldehyde in recrystallized DNPH reagent or below the sensitivity (ppb, v/v) level indicated in Table 3 for the anticipated sample volume.

A.6 If the impurity level is not satisfactory, pipet off the solution to waste, repeat the recrystallization as in Sec. A.4 but rinse with two 25 mL portions of acetonitrile. Prep and analyze the second rinse as in Sec. A.5.

A.7 When the impurity level is satisfactory, place the crystals in an all-glass reagent bottle, add another 25 mL of acetonitrile, stopper, and shake the bottle. Use clean pipets when removing the saturated DNPH stock solution to reduce the possibility of contamination of the solution. Maintain only a minimum volume of the saturated solution adequate for day to day operation to minimize waste of the purified reagent.

METHOD 8316

ACRYLAMIDE, ACRYLONITRILE AND ACROLEIN BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Acrylamide	79-06-1
Acrylonitrile	107-13-1
Acrolein (Propenal)	107-02-8

[a] Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) for the target analytes in organic-free reagent water are listed in Table 1. The method may be applicable to other matrices.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatographs and skilled in the interpretation of high performance liquid chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Water samples are analyzed by high performance liquid chromatography (HPLC). A 200 μL aliquot is injected onto a C-18 reverse-phase column, and compounds in the effluent are detected with an ultraviolet (UV) detector.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 One high pressure pump.

4.1.2 Octadecyl Silane (ODS, C-18) reverse phase HPLC column, 25 cm x 4.6 mm, 10 μm, (Zorbax, or equivalent).

4.1.3 Variable wavelength UV detector.

4.1.4 Data system.

4.2 Other apparatus

4.2.1 Water degassing unit - 1 liter filter flask with stopper and pressure tubing.

4.2.2 Analytical balance - $\pm$ 0.0001 g.

4.2.3 Magnetic stirrer and magnetic stirring bar.

4.2.4 Sample filtration unit - syringe filter with 0.45 μm filter membrane, or equivalent disposable filter unit.

4.3 Materials

4.3.1 Syringes - 10, 25, 50 and 250 μL and 10 mL.

4.3.2 Volumetric pipettes, Class A, glass - 1, 5 and 10 mL.

4.3.3 Volumetric flasks - 5, 10, 50 and 100 mL.

4.3.4 Vials - 25 mL, glass with Teflon lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Acrylamide, CH_2:$CHCONH_2$, 99+% purity, electrophoresis reagent grade.

5.3 Acrylonitrile, H_2C:CHCN, 99+% purity.

5.4 Acrolein, CH_2:CHCHO, 99+% purity.

5.5 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One. Sparge with He to eliminate O_2 to prevent significant absorption interference from O_2 at the 195 nm wavelength.

5.6 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are certified by the manufacturer and verified against a standard made from pure material.

5.6.1 Acrylamide

5.6.1.1 Weigh 0.0100 g of acrylamide neat standard into a 100 mL volumetric flask, and dilute to the mark with organic-free reagent water. Calculate the concentration of the standard solution from the actual weight used. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

5.6.1.2 Transfer the stock solution into vials with Teflon lined screw caps or crimp tops. Store at 4°C, protected from light.

5.6.1.3 Stock solutions must be replaced after six months, or sooner if comparison with the check standards indicates a problem.

5.6.2 Acrylonitrile and Acrolein - Prepare separate stock solutions for acrylonitrile and acrolein.

5.6.2.1 Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.0001 g. Add two drops of neat standard, using a 50 µL syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask.

<u>CAUTION</u>: Acrylonitrile and acrolein are toxic. Standard preparation should be performed in an laboratory fume hood.

5.6.2.2 Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

5.6.2.3 Stock solutions must be replaced after six months, or sooner if comparison with the check standards indicates a problem.

5.7 Calibration standards

5.7.1 Prepare calibration standards at a minimum of five concentrations by diluting the stock solutions with organic-free reagent water.

5.7.2 One calibration standard should be prepared at a concentration near, but above, the method detection limit; the remaining standards should correspond to the range of concentrations found in real samples, but should not exceed the working range of the HPLC system (1 mg/L to 10 mg/L).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 HPLC Conditions

Mobile Phase:	Degassed organic-free reagent water
Injection Volume:	200 µL
Flow Rate:	2.0 mL/min
Pressure:	38 atm
Temperature:	25°C
Detector UV wavelength:	195 nm

7.2 Calibration:

7.2.1 Prepare standard solutions of acrylamide as described in Sec. 5.7.1. Inject 200 µL aliquots of each solution into the chromatograph. See Method 8000 for additional guidance on calibration by the external standard method.

7.3 Chromatographic analysis:

7.3.1 Analyze the samples using the same chromatographic conditions used to prepare the standard curve. Suggested chromatographic conditions are given in Sec. 7.1. Table 1 provides the retention times that were obtained under these conditions during method development.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank, that all glassware and reagents are interference free.

9.0 METHOD PERFORMANCE

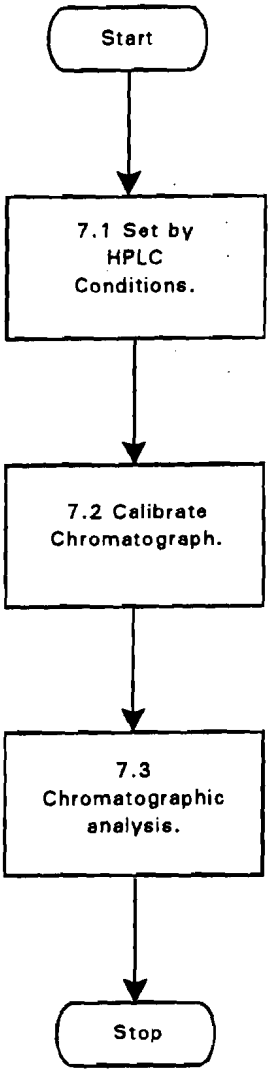
9.1 Method performance data are not available.

10.0 REFERENCES

1. Hayes, Sam; "Acrylamide, Acrylonitrile, and Acrolein Determination in Water by High Pressure Liquid Chromatography," USEPA.

TABLE 1
ANALYTE RETENTION TIMES AND METHOD DETECTION LIMITS

Compound	Retention Time (min)	MDL (µg/L)
Acrylamide	3.5	10
Acrylonitrile	8.9	20
Acrolein (Propenal)	10.1	30


Start
7.1 Set by HPLC Conditions.
7.2 Calibrate Chromatograph.
7.3 Chromatographic analysis.
Stop

METHOD 8318

N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8318 is used to determine the concentration of N-methylcarbamates in soil, water and waste matrices. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Aldicarb (Temik)	116-06-3
Aldicarb Sulfone	1646-88-4
Carbaryl (Sevin)	63-25-2
Carbofuran (Furadan)	1563-66-2
Dioxacarb	6988-21-2
3-Hydroxycarbofuran	16655-82-6
Methiocarb (Mesurol)	2032-65-7
Methomyl (Lannate)	16752-77-5
Promecarb	2631-37-0
Propoxur (Baygon)	114-26-1

[a] Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) of Method 8318 for determining the target analytes in organic-free reagent water and in soil are listed in Table 1.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high performance liquid chromatography (HPLC) and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 N-methylcarbamates are extracted from aqueous samples with methylene chloride, and from soils, oily solid waste and oils with acetonitrile. The extract solvent is exchanged to methanol/ethylene glycol, and then the extract is cleaned up on a C-18 cartridge, filtered, and eluted on a C-18 analytical column. After separation, the target analytes are hydrolyzed and derivatized post-column, then quantitated fluorometrically.

2.2 Due to the specific nature of this analysis, confirmation by a secondary method is not essential. However, fluorescence due to post-column derivatization may be confirmed by substituting the NaOH and o-phthalaldehyde solutions with organic-free reagent water and reanalyzing the sample. If

fluorescence is still detected, then a positive interference is present and care should be taken in the interpretation of the results.

2.3 The sensitivity of the method usually depends on the level of interferences present, rather than on the instrumental conditions. Waste samples with a high level of extractable fluorescent compounds are expected to yield significantly higher detection limits.

3.0 INTERFERENCES

3.1 Fluorescent compounds, primarily alkyl amines and compounds which yield primary alkyl amines on base hydrolysis, are potential sources of interferences.

3.2 Coeluting compounds that are fluorescence quenchers may result in negative interferences.

3.3 Impurities in solvents and reagents are additional sources of interferences. Before processing any samples, the analyst must demonstrate daily, through the analysis of solvent blanks, that the entire analytical system is interference free.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 An HPLC system capable of injecting 20 µL aliquots and performing multilinear gradients at a constant flow. The system must also be equipped with a data system to measure the peak areas.

4.1.2 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5 µm).

4.1.3 Post Column Reactor with two solvent delivery systems (Kratos PCRS 520 with two Kratos Spectroflow 400 Solvent Delivery Systems, or equivalent).

4.1.4 Fluorescence detector (Kratos Spectroflow 980, or equivalent).

4.2 Other apparatus

4.2.1 Centrifuge.

4.2.2 Analytical balance - ± 0.0001 g.

4.2.3 Top loading balance - ± 0.01 g.

4.2.4 Platform shaker.

4.2.5 Heating block, or equivalent apparatus, that can accommodate 10 mL graduated vials (Sec. 4.3.11).

4.3 Materials

4.3.1 HPLC injection syringe - 50 μL.

4.3.2 Filter paper, (Whatman #113 or #114, or equivalent).

4.3.3 Volumetric pipettes, Class A, glass, assorted sizes.

4.3.4 Reverse phase cartridges, (C-18 Sep-Pak^R [Waters Associates], or equivalent).

4.3.5 Glass syringes - 5 mL.

4.3.6 Volumetric flasks, Class A - Sizes as appropriate.

4.3.7 Erlenmeyer flasks with teflon-lined screw caps, 250 mL.

4.3.8 Assorted glass funnels.

4.3.9 Separatory funnels, with ground glass stoppers and teflon stopcocks - 250 mL.

4.3.10 Graduated cylinders - 100 mL.

4.3.11 Graduated glass vials - 10 mL, 20 mL.

4.3.12 Centrifuge tubes - 250 mL.

4.3.13 Vials - 25 mL, glass with Teflon lined screw caps or crimp tops.

4.3.14 Positive displacement micro-pipettor, 3 to 25 μL displacement, (Gilson Microman [Rainin #M-25] with tips, [Rainin #CP-25], or equivalent).

4.3.15 Nylon filter unit, 25 mm diameter, 0.45 μm pore size, disposable (Alltech Associates, #2047, or equivalent).

5.0 REAGENTS

5.1 HPLC grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

5.2 General

5.2.1 Acetonitrile, CH_3CN - HPLC grade - minimum UV cutoff at 203 nm (EM Omnisolv #AX0142-1, or equivalent).

5.2.2 Methanol, CH_3OH - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #MX0488-1, or equivalent).

5.2.3 Methylene chloride, CH_2Cl_2 - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #DX0831-1, or equivalent).

5.2.4 Hexane, C_6H_{14} - pesticide grade - (EM Omnisolv #HX0298-1, or equivalent).

5.2.5 Ethylene glycol, $HOCH_2CH_2OH$ - Reagent grade - (EM Science, or equivalent).

5.2.6 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.7 Sodium hydroxide, NaOH - reagent grade - 0.05N NaOH solution.

5.2.8 Phosphoric acid, H_3PO_4 - reagent grade.

5.2.9 pH 10 borate buffer (J.T. Baker #5609-1, or equivalent).

5.2.10 o-Phthalaldehyde, o-$C_6H_4(CHO)_2$ - reagent grade (Fisher #0-4241, or equivalent).

5.2.11 2-Mercaptoethanol, $HSCH_2CH_2OH$ - reagent grade (Fisher #0-3446, or equivalent).

5.2.12 N-methylcarbamate neat standards (equivalence to EPA standards must be demonstrated for purchased solutions).

5.2.13 Chloroacetic acid, $ClCH_2COOH$, 0.1 N.

5.3 Reaction solution

5.3.1 Dissolve 0.500 g of o-phthalaldehyde in 10 mL of methanol, in a 1 L volumetric flask. To this solution, add 900 mL of organic-free reagent water, followed by 50 mL of the borate buffer (pH 10). After mixing well, add 1 mL of 2-mercaptoethanol, and dilute to the mark with organic-free reagent water. Mix the solution thoroughly. Prepare fresh solutions on a weekly basis, as needed. Protect from light and store under refrigeration.

5.4 Standard solutions

5.4.1 Stock standard solutions: prepare individual 1000 mg/L solutions by adding 0.025 g of carbamate to a 25 mL volumetric flask, and diluting to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every six months.

5.4.2 Intermediate standard solution: prepare a mixed 50.0 mg/L solution by adding 2.5 mL of each stock solution to a 50 mL volumetric flask, and diluting to the mark with methanol. Store solutions, under

refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every three months.

5.4.3 Working standard solutions: prepare 0.5, 1.0, 2.0, 3.0 and 5.0 mg/L solutions by adding 0.25, 0.5, 1.0, 1.5 and 2.5 mL of the intermediate mixed standard to respective 25 mL volumetric flasks, and diluting each to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every two months, or sooner if necessary.

5.4.4 Mixed QC standard solution: prepare a 40.0 mg/L solution from another set of stock standard solutions, prepared similarly to those described in Sec. 5.4.1. Add 2.0 mL of each stock solution to a 50 mL volumetric flask and dilute to the mark with methanol. Store the solution, under refrigeration, in a glass vial with a Teflon lined screw cap or crimp top. Replace every three months.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Due to the extreme instability of N-methylcarbamates in alkaline media, water, waste water and leachates should be preserved immediately after collection by acidifying to pH 4-5 with 0.1 N chloroacetic acid.

6.2 Store samples at 4°C and out of direct sunlight, from the time of collection through analysis. N-methylcarbamates are sensitive to alkaline hydrolysis and heat.

6.3 All samples must be extracted within seven days of collection, and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Water, domestic wastewater, aqueous industrial wastes, and leachates

7.1.1.1 Measure 100 mL of sample into a 250 mL separatory funnel and extract by shaking vigorously for about 2 minutes with 30 mL of methylene chloride. Repeat the extraction two more times. Combine all three extracts in a 100 mL volumetric flask and dilute to volume with methylene chloride. If cleanup is required, go to Sec. 7.2. If cleanup is not required, proceed directly to Sec. 7.3.1.

7.1.2 Soils, solids, sludges, and heavy aqueous suspensions

7.1.2.1 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.1.2.1.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.1.2.2 Extraction - Weigh out 20 ± 0.1 g of sample into a 250 mL Erlenmeyer flask with a Teflon-lined screw cap. Add 50 mL of acetonitrile and shake for 2 hours on a platform shaker. Allow the mixture to settle (5-10 min), then decant the extract into a 250 mL centrifuge tube. Repeat the extraction two more times with 20 mL of acetonitrile and 1 hour shaking each time. Decant and combine all three extracts. Centrifuge the combined extract at 200 rpm for 10 min. Carefully decant the supernatant into a 100 mL volumetric flask and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Sec. 7.3.2.

7.1.3 Soils heavily contaminated with non-aqueous substances, such as oils

7.1.3.1 Determination of sample % dry weight - Follow Secs. 7.1.2.1 through 7.1.2.1.1.

7.1.3.2 Extraction - Weigh out 20 ± 0.1 g of sample into a 250 mL Erlenmeyer flask with a Teflon-lined screw cap. Add 60 mL of hexane and shake for 1 hour on a platform shaker. Add 50 mL of acetonitrile and shake for an additional 3 hours. Allow the mixture to settle (5-10 min), then decant the solvent layers into a 250 mL separatory funnel. Drain the acetonitrile (bottom layer) through filter paper into a 100 mL volumetric flask. Add 60 mL of hexane and 50 mL of acetonitrile to the sample extraction flask and shake for 1 hour. Allow the mixture to settle, then decant the mixture into the separatory funnel containing the hexane from the first extraction. Shake the separatory funnel for 2 minutes, allow the phases to separate, drain the acetonitrile layer through filter paper into the volumetric flask, and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Sec. 7.3.2.

7.1.4 Non-aqueous liquids such as oils

7.1.4.1 Extraction - Weigh out 20 ± 0.1 g of sample into a 125 mL separatory funnel. Add 40 mL of hexane and 25 mL of acetonitrile and vigorously shake the sample mixture for 2 minutes. Allow the phases to separate, then drain the acetonitrile (bottom layer) into a 100 mL volumetric flask. Add 25 mL of acetonitrile to the sample funnel, shake for 2 minutes, allow the phases to

Repeat the extraction with another 25 mL portion of acetonitrile, combining the extracts. Dilute to volume with acetonitrile. (Dilution factor = 5). Proceed to Sec. 7.3.2.

7.2 Cleanup - Pipet 20.0 mL of the extract into a 20 mL glass vial containing 100 μL of ethylene glycol. Place the vial in a heating block set at 50^{0} C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Dissolve the ethylene glycol residue in 2 mL of methanol, pass the extract through a pre-washed C-18 reverse phase cartridge, and collect the eluate in a 5 mL volumetric flask. Elute the cartridge with methanol, and collect the eluate until the final volume of 5.0 mL is obtained. (Dilution factor = 0.25) Using a disposable 0.45 μm filter, filter an aliquot of the clean extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Sec. 7.4.

7.3 Solvent Exchange

7.3.1 Water, domestic wastewater, aqueous industrial wastes, and leachates:

Pipet 10.0 mL of the extract into a 10 mL graduated glass vial containing 100 μL of ethylene glycol. Place the vial in a heating block set at 50^{0} C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Dilution factor = 0.1). Using a disposable 0.45 μm filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Sec. 7.4.

7.3.2 Soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids:

Elute 15 mL of the acetonitrile extract through a C-18 reverse phase cartridge, prewashed with 5 mL of acetonitrile. Discard the first 2 mL of eluate and collect the remainder. Pipet 10.0 mL of the clean extract into a 10 mL graduated glass vial containing 100 μL of ethylene glycol. Place the vial in a heating block set at 50^{0} C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Additional dilution factor = 0.1; overall dilution factor = 0.5). Using a disposable 0.45 μm filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Sec. 7.4.

7.4 Sample Analysis

7.4.1 Analyze the samples using the chromatographic conditions, post-column reaction parameters and instrument parameters given in Secs. 7.4.1.1, 7.4.1.2, 7.4.1.3 and 7.4.1.4. Table 2 provides the retention times that were obtained under these conditions during method development. A chromatogram of the separation is shown in Figure 1.

7.4.1.1 Chromatographic Conditions (Recommended)

Solvent A: Organic-free reagent water, acidified with 0.4 mL of phosphoric acid per liter of water
Solvent B: Methanol/acetonitrile (1:1, v/v)
Flow rate: 1.0 mL/min
Injection Volume: 20 µL
Solvent delivery system program:

Time (min)	Function	Value	Duration (min)	File
0.00	FR	1.0		0
0.00	B%	10%		0
0.02	B%	80%	20	0
20.02	B%	100%	5	0
25.02	B%	100%	5	0
30.02	B%	10%	3	0
33.02	B%	10%	7	0
36.02	ALARM		0.01	0

7.4.1.2 Post-column Hydrolysis Parameters (Recommended)

Solution: 0.05 N aqueous sodium hydroxide
Flow Rate: 0.7 mL/min
Temperature: 95° C
Residence Time: 35 seconds (1 mL reaction coil)

7.4.1.3 Post-column Derivatization Parameters (Recommended)

Solution: o-phthalaldehyde/2-mercaptoethanol (Sec. 5.3.1)
Flow Rate: 0.7 mL/min
Temperature: 40° C
Residence time: 25 seconds (1 mL reaction coil)

7.4.1.4 Fluorometer Parameters (Recommended)

Cell: 10 µL
Excitation wavelength: 340 nm
Emission wavelength: 418 nm cutoff filter
Sensitivity wavelength: 0.5 µA
PMT voltage: -800 V
Time constant: 2 sec

7.4.2 If the peak areas of the sample signals exceed the calibration range of the system, dilute the extract as necessary and reanalyze the diluted extract.

7.5 Calibration:

7.5.1 Analyze a solvent blank (20 μL of methanol) to ensure that the system is clean. Analyze the calibration standards (Sec. 5.4.3), starting with the 0.5 mg/L standards and ending with the 5.0 mg/L standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.5.2 Using the established calibration mean response factors, check the calibration of the instrument at the beginning of each day by analyzing the 2.0 mg/L mixed standard. If the concentration of each analyte falls within the range of 1.70 to 2.30 mg/L (i.e., within $\pm$ 15% of the true value), the instrument is considered to be calibrated and the analysis of samples may proceed. If the observed value of any analyte exceeds its true value by more than $\pm$ 15%, the instrument must be recalibrated (Sec. 7.5.1).

7.5.3 After 10 sample runs, or less, the 2.0 mg/L standards must be analyzed to ensure that the retention times and response factors are still within acceptable limits. Significant variations (i.e., observed concentrations exceeding the true concentrations by more than $\pm$ 15%) may require a re-analysis of the samples.

7.6 Calculations

7.6.1 Calculate each response factor as follows (mean value based on 5 points):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean } RF = \overline{RF} = \frac{(\sum_{i}^{5} RF_i)}{5}$$

$$\%RSD \text{ of } \overline{RF} = \frac{[(\sum_{i}^{5} RF_i - \overline{RF})^2]^{1/2} / 4}{\overline{RF}} \quad X\ 100\%$$

7.6.2 Calculate the concentration of each N-methylcarbamate as follows:

μg/g or mg/L = ($\overline{RF}$) (area of signal) (dilution factor)

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank for each matrix type, that all glassware and reagents are interference free. Each time there is a change of reagents, a method blank must be processed as a safeguard against laboratory contamination.

8.2 A QC check solution must be prepared and analyzed with each sample batch that is processed. Prepare this solution, at a concentration of 2.0 mg/L of each analyte, from the 40.0 mg/L mixed QC standard solution (Sec. 5.4.4). The acceptable response range is 1.7 to 2.3 mg/L for each analyte.

8.3 Negative interference due to quenching may be examined by spiking the extract with the appropriate standard, at an appropriate concentration, and examining the observed response against the expected response.

8.4 Confirm any detected analytes by substituting the NaOH and OPA reagents in the post column reaction system with deionized water, and reanalyze the suspected extract. Continued fluorescence response will indicate that a positive interference is present (since the fluorescence response is not due to the post column derivatization). Exercise caution in the interpretation of the chromatogram.

9.0 METHOD PERFORMANCE

9.1 Table 1 lists the single operator method detection limit (MDL) for each compound in organic-free reagent water and soil. Seven/ten replicate samples were analyzed, as indicated in the table. See reference 7 for more details.

9.2 Tables 2, 3 and 4 list the single operator average recoveries and standard deviations for organic-free reagent water, wastewater and soil. Ten replicate samples were analyzed at each indicated spike concentration for each matrix type.

9.3 The method detection limit, accuracy and precision obtained will be determined by the sample matrix.

10.0 REFERENCES

1. California Department of Health Services, Hazardous Materials Laboratory, "N-Methylcarbamates by HPLC", Revision No. 1.0, September 14, 1989.

2. Krause, R.T. Journal of Chromatographic Science, 1978, vol. 16, pg 281.

3. Klotter, Kevin, and Robert Cunico, "HPLC Post Column Detection of Carbamate Pesticides", Varian Instrument Group, Walnut Creek, CA 94598.

4. USEPA, "Method 531. Measurement of N-Methylcarbomyloximes and N-Methylcarbamates in Drinking Water by Direct Aqueous Injection HPLC with Post Column Derivatization", EPA 600/4-85-054, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

5. USEPA, "Method 632. The Determination of Carbamate and Urea Pesticides in Industrial and Municipal Wastewater", EPA 600/4-21-014, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

6. Federal Register, "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11", Friday, October 26, 1984, 49, No. 209, 198-199.

7. Okamoto, H.S., D. Wijekoon, C. Esperanza, J. Cheng, S. Park, J. Garcha, S. Gill, K. Perera "Analysis for N-Methylcarbamate Pesticides by HPLC in Environmental Samples", Proceedings of the Fifth Annual USEPA Symposium on Waste Testing and Quality Assurance, July 24-28, 1989, Vol. II, 57-71.

TABLE 1
ELUTION ORDER, RETENTION TIMES[a] AND
SINGLE OPERATOR METHOD DETECTION LIMITS

Compound	Retention Time (min)	Method Detection Limits[b] Organic-free Reagent Water (µg/L)	Soil (µg/kg)
Aldicarb Sulfone	9.59	1.9[c]	44[c]
Methomyl (Lannate)	9.59	1.7	12
3-Hydroxycarbofuran	12.70	2.6	10[c]
Dioxacarb	13.50	2.2	>50[c]
Aldicarb (Temik)	16.05	9.4[c]	12[c]
Propoxur (Baygon)	18.06	2.4	17
Carbofuran (Furadan)	18.28	2.0	22
Carbaryl (Sevin)	19.13	1.7	31
α-Naphthol[d]	20.30	-	-
Methiocarb (Mesurol)	22.56	3.1	32
Promecarb	23.02	2.5	17

a See Sec. 7.4 for chromatographic conditions

b MDL for organic-free reagent water, sand, soil were determined by analyzing 10 low concentration spike replicate for each matrix type (except where noted). See reference 7 for more details.

c MDL determined by analyzing 7 spiked replicates.

d Breakdown product of Carbaryl.

TABLE 2
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR ORGANIC-FREE REAGENT WATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	225	75.0	7.28	3.24
Methomyl (Lannate)	244	81.3	8.34	3.42
3-Hydroxycarbofuran	210	70.0	7.85	3.74
Dioxacarb	241	80.3	8.53	3.54
Aldicarb (Temik)	224	74.7	13.5	6.03
Propoxur (Baygon)	232	77.3	10.6	4.57
Carbofuran (Furadan)	239	79.6	9.23	3.86
Carbaryl (Sevin)	242	80.7	8.56	3.54
Methiocarb (Mesurol)	231	77.0	8.09	3.50
Promecarb	227	75.7	9.43	4.1

[a] Spike Concentration = 300 μg/L of each compound, n = 10

TABLE 3
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR WASTEWATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	235	78.3	17.6	7.49
Methomyl (Lannate)	247	82.3	29.9	12.10
3-Hydroxycarbofuran	251	83.7	25.4	10.11
Dioxacarb	b	-	-	-
Aldicarb (Temik)	258	86.0	16.4	6.36
Propoxur (Baygon)	263	87.7	16.7	6.47
Carbofuran (Furadan)	262	87.3	15.7	5.99
Carbaryl (Sevin)	262	87.3	17.2	6.56
Methiocarb (Mesurol)	254	84.7	19.9	7.83
Promecarb	263	87.7	15.1	5.74

a Spike Concentration = 300 μg/L of each compound, n = 10

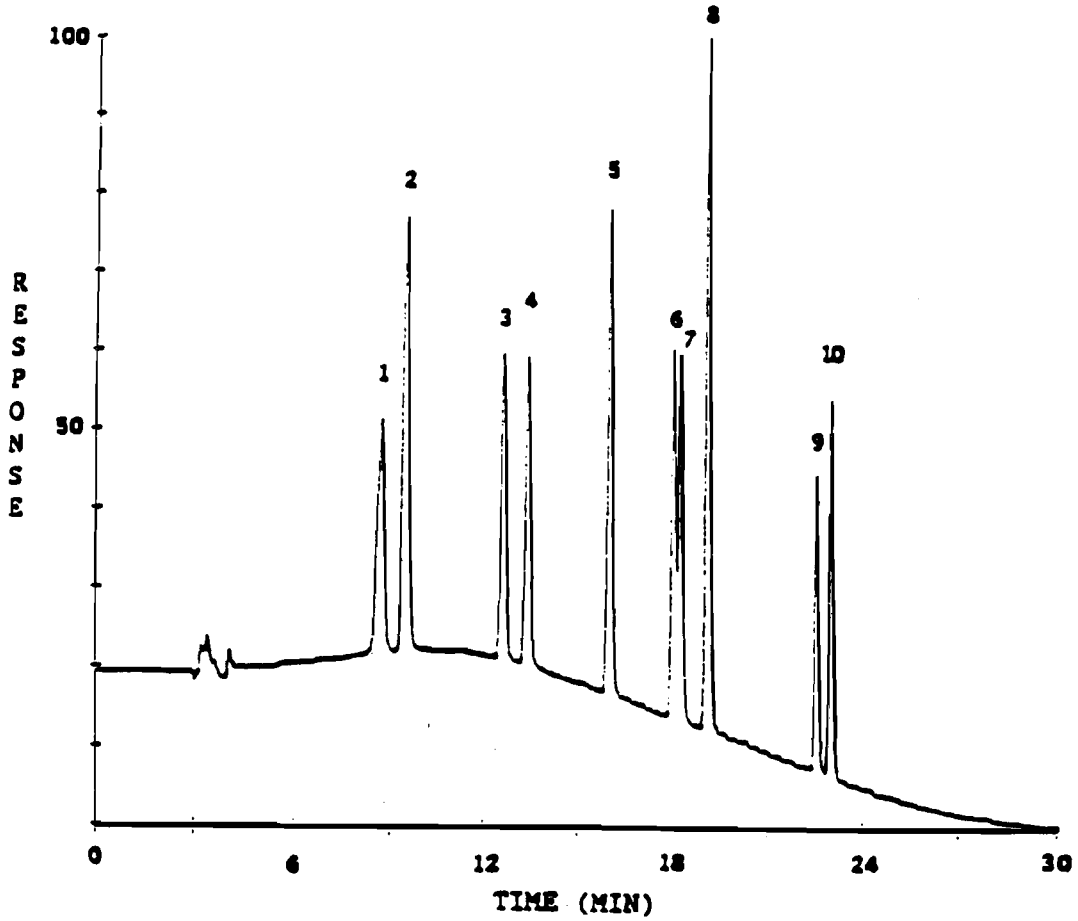
b No recovery

TABLE 4
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR SOIL

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	1.57	78.5	0.069	4.39
Methomyl (Lannate)	1.48	74.0	0.086	5.81
3-Hydroxycarbofuran	1.60	80.0	0.071	4.44
Dioxacarb	1.51	75.5	0.073	4.83
Aldicarb (Temik)	1.29	64.5	0.142	11.0
Propoxur (Baygon)	1.33	66.5	0.126	9.47
Carbofuran (Furadan)	1.46	73.0	0.092	6.30
Carbaryl (Sevin)	1.53	76.5	0.076	4.90
Methiocarb (Mesurol)	1.45	72.5	0.071	4.90
Promecarb	1.29	64.7	0.124	9.61

[a] Spike Concentration = 2.00 mg/kg of each compound, n = 10

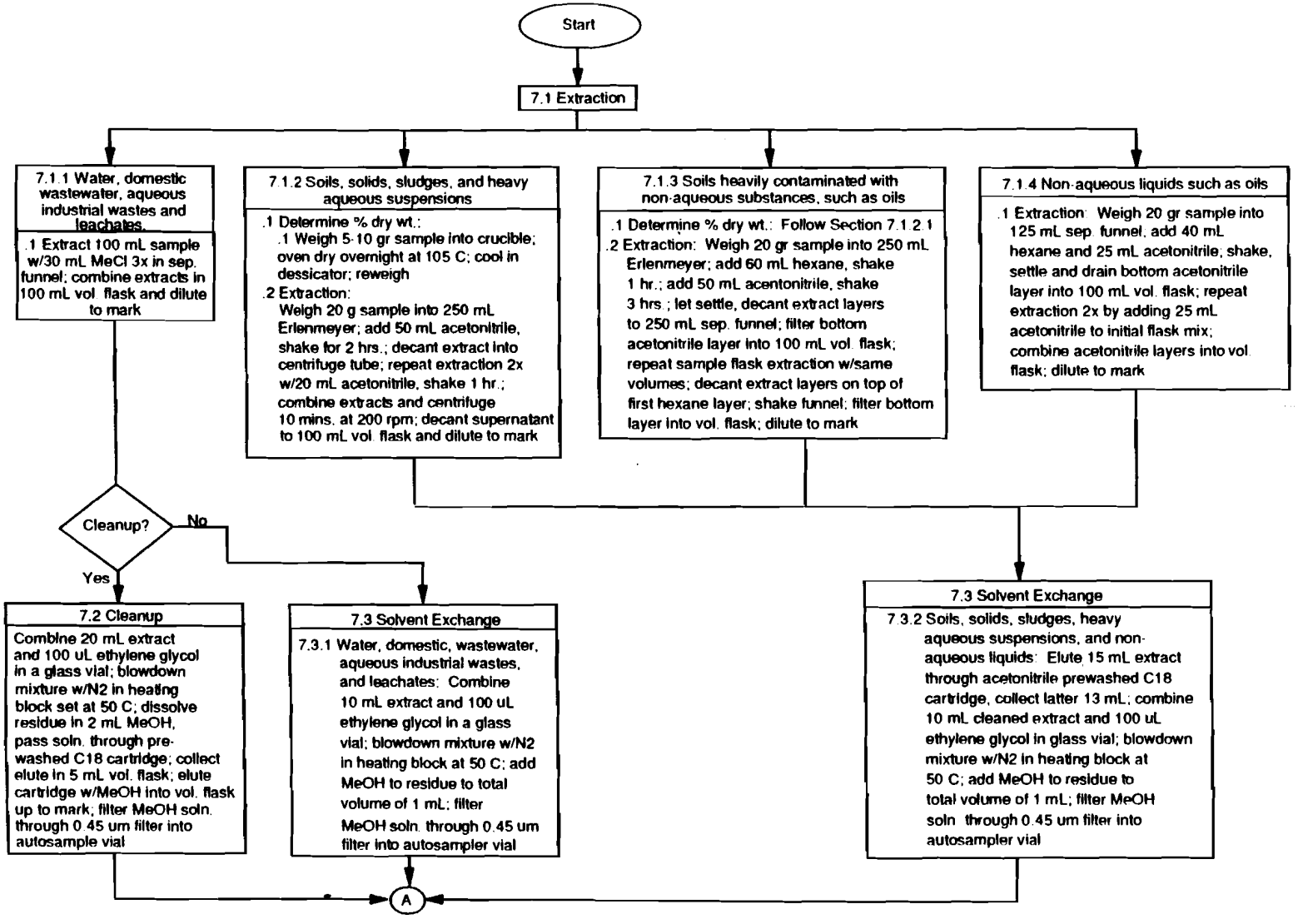
FIGURE 1

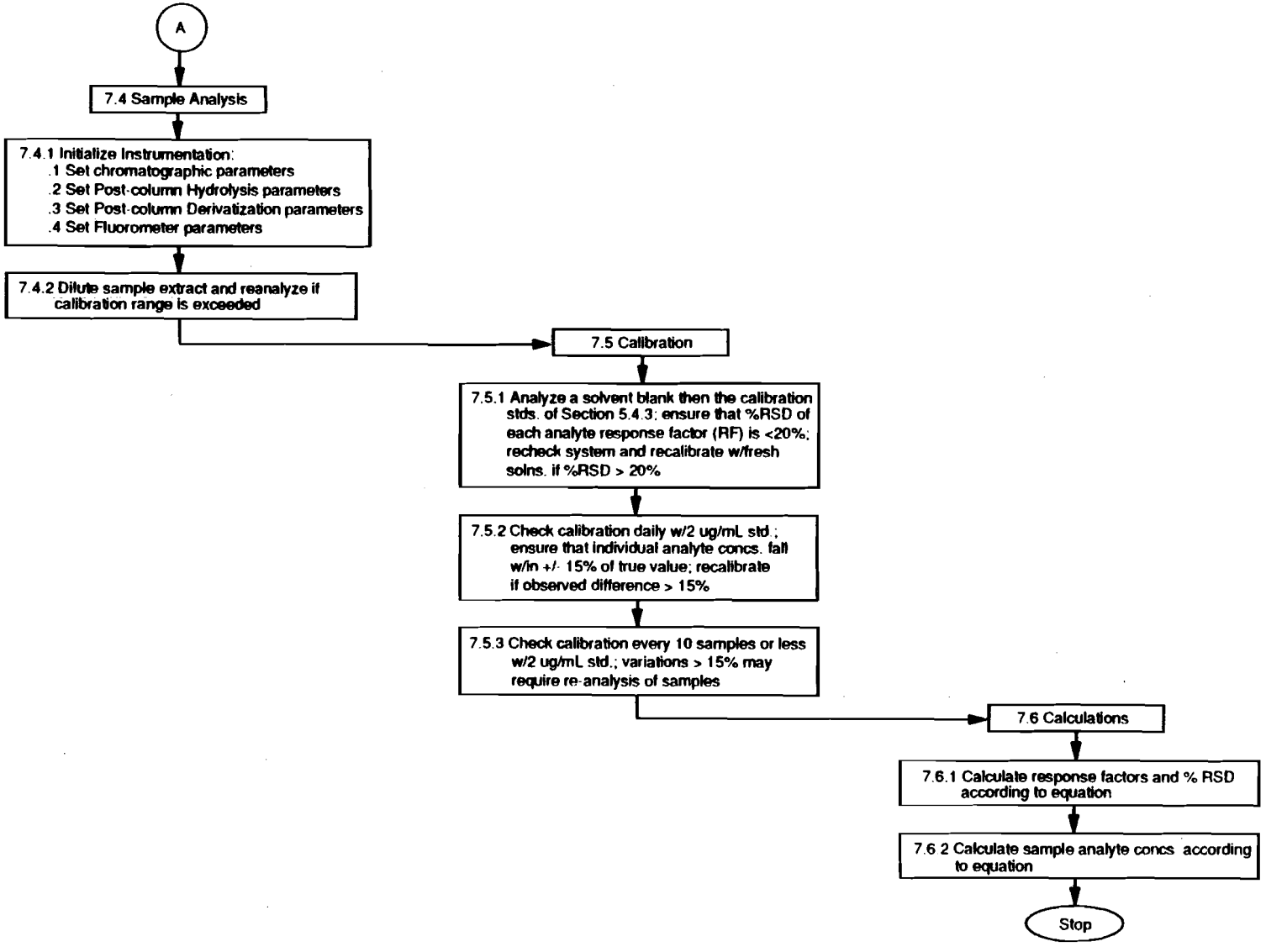


1.00 μg/mL EACH OF:

1. ALDICARB SULFONE
2. METHOMYL
3. 3-HYDROXYCARBOFURAN
4. DIOXACARB
5. ALDICARB
6. PROPOXUR
7. CARBOFURAN
8. CARBARYL
9. METHIOCARB
10. PROMECARB

METHOD 8318
N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)




A
7.4 Sample Analysis
7.4.1 Initialize Instrumentation:
.1 Set chromatographic parameters
.2 Set Post-column Hydrolysis parameters
.3 Set Post-column Derivatization parameters
.4 Set Fluorometer parameters
7.4.2 Dilute sample extract and reanalyze if calibration range is exceeded
7.5 Calibration
7.5.1 Analyze a solvent blank then the calibration stds. of Section 5.4.3; ensure that %RSD of each analyte response factor (RF) is <20%; recheck system and recalibrate w/fresh solns. if %RSD > 20%
7.5.2 Check calibration daily w/2 ug/mL std.; ensure that individual analyte concs. fall w/in +/- 15% of true value; recalibrate if observed difference > 15%
7.5.3 Check calibration every 10 samples or less w/2 ug/mL std.; variations > 15% may require re-analysis of samples
7.6 Calculations
7.6.1 Calculate response factors and % RSD according to equation
7.6 2 Calculate sample analyte concs according to equation
Stop

METHOD 8321

SOLVENT EXTRACTABLE NON-VOLATILE COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/MASS SPECTROMETRY (HPLC/TSP/MS) OR ULTRAVIOLET (UV) DETECTION

1.0 SCOPE AND APPLICATION

1.1 This method covers the use of high performance liquid chromatography (HPLC), coupled with either thermospray-mass spectrometry (TSP-MS), and/or ultraviolet (UV), for the determination of disperse azo dyes, organophosphorus compounds, and Tris-(2,3-dibromopropyl)phosphate in wastewater, ground water, sludge, and soil/sediment matrices, and chlorinated phenoxyacid compounds and their esters in wastewater, ground water, and soil/sediment matrices. Data are also provided for chlorophenoxy acid herbicides in fly ash (Table 15), however, recoveries for most compounds are very poor indicating poor extraction efficiency for these analytes using the extraction procedure included in this method. Additionally, this method may apply to other non-volatile compounds that are solvent extractable, are amenable to HPLC, and are ionizable under thermospray introduction for mass spectrometric detection. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Azo Dyes	
Disperse Red 1	2872-52-8
Disperse Red 5	3180-81-2
Disperse Red 13	2832-40-8
Disperse Yellow 5	6439-53-8
Disperse Orange 3	730-40-5
Disperse Orange 30	5261-31-4
Disperse Brown 1	17464-91-4
Solvent Red 3	6535-42-8
Solvent Red 23	85-86-9
Anthraquinone Dyes	
Disperse Blue 3	2475-46-9
Disperse Blue 14	2475-44-7
Disperse Red 60	17418-58-5
Coumarin Dyes	
(Fluorescent Brighteners)	
Fluorescent Brightener 61	8066-05-5
Fluorescent Brightener 236	63590-17-0
Alkaloids	
Caffeine	58-08-2
Strychnine	57-24-9

Compound Name	CAS No.[a]
Organophosphorus Compounds	
Methomyl	16752-77-5
Thiofanox	39196-18-4
Famphur	52-85-7
Asulam	3337-71-1
Dichlorvos	62-73-7
Dimethoate	60-51-5
Disulfoton	298-04-4
Fensulfothion	115-90-2
Merphos	150-50-5
Methyl parathion	298-00-0
Monocrotophos	919-44-8
Naled	300-76-5
Phorate	298-02-2
Trichlorfon	52-68-6
Tris-(2,3-Dibromopropyl) phosphate, (Tris-BP)	126-72-7
Chlorinated Phenoxyacid Compounds	
Dalapon	75-99-0
Dicamba	1918-00-9
2,4-D	94-75-7
MCPA	94-74-6
MCPP	7085-19-0
Dichlorprop	120-36-5
2,4,5-T	93-76-5
Silvex (2,4,5-TP)	93-72-1
Dinoseb	88-85-7
2,4-DB	94-82-6
2,4-D, butoxyethanol ester	1929-73-3
2,4-D, ethylhexyl ester	1928-43-4
2,4,5-T, butyl ester	93-79-8
2,4,5-T, butoxyethanol ester	2545-59-7

[a] Chemical Abstract Services Registry Number.

1.2 This method may be applicable to the analysis of other non-volatile or semivolatile compounds.

1.3 Tris-BP has been classified as a carcinogen. Purified standard material and stock standard solutions should be handled in a hood.

1.4 Method 8321 is designed to detect the chlorinated phenoxyacid compounds (free acid form) and their esters without the use of hydrolysis and esterification in the extraction procedure.

1.5 The compounds were chosen for analysis by HPLC/MS because they have been designated as problem compounds that are hard to analyze by traditional chromatographic methods (e.g. gas chromatography). The sensitivity of this method is dependent upon the level of interferants within a given matrix, and varies with compound class and even with compounds within that class. Additionally, the limit of detection (LOD) is dependent upon the mode of operation of the mass spectrometer. For example, the LOD for caffeine in the selected reaction monitoring (SRM) mode is 45 pg of standard injected (10 μL injection), while for Disperse Red 1 the LOD is 180 pg. The LOD for caffeine under single quadrupole scanning is 84 pg and is 600 pg for Disperse Red 1 under similar scanning conditions.

1.6 The experimentally determined limits of detection (LOD) for the target analytes are presented in Tables 3, 10, 13, and 14. For further compound identification, MS/MS (CAD - collision activated dissociation) can be used as an optional extension of this method.

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatographs/mass spectrometers and skilled in the interpretation of liquid chromatograms and mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides reverse phase high performance liquid chromatographic (RP/HPLC) and thermospray (TSP) mass spectrometric (MS) conditions for the detection of the target analytes. Quantitative analysis is performed by TSP/MS, using an external standard approach. Sample extracts can be analyzed by direct injection into the thermospray or onto a liquid chromatographic-thermospray interface. A gradient elution program is used on the chromatograph to separate the compounds. Detection is achieved both by negative ionization (discharge electrode) and positive ionization, with a single quadrupole mass spectrometer. Since this method is based on an HPLC technique, the use of ultraviolet (UV) detection is optional on routine samples.

2.2 Prior to the use of this method, appropriate sample preparation techniques must be used.

2.2.1 Samples for analysis of chlorinated phenoxyacid compounds are prepared by a modification of Method 8151 (see Sec. 7.1.2). In general, one liter of aqueous sample or fifty grams of solid sample are pH adjusted, extracted with diethyl ether, concentrated and solvent exchanged to acetonitrile.

2.2.2 Samples for analysis of the other target analytes are prepared by established extraction techniques. In general, water samples are extracted at a neutral pH with methylene chloride, using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet (Methods 3540/3541) or ultrasonic (Method 3550) extraction using methylene chloride/acetone (1:1) is used for solid samples. A

micro-extraction technique is included for the extraction of Tris-BP from aqueous and non-aqueous matrices.

2.3 An optional thermospray-mass spectrometry/mass spectrometry (TS-MS/MS) confirmatory method is provided. Confirmation is obtained by using MS/MS collision activated dissociation (CAD) or wire-repeller CAD.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, 8000 and 8150/8151.

3.2 The use of Florisil Column Cleanup (Method 3620) has been demonstrated to yield recoveries less than 85% for some of the compounds in this method, and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorus compounds as a function of Florisil fractions.

3.3 Compounds with high proton affinity may mask some of the target analytes. Therefore, an HPLC must be used as a chromatographic separator, for quantitative analysis.

3.4 Analytical difficulties encountered with specific organophosphorus compounds, as applied in this method, may include (but are not limited to) the following:

3.4.1 Methyl parathion shows some minor degradation upon analysis.

3.4.2 Naled can undergo debromination to form dichlorvos.

3.4.3 Merphos often contains contamination from merphos oxide. Oxidation of merphos can occur during storage, and possibly upon introduction into the mass spectrometer.

Refer to Method 8141 for other compound problems as related to the various extraction methods.

3.5 The chlorinated phenoxy acid compounds, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.6 Due to the reactivity of the chlorinated herbicides, the standards must be prepared in acetonitrile. Methylation will occur if prepared in methanol.

3.7 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines, or both, causing misinterpretation of chromatograms or spectra. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.8 Interferants co-extracted from the sample will vary considerably from source to source. Retention times of target analytes must be verified by using reference standards.

3.9 The optional use of HPLC/MS/MS methods aids in the confirmation of specific analytes. These methods are less subject to chemical noise than other mass spectrometric methods.

4.0 APPARATUS AND MATERIALS

4.1 HPLC/MS

4.1.1 High Performance Liquid Chromatograph (HPLC) - An analytical system with programmable solvent delivery system and all required accessories including 10 µL injection loop, analytical columns, purging gases, etc. The solvent delivery system must be capable, at a minimum, of a binary solvent system. The chromatographic system must be capable of interfacing with a Mass Spectrometer (MS).

4.1.1.1 HPLC Post-Column Addition Pump - A pump for post-column addition should be used. Ideally, this pump should be a syringe pump, and does not have to be capable of solvent programming.

4.1.1.2 Recommended HPLC Columns - A guard column and an analytical column are required.

4.1.1.2.1 Guard Column - C_{18} reverse phase guard column, 10 mm x 2.6 mm ID, 0.5 µm frit, or equivalent.

4.1.1.2.2 Analytical Column - C_{18} reverse phase column, 100 mm x 2 mm ID, 5 µm particle size of ODS-Hypersil; or C_8 reversed phase column, 100 mm x 2 mm ID, 3 µm particle size of MOS2-Hypersil, or equivalent.

4.1.2 HPLC/MS interface(s)

4.1.2.1 Micromixer - 10 µL, interfaces HPLC column system with HPLC post-column addition solvent system.

4.1.2.2 Interface - Thermospray ionization interface and source that will give acceptable calibration response for each analyte of interest at the concentration required. The source must be capable of generating both positive and negative ions, and have a discharge electrode or filament.

4.1.3 Mass spectrometer system - A single quadrupole mass spectrometer capable of scanning from 1 to 1000 amu. The spectrometer must also be capable of scanning from 150 to 450 amu in 1.5 sec or less, using 70 volts (nominal) electron energy in the positive or negative electron impact modes. In addition, the mass spectrometer must be capable

of producing a calibrated mass spectrum for PEG 400, 600, or 800 (see Sec. 5.14).

4.1.3.1 Optional triple quadrupole mass spectrometer - capable of generating daughter ion spectra with a collision gas in the second quadrupole and operation in the single quadrupole mode.

4.1.4 Data System - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows any MS data file to be searched for ions of a specified mass, and such ion abundances to be plotted versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integration of the abundances in any EICP between specified time or scan-number limits. There must be computer software available to operate the specific modes of the mass spectrometer.

4.2 HPLC with UV detector - An analytical system with solvent programmable pumping system for at least a binary solvent system, and all required accessories including syringes, 10 μL injection loop, analytical columns, purging gases, etc. An automatic injector is optional, but is useful for multiple samples. The columns specified in Sec. 4.1.1.2 are also used with this system.

4.2.1 If the UV detector is to be used in tandem with the thermospray interface, then the detector cell must be capable of withstanding high pressures (up to 6000 psi). However, the UV detector may be attached to an HPLC independent of the HPLC/TS/MS and, in that case, standard HPLC pressures are acceptable.

4.3 Purification Equipment for Azo Dye Standards

4.3.1 Soxhlet extraction apparatus.

4.3.2 Extraction thimbles, single thickness, 43 x 123 mm.

4.3.3 Filter paper, 9.0 cm (Whatman qualitative No. 1 or equivalent).

4.3.4 Silica-gel column - 3 in. x 8 in., packed with Silica gel (Type 60, EM reagent 70/230 mesh).

4.4 Extraction equipment for Chlorinated Phenoxyacid Compounds

4.4.1 Erlenmeyer flasks - 500-mL wide-mouth Pyrex, 500-mL Pyrex, with 24/40 ground glass joint, 1000-mL pyrex.

4.4.2 Separatory funnel - 2000 mL.

4.4.3 Graduated cylinder - 1000 mL.

4.4.4 Funnel - 75 mm diameter.

4.4.5 Wrist shaker - Burrell Model 75 or equivalent.

4.4.6 pH meter.

4.5 Kuderna-Danish (K-D) apparatus (optional).

4.5.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.5.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.5.3 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.5.4 Springs - 1/2 in. (Kontes K-662750 or equivalent).

4.6 Disposable serological pipets - 5 mL x 1/10, 5.5 mm ID.

4.7 Collection tube - 15 mL conical, graduated (Kimble No. 45165 or equivalent).

4.8 Vials - 5 mL conical, glass, with Teflon lined screw-caps or crimp tops.

4.9 Glass wool - Supelco No. 2-0411 or equivalent.

4.10 Microsyringes - 100 µL, 50 µL, 10 µL (Hamilton 701 N or equivalent), and 50 µL (Blunted, Hamilton 705SNR or equivalent).

4.11 Rotary evaporator - Equipped with 1000 mL receiving flask.

4.12 Balances - Analytical, 0.0001 g, Top-loading, 0.01 g.

4.13 Volumetric flasks, Class A - 10 mL to 1000 mL.

4.14 Graduated cylinder - 100 mL.

4.15 Separatory funnel - 250 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

5.4 Ammonium acetate, NH_4OOCCH_3, solution (0.1 M). Filter through a 0.45 micron membrane filter (Millipore HA or equivalent).

5.5 Acetic acid, CH_3CO_2H

5.6 Sulfuric acid solution

5.6.1 ((1:1) (v/v)) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6.2 ((1:3) (v/v)) - slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of water.

5.7 Argon gas, 99+% pure.

5.8 Solvents

5.8.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.8.2 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.8.3 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.8.4 Diethyl Ether, $C_2H_5OC_2H_5$ - Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.8.5 Methanol, CH_3OH - HPLC quality or equivalent.

5.8.6 Acetonitrile, CH_3CN - HPLC quality or equivalent.

5.8.7 Ethyl acetate $CH_3CO_2C_2H_5$ - Pesticide quality or equivalent.

5.9 Standard Materials - pure standard materials or certified solutions of each analyte targeted for analysis. Disperse azo dyes must be purified before use according to Sec. 5.10.

5.10 Disperse Azo Dye Purification

5.10.1 Two procedures are involved. The first step is the Soxhlet extraction of the dye for 24 hours with toluene and evaporation of the liquid extract to dryness, using a rotary evaporator. The solid is then recrystallized from toluene, and dried in an oven at approximately 100°C. If this step does not give the required purity, column

chromatography should be employed. Load the solid onto a 3 x 8 inch silica gel column (Sec. 4.3.4), and elute with diethyl ether. Separate impurities chromatographically, and collect the major dye fraction.

5.11 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions.

5.11.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in methanol or other suitable solvent (e.g. prepare Tris-BP in ethyl acetate), and dilute to known volume in a volumetric flask.

NOTE: Due to the reactivity of the chlorinated herbicides, the standards must be prepared in acetonitrile. Methylation will occur if prepared in methanol.

If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.11.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp-tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards.

5.12 Calibration standards - A minimum of five concentrations for each parameter of interest should be prepared through dilution of the stock standards with methanol (or other suitable solvent). One of these concentrations should be near, but above, the MDL. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the HPLC-UV/VIS or HPLC-TSP/MS. Calibration standards must be replaced after one or two months, or sooner if comparison with check standards indicates a problem.

5.13 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, along with the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g., organophosphorus or chlorinated phenoxyacid compounds not expected to be present in the sample).

5.14 HPLC/MS tuning standard - Polyethylene glycol 400 (PEG-400), PEG-600 or PEG-800. Dilute to 10 percent (v/v) in methanol. Dependent upon analyte molecular weight range: m.w. < 500 amu, use PEG-400; m.w. > 500 amu, use PEG-600, or PEG-800.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample preparation - Samples for analysis of disperse azo dyes and organophosphorus compounds must be prepared by one of the following methods prior to HPLC/MS analysis:

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3541, 3550
Waste	3540, 3541, 3550, 3580

Samples for the analysis of Tris-(2,3-dibromopropyl)phosphate in wastewater must be prepared according to Sec. 7.1.1 prior to HPLC/MS analysis. Samples for the analysis of chlorinated phenoxyacid compounds and their esters should be prepared according to Sec. 7.1.2 prior to HPLC/MS analysis.

7.1.1 Microextraction for Tris-BP:

7.1.1.1 Solid Samples

7.1.1.1.1 Weigh a 1 gram portion of the sample into a tared beaker. If the sample appears moist, add an equivalent amount of anhydrous sodium sulfate and mix well. Add 100 µL of Tris-BP (approximate concentration 1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 100 ng/µL in the 1 mL extract.

7.1.1.1.2 Remove the glass wool plug from a disposable serological pipet. Insert a 1 cm plug of clean silane treated glass wool to the bottom (narrow end) of the pipet. Pack 2 cm of anhydrous sodium sulfate onto the top of the glass wool. Wash pipet and contents with 3 - 5 mL of methanol.

7.1.1.1.3 Pack the sample into the pipet prepared according to Sec. 7.1.1.1.2. If packing material has dried, wet with a few mL of methanol first, then pack sample into the pipet.

7.1.1.1.4 Extract the sample with 3 mL of methanol followed by 4 mL of 50% (v/v) methanol/methylene chloride (rinse the sample beaker with each volume of extraction solvent prior to adding it to the pipet containing the sample). Collect the extract in a 15 mL graduated glass tube.

7.1.1.1.5 Evaporate the extract to 1 mL using the nitrogen blowdown technique (Sec. 7.1.1.1.6). Record the volume. It may not be possible to evaporate some sludge samples to a reasonable concentration.

7.1.1.1.6 Nitrogen Blowdown Technique

7.1.1.1.6.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.1.1.1.6.2 The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry. Proceed to Sec. 7.1.1.1.7.

7.1.1.1.7 Transfer the extract to a glass vial with a Teflon lined screw-cap or crimp-top and store refrigerated at 4°C. Proceed with HPLC analysis.

7.1.1.1.8 Determination of percent dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data are desired, or required, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

7.1.1.1.9 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.1.1.2 Aqueous Samples

7.1.1.2.1 Using a 100 mL graduated cylinder, measure 100 mL of sample and transfer it to a 250 mL separatory funnel. Add 200 μL of Tris-BP (approximate concentration 1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 200 ng/μL in the 1 mL extract.

7.1.1.2.2 Add 10 mL of methylene chloride to the separatory funnel. Seal and shake the separatory funnel three times, approximately 30 seconds each time, with periodic venting to release excess pressure. NOTE: Methylene chloride creates excessive pressure rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Methylene chloride is a suspected carcinogen, use necessary safety precautions.

7.1.1.2.3 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete phase separation. See Sec. 7.5, Method 3510.

7.1.1.2.4 Collect the extract in a 15 mL graduated glass tube. Proceed as in Sec. 7.1.1.1.5.

7.1.2 Extraction for chlorinated phenoxyacid compounds - Preparation of soil, sediment, and other solid samples must follow Method 8151, with the exception of no hydrolysis or esterification. Sec. 7.1.2.1 presents an outline of the procedure with the appropriate changes necessary for determination by Method 8321. Sec. 7.1.2.2 describes the extraction procedure for aqueous samples.

7.1.2.1 Extraction of solid samples

7.1.2.1.1 Add 50 g of soil/sediment sample to a 500 mL, wide mouth Erlenmeyer. Add spiking solutions if required, mix well and allow to stand for 15 minutes. Add 50 mL of organic-free reagent water and stir for 30 minutes. Determine the pH of the sample with a glass electrode and pH meter, while stirring. Adjust the pH to 2 with cold H_2SO_4 (1:1) and monitor the pH for 15 minutes, with stirring. If necessary, add additional H_2SO_4 until the pH remains at 2.

7.1.2.1.2 Add 20 mL of acetone to the flask, and mix the contents with the wrist shaker for 20 minutes. Add 80 mL of diethyl ether to the same flask, and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.1.2.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.1.2.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2000 mL separatory funnel containing 250 mL of reagent water. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.1.2.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until the extract is stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker, and the extract phase (top layer) in a 500 mL ground-glass Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask.

7.1.2.1.6 Add 45 - 50 g acidified anhydrous sodium sulfate to the combined ether extracts. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

> NOTE: The drying step is very critical. Any moisture remaining in the ether will result in low recoveries. The amount of sodium sulfate used is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum; however, the extracts may be held overnight in contact with the sodium sulfate.

7.1.2.1.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer. Reduce the volume of the extract using the macro K-D technique (Sec. 7.1.2.1.8).

7.1.2.1.8 Add one or two clean boiling chips to the flask and attach a three ball macro-Snyder column. Prewet

the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.1.2.1.9 Exchange the solvent of the extract to acetonitrile by quantitatively transferring the extract with acetonitrile to a blow-down apparatus. Add a total of 5 mL acetonitrile. Reduce the extract volume according to Sec. 7.1.1.1.6, and adjust the final volume to 1 mL.

7.1.2.2 Preparation of aqueous samples

7.1.2.2.1 Using a 1000 mL graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL, and transfer it to a separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.1.2.2.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1000 mL Erlenmeyer flask.

7.1.2.2.3 Repeat the extraction two more times using 100 mL of diethyl ether each time. Combine the extracts in a 500 mL Erlenmeyer flask. (Rinse the 1000 mL flask with each additional aliquot of extracting solvent to make a quantitative transfer.)

7.1.2.2.4 Proceed to Sec. 7.1.2.1.6 (drying, K-D concentration, solvent exchange, and final volume adjustment).

7.2 Prior to HPLC analysis, the extraction solvent must be exchanged to methanol or acetonitrile (Sec. 7.1.2.1.9). The exchange is performed using the K-D procedures listed in all of the extraction methods.

7.3 HPLC Chromatographic Conditions:

7.3.1 Analyte-specific chromatographic conditions are shown in Table 1. Chromatographic conditions which are not analyte-specific are as follows:

Flow rate:	0.4 mL/min
Post-column mobile phase:	0.1 M ammonium acetate (1% methanol) (0.1 M ammonium acetate for phenoxyacid compounds)
Post-column flow rate:	0.8 mL/min

7.3.2 If there is a chromatographic problem from compound retention when analyzing for disperse azo dyes, organophosphorus compounds, or Tris-(2,3-dibromopropyl)phosphate, a 2% constant flow of methylene chloride may be applied as needed. Methylene chloride/aqueous methanol solutions must be used with caution as HPLC eluants. Acetic acid (1%), another mobile phase modifier, can be used with compounds with acid functional groups.

7.3.3 A total flow rate of 1.0 to 1.5 mL/min is necessary to maintain thermospray ionization.

7.3.4 Retention times for organophosphorus compounds on the specified analytical column are presented in Table 9.

7.4 Recommended HPLC/Thermospray/MS operating conditions:

7.4.1 Positive Ionization mode

Repeller (wire or plate, optional): 170 to 250 v (sensitivity optimized). See Figure 2 for schematic of source with wire repeller.

Mass range: 150 to 450 amu (compound dependent, expect 1 to 18 amu higher than molecular weight of the compound).
Scan time: 1.50 sec/scan.

7.4.2 Negative Ionization mode

Discharge electrode:	on
Filament:	off
Mass Range:	135 to 450 amu
Scan time:	1.50 sec/scan.

7.4.3 Thermospray temperatures:

Vaporizer control	110°C to 130°C.
Vaporizer tip	200°C to 215°C.

Jet	210°C to 220°C.
Source block	230°C to 265°C. (Some compounds may degrade in the source block at higher temperatures, the operator should use knowledge of chemical properties to estimate proper source temperature).

7.4.4 Sample injection volume: 20 µL is necessary in order to overfill the 10 µL injection loop. If solids are present in the extract, allow them to settle or centrifuge the extract and withdraw the injection volume from the clear layer.

7.5 Calibration:

7.5.1 Thermospray/MS system - Must be hardware-tuned on quadrupole 1 (and quadrupole 3 for triple quadrupoles) for accurate mass assignment, sensitivity, and resolution. This is accomplished using polyethylene glycol (PEG) 400, 600, or 800 (see Sec. 5.14) which have average molecular weights of 400, 600, and 800, respectively. A mixture of these PEGs can be made such that it will approximate the expected working mass range for the analyses. Use PEG 400 for analysis of chlorinated phenoxyacid compounds. The PEG is introduced via the thermospray interface, circumventing the HPLC.

7.5.1.1 The mass calibration parameters are as follows:

for PEG 400 and 600	for PEG 800
Mass range: 15 to 765 amu	Mass range: 15 to 900 amu
Scan time: 5.00 sec/scan	Scan time: 5.00 sec/scan

Approximately 100 scans should be acquired, with 2 to 3 injections made. The scan with the best fit to the accurate mass table (see Tables 7 and 8) should be used as the calibration table.

7.5.1.2 The low mass range from 15 to 100 amu is covered by the ions from the ammonium acetate buffer used in the thermospray process: NH_4^+ (18 amu), $NH_4^+ \cdot H_2O$ (36), $CH_3OH \cdot NH_4^+$ (50) (methanol), or $CH_3CN \cdot NH_4^+$ (59) (acetonitrile), and $CH_3COOH \cdot NH_4^+$ (78) (acetic acid). The appearance of the m/z 50 or 59 ion depends upon the use of methanol or acetonitrile as the organic modifier. The higher mass range is covered by the ammonium ion adducts of the various ethylene glycols (e.g. $H(OCH_2CH_2)_nOH$ where n=4, gives the $H(OCH_2CH_2)_4OH \cdot NH_4^+$ ion at m/z 212).

7.5.2 Liquid Chromatograph

7.5.2.1 Prepare calibration standards as outlined in Sec. 5.12.

7.5.2.2 Choose the proper ionization conditions, as outlined in Sec. 7.4. Inject each calibration standard onto the HPLC, using the chromatographic conditions outlined in Table 1. Calculate the area under the curve for the mass chromatogram of each

quantitation ion. For example, Table 9 lists the retention times and the major ions (>5%) present in the positive ionization thermospray single quadrupole spectra of the organophosphorus compounds. In most cases the $(M^+H)^+$ and $(M^+NH_4)^+$ adduct ions are the only ions of significant abundance. Plot these ions as area response versus the amount injected. The points should fall on a straight line, with a correlation coefficient of at least 0.99 (0.97 for chlorinated phenoxyacid analytes).

7.5.2.3 If HPLC-UV detection is also being used, calibrate the instrument by preparing calibration standards as outlined in Sec. 5.12, and injecting each calibration standard onto the HPLC using the chromatographic conditions outlined in Table 1. Integrate the area under the full chromatographic peak for each concentration. Quantitation by HPLC-UV may be preferred if it is known that sample interference and/or analyte coelution are not a problem.

7.5.2.4 For the methods specified in Sec. 7.5.2.2 and 7.5.2.3, the retention time of the chromatographic peak is an important variable in analyte identification. Therefore, the ratio of the retention time of the sample analyte to the standard analyte should be 1.0 - 0.1.

7.5.2.5 The concentration of the sample analyte will be determined by using the calibration curves determined in Secs. 7.5.2.2 and 7.5.2.3. These calibration curves must be generated on the same day as each sample is analyzed. At least duplicate determinations should be made for each sample extract. Samples whose concentrations exceed the standard calibration range should be diluted to fall within the range.

7.5.2.6 Refer to Method 8000 for further information on calculations.

7.5.2.7 Precision can also be calculated from the ratio of response (area) to the amount injected; this is defined as the calibration factor (CF) for each standard concentration. If the percent relative standard deviation (%RSD) of the CF is less than 20 percent over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The CF and %RSD can be calculated as follows:

$$CF = \text{Total Area of Peak/Mass injected (ng)}$$

$$\%RSD = SD/\overline{CF} \times 100$$

where:

SD = Standard deviation between CFs

$\overline{CF}$ = Average CF

7.6 Sample Analysis

7.6.1 Once the LC/MS system has been calibrated as outlined in Sec. 7.5, it is ready for sample analysis. It is recommended that the samples initially be analyzed in the negative ionization mode. If low levels of compounds are suspected, then the samples should also be screened in the positive ionization mode.

7.6.1.1 A blank 20 µL injection (methanol) must be analyzed after the standard(s) analyses, in order to determine any residual contamination of the Thermospray/HPLC/MS system.

7.6.1.2 Take a 20 µL aliquot of the sample extract from Sec. 7.4.4. Start the HPLC gradient elution, load and inject the sample aliquot, and start the mass spectrometer data system analysis.

7.7 Calculations

7.7.1 Using the external standard calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample reconstructed ion chromatogram which corresponds to the compounds used for calibration processes. See Method 8000 for calculation equations.

7.7.2 The retention time of the chromatographic peak is an important parameter for the identity of the analyte. However, because matrix interferences can change chromatographic column conditions, the retention times are not as significant, and the mass spectra confirmations are important criteria for analyte identification.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Tables 4, 5, 6, 11, 12, and 15 indicate the single operator accuracy and precision for this method. Compare the results obtained with the results in the tables to determine if the data quality is acceptable. Tables 4, 5, and 6 provide single lab data for Disperse Red 1, Table 11 with organophoshorus pesticides, Table 12 with Tris-BP and Table 15 with chlorophenoxyacid herbicides.

8.2.1 If recovery is not acceptable, check the following:

8.2.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.2.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.2.1.3 If no problem is found, re-extract and re-analyze the sample.

8.2.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.3 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.3.1 See Sec. 7.5.2.7 for required HPLC/MS parameters for standard calibration curve %RSD limits.

8.3.2 See Sec. 7.5.2.4 regarding retention time window QC limits.

8.3.3 If any of the chromatographic QC limits are not met, the analyst should examine the LC system for:

- Leaks,
- Proper pressure delivery,
- A dirty guard column; may need replacing or repacking, and
- Possible partial thermospray plugging.

Any of the above items will necessitate shutting down the HPLC/TSP system, making repairs and/or replacements, and then restarting the analyses. The calibration standard should be reanalyzed before any sample analyses, as described in Sec. 7.5.

8.3.4 The experience of the analyst performing liquid chromatography is invaluable to the success of the method. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. If any changes are made to the system (e.g. column change), the system must be recalibrated.

8.4 Optional Thermospray HPLC/MS/MS confirmation

8.4.1 With respect to this method, MS/MS shall be defined as the daughter ion collision activated dissociation acquisition with quadrupole one set on one mass (parent ion), quadrupole two pressurized with argon and with a higher offset voltage than normal, and quadrupole three set to scan desired mass range.

8.4.2 Since the thermospray process often generates only one or two ions per compound, the use of MS/MS is a more specific mode of operation, yielding molecular structural information. In this mode, fast screening of samples can be accomplished through direct injection of the sample into the thermospray.

8.4.3 For MS/MS experiments, the first quadrupole should be set to the protonated molecule or ammoniated adduct of the analyte of interest. The third quadrupole should be set to scan from 30 amu to just above the mass region of the protonated molecule.

8.4.4 The collision gas pressure (Ar) should be set at about 1.0 mTorr and the collision energy at 20 eV. If these parameters fail to give considerable fragmentation, they may be raised above these settings to create more and stronger collisions.

8.4.5 For analytical determinations, the base peak of the collision spectrum shall be taken as the quantification ion. For extra specificity, a second ion should be chosen as a backup quantification ion.

8.4.6 Generate a calibration curve as outlined in Sec. 7.5.2.

8.4.7 For analytical determinations, calibration blanks must be run in the MS/MS mode to determine specific ion interferences. If no calibration blanks are available, chromatographic separation must be performed to assure no interferences at specific masses. For fast screening, the MS/MS spectra of the standard and the analyte could be compared and the ratios of the three major (most intense) ions examined. These ratios should be approximately the same, unless there is an interference. If an interference appears, chromatography must be utilized.

8.4.8 For unknown concentrations, the total area of the quantitation ion(s) is calculated and the calibration curves generated as in Sec. 7.5 are used to attain an injected weight number.

8.4.9 MS/MS techniques can also be used to perform structural analysis on ions represented by unassigned m/z ratios. The procedure for compounds of unknown structures is to set up a CAD experiment on the ion of interest. The spectrum generated from this experiment will reflect the structure of the compound by its fragmentation pattern. A trained mass spectroscopist and some history of the sample are usually needed to interpret the spectrum. (CAD experiments on actual standards of the expected compound are necessary for confirmation or denial of that substance.)

8.5 Optional wire-repeller CAD confirmation

8.5.1 See Figure 3 for the correct position of the wire-repeller in the thermospray source block.

8.5.2 Once the wire-repeller is inserted into the thermospray flow, the voltage can be increased to approximately 500 - 700 v. Enough voltage is necessary to create fragment ions, but not so much that shorting occurs.

8.5.3 Continue as outlined in Sec. 7.6.

9.0 METHOD PERFORMANCE

9.1 Single operator accuracy and precision studies have been conducted using spiked sediment, wastewater, sludge, and water samples. The results are presented in Tables 4, 5, 6, 11, 12, and 15. Tables 4, 5, and 6 provide single

lab data for Disperse Red 1, Table 11 for organophoshorus pesticides, Table 12 for Tris-BP and Table 15 with chlorophenoxyacid herbicides.

9.2 LODs should be calculated for the known analytes, on each instrument to be used. Tables 3, 10, and 13 list limits of detection (LOD) and/or estimated quantitation limits (EQL) that are typical with this method.

9.2.1 The LODs presented in this method were calculated by analyzing three replicates of four standard concentrations, with the lowest concentration being near the instrument detection limit. A linear regression was performed on the data set to calculate the slope and intercept. Three times the standard deviation (3σ) of the lowest standard amount, along with the calculated slope and intercept, were used to find the LOD. The LOD was not calculated using the specifications in Chapter One, but according to the ACS guidelines specified in Reference 4.

9.2.2 Table 17 presents a comparison of the LODs from Method 8151 and Method 8321 for the chlorinated phenoxyacid compounds.

9.3 Table 16 presents multilaboratory accuracy and precision data for the chlorinated phenoxyacid herbicides. The data summary is based on data from three laboratories that analyzed duplicate solvent solutions at each concentration specified in the Table.

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TABLE 1.
RECOMMENDED HPLC CHROMATOGRAPHIC CONDITIONS

Analytes	Initial Mobile Phase (%)	Initial Time (min)	Gradient (linear) (min)	Final Mobile Phase (%)	Final Time (min)
Organophosphorus Compounds	50/50 (water/ methanol)	0	10	100 (methanol)	5
Azo Dyes (e.g. Disperse Red 1)	50/50 (water/CH_3CN)	0	5	100 (CH_3CN)	5
Tris-(2,3-dibromo-propyl)phosphate	50/50 (water/methanol)	0	10	100 (methanol)	5
Chlorinated phenoxyacid compounds	75/25 (A/methanol)	2	15	40/60 (A/methanol)*	
	40/60 (A/methanol)	3	5	75/25 (A/methanol)*	10

* Where A = 0.01 M ammonium acetate (1% acetic acid)

TABLE 2.
COMPOUNDS AMENABLE TO THERMOSPRAY MASS SPECTROMETRY

Disperse Azo Dyes	Alkaloids
Methine Dyes	Aromatic ureas
Arylmethane Dyes	Amides
Coumarin Dyes	Amines
Anthraquinone Dyes	Amino acids
Xanthene Dyes	Organophosphorus Compounds
Flame retardants	Chlorinated Phenoxyacid Compounds

TABLE 3.
LIMITS OF DETECTION (LOD) AND METHOD SENSITIVITIES
FOR DISPERSE RED 1 AND CAFFEINE

Compound	Mode	LOD (pg)	EQL(7s) (pg)	EQL(10s) (pg)
Disperse Red 1	SRM	180	420	600
	Single Quad	600	1400	2000
	CAD	2,000	4700	6700
Caffeine	SRM	45	115	150
	Single Quad	84	200	280
	CAD	240	560	800

EQL = Estimated Quantitation Limit

Data from Reference 16.

TABLE 4.
PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH
HPLC/UV FOR ORGANIC-FREE REAGENT WATER SPIKED WITH DISPERSE RED 1

Sample	Percent Recovery			
	HPLC/UV	MS	CAD	SRM
Spike 1	82.2 ± 0.2	92.5 ± 3.7	87.6 ± 4.6	95.5 ± 17.1
Spike 2	87.4 ± 0.6	90.2 ± 4.7	90.4 ± 9.9	90.0 ± 5.9
RPD	6.1%	2.5%	3.2%	5.9%

Data from Reference 16.

TABLE 5.
PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH
HPLC/UV FOR MUNICIPAL WASTEWATER SPIKED WITH DISPERSE RED 1

Sample	Percent Recovery		
	HPLC/UV	MS	CAD
Spike 1	93.4 ± 0.3	102.0 ± 31	82.7 ± 13
Spike 2	96.2 ± 0.1	79.7 ± 15	83.7 ± 5.2
RPD	3.0%	25%	1.2%

Data from Reference 16.

TABLE 6.
RESULTS FROM ANALYSES OF ACTIVATED SLUDGE PROCESS WASTEWATER

Sample	Recovery of Disperse Red 1 (mg/L)		
	HPLC/UV	MS	CAD
5 mg/L Spiking Concentration			
1	0.721 ± 0.003	0.664 ± 0.030	0.796 ± 0.008
1-D	0.731 ± 0.021	0.600 ± 0.068	0.768 ± 0.093
2	0.279 ± 0.000	0.253 ± 0.052	0.301 ± 0.042
3	0.482 ± 0.001	0.449 ± 0.016	0.510 ± 0.091
RPD	1.3%	10.1%	3.6%
Unspiked Sample			
1	0.000	0.005 ± 0.0007	<0.001
1-D	0.000	0.006 ± 0.001	<0.001
2	0.000	0.002 ± 0.0003	<0.001
3	0.000	0.003 ± 0.0004	<0.001
RPD	--	18.2%	--

Data from Reference 16.

TABLE 7.
CALIBRATION MASSES AND % RELATIVE ABUNDANCES
OF PEG 400

Mass	% Relative Abundances[a]
18.0	32.3
35.06	13.5
36.04	40.5
50.06	94.6
77.04	27.0
168.12	5.4
212.14	10.3
256.17	17.6
300.20	27.0
344.22	45.9
388.25	64.9
432.28	100
476.30	94.6
520.33	81.1
564.35	67.6
608.38	32.4
652.41	16.2
653.41	4.1
696.43	8.1
697.44	2.7

[a] Intensity is normalized to mass 432.

TABLE 8.
CALIBRATION MASSES AND % RELATIVE ABUNDANCES
OF PEG 600

Mass	% Relative Abundances[a]
18.0	4.7
36.04	11.4
50.06	64.9
77.04	17.5
168.12	9.3
212.14	43.9
256.17	56.1
300.20	22.8
344.22	28.1
388.25	38.6
432.28	54.4
476.30	64.9
520.33	86.0
564.35	100
608.38	63.2
652.41	17.5
653.41	5.6
696.43	1.8

[a] Intensity is normalized to mass 564.

TABLE 9.
RETENTION TIMES AND THERMOSPRAY MASS SPECTRA
OF ORGANOPHOSPHORUS COMPOUNDS

Compound	Retention Time (minutes)	Mass Spectra (% Relative Abundance)[a]
Monocrotophos	1:09	241 (100), 224 (14)
Trichlorfon	1:22	274 (100), 257 (19), 238 (19)
Dimethoate	1:28	230 (100), 247 (20)
Dichlorvos	4:40	238 (100), 221 (40)
Naled	9:16	398 (100), 381 (23), 238 (5), 221 (2)
Fensulfothion	9:52	326 (10), 309 (100)
Methyl parathion	10:52	281 (100), 264 (8), 251 (21), 234 (48)
Phorate	13:30	278 (4), 261 (100)
Disulfoton	13:55	292 (10), 275 (100)
Merphos	18:51	315 (100), 299 (15)

[a] For molecules containing Cl, Br and S, only the base peak of the isotopic cluster is listed.

Data from Reference 17.

TABLE 10.
PRECISION AND METHOD DETECTION LIMITS (MDLs) FOR
ORGANOPHOSPHORUS COMPOUND STANDARDS

Compound	Ion	Standard Quantitation Concentration (ng/μL)	%RSD	MDL (ng)
Dichlorvos	238	2	16	
		12.5	13	
		25	5.7	
		50	4.2	4
Dimethoate	230	2	2.2	
		12.5	4.2	
		25	13	
		50	7.3	2
Phorate	261	2	0.84	
		12.5	14	
		25	7.1	
		50	4.0	2
Disulfoton	275	2	2.2	
		12.5	14	
		25	6.7	
		50	3.0	1
Fensulfothion	309	2	4.1	
		12.5	9.2	
		25	9.8	
		50	2.5	0.4
Naled	398	2	9.5	
		12.5	9.6	
		25	5.2	
		50	6.3	0.2
Merphos	299	2	5.5	
		12.5	17	
		25	3.9	
		50	5.3	1
Methyl parathion	281	2	--	
		12.5	7.1	
		25	4.8	
		50	1.5	30

Data from Reference 17.

TABLE 11.
SINGLE OPERATOR ACCURACY AND PRECISION FOR LOW CONCENTRATION DRINKING WATER (A), LOW CONCENTRATION SOIL (B), MEDIUM CONCENTRATION DRINKING WATER (C), MEDIUM CONCENTRATION SEDIMENT (D)

Compound	Average Recovery (%)	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
A			µg/L		
Dimethoate	70	7.7	5	54 - 85	15
Dichlorvos	40	12	5	14 - 64	15
Naled	0.5	1.0	5	0 - 2	15
Fensulfothion	112	3.3	5	106 - 119	15
Methyl parathion	50	28	10	0 - 105	15
Phorate	16	35	5	0 - 86	15
Disulfoton	3.5	8	5	0 - 19	15
Merphos	237	25	5	187 -287	15
B			µg/kg		
Dimethoate	16	4	50	7 - 24	15
Dichlorvos	ND	--	50	--	15
Naled	ND	--	50	--	15
Fensulfothion	45	5	50	34 - 56	15
Methyl parathion	ND	--	100	--	15
Phorate	78	15	50	48 - 109	15
Disulfoton	36	7	50	22 - 49	15
Merphos	118	19	50	81 - 155	15
C			µg/L		
Dimethoate	52	4	50	43 - 61	12
Dichlorvos	146	29	50	89 - 204	12
Naled	4	3	50	0 - 9	12
Fensulfothion	65	7	50	51 - 79	12
Methyl parathion	85	24	100	37 - 133	12
Phorate	10	15	50	0 - 41	12
Disulfoton	2	1	50	0 - 4	12
Merphos	101	13	50	75 - 126	12
D			mg/kg		
Dimethoate	74	8.5	2	57 - 91	15
Dichlorvos	166	25	2	115 - 216	15
Naled	ND	--	2	--	15
Fensulfothion	72	8.6	2	55 - 90	15
Methyl parathion	84	9	3	66 - 102	15
Phorate	58	6	2	46 - 70	15
Disulfoton	56	5	2	47 - 66	15
Merphos	78	4	2	70 - 86	12

Data from Reference 17.

TABLE 12
SINGLE OPERATOR ACCURACY AND PRECISION FOR MUNICIPAL WASTE WATER (A), DRINKING WATER (B), CHEMICAL SLUDGE WASTE (C)

Compound		Average Recovery (%)	Standard Deviation	Spike Amount (ng/µL)	Range of % Recovery	Number of Analyses
Tris-BP	(A)	25	8.0	2	41 - 9.0	15
	(B)	40	5.0	2	50 - 30	12
	(C)	63	11	100	84 - 42	8

Data from Reference 18.

TABLE 13.
SINGLE OPERATOR ESTIMATED QUANTITATION LIMIT (EQL) TABLE FOR TRIS-BP

Concentration (ng/μL)	Average Area	Standard Deviation	3*Std Dev.	7*Std Dev.	10*Std Dev.	LOD (ng/μL)	Lower EQL (ng/μL)	Upper EQL (ng/μL)
50	2675	782	2347	5476	7823	33	113	172
100	5091	558						
150	7674	2090						
200	8379	2030						

Data from Reference 18.

TABLE 14
LIMITS OF DETECTION (LOD) IN THE POSITIVE AND NEGATIVE ION MODES
FOR THE CHLORINATED PHENOXYACID HERBICIDES AND FOUR ESTERS

Compound	Positive Mode Quantitation Ion	LOD (ng)	Negative Mode Quantitation Ion	LOD (ng)
Dalapon	Not detected		141 $(M-H)^-$	11
Dicamba	238 $(M+NH_4)^+$	13	184 $(M-HCl)^-$	3.0
2,4-D	238 $(M+NH_4)^+$	2.9	184 $(M-HCl)^-$	50
MCPA	218 $(M+NH_4)^+$	120	199 $(M-1)^-$	28
Dichlorprop	252 $(M+NH_4)^+$	2.7	235 $(M-1)^-$	25
MCPP	232 $(M+NH_4)^+$	5.0	213 $(M-1)^-$	12
2,4,5-T	272 $(M+NH_4)^+$	170	218 $(M-HCl)^-$	6.5
2,4,5-TP (Silvex)	286 $(M+NH_4)^+$	160	269 $(M-1)^-$	43
Dinoseb	228 $(M+NH_4-NO)^+$	24	240 $(M)^-$	19
2,4-DB	266 $(M+NH_4)^+$	3.4	247 $(M-1)^-$	110
2,4-D,Butoxy ethanol ester	321 $(M+H)^+$	1.4	185 $(M-C_6H_{13}O_1)^-$	
2,4,5-T,Butoxy ethanol ester	372 $(M+NH_4)^+$	0.6	195 $(M-C_8H_{15}O_3)^-$	
2,4,5-T,Butyl ester	328 $(M+NH_4)^+$	8.6	195 $(M-C_6H_{11}O_2)^-$	
2,4-D,ethyl-hexyl ester	350 $(M+NH_4)^+$	1.2	161 $(M-C_{10}H_{19}O_3)^-$	

Data from Reference 19.

TABLE 15
SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compound	Average Recovery(%)[a]	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
	LOW LEVEL DRINKING WATER		µg/L		
Dicamba	63	22	5	33 - 86	9
2,4-D	26	13	5	0 - 37	9
MCPA	60	23	5	37 - 92	9
MCPP	78	21	5	54 - 116	9
Dichlorprop	43	18	5	0 - 61	9
2,4,5-T	72	31	5	43 - 138	9
Silvex	62	14	5	46 - 88	9
2,4-DB	29	24	5	0 - 62	9
Dinoseb	73	11	5	49 - 85	9
Dalapon	ND	ND	5	ND	9
2,4-D,ester	73	17	5	48 - 104	9
	HIGH LEVEL DRINKING WATER		µg/L		
Dicamba	54	30	50	26 - 103	9
2,4-D	60	35	50	35 - 119	9
MCPA	67	41	50	32 - 128	9
MCPP	66	33	50	35 - 122	9
Dichlorprop	66	33	50	27 - 116	9
2,4,5-T	61	23	50	44 - 99	9
Silvex	74	35	50	45 - 132	9
2,4-DB	83	25	50	52 - 120	9
Dinoseb	91	10	50	76 - 102	9
Dalapon	43	9.6	50	31 - 56	6
2,4-D,ester	97	19	50	76 - 130	9
	LOW LEVEL SAND		µg/g		
Dicamba	117	26	.1	82 - 147	10
2,4-D	147	23	.1	118 - 180	10
MCPA	167	79	.1	78 - 280	10
MCPP	142	39	.1	81 - 192	10
Dichlorprop	ND	ND	.1	ND	10
2,4,5-T	134	27	.1	99 - 171	10
Silvex	121	23	.1	85 - 154	10
2,4-DB	199	86	.1	0 - 245	10
Dinoseb	76	74	.1	6 - 210	10
Dalapon	ND	ND	.1	ND	10
2,4-D,ester	180	58	.1	59 - 239	7

[a]All recoveries are in negative ionization mode, except for 2,4-D,ester.
ND = Not Detected.

TABLE 15 (cont.)
SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compound	Average Recovery(%)[a]	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
	HIGH LEVEL SAND		µg/g		
Dicamba	153	33	1	119 - 209	9
2,4-D	218	27	1	187 - 276	9
MCPA	143	30	1	111 - 205	9
MCPP	158	34	1	115 - 226	9
Dichlorprop	92	37	1	51 - 161	9
2,4,5-T	160	29	1	131 - 204	9
Silvex	176	34	1	141 - 225	9
2,4-DB	145	22	1	110 - 192	9
Dinoseb	114	28	1	65 - 140	9
Dalapon	287	86	1	166 - 418	9
2,4-D,ester	20	3.6	1	17 - 25	7
	LOW LEVEL MUNICIPAL ASH		µg/g		
Dicamba	83	22	.1	48 - 104	9
2,4-D	ND	ND	.1	ND	9
MCPA	ND	ND	.1	ND	9
MCPP	ND	ND	.1	ND	9
Dichlorprop	ND	ND	.1	ND	9
2,4,5-T	27	25	.1	0 - 60	9
Silvex	68	38	.1	22 - 128	9
2,4-DB	ND	ND	.1	ND	9
Dinoseb	44	13	.1	26 - 65	9
Dalapon	ND	ND	.1	ND	9
2,4-D,ester	29	23	.1	0 - 53	6
	HIGH LEVEL MUNICIPAL ASH		µg/g		
Dicamba	66	21	1	41 - 96	9
2,4-D	8.7	4.8	1	5 - 21	9
MCPA	3.2	4.8	1	0 - 10	9
MCPP	10	4.3	1	4.7 - 16	9
Dichlorprop	ND	ND	1	ND	9
2,4,5-T	2.9	1.2	1	0 - 3.6	9
Silvex	6.0	3.1	1	2.8 - 12	9
2,4-DB	ND	ND	1	ND	9
Dinoseb	16	6.8	1	0 - 23	9
Dalapon	ND	ND	1	ND	9
2,4-D,ester	1.9	1.7	1	0 - 6.7	6

[a]All recoveries are in negative ionization mode, except for 2,4-D,ester.
ND = Not Detected.

TABLE 16
MULTILABORATORY ACCURACY AND PRECISION DATA
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compounds	Spiking Concentration	Mean (% Recovery)[a]	% Relative Standard Deviation[b]
	500 mg/L		
2,4,5-T		90	23
2,4,5-T,butoxy		90	29
2,4-D		86	17
2,4-DB		95	22
Dalapon		83	13
Dicamba		77	25
Dichlorprop		84	20
Dinoseb		78	15
MCPA		89	11
MCPP		86	12
Silvex		96	27
	50 mg/L		
2,4,5-T		62	68
2,4,5-T,butoxy		85	9
2,4-D		64	80
2,4-DB		104	28
Dalapon		121	99
Dicamba		90	23
Dichlorprop		96	15
Dinoseb		86	57
MCPA		96	20
MCPP		76	74
Silvex		65	71
	5 mg/L		
2,4,5-T		90	28
2,4,5-T,butoxy		99	17
2,4-D		103	31
2,4-DB		96	21
Dalapon		150	4
Dicamba		105	12
Dichlorprop		102	22
Dinoseb		108	30
MCPA		94	18
MCPP		98	15
Silvex		87	15

Data from Reference 20.
[a] Mean of duplicate data from 3 laboratories.
[b] % RSD of duplicate data from 3 laboratories.

TABLE 17
COMPARISON OF LODs: METHOD 8151 vs. METHOD 8321

Compound	Method 8151 LOD(μg/L)	Method 8321 LOD (μg/L)	Ionization Mode
Dalapon	1.3	1.1	(-)
Dicamba	0.8	0.3	(-)
2,4-D	0.2	0.29	(+)
MCPA	0.06	2.8	(-)
Dichloroprop	0.26	0.27	(+)
MCPP	0.09	0.50	(+)
2,4,5-T	0.08	0.65	(-)
2,4,5-TP (Silvex)	0.17	4.3	(-)
2,4-DB	0.8	0.34	(+)
Dinoseb	0.19	1.9	(-)

FIGURE 1.
SCHEMATIC OF THE THERMOSPRAY PROBE AND ION SOURCE

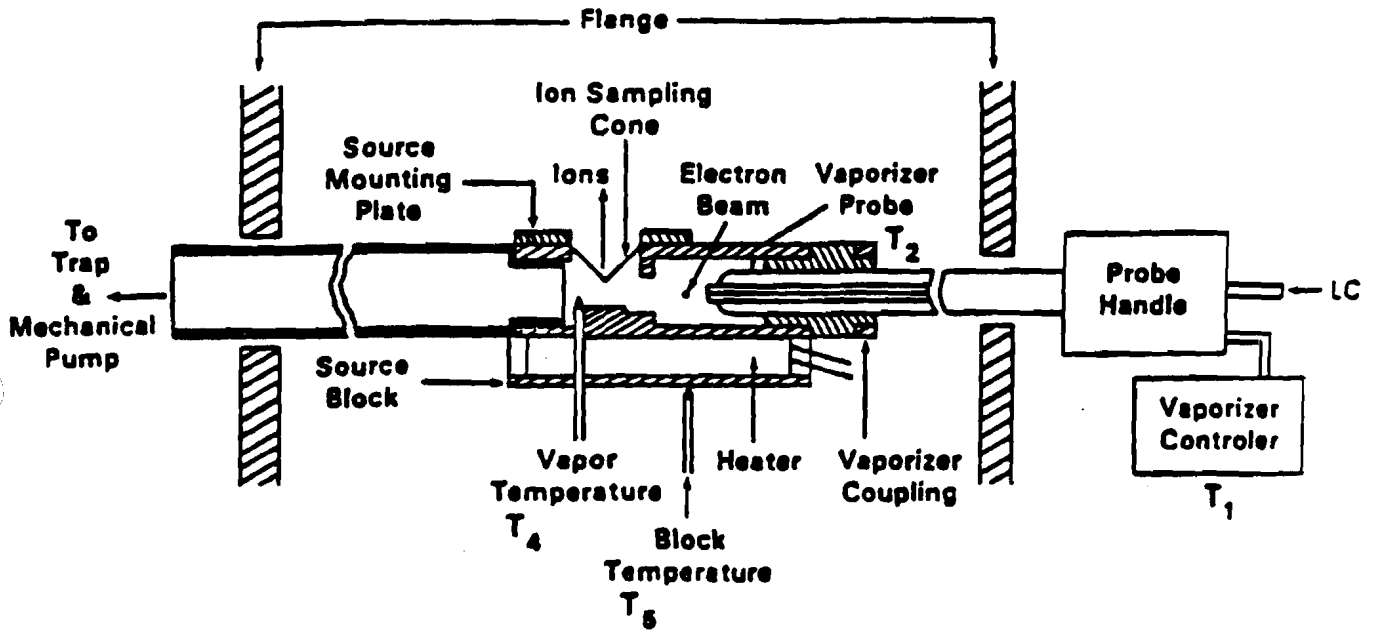


FIGURE 2.
THERMOSPRAY SOURCE WITH WIRE-REPELLER
(High sensitivity configuration)

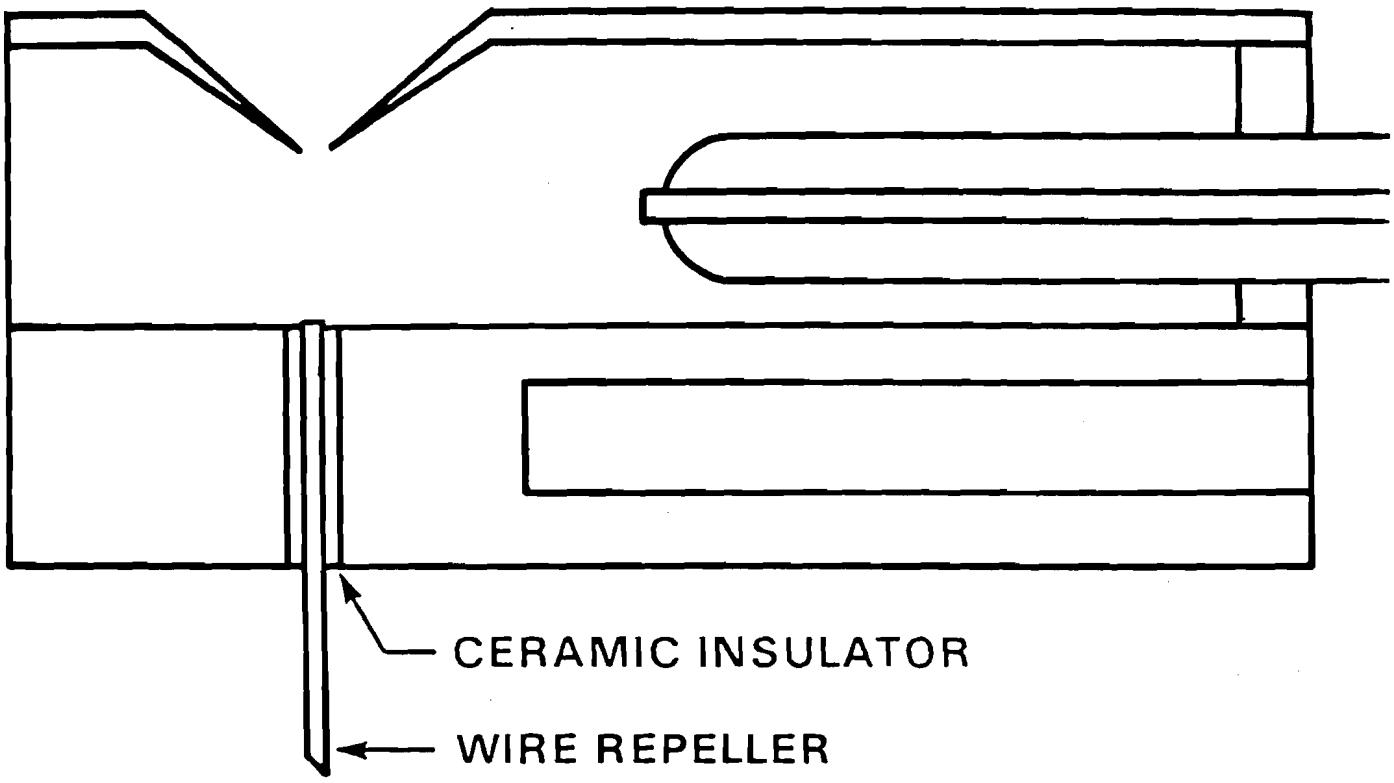
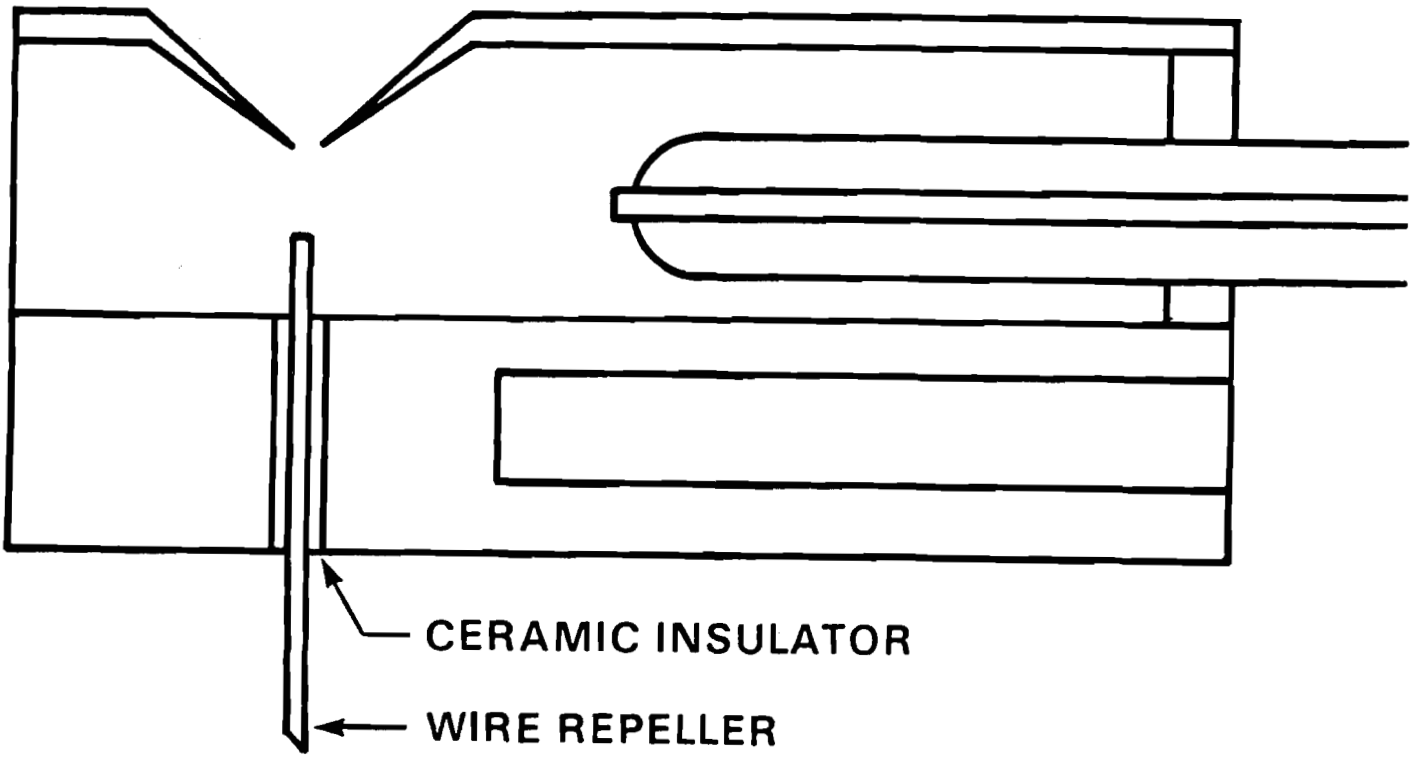
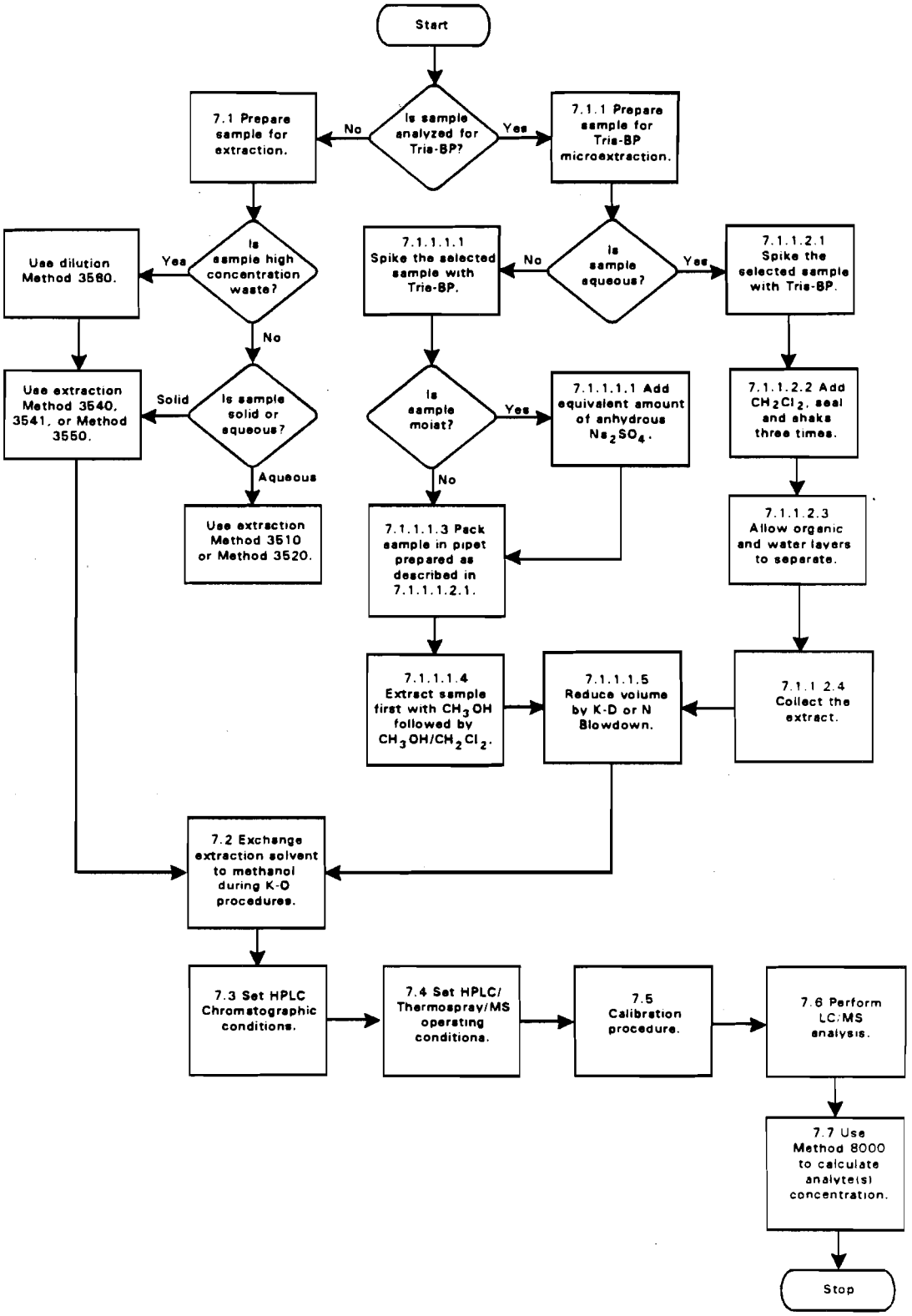


FIGURE 3.
THERMOSPRAY SOURCE WITH WIRE-REPELLER
(CAD configuration)



METHOD 8321
SOLVENT EXTRACTABLE NON-VOLATILE COMPOUNDS BY
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/MASS SPECTROMETRY
(HPLC/TSP/MS) OR ULTRAVIOLET (UV) DETECTION



METHOD 8330

NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8330 is intended for the trace analysis of explosives residues by high performance liquid chromatography using a UV detector. This method is used to determine the concentration of the following compounds in a water, soil, or sediment matrix:

Compound	Abbreviation	CAS No[a]
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	1946-51-0
2-Amino-4, 6-dinitrotoluene	2-Am-DNT	355-72-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0

a Chemical Abstracts Service Registry number

1.2 Method 8330 provides a salting-out extraction procedure for low concentration (parts per trillion, or nanograms per liter) of explosives residues in surface or ground water. Direct injection of diluted and filtered water samples can be used for water samples of higher concentration (See Table 1).

1.3 All of these compounds are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. When making stock solutions for calibration, treat each explosive compound with caution. See NOTE in Sec. 5.3.1 and Sec. 11 on Safety.

1.4 The estimated quantitation limits (EQLs) of target analytes determined by Method 8330 in water and soil are presented in Table 1.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. (See Sec. 11.0

on SAFETY.) Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Method 8330 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosives residues in water, soil and sediment matrix. Prior to use of this method, appropriate sample preparation techniques must be used.

2.2 Low-Level Salting-out Method With No Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure with acetonitrile and sodium chloride. The small volume of acetonitrile that remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is diluted 1:1 with reagent grade water. An aliquot is separated on a C-18 reverse phase column, determined at 254 nm, and confirmed on a CN reverse phase column.

2.3 High-level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1/1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, determine at 254 nm, and confirmed on a CN reverse phase column. If HMX is an important target analyte, methanol is preferred.

2.4 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered and chromatographed as in Sec. 2.3.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

3.2 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

3.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration and acidified to pH <3. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

3.4 Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 HPLC - equipped with a pump capable of achieving 4000 psi, a 100 µl loop injector and a 254 nm UV detector (Perkin Elmer Series 3, or equivalent). For the low concentration option, the detector must be capable of a stable baseline at 0.001 absorbance units full scale.

4.1.2 Recommended Columns:

4.1.2.1 Primary column: C-18 Reverse phase HPLC column, 25 cm x 4.6 mm (5 µm), (Supelco LC-18, or equivalent).

4.1.2.2 Secondary column: CN Reverse phase HPLC column, 25 cm x 4.6 mm (5 µm), (Supelco LC-CN, or equivalent).

4.1.3 Strip chart recorder.

4.1.4 Digital integrator (optional).

4.1.5 Autosampler (optional).

4.2 Other Equipment

4.2.1 Temperature controlled ultrasonic bath.

4.2.2 Vortex mixer.

4.2.3 Balance, ± 0.0001 g.

4.2.4 Magnetic stirrer with stirring pellets.

4.2.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.2.6 Oven - Forced air, without heating.

4.3 Materials

4.3.1 High pressure injection syringe - 500 µL, (Hamilton liquid syringe or equivalent).

4.3.2 Disposable cartridge filters - 0.45 µm Teflon filter.

4.3.3 Pipets - Class A, glass, Appropriate sizes.

4.3.4 Pasteur pipets.

4.3.5 Scintillation Vials - 20 mL, glass.

4.3.6 Vials - 15 mL, glass, Teflon-lined cap.

4.3.7 Vials- 40 mL, glass, Teflon-lined cap.

4.3.8 Disposable syringes - Plastipak, 3 mL and 10 mL or equivalent.

4.3.9 Volumetric flasks - Appropriate sizes with ground glass stoppers, Class A.

NOTE: The 100 mL and 1 L volumetric flasks used for magnetic stirrer extraction must be round.

4.3.10 Vacuum desiccator - Glass.

4.3.11 Mortar and pestle - Steel.

4.3.12 Sieve - 30 mesh.

4.3.13 Graduated cylinders - Appropriate sizes.

4.4 Preparation of Materials

4.4.1 Prepare all materials to be used as described in Chapter 4 for semivolatile organics.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

5.1.1 Acetonitrile, CH_3CN - HPLC grade.

5.1.2 Methanol, CH_3OH - HPLC grade.

5.1.3 Calcium chloride, $CaCl_2$ - Reagent grade. Prepare an aqueous solution of 5 g/L.

5.1.4 Sodium chloride, NaCl, shipped in glass bottles - reagent grade.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock Standard Solutions

5.3.1 Dry each solid analyte standard to constant weight in a vacuum desiccator in the dark. Place about 0.100 g (weighed to 0.0001 g) of a single analyte into a 100 mL volumetric flask and dilute to volume with acetonitrile. Invert flask several times until dissolved. Store in

refrigerator at 4°C in the dark. Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1,000 mg/L). Stock solutions may be used for up to one year.

> NOTE: The HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material should be handled carefully. See SAFETY in Sec. 11 for guidance. HMX, RDX, and Tetryl reference materials are shipped under water. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES!

5.4 Intermediate Standards Solutions

5.4.1 If both 2,4-DNT and 2,6-DNT are to be determined, prepare two separate intermediate stock solutions containing (1) HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, 2,4,6-TNT, and 2,4-DNT and (2) Tetryl, 2,6-DNT, 2-NT, 3-NT, and 4-NT. Intermediate stock standard solutions should be prepared at 1,000 µg/L, in acetonitrile when analyzing soil samples, and in methanol when analyzing aqueous samples.

5.4.2 Dilute the two concentrated intermediate stock solutions, with the appropriate solvent, to prepare intermediate standard solutions that cover the range of 2.5 - 1,000 µg/L. These solutions should be refrigerated on preparation, and may be used for 30 days.

5.4.3 For the low-level method, the analyst must conduct a detection limit study and devise dilution series appropriate to the desired range. Standards for the low level method must be prepared immediately prior to use.

5.5 Working standards

5.5.1 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the intermediate standards solutions by 50% (v/v) with 5 g/L calcium chloride solution (Sec. 5.1.3). These solutions must be refrigerated and stored in the dark, and prepared fresh on the day of calibration.

5.6 Surrogate Spiking Solution

5.6.1 The analyst should monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., analytes not expected to be present in the sample).

5.7 Matrix Spiking Solutions

5.7.1 Prepare matrix spiking solutions in methanol such that the concentration in the sample is five times the Estimated Quantitation Limit (Table 1). All target analytes should be included.

5.8 HPLC Mobile Phase

5.8.1 To prepare 1 liter of mobile phase, add 500 mL of methanol to 500 mL of organic-free reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Follow conventional sampling and sample handling procedures as specified for semivolatile organics in Chapter Four.

6.2 Samples and sample extracts must be stored in the dark at 4°C. Holding times are the same as for semivolatile organics.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Aqueous Samples: It is highly recommended that process waste samples be screened with the high-level method to determine if the low level method (1-50 μg/L) is required. Most groundwater samples will fall into the low level method.

7.1.1.1 Low-Level Method (salting-out extraction)

7.1.1.1.1 Add 251.3 g of sodium chloride to a 1 L volumetric flask (round). Measure out 770 mL of a water sample (using a 1 L graduated cylinder) and transfer it to the volumetric flask containing the salt. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

7.1.1.1.2 Add 164 mL of acetonitrile (measured with a 250 mL graduated cylinder) while the solution is being stirred and stir for an additional 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.

7.1.1.1.3 Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipet and transfer it to a 100 mL volumetric flask (round). Add 10 mL of fresh acetonitrile to the water sample in the 1 L flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

7.1.1.1.4 Add 84 mL of salt water (325 g NaCl per 1000 mL of reagent water) to the acetonitrile extract in the 100 mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 minutes, followed by 10 minutes for phase separation. Carefully transfer the acetonitrile phase

to a 10 mL graduated cylinder using a Pasteur pipet. At this stage, the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram, where it could interfere with the HMX determination.

7.1.1.1.5 Add an additional 1.0 mL of acetonitrile to the 100 mL volumetric flask. Again stir the contents of the flask for 15 minutes, followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract in the 10 mL graduated cylinder (transfer to a 25 mL graduated cylinder if the volume exceeds 5 mL). Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [V_t] in the calculation of concentration after converting to μL). The resulting extract, about 5 - 6 mL, is then diluted 1:1 with organic-free reagent water (with pH <3 if tetryl is a suspected analyte) prior to analysis.

7.1.1.1.6 If the diluted extract is turbid, filter it through a 0.45 - μm Teflon filter using a disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4.

7.1.1.2 High-Level Method

7.1.1.2.1 Sample filtration: Place a 5 mL aliquot of each water sample in a scintillation vial, add 5 mL of acetonitrile, shake thoroughly, and filter through a 0.45-μm Teflon filter using a disposable syringe. Discard the first 3 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

7.1.2 Soil and Sediment Samples

7.1.2.1 Sample homogenization: Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile-rinsed mortar to pass a 30 mesh sieve.

<u>NOTE</u>: Soil samples should be screened by Method 8515 prior to grinding in a mortar and pestle (See Safety Sec. 11.2).

7.1.2.2 Sample extraction

7.1.2.2.1 Place a 2.0 g subsample of each soil sample in a 15 mL glass vial. Add 10.0 mL of acetonitrile, cap with

Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

7.1.2.2.2 After sonication, allow sample to settle for 30 minutes. Remove 5.0 mL of supernatant, and combine with 5.0 mL of calcium chloride solution (Sec. 5.1.3) in a 20 mL vial. Shake, and let stand for 15 minutes.

7.1.2.2.3 Place supernatant in a disposable syringe and filter through a 0.45-µm Teflon filter. Discard first 3 mL and retain remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4.

7.2 Chromatographic Conditions (Recommended)

Primary Column:	C-18 reverse phase HPLC column, 25-cm x 4.6-mm, 5 µm, (Supelco LC-18 or equivalent).
Secondary Column:	CN reverse phase HPLC column, 25-cm x 4.6-mm, 5 µm, (Supelco LC-CN or equivalent).
Mobile Phase:	50/50 (v/v) methanol/organic-free reagent water.
Flow Rate:	1.5 mL/min
Injection volume:	100-µL
UV Detector:	254 nm

7.3 Calibration of HPLC

7.3.1 All electronic equipment is allowed to warm up for 30 minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (approximately 20 min at 1.5 mL/min) and continued until the baseline is level at the UV detector's greatest sensitivity.

7.3.2 Initial Calibration. Injections of each calibration standard over the concentration range of interest are made sequentially into the HPLC in random order. Peak heights or peak areas are obtained for each analyte. Experience indicates that a linear calibration curve with zero intercept is appropriate for each analyte. Therefore, a response factor for each analyte can be taken as the slope of the best-fit regression line.

7.3.3 Daily Calibration. Analyze midpoint calibration standards, at a minimum, at the beginning of the day, singly at the midpoint of the run, and singly after the last sample of the day (assuming a sample group of 10 samples or less). Obtain the response factor for each analyte from the mean peak heights or peak areas and compare it with the response factor obtained for the initial calibration. The mean response factor for the

daily calibration must agree within ±15% of the response factor of the initial calibration. The same criteria is required for subsequent standard responses compared to the mean response of the triplicate standards beginning the day. If this criterion is not met, a new initial calibration must be obtained.

7.4 HPLC Analysis

7.4.1 Analyze the samples using the chromatographic conditions given in Sec. 7.2. All positive measurements observed on the C-18 column must be confirmed by injection onto the CN column.

7.4.2 Follow Sec. 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence. If column temperature control is not employed, special care must be taken to ensure that temperature shifts do not cause peak misidentification.

7.4.3 Table 2 summarizes the estimated retention times on both C-18 and CN columns for a number of analytes analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the resulting peak sizes in peak heights or area units. The use of peak heights is recommended to improve reproducibility of low level samples.

7.4.5 Calculation of concentration is covered in Sec. 7.0 of Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500.

8.2 Quality control required to validate the HPLC system operation is found in Method 8000, Sec. 8.0.

8.3 Prior to preparation of stock solutions, acetonitrile, methanol, and water blanks should be run to determine possible interferences with analyte peaks. If the acetonitrile, methanol, or water blanks show contamination, a different batch should be used.

9.0 METHOD PERFORMANCE

9.1 Table 3 presents the single laboratory precision based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.2 Table 4 presents the multilaboratory error based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.3 Table 5 presents the multilaboratory variance of the high concentration method for water based on data from nine laboratories.

9.4 Table 6 presents multilaboratory recovery data from the analysis of spiked soil samples by seven laboratories.

9.5 Table 7 presents a comparison of method accuracy for soil and aqueous samples (high concentration method).

9.6 Table 8 contains precision and accuracy data for the salting-out extraction method.

10.0 REFERENCES

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7. Jenkins, T.F., P.W. Schumacher, M.E. Walsh and C.F. Bauer (1988b) Development of an analytical method for the determination of explosive residues in soil. Part II: Further development and ruggedness testing. USA Cold Regions Research and Engineering Laboratory, CRREL Report 88-8.

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11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by Method 8330. The only extra caution that should be taken is when handling the analytical standard neat material for the explosives themselves and in rare cases where soil or waste samples are highly contaminated with the explosives. Follow the note for drying the neat materials at ambient temperatures.

11.2 It is advisable to screen soil or waste samples using Method 8515 to determine whether high concentrations of explosives are present. Soil samples as high as 2% 2,4,6-TNT have been safely ground. Samples containing higher concentrations should not be ground in the mortar and pestle. Method 8515 is for 2,4,6-TNT, however, the other nitroaromatics will also cause a color to be developed and provide a rough estimation of their concentrations. 2,4,6-TNT is the analyte most often detected in high concentrations in soil samples. Visual observation of a soil sample is also important when the sample is taken from a site expected to contain explosives. Lumps of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

TABLE 1
ESTIMATED QUANTITATION LIMITS

Compounds	Water (µg/L) Low-Level	Water (µg/L) High-Level	Soil (mg/kg)
HMX	-	13.0	2.2
RDX	0.84	14.0	1.0
1,3,5-TNB	0.26	7.3	0.25
1,3-DNB	0.11	4.0	0.25
Tetryl	-	4.0	0.65
NB	-	6.4	0.26
2,4,6-TNT	0.11	6.9	0.25
4-Am-DNT	0.060	-	-
2-Am-DNT	0.035	-	-
2,6-DNT	0.31	9.4	0.26
2,4-DNT	0.020	5.7	0.25
2-NT	-	12.0	0.25
4-NT	-	8.5	0.25
3-NT	-	7.9	0.25

TABLE 2
RETENTION TIMES AND CAPACITY FACTORS ON LC-18 AND LC-CN COLUMNS

	Retention time (min)		Capacity factor (k)*	
Compound	LC-18	LC-CN	LC-18	LC-CN
HMX	2.44	8.35	0.49	2.52
RDX	3.73	6.15	1.27	1.59
1,3,5-TNB	5.11	4.05	2.12	0.71
1,3-DNB	6.16	4.18	2.76	0.76
Tetryl	6.93	7.36	3.23	2.11
NB	7.23	3.81	3.41	0.61
2,4,6-TNT	8.42	5.00	4.13	1.11
4-Am-DNT	8.88	5.10	4.41	1.15
2-Am-DNT	9.12	5.65	4.56	1.38
2,6-DNT	9.82	4.61	4.99	0.95
2,4-DNT	10.05	4.87	5.13	1.05
2-NT	12.26	4.37	6.48	0.84
4-NT	13.26	4.41	7.09	0.86
3-NT	14.23	4.45	7.68	0.88

* Capacity factors are based on an unretained peak for nitrate at 1.71 min on LC-18 and at 2.00 min on LC-CN.

TABLE 3
SINGLE LABORATORY PRECISION OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%RSD	Mean Conc. (mg/kg)	SD	%RSD
HMX	46	1.7	3.7	14	1.8	12.8
				153	21.6	14.1
RDX	60	1.4	2.3	104	12	11.5
				877	29.6	3.4
1,3,5-TNB	8.6	0.4	4.6	2.8	0.2	7.1
	46	1.9	4.1	72	6.0	8.3
1,3-DNB	3.5	0.14	4.0	1.1	0.11	9.8
Tetryl	17	3.1	17.9	2.3	0.41	18.0
2,4,6-TNT	40	1.4	3.5	7.0	0.61	9.0
				669	55	8.2
2,4-DNT	5.0	0.17	3.4	1.0	0.44	42.3

TABLE 4
MULTILABORATORY ERROR OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%RSD	Mean Conc. (mg/kg)	SD	%RSD
HMX	46	2.6	5.7	14	3.7	26.0
				153	37.3	24.0
RDX	60	2.6	4.4	104	17.4	17.0
				877	67.3	7.7
1,3,5-TNB	8.6	0.61	7.1	2.8	0.23	8.2
	46	2.97	6.5	72	8.8	12.2
1,3-DNB	3.5	0.24	6.9	1.1	0.16	14.5
Tetryl	17	5.22	30.7	2.3	0.49	21.3
2,4,6-TNT	40	1.88	4.7	7.0	1.27	18.0
				669	63.4	9.5
2,4-DNT	5.0	0.22	4.4	1.0	0.74	74.0

TABLE 5
MULTILABORATORY VARIANCE OF METHOD FOR WATER SAMPLES[a]

Compounds	Mean Conc. (µg/L)	SD	%RSD
HMX	203	14.8	7.3
RDX	274	20.8	7.6
2,4-DNT	107	7.7	7.2
2,4,6-TNT	107	11.1	10.4

[a] Nine Laboratories

TABLE 6
MULTILABORATORY RECOVERY DATA FOR SPIKED SOIL SAMPLES

	Concentration (μg/g)						
Laboratory	HMX	RDX	1,3,5-TNB	1,3-DNB	Tetryl	2,4,6-TNT	2,4-DNT
1	44.97	48.78	48.99	49.94	32.48	49.73	51.05
3	50.25	48.50	45.85	45.96	47.91	46.25	48.37
4	42.40	44.00	43.40	49.50	31.60	53.50	50.90
5	46.50	48.40	46.90	48.80	32.10	55.80	49.60
6	56.20	55.00	41.60	46.30	13.20	56.80	45.70
7	41.50	41.50	38.00	44.50	2.60	36.00	43.50
8	52.70	52.20	48.00	48.30	44.80	51.30	49.10
True Conc	50.35	50.20	50.15	50.05	50.35	50.65	50.05
Mean	47.79	48.34	44.68	47.67	29.24	49.91	48.32
Std Dev	5.46	4.57	3.91	2.09	16.24	7.11	2.78
% RSD	11.42	9.45	8.75	4.39	55.53	14.26	5.76
% Diff*	5.08	3.71	10.91	4.76	41.93	1.46	3.46
Mean % Recovery	95	96	89	95	58	98	96

* Between true value and mean determined value.

TABLE 7
COMPARISON OF METHOD ACCURACY FOR SOIL AND AQUEOUS SAMPLES
(HIGH CONCENTRATION METHOD)

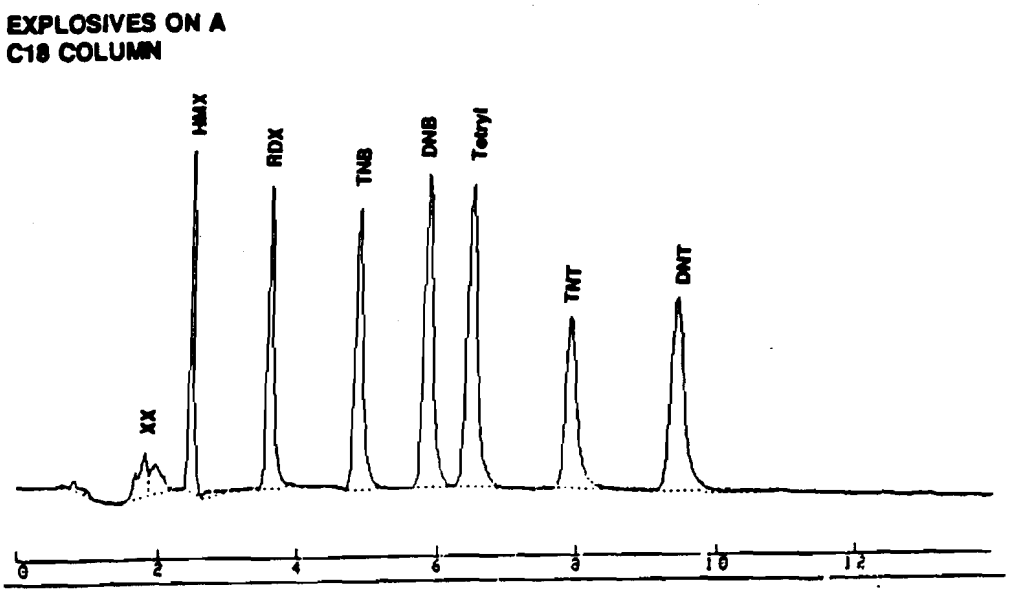
Analyte	Recovery (%)	
	Soil Method*	Aqueous Method**
2,4-DNT	96.0	98.6
2,4,6-TNT	96.8	94.4
RDX	96.8	99.6
HMX	95.4	95.5

* Taken from Bauer et al. (1989), Reference 1.
** Taken from Jenkins et al. (1984), Reference 3.

TABLE 8
PRECISION AND ACCURACY DATA FOR THE SALTING-OUT EXTRACTION METHOD

Analyte	No. of Samples[1]	Precision (% RSD)	Ave. Recovery (%)	Conc. Range (µg/L)
HMX	20	10.5	106	0-1.14
RDX	20	8.7	106	0-1.04
1,3,5-TNB	20	7.6	119	0-0.82
1,3-DNB	20	6.6	102	0-1.04
Tetryl	20	16.4	93	0-0.93
2,4,6-TNT	20	7.6	105	0-0.98
2-Am-DNT	20	9.1	102	0-1.04
2,4-DNT	20	5.8	101	0-1.01
1,2-NT	20	9.1	102	0-1.07
1,4-NT	20	18.1	96	0-1.06
1,3-NT	20	12.4	97	0-1.23

[1]Reagent water



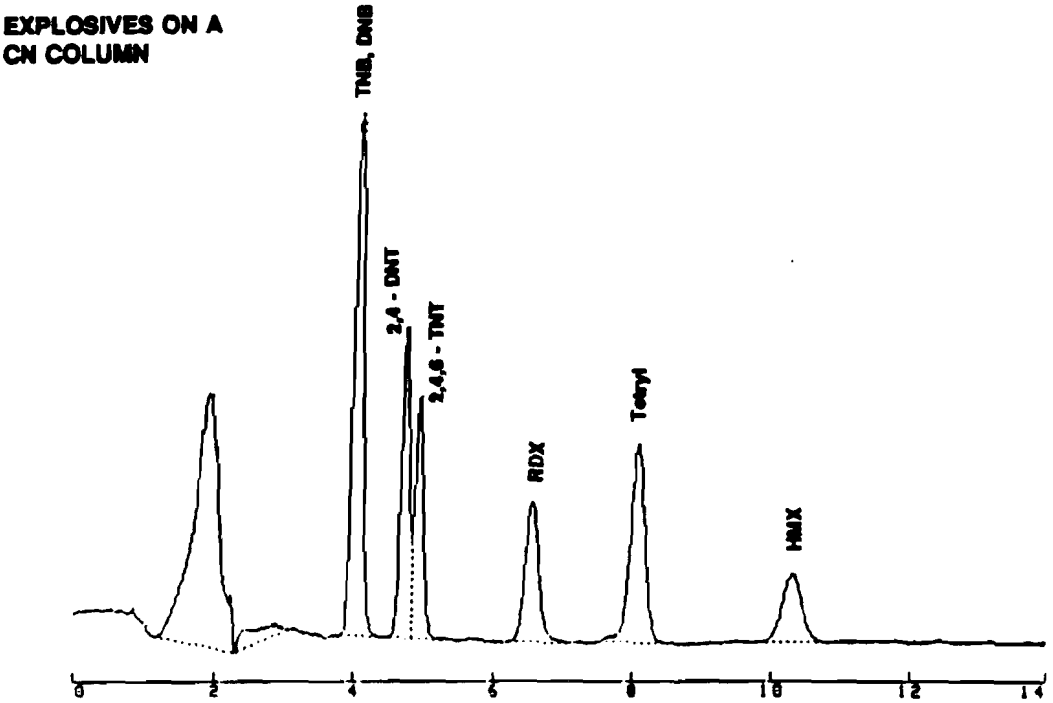
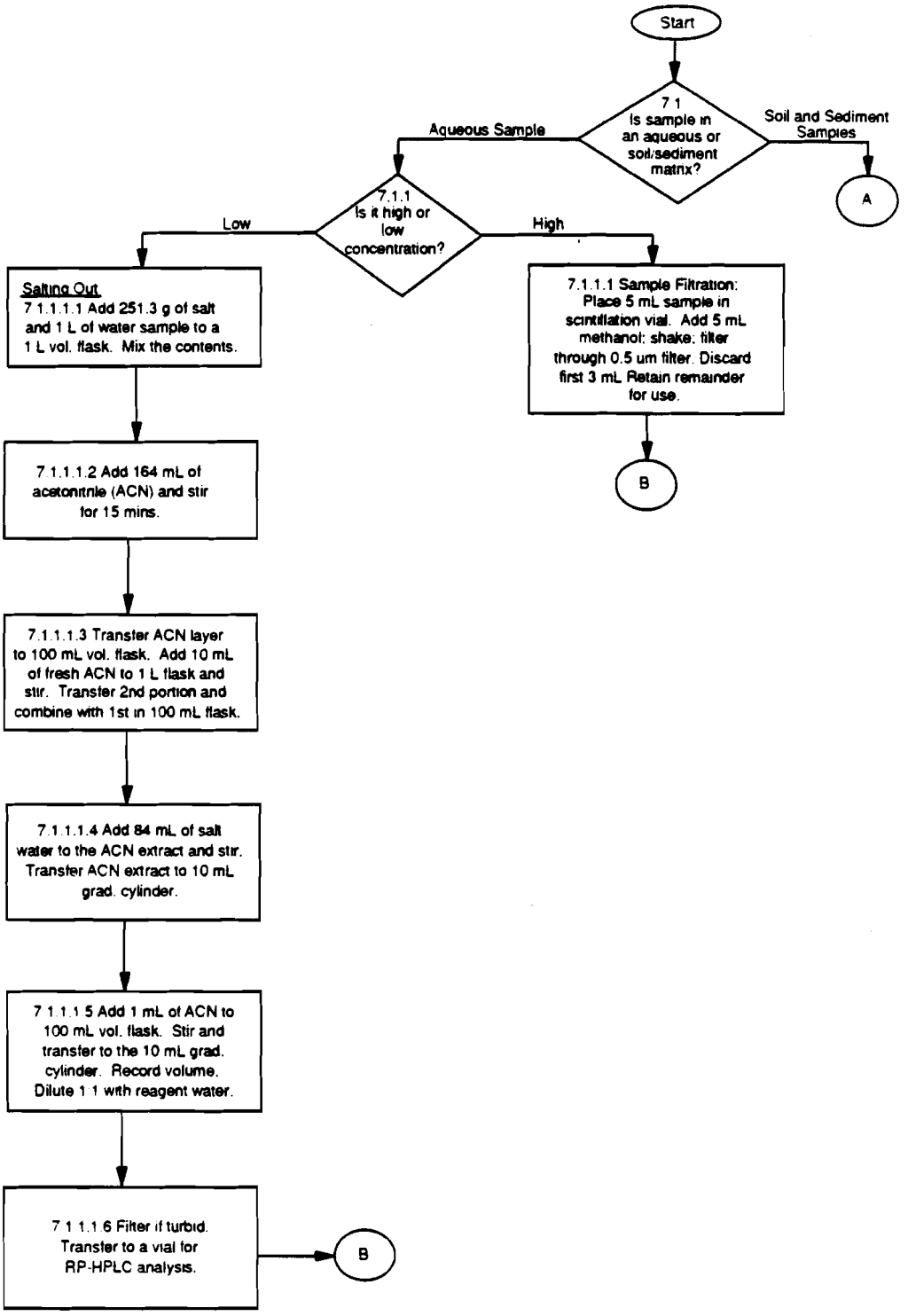
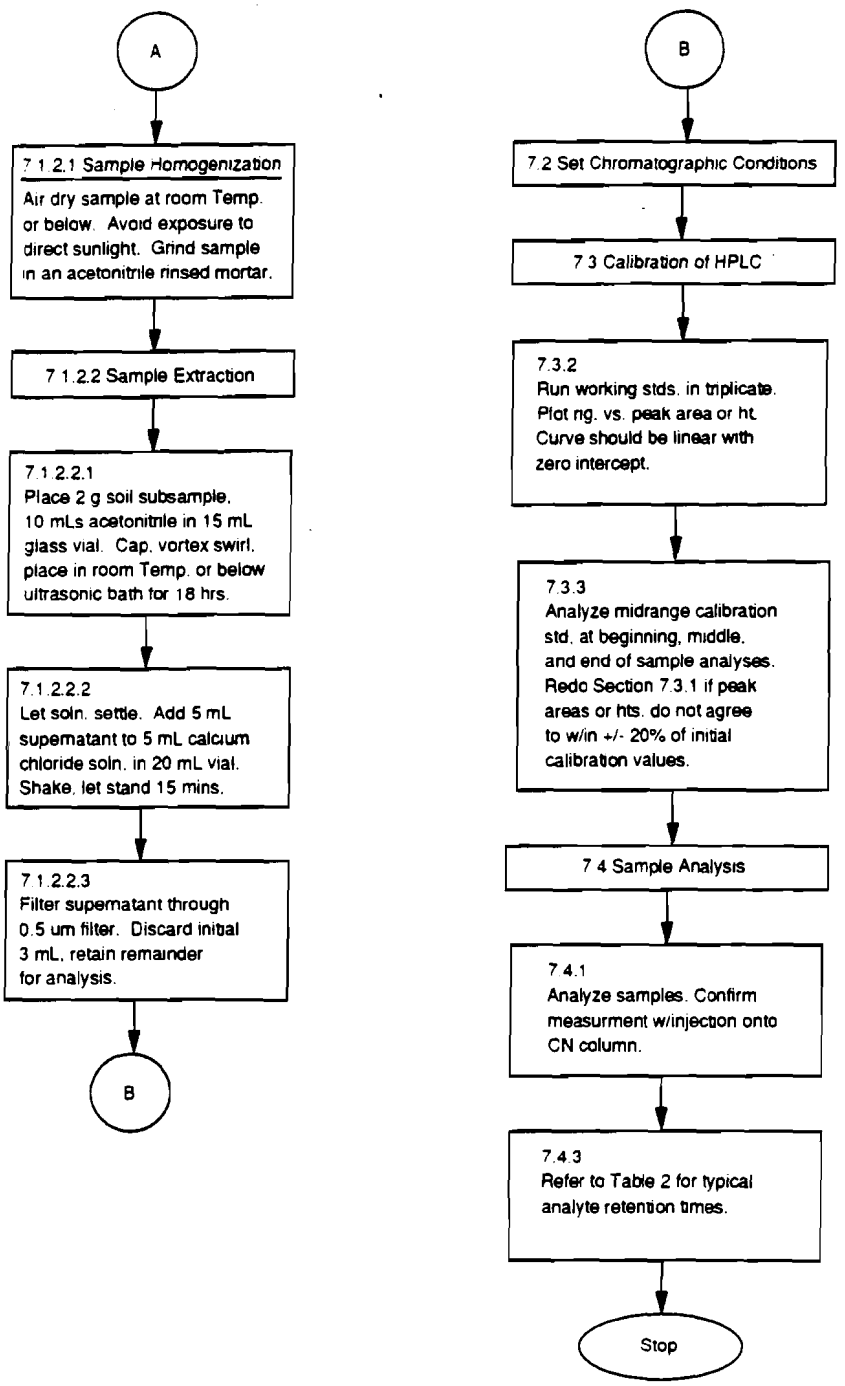


FIGURE 1
CHROMATOGRAMS FOR COLUMNS DESCRIBED IN Sec. 4.1.2.
COURTESY OF U.S. ARMY CORPS OF ENGINEERS, OMAHA, NE.


Start
7.1 Is sample in an aqueous or soil/sediment matrix?
Aqueous Sample
Soil and Sediment Samples
A
7.1.1 Is it high or low concentration?
Low
High
Salting Out
7.1.1.1 Add 251.3 g of salt and 1 L of water sample to a 1 L vol. flask. Mix the contents.
7.1.1.1.2 Add 164 mL of acetonitrile (ACN) and stir for 15 mins.
7.1.1.1.3 Transfer ACN layer to 100 mL vol. flask. Add 10 mL of fresh ACN to 1 L flask and stir. Transfer 2nd portion and combine with 1st in 100 mL flask.
7.1.1.1.4 Add 84 mL of salt water to the ACN extract and stir. Transfer ACN extract to 10 mL grad. cylinder.
7.1.1.1.5 Add 1 mL of ACN to 100 mL vol. flask. Stir and transfer to the 10 mL grad. cylinder. Record volume. Dilute 1:1 with reagent water.
7.1.1.1.6 Filter if turbid. Transfer to a vial for RP-HPLC analysis.
B
7.1.1.1 Sample Filtration: Place 5 mL sample in scintillation vial. Add 5 mL methanol; shake; filter through 0.5 um filter. Discard first 3 mL. Retain remainder for use.
B


A
7.1.2.1 Sample Homogenization
Air dry sample at room Temp. or below. Avoid exposure to direct sunlight. Grind sample in an acetonitrile rinsed mortar.
7.1.2.2 Sample Extraction
7.1.2.2.1
Place 2 g soil subsample, 10 mLs acetonitrile in 15 mL glass vial. Cap, vortex swirl, place in room Temp. or below ultrasonic bath for 18 hrs.
7.1.2.2.2
Let soln. settle. Add 5 mL supernatant to 5 mL calcium chloride soln. in 20 mL vial. Shake, let stand 15 mins.
7.1.2.2.3
Filter supernatant through 0.5 um filter. Discard initial 3 mL, retain remainder for analysis.
B
B
7.2 Set Chromatographic Conditions
7.3 Calibration of HPLC
7.3.2
Run working stds. in triplicate. Plot ng. vs. peak area or ht. Curve should be linear with zero intercept.
7.3.3
Analyze midrange calibration std. at beginning, middle, and end of sample analyses. Redo Section 7.3.1 if peak areas or hts. do not agree to w/in +/- 20% of initial calibration values.
7.4 Sample Analysis
7.4.1
Analyze samples. Confirm measurment w/injection onto CN column.
7.4.3
Refer to Table 2 for typical analyte retention times.
Stop

METHOD 8331

TETRAZENE BY REVERSE PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 This method is intended for the analysis of tetrazene, an explosive residue, in soil and water. This method is limited to use by analysts experienced in handling and analyzing explosive materials. The following compounds can be determined by this method:

Compound	CAS No[a]
Tetrazene	31330-63-9

[a] Chemical Abstracts Service Registry number

1.2 Tetrazene degrades rapidly in water and methanol at room temperature. Special care must be taken to refrigerate or cool all solutions throughout the analytical process.

1.3 Tetrazene, in its dry form, is extremely explosive. Caution must be taken during preparation of standards.

1.4 The estimated quantitation limit (EQL) of Method 8331 for determining the concentration of tetrazene is approximately 7 µg/L in water and approximately 1 mg/kg in soil.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A 10 mL water sample is filtered, eluted on a C-18 column using ion pairing reverse phase HPLC, and quantitated at 280 nm.

2.2 2 g of soil are extracted with 55:45 v/v methanol-water and 1-decanesulfonic acid on a platform shaker, filtered, and eluted on a C-18 column using ion pairing reverse phase HPLC, and quantitated at 280 nm.

3.0 INTERFERENCES

3.1 No interferences are known. Tetrazene elutes early, however, and if a computing integrator is used for peak quantification, the baseline setting may have to be set to exclude baseline aberrations. Baseline setting is particularly important at low concentrations of analyte.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 HPLC - Pump capable of achieving 4000 psi.

4.1.2 100 μL loop injector.

4.1.3 Variable or fixed wavelength detector capable of reading 280 nm.

4.1.4 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5 μm) (Supelco LC-18, or equivalent).

4.1.5 Digital integrator - HP 3390A (or equivalent)

4.1.6 Strip chart recorder.

4.2 Other apparatus

4.2.1 Platform orbital shaker.

4.2.2 Analytical balance - $\pm$ 0.0001 g.

4.2.3 Desiccator.

4.3 Materials

4.3.1 Injection syringe - 500 μL.

4.3.2 Filters - 0.5 μm Millex-SR and 0.5 μm Millex-HV, disposable, or equivalent.

4.3.3 Pipets - volumetric, glass, Class A.

4.3.4 Scintillation vials - 20 mL, glass.

4.3.5 Syringes - 10 mL.

4.3.6 Volumetric flasks, Class A - 100 mL, 200 mL.

4.3.7 Erlenmeyer flasks with ground glass stoppers - 125 mL.

4.4 Preparation

4.4.1 Prepare all materials as described in Chapter 4 for volatile organics.

5.0 REAGENTS

5.1 HPLC grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

5.2 General

5.2.1 Methanol, CH_3OH - HPLC grade.

5.2.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.3 1-Decanesulfonic acid, sodium salt, $C_{10}H_{21}SO_3Na$ - HPLC grade.

5.2.4 Acetic acid (glacial), CH_3COOH - reagent grade.

5.3 Standard Solutions

5.3.1 Tetrazene - Standard Analytical Reference Material.

5.3.2 Stock standard solution - Dry tetrazene to constant weight in a vacuum desiccator in the dark. (Tetrazene is extremely explosive in the dry state. Do not dry more reagent than is necessary to prepare stock solutions.) Place about 0.0010 g (weighed to 0.0001 g) into a 100-ml volumetric flask and dilute to volume with methanol. Invert flask several times until tetrazene is dissolved. Store in freezer at -10°C. Stock solution is about 100 mg/L. Replace stock standard solution every week.

5.3.3 Intermediate standard solutions

5.3.3.1 Prepare a 4 mg/L standard by diluting the stock solution 1/25 v/v with methanol.

5.3.3.2 Pipet 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 mL of the 4 mg/L standard solution into 6 separate 100 mL volumetric flasks, and make up to volume with methanol. Pipet 25.0 mL of the 4 mg/L standard solution into a 50 mL volumetric flask, and make up to volume with methanol. This results in intermediate standards of about 0.02, 0.04, 0.08, 0.2, 0.4, 0.8, 2 and 4 mg/L.

5.3.3.3 Cool immediately on preparation in refrigerator or ice bath.

5.3.4 Working standard solutions

5.3.4.1 Inject 4 mL of each of the intermediate standard solutions into 6.0 mL of water. This results in concentrations of about 0.008, 0.016, 0.032, 0.08, 0.16, 0.3, 0.8 and 1.6 mg/L.

5.3.4.2 Cool immediately on preparation in refrigerator or ice bath.

5.5 QC spike concentrate solution

5.5.1 Dry tetrazene to constant weight in a vacuum desiccator in the dark. (Tetrazene is extremely explosive in the dry state. Do not dry any more than necessary to prepare standards.) Place about 0.0011 g (weighed to 0.0001 g) into a 200-ml volumetric flask and dilute to volume with methanol. Invert flask several times until tetrazene is dissolved. Store in freezer at -10°C. QC spike concentrate solution is about 55 mg/L. Replace stock standard solution every week.

5.5.2 Prepare spiking solutions, at concentrations appropriate to the concentration range of the samples being analyzed, by diluting the QC spike concentrate solution with methanol. Cool on preparation in refrigerator or ice bath.

5.6 Eluent

5.6.1 To make about 1 liter of eluent, add 2.44 g of 1-decanesulfonic acid, sodium salt to 400/600 v/v methanol/water, and add 2.0 mL of glacial acetic acid.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1.

6.2 Samples must be collected and stored in glass containers. Follow conventional sampling procedures.

6.3 Samples must be kept below 4°C from the time of collection through analysis.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Filtration of Water Samples

7.1.1.1 Place a 10 mL portion of each water sample in a syringe and filter through a 0.5 μm Millex-HV filter unit. Discard first 5 mL of filtrate, and retain 5 mL for analysis.

7.1.2 Extraction and Filtration of Soil Samples

7.1.2.1 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.1.2.1.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample} \times 100}{\text{g of sample}}$$

7.1.2.2 Weigh 2 g soil subsamples into 125 mL Erlenmeyer flasks with ground glass stoppers.

7.1.2.3 Add 50 mL of 55/45 v/v methanol-water with 1-decanesulfonic acid, sodium salt added to make a 0.1 M solution.

7.1.2.4 Vortex for 15 seconds.

7.1.2.5 Shake for 5 hr at 2000 rpm on platform shaker.

7.1.2.6 Place a 10 mL portion of each soil sample extract in a syringe and filter through a 0.5 µm Millex-SR filter unit. Discard first 5 mL of filtrate, and retain 5 mL for analysis.

7.2 Sample Analysis

7.2.1 Analyze the samples using the chromatographic conditions given in Section 7.2.1.1. Under these conditions, the retention time of tetrazene is 2.8 min. A sample chromatogram, including other compounds likely to be present in samples containing tetrazene, is shown in Figure 1.

7.2.1.1 Chromatographic Conditions

Solvent:	0.01 M 1-decanesulfonic acid, in acidic methanol/water (Section 5.5)
Flow rate:	1.5 mL/min
Injection volume:	100 µL
UV Detector:	280 nm

7.3 Calibration of HPLC

7.3.1 Initial Calibration - Analyze the working standards (Section 5.3.4), starting with the 0.008 mg/L standards and ending with the 0.30 mg/L standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.3.2 Continuing Calibration - On a daily basis, inject 250 μL of stock standard into 20 mL water. Keep solution in refrigerator until analysis. Analyze in triplicate (by overfilling loop) at the beginning of the day, singly after each five samples, and singly after the last sample of the day. Compare response factors from the mean peak area or peak height obtained over the day with the response factor at initial calibration. If these values do not agree within 10%, recalibrate.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol should be analyzed to determine possible interferences with the tetrazene peak. If the methanol shows contamination, a different batch of methanol should be used.

8.3 Method Blanks

8.3.1 Method blanks for the analysis of water samples should be organic-free reagent water carried through all sample storage and handling procedures.

8.3.2 Method blanks for the analysis of soil samples should be uncontaminated soil carried through all sample storage, extraction, and handling procedures.

9.0 METHOD PERFORMANCE

9.1 Method 8331 was tested in a laboratory over a period of four days. Spiked organic-free reagent water and standard soil were analyzed in duplicate each day for four days. The HPLC was calibrated daily according to the procedures given in Section 7.1. Method performance data are presented in Tables 1 and 2.

10.0 REFERENCES

1. Walsh, M.E., and T.F. Jenkins, "Analytical Method for Determining Tetrazene in Water," U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 87-25, 1987.

2. Walsh, M.E., and T.F. Jenkins, "Analytical Method for Determining Tetrazene in Soil," U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 88-15, 1988.

11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for safe handling of the analytes targeted by Method 8331.

FIGURE 1

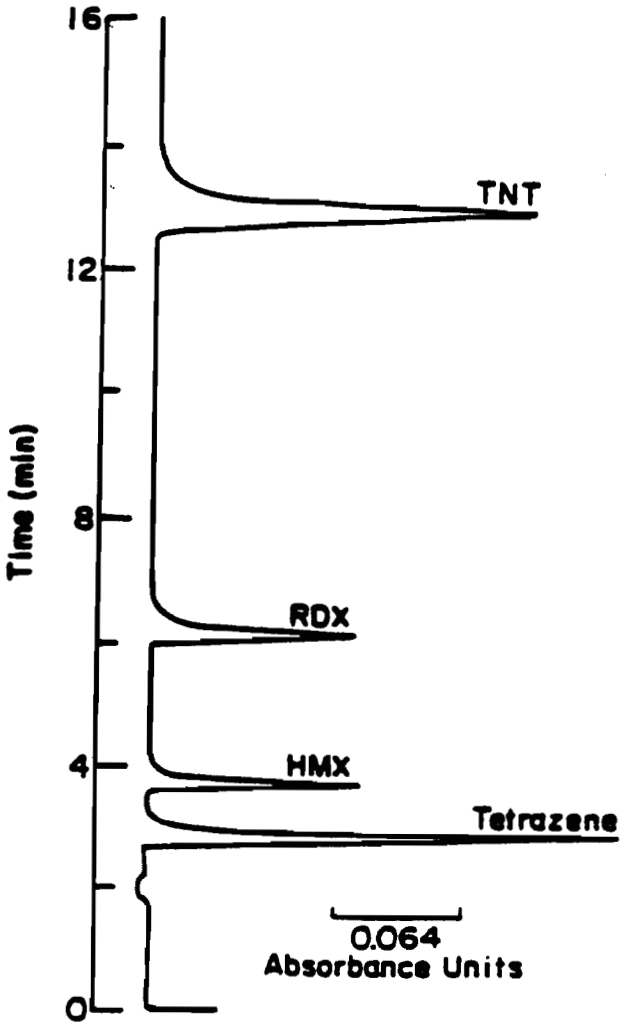

16
12
8
4
0
Time (min)
TNT
RDX
HMX
Tetrazene
0.064
Absorbance Units

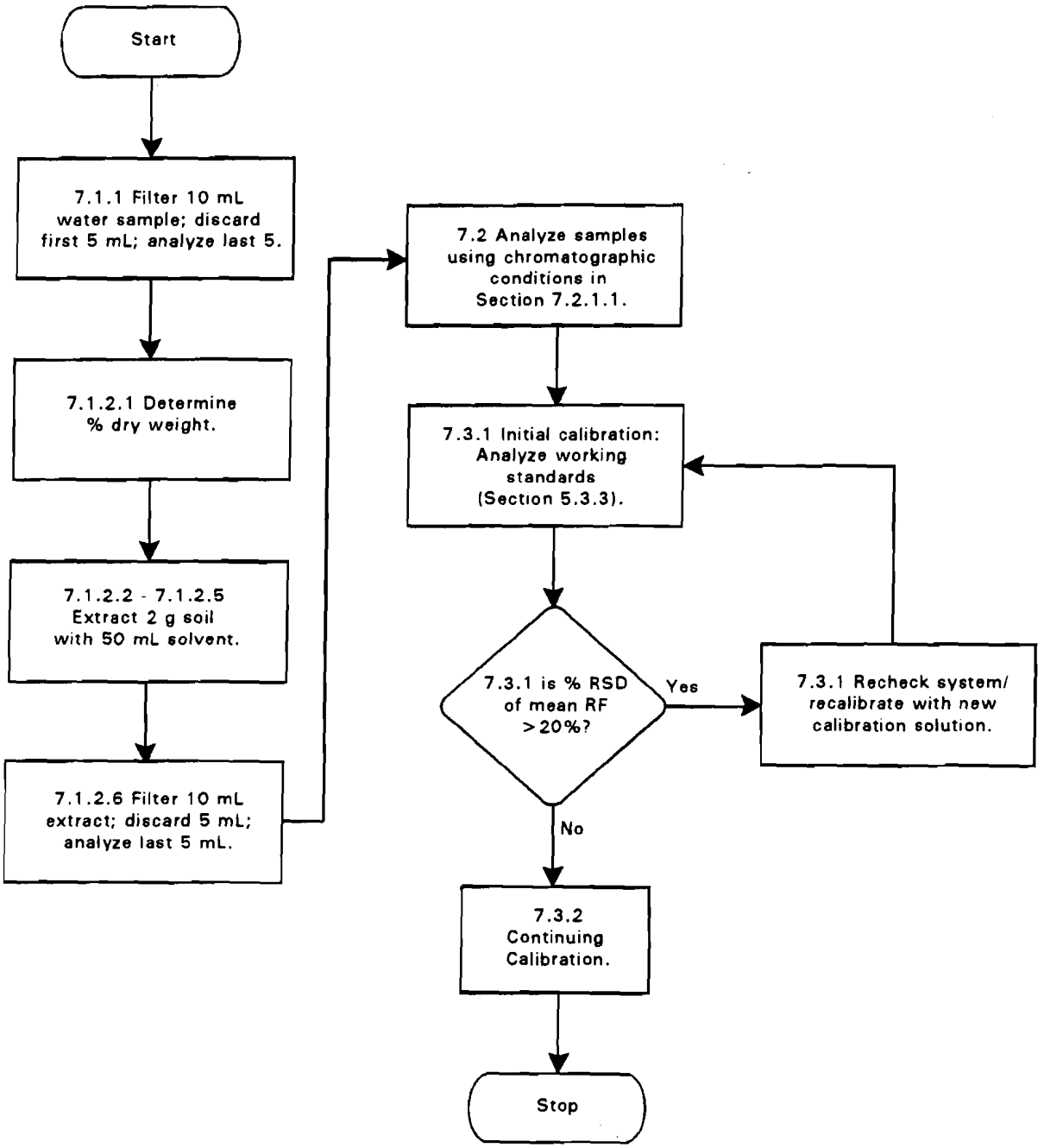
TABLE 1.
METHOD PERFORMANCE, WATER MATRIX

Spike Conc. (µg/L)	Replicate	Avg % Recovery Day 1	Day 2	Day 3	Day 4	Average % Recovery
0.00	Replicate 1	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
	Replicate 2	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
7.25	Replicate 1	8.9	7.8	7.4	9.4	
	% Recovery	122	108	102	130	116
	Replicate 2	6.6	9.9	8.5	6.7	
	% Recovery	91	137	117	92	109
14.5	Replicate 1	14.6	14.6	13.8	14.6	
	% Recovery	101	101	95	101	99
	Replicate 2	14.8	14.1	14.1	15.2	
	% Recovery	102	97	98	105	100
29	Replicate 1	31.8	30.0	30.8	28.7	
	% Recovery	110	103	106	99	105
	Replicate 2	29.5	29.7	30.4	30.7	
	% Recovery	102	102	105	106	104
72.5	Replicate 1	71.1	73.6	75.7	73.9	
	% Recovery	98	102	104	102	101
	Replicate 2	71.2	71.3	70.7	71.6	
	% Recovery	98	98	98	99	98
145	Replicate 1	140.6	143.8	144.7	142.1	
	% Recovery	97	99	100	98	98
	Replicate 2	138.5	140.8	140.9	136.9	
	% Recovery	96	97	97	94	96
290	Replicate 1	289.4	288.5	291.0	289.8	
	% Recovery	100	99	100	100	100
	Replicate 2	282.0	284.2	281.9	282.5	
	% Recovery	97	98	97	97	97
725	Replicate 1	737.6	707.2	714.3	722.0	
	% Recovery	102	98	99	100	99
	Replicate 2	700.2	695.8	714.2	716.3	
	% Recovery	97	96	99	99	97
OVERALL						102

TABLE 2
METHOD PERFORMANCE, SOIL MATRIX

Spike Conc. (µg/L)	Replicate	Avg % Recovery Day 1	Day 2	Day 3	Day 4	Average % Recovery
0.00	Replicate 1	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
	Replicate 2	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
1.28	Replicate 1	0.6	0.9	0.6	1.0	
	% Recovery	49	73	48	74	61
	Replicate 2	1.2	0.7	0.8	0.7	
	% Recovery	92	56	63	56	67
2.56	Replicate 1	1.4	1.5	1.6	1.6	
	% Recovery	56	58	61	61	59
	Replicate 2	1.5	2.0	1.4	1.3	
	% Recovery	59	79	56	50	61
5.12	Replicate 1	2.9	3.0	2.9	2.9	
	% Recovery	57	58	56	56	57
	Replicate 2	3.0	3.0	3.5	3.1	
	% Recovery	58	59	69	60	61
12.8	Replicate 1	7.8	7.6	7.8	8.1	
	% Recovery	61	59	61	63	61
	Replicate 2	8.0	8.4	7.7	8.2	
	% Recovery	62	66	60	64	63
25.6	Replicate 1	17.2	16.7	17.4	17.3	
	% Recovery	67	65	68	68	67
	Replicate 2	16.7	16.8	17.6	17.2	
	% Recovery	65	66	69	67	67
OVERALL						62

METHOD 8331
TETRAZENE BY REVERSE PHASE
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)



4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.4 FOURIER TRANSFORM INFRARED METHODS

The following method is included in this section:

Method 8410: Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column

METHOD 8410

GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED (GC/FT-IR) SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN

1.0 SCOPE AND APPLICATION

1.1 This method covers the automated identification, or compound class assignment of unidentifiable compounds, of solvent extractable semivolatile organic compounds which are amenable to gas chromatography, by GC/FT-IR. GC/FT-IR can be a useful complement to GC/MS analysis (Method 8270). It is particularly well suited for the identification of specific isomers that are not differentiated using GC/MS. Compound class assignments are made using infrared group absorption frequencies. The presence of an infrared band in the appropriate group frequency region may be taken as evidence of the possible presence of a particular compound class, while its absence may be construed as evidence that the compound class in question is not present. This evidence will be further strengthened by the presence of confirmatory group frequency bands. Identification limits of the following compounds have been demonstrated by this method.

Compound Name	CAS No.[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benzo(a)anthracene	56-55-3
Benzo(a)pyrene	50-32-8
Benzoic acid	65-85-0
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	39638-32-9
Bis(2-ethylhexyl) phthalate	117-81-7
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
4-Chloroaniline	106-47-8
4-Chloro-3-methylphenol	59-50-7
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
4-Chlorophenyl phenyl ether	7005-72-3
Chrysene	218-01-9
Dibenzofuran	132-64-9
Di-n-butyl phthalate	84-74-2
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
2,4-Dichlorophenol	120-83-2

Compound Name	CAS No.[a]
Dimethyl phthalate	131-11-3
Diethyl phthalate	84-66-2
4,6-Dinitro-2-methylphenol	534-52-1
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Di-n-octyl phthalate	117-84-0
Di-n-propyl phthalate	131-16-8
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
1,3-Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Isophorone	78-59-1
2-Methylnaphthalene	91-57-6
2-Methylphenol	95-48-7
4-Methylphenol	106-44-5
Naphthalene	91-20-3
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-9
N-Nitroso-di-n-propylamine	621-64-7
Pentachlorophenol	87-86-5
Phenanthrene	85-01-8
Phenol	108-95-2
Pyrene	129-00-0
1,2,4-Trichlorobenzene	120-82-1
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2

[a] Chemical Abstract Services Registry Number.

1.2 This method is applicable to the determination of most extractable, semivolatile-organic compounds in wastewater, soils and sediments, and solid wastes. Benzidine can be subject to losses during solvent concentration and GC analysis; α-BHC, β-BHC, Endosulfan I and II, and Endrin are subject to decomposition under the alkaline conditions of the extraction step; Endrin is subject to decomposition during GC analysis; and Hexachlorocyclopentadiene and N-Nitrosodiphenylamine may decompose during extraction and GC analysis. Other extraction and/or instrumentation procedures should be considered for unstable analytes.

1.3 The identification limit of this method may depend strongly upon the level and type of gas chromatographable (GC) semivolatile extractants. The values listed in Tables 1 and 2 represent the minimum quantities of semivolatile organic compounds which have been identified by the specified GC/FT-IR system, using this method and under routine environmental analysis conditions. Capillary GC/FT-IR wastewater identification limits of 25 µg/L may be achieved for weak infrared absorbers with this method, while the corresponding identification limits for strong infrared absorbers is 2 µg/L. Identification limits for other sample matrices can be calculated from the wastewater values after choice of the proper sample workup procedure (see Sec. 7.1).

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and uses FT-IR for detection and quantitation of the target analytes.

3.0 INTERFERENCES

3.1 Glassware and other sample processing hardware must be thoroughly cleaned to prevent contamination and misinterpretation. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents or purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interference will vary considerably from source to source, depending upon the diversity of the residual waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup to isolate the analytes of interest from interferences in order to achieve maximum sensitivity.

3.3 4-Chlorophenol and 2-nitrophenol are subject to interference from co-eluting compounds.

3.4 Clean all glassware as soon as possible after use by rinsing with the last solvent used. Glassware should be sealed/stored in a clean environment immediately after drying to prevent any accumulation of dust or other contaminants.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatographic/Fourier Transform Infrared Spectrometric Equipment

4.1.1 Fourier Transform-Infrared Spectrometer - A spectrometer capable of collecting at least one scan set per second at 8 cm^{-1} resolution is required. In general, a spectrometer purchased after 1985, or retrofitted to meet post-1985 FT-IR improvements, will be necessary to

meet the detection limits of this protocol. A state-of-the-art A/D converter is required, since it has been shown that the signal-to-noise ratio of single beam GC/FT-IR systems is A/D converter limited.

4.1.2 GC/FT-IR Interface - The interface should be lightpipe volume-optimized for the selected chromatographic conditions (lightpipe volume of 100-200 μL for capillary columns). The shortest possible inert transfer line (preferably fused silica) should be used to interface the end of the chromatographic column to the lightpipe. If fused silica capillary columns are employed, the end of the GC column can serve as the transfer line if it is adequately heated. It has been demonstrated that the optimum lightpipe volume is equal to the full width at half height of the GC eluate peak.

4.1.3 Capillary Column - A fused silica DB-5 30 m x 0.32 mm capillary column with 1.0 μm film thickness (or equivalent).

4.1.4 Data Acquisition - A computer system dedicated to the GC/FT-IR system to allow the continuous acquisition of scan sets for a full chromatographic run. Peripheral data storage systems should be available (magnetic tape and/or disk) for the storage of all acquired data. Software should be available to allow the acquisition and storage of every scan set to locate the file numbers and transform high S/N scan sets, and to provide a real time reconstructed chromatogram.

4.1.5 Detector - A cryoscopic, medium-band HgCdTe (MCT) detector with the smallest practical focal area. Typical narrow-band MCT detectors operate from 3800-800 cm^{-1}, but medium-band MCT detectors can reach 650 cm^{-1}. A 750 cm^{-1} cutoff (or lower) is desirable since it allows the detection of typical carbon-chlorine stretch and aromatic out-of-plane carbon-hydrogen vibrations of environmentally important organo-chlorine and polynuclear aromatic compounds. The MCT detector sensitivity $(D)^*$ should be $\geq 1 \times 10^{10}$ cm.

4.1.6 Lightpipe - Constructed of inert materials, gold coated, and volume-optimized for the desired chromatographic conditions (see Sec. 7.3).

4.1.7 Gas Chromatograph - The FT-IR spectrometer should be interfaced to a temperature programmable gas chromatograph equipped with a Grob-type (or equivalent) purged splitless injection system suitable for capillary glass columns or an on-column injector system.

A short, inert transfer line should interface the gas chromatograph to the FT-IR lightpipe and, if applicable, to the GC detector. Fused silica GC columns may be directly interfaced to the lightpipe inlet and outlet.

4.2 Dry Purge Gas - If the spectrometer is the purge-type, provisions should be made to provide a suitable continuous source of dry purge-gas to the FT-IR spectrometer.

4.3 Dry Carrier Gas - The carrier gas should be passed through an efficient cartridge-type drier.

4.4 Syringes - 1-μL, 10-μL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Acetone, CH_3COCH_3 - Pesticide quality, or equivalent.

5.3.2 Methylene chloride, CH_2Cl_2 - Pesticide quality, or equivalent.

5.4 Stock Standard Solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as a certified solution.

5.4.1 Prepare stock standard solutions by accurately weighing 0.1000 $\pm$ 0.0010 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after 6 months or sooner if comparison with quality control reference samples indicates a problem.

5.5 Calibration Standards and Internal Standards - For use in situations where GC/FT-IR will be used for primary quantitation of analytes rather than confirmation of GC/MS identification.

5.5.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be

prepared at concentrations that will completely bracket the working range of the chromatographic system (at least one order of magnitude is suggested).

5.5.2 Prepare internal standard solutions. Suggested internal standards are 1-Fluoronaphthalene, Terphenyl, 2-Chlorophenol, Phenol, Bis(2-chloroethoxy)methane, 2,4-Dichlorophenol, Phenanthrene, Anthracene, and Butyl benzyl phthalate. Determine the internal standard concentration levels from the minimum identifiable quantities. See Tables 1 and 2.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample Preparation - Samples must be prepared by one of the following methods prior to GC/FT-IR analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3541, 3550
Waste	3540, 3541, 3550, 3580

7.2 Extracts may be cleaned up by Method 3640, Gel-Permeation Cleanup.

7.3 Initial Calibration - Recommended GC/FT-IR conditions:

Scan time:	At least 2 scan/sec.
Initial column temperature and hold time:	40°C for 1 minute.
Column temperature program:	40-280°C at 10°C/min.
Final column temperature hold:	280°C.
Injector temperature:	280-300°C.
Transfer line temperature:	270°C.
Lightpipe:	280°C.
Injector:	Grob-type, splitless or on-column.
Sample volume:	2-3 µL.
Carrier gas:	Dry helium at about 1 mL/min.

7.4 With an oscilloscope, check the detector centerburst intensity versus the manufacturer's specifications. Increase the source voltage, if necessary, to meet these specifications. For reference purposes, laboratories should prepare a plot of time versus detector voltage over at least a 5 day period.

7.5 Capillary Column Interface Sensitivity Test - Install a 30 m x 0.32 mm fused silica capillary column coated with 1.0 µm of DB-5 (or equivalent). Set the lightpipe and transfer lines at 280°C, the injector at 225°C and the GC detector at 280°C (if used). Under splitless Grob-type or on-

column injection conditions, inject 25 ng of nitrobenzene, dissolved in 1 μL of methylene chloride. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).

7.6 Interferometer - If the interferometer is air-driven, adjust the interferometer drive air pressure to manufacturer's specifications.

7.7 MCT Detector Check - If the centerburst intensity is 75 percent or less of the mean intensity of the plot maximum obtained by the procedure of Sec. 7.4, install a new source and check the MCT centerburst with an oscilloscope versus the manufacturer's specifications (if available). Allow at least five hours of new source operation before data acquisition.

7.8 Frequency Calibration - At the present time, no consensus exists within the spectroscopic community on a suitable frequency reference standard for vapor-phase FT-IR. One reviewer has suggested the use of indene as an on-the-fly standard.

7.9 Minimum Identifiable Quantities - Using the GC/FT-IR operating parameters specified in Sec. 7.3, determine the minimum identifiable quantities for the compounds of interest.

7.9.1 Prepare a plot of lightpipe temperature versus MCT centerburst intensity (in volts or other vertical height units). This plot should span the temperature range between ambient and the lightpipe thermal limit in increments of about 20°C. Use this plot for daily QA/QC (see Sec. 8.4). Note that modern GC/FT-IR interfaces (1985 and later) may have eliminated most of this temperature effect.

7.10 GC/FT-IR Extract Analysis

7.10.1 Analysis - Analyze the dried methylene chloride extract using the chromatographic conditions specified in Sec. 7.3 for capillary column interfaces.

7.10.2 GC/FT-IR Identification - Visually compare the analyte infrared (IR) spectrum versus the search library spectrum of the most promising on-line library search hits. Report, as identified, those analytes with IR frequencies for the five (maximum number) most intense IR bands ($S/N \geq 5$) which are within $\pm$ 5.0 cm^{-1} of the corresponding bands in the library spectrum. Choose IR bands which are sharp and well resolved. The software used to locate spectral peaks should employ the peak "center of gravity" technique. In addition, the IR frequencies of the analyte and library spectra should be determined with the same computer software.

7.10.3 Retention Time Confirmation - After visual comparison of the analyte and library spectrum as described in Sec. 7.10.2, compare the relative retention times (RRT) of the analyte and an authentic standard of the most promising library search hit. The standard and analyte RRT should agree within $\pm$ 0.01 RRT units when both are determined at the same chromatographic conditions.

7.10.4 Compound Class or Functionality Assignment - If the analyte cannot be unequivocally identified, report its compound class or functionality. See Table 3 for gas-phase group frequencies to be used as an aid for compound class assignment. It should be noted that FT-IR gas-phase group stretching frequencies are 0-30 cm^{-1} higher in frequency than those of the condensed phase.

7.10.5 Quantitation - This protocol can be used to confirm GC/MS identifications, with subsequent quantitation. Two FT-IR quantitation and a supplemental GC detector technique are also provided.

7.10.5.1 Integrated Absorbance Technique - After analyte identification, construct a standard calibration curve of concentration versus integrated infrared absorbance. For this purpose, choose for integration only those FT-IR scans which are at or above the peak half-height. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration.

7.10.5.2 Maximum Absorbance Infrared Band Technique - Following analyte identification, construct a standard calibration curve of concentration versus maximum infrared band intensity. For this purpose, choose an intense, symmetrical and well resolved IR absorbance band.

(Note that IR transmission is not proportional to concentration). Select the FT-IR scan with the highest absorbance to plot against concentration. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses. It is more sensitive than the integrated absorbance technique.

7.10.5.3 Supplemental GC Detector Technique - If a GC detector is used in tandem with the FT-IR detector, the following technique may be used: following analyte identification, construct a standard calibration curve of concentration versus integrated peak area. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 One Hundred Percent Line Test - Set the GC/FT-IR operating conditions to those employed for the Sensitivity Test (see Sec. 7.5). Collect 16 scans over the entire detector spectral range. Plot the test and measure the peak-to-peak

noise between 1800 and 2000 cm^{-1}. This noise should be $\leq$ 0.15%. Store this plot for future reference.

8.3 Single Beam Test - With the GC/FT-IR at analysis conditions, collect 16 scans in the single beam mode. Plot the co-added file and compare with a subsequent file acquired in the same fashion several minutes later. Note if the spectrometer is at purge equilibrium. Also check the plot for signs of deterioration of the lightpipe potassium bromide windows. Store this plot for future reference.

8.4 Align Test - With the lightpipe and MCT detector at thermal equilibrium, check the intensity of the centerburst versus the signal temperature calibration curve. Signal intensity deviation from the predicted intensity may mean thermal equilibrium has not yet been achieved, loss of detector coolant, decrease in source output, or a loss in signal throughput resulting from lightpipe deterioration.

8.5 Mirror Alignment - Adjust the interferometer mirrors to attain the most intense signal. Data collection should not be initiated until the interferogram is stable. If necessary, align the mirrors prior to each GC/FT-IR run.

8.6 Lightpipe - The lightpipe and lightpipe windows should be protected from moisture and other corrosive substances at all times. For this purpose, maintain the lightpipe temperature above the maximum GC program temperature but below its thermal degradation limit. When not in use, maintain the lightpipe temperature slightly above ambient. At all times, maintain a flow of dry, inert, carrier gas through the lightpipe.

8.7 Beamsplitter - If the spectrometer is thermostated, maintain the beamsplitter at a temperature slightly above ambient at all times. If the spectrometer is not thermostated, minimize exposure of the beamsplitter to atmospheric water vapor.

9.0 METHOD PERFORMANCE

9.1 Method 8410 has been in use at the U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory for more than two years. Portions of it have been reviewed by key members of the FT-IR spectroscopic community (9). Side-by-side comparisons with GC/MS sample analyses indicate similar demands upon analytical personnel for the two techniques. Extracts previously subjected to GC/MS analysis are generally compatible with GC/FT-IR. However, it should be kept in mind that lightpipe windows are typically water soluble. Thus, extracts must be vigorously dried prior to analysis.

9.2 Table 4 provides performance data for this method.

10.0 REFERENCES

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TABLE 1.
FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED IDENTIFICATION LIMITS FOR BASE/NEUTRAL EXTRACTABLES

Compound	Identification Limit ng injected[a]	Identification Limit µg/L[b]	νmax, cm^{-1}[c]
Acenaphthene	40(25)	20(12.5)	799
Acenaphthylene	50(50)	25(25)	799
Anthracene	40(50)	20(25)	874
Benzo(a)anthracene	(50)	(25)	745
Benzo(a)pyrene	(100)	(50)	756
Bis(2-chloroethyl) ether	70(10)	35(5)	1115
Bis(2-chloroethoxy)methane	50(10)	25(5)	1084
Bis(2-chloroisopropyl) ether	50(10)	25(5)	1088
Butyl benzyl phthalate	25(10)	12.5(5)	1748
4-Bromophenyl phenyl ether	40(5)	20(2.5)	1238
2-Chloronaphthalene	110	55	851
4-Chloroaniline	40	20	1543
4-Chlorophenyl phenyl ether	20(5)	10(2.5)	1242
Chrysene	(100)	(50)	757
Di-n-butyl phthalate	20(5)	10(2.5)	1748
Dibenzofuran	40	20	1192
Diethyl phthalate	20(5)	10(2.5)	1748
Dimethyl phthalate	20(5)	10(2.5)	1751
Di-n-octyl phthalate	25(10)	12.5(5)	1748
Di-n-propyl phthalate	25(5)	12.5(2.5)	1748
1,2-Dichlorobenzene	50	25	1458
1,3-Dichlorobenzene	50	25	779
1,4-Dichlorobenzene	50	25	1474
2,4-Dinitrotoluene	20	10	1547
2,6-Dinitrotoluene	20	10	1551
Bis-(2-ethylhexyl) phthalate	25(10)	12.5(5)	1748
Fluoranthene	100(50)	50(25)	773
Fluorene	40(50)	20(25)	737
Hexachlorobenzene	40	20	1346
Hexachlorocyclopentadiene	120	60	814
Hexachloroethane	50	25	783
1,3-Hexachlorobutadiene	120	60	853
Isophorone	40	20	1690
2-Methylnaphthalene	110	55	3069
Naphthalene	40(25)	20(12.5)	779
Nitrobenzene	25	12.5	1539
N-Nitrosodimethylamine	20(5)	10(2.5)	1483
N-Nitrosodi-n-propylamine	50(5)	25(2.5)	1485
N-Nitrosodiphenylamine[d]	40	20	1501
2-Nitroaniline	40	20	1564
3-Nitroaniline	40	20	1583

TABLE 1.
(Continued)

Compound	Identification Limit ng injected[a]	Identification Limit µg/L[b]	νmax, cm^{-1}[c]
4-Nitroaniline	40	20	1362
Phenanthrene	50(50)	25(25)	729
Pyrene	100(50)	50(25)	820
1,2,4-Trichlorobenzene	50(25)	25(12.5)	750

[a] Determined using on-column injection and the conditions of Sec. 7.3. A medium band HgCdTe detector [3800-700 cm^{-1}; D*value (λpeak 1000 Hz, 1) 4.5 x 10^{10} cm $Hz^{1/2}W^{-1}$] type with a 0.25 mm^2 focal chip was used. The GC/FT-IR system is a 1976 retrofitted model. Values in parentheses were determined with a new (1986) GC/FT-IR system. A narrow band HgCdTe detector [3800-750cm^{-1}; D*value (λpeak 1000 Hz, 1) 4 x 10^{10} cm $Hz^{1/2}W^{-1}$] was used. Chromatographic conditions are those of Sec. 7.3.

[b] Based on a 2 µL injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 mL. Values in parentheses were determined with a new (1986) GC/FT-IR system. A narrow band HgCdTe detector [3800-750cm^{-1}; D*value (λpeak 1000 Hz, 1) 4 x 10^{10} cm $Hz^{1/2}W^{-1}$] was used. Chromatographic conditions are those of Sec. 7.3.

[c] Most intense IR peak and suggested quantitation peak.

[d] Detected as diphenylamine.

TABLE 2.
FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR ACIDIC EXTRACTABLES

Compound	Identification Limit		
	ng injected[a]	μg/L[b]	νmax, cm^{-1}[c]
Benzoic acid	70	35	1751
2-Chlorophenol	50	25	1485
4-Chlorophenol[d]	100	50	1500
4-Chloro-3-methylphenol	25	12.5	1177
2-Methylphenol	50	25	748
4-Methylphenol	50	25	1177
2,4-Dichlorophenol	50	25	1481
2,4-Dinitrophenol	60	30	1346
4,6-Dinitro-2-methylphenol	60	30	1346
2-Nitrophenol[d]	40	20	1335
4-Nitrophenol	50	25	1350
Pentachlorophenol	50	25	1381
Phenol	70	35	1184
2,4,6-Trichlorophenol	120	60	1470
2,4,5-Trichlorophenol	120	60	1458

[a] Operating conditions are the same as those cited in Sec. 7.3.

[b] Based on a 2 μL injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 mL.

[c] Most intense IR peak and suggested quantitation peak.

[d] Subject to interference from co-eluting compounds.

TABLE 3.
GAS-PHASE GROUP FREQUENCIES

Functionality	Class	Number of Compounds	Frequency Range, νcm^{-1}
Ether	Aryl, Alkyl	14	1215-1275
	Benzyl, Alkyl	3	1103-1117
	Diaryl	5	1238-1250
	Dialkyl	12	1084-1130
	Alkyl, Vinyl	3	1204-1207
			1128-1142
Ester	Unsubstituted Aliphatic	29	1748-1761
	Aromatic	11	1703-1759
	Monosubstituted Acetate	34	1753-1788
Nitro	Aliphatic	5	1566-1594
			1548-1589
			1377-1408
			1327-1381
	Aromatic	18	1535-1566
			1335-1358
Nitrile	Aliphatic	9	2240-2265
	Aromatic	9	2234-2245
Ketone	Aliphatic (acyclic)	13	1726-1732
	(α,β unsaturated)	2	1638-1699
	Aromatic	16	1701-1722
Amide	Substituted Acetamides	8	1710-1724
Alkyne	Aliphatic	8	3323-3329
Acid	Aliphatic	24	3574-3580
		22	1770-1782
	Dimerized-Aliphatic	2	3586-3595
	Aromatic	10	3574-3586
		10	1757-1774
Phenol	1,4-Disubstituted	15	3645-3657
		15	1233-1269
		15	1171-1190
	1,3-Disubstituted	10	3643-3655
		10	1256-1315
		10	1157-1198
	1,2-Disubstituted	6	3582-3595
			1255-1274

(continued)

TABLE 3.
(Continued)

Functionality	Class	Number of Compounds	Frequency Range, νcm^{-1}
Alcohol	Primary Aliphatic	20	3630-3680
		11	1206-1270
		16	1026-1094
	Secondary Aliphatic	17	3604-3665
		10	1231-1270
	Tertiary Aliphatic	10	3640-3670
		6	1213-1245
Amine	Primary Aromatic	15	3480-3532
	Secondary Aromatic	5	3387-3480
	Aliphatic	10	760- 785
Alkane		14	2930-2970
			2851-2884
			1450-1475
			1355-1389
Aldehyde	Aromatic	12	1703-1749
		12	2820-2866
		12	2720-2760
	Aliphatic	6	1742-1744
		6	2802-2877
		6	2698-2712
Benzene	Monosubstituted	7	1707-1737
		24	1582-1630
		24	1470-1510
		11	831- 893
		23	735- 790
		25	675- 698

TABLE 4. FUSED SILICA CAPILLARY COLUMN GC/FT-IR QUANTITATION RESULTS

Compound	Concentration Range, and Identification Limit, ng[a]	Maximum Absorbance[b] Correlation Coefficient[d]	Integrated Absorbance[c] Correlation Coefficient[d]
Acenaphthene	25-250	0.9995	0.9985
Acenaphthylene	25-250	0.9959	0.9985
Anthracene	50-250	0.9969	0.9971
Benzo(a)anthracene	50-250	0.9918	0.9921
Benzoic acid	50-250	0.9864	0.9892
Benzo(a)pyrene	100-250	0.9966	0.9074
Bis(2-chloroethoxy)methane	25-250	0.9992	0.9991
Bis(2-chloroethyl) ether	25-250	0.9955	0.9992
Bis(2-chloroisopropyl) ether	50-250	0.9981	0.9998
4-Bromophenyl phenyl ether	25-250	0.9995	0.9996
Butyl benzyl phthalate	25-250	0.9999	0.9994
4-Chloroaniline	25-250	0.9991	0.9965
4-Chloro-3-methylphenol	25-250	0.9975	0.9946
2-Chloronaphthalene	100-250	0.9897	0.9988
2-Chlorophenol	25-250	0.9976	0.9965
4-Chlorophenol[e]			
4-Chlorophenyl phenyl ether	25-250	0.9999	0.9997
Chrysene	100-250	0.9985	0.9984
Dibenzofuran	25-250	0.9697	0.8579
Di-n-butyl phthalate	25-250	0.9998	0.9996
1,2-Dichlorobenzene	25-250	0.9937	0.9947
1,3-Dichlorobenzene	25-250	0.9985	0.9950
1,4-Dichlorobenzene	25-250	0.9994	0.9994
2,4-Dichlorophenol	25-250	0.9964	0.9969
Dimethyl phthalate	25-250	0.9998	0.9996
Dimethyl phthalate	25-250	0.9998	0.9997
Dinitro-2-methylphenol	50-250	0.9936	0.9967
2,4-Dinitrophenol	50-250	0.9920	0.9916
2,4-Dinitrotoluene	25-250	0.9966	0.9928
2,6-Dinitrotoluene	25-250	0.9947	0.9966
Di-n-octyl phthalate	25-250	0.9983	0.9991
Bis(2-ethylhexyl) phthalate	25-250	0.9991	0.9993
Fluoranthene	25-250	0.9983	0.9966
Fluorene	25-250	0.9987	0.9989
Hexachlorobenzene	50-250	0.9981	0.9995
1,3-Hexachlorobutadiene	50-250	0.9960	0.9979
Hexachlorocyclopentadiene	100-250	0.9862	0.9845
Hexachloroethane	25-250	0.9986	0.9992
Isophorone	25-250	0.9984	0.9990
2-Methylnaphthalene	50-250	0.9981	0.9950

(continued)

TABLE 4. (Continued)

Compound	Concentration Range, and Identification Limit, ng[a]	Maximum Absorbance[b] Correlation Coefficient[d]	Integrated Absorbance[c] Correlation Coefficient[d]
2-Methylphenol	25-250	0.9972	0.9964
4-Methylphenol	25-250	0.9972	0.9959
Naphthalene	25-250	0.9956	0.9954
2-Nitroaniline	25-250	0.9996	0.9994
3-Nitroaniline	25-250	0.9985	0.9990
4-Nitroaniline	25-250	0.9936	0.9992
Nitrobenzene	25-250	0.9997	0.9979
2-Nitrophenol[e]			
4-Nitrophenol	50-250	0.9951	0.9953
N-Nitrosodimethylamine	25-250	0.9982	0.9993
N-Nitrosodiphenylamine	25-250	0.9994	0.9971
N-Nitrosodi-n-propylamine	25-250	0.9991	0.9995
Pentachlorophenol	50-250	0.9859	0.9883
Phenanthrene	25-250	0.9941	0.9989
Phenol	25-250	0.9978	0.9966
Pyrene	50-250	0.9971	0.9977
1,2,4-Trichlorobenzene	50-250	0.9969	0.991
2,4,5-Trichlorophenol	25-250	0.9952	0.9966
2,4,6-Trichlorophenol	25-250	0.9969	0.9965

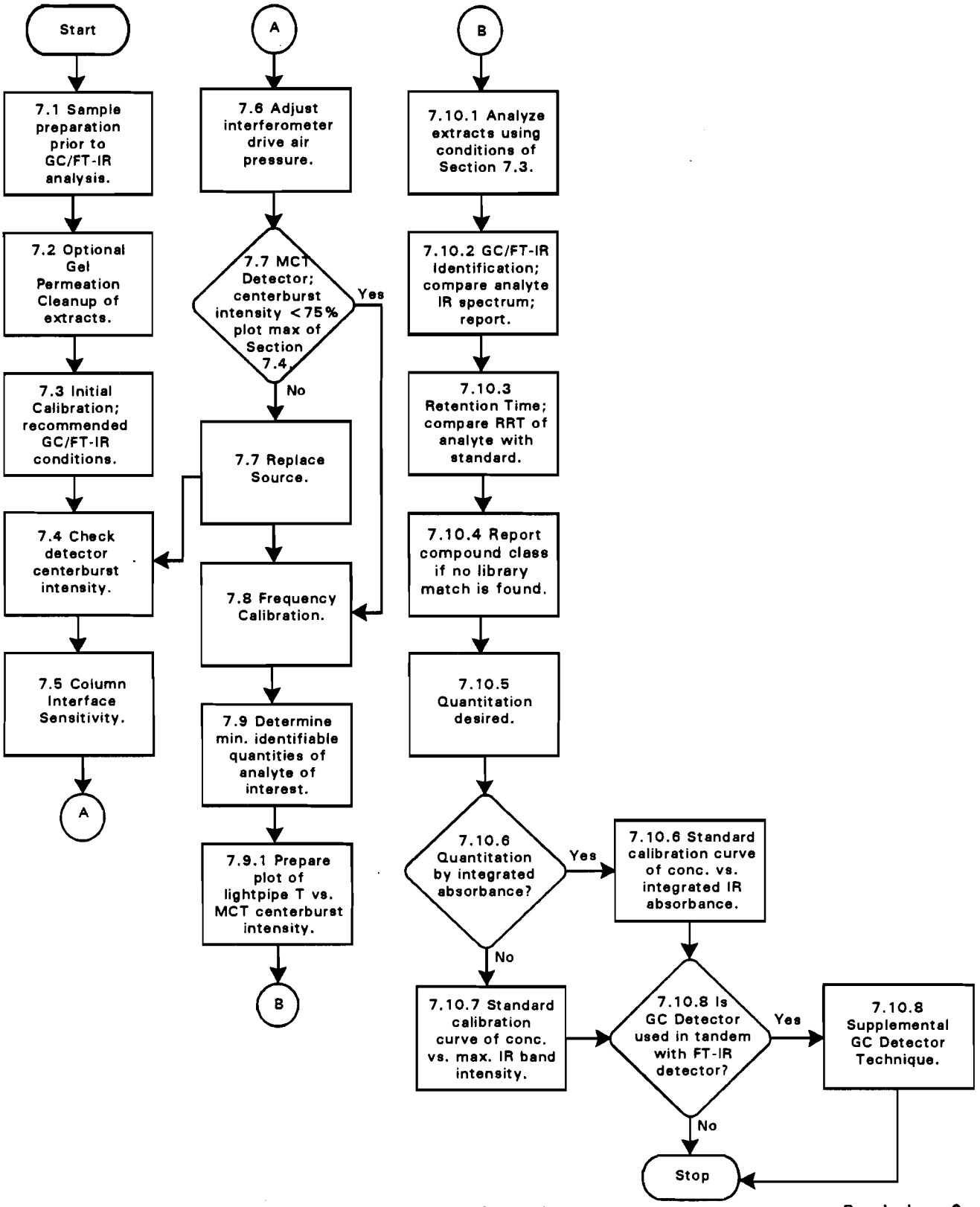
[a] Lower end of range is at or near the identification limit.

[b] FT-IR scan with highest absorbance plotted against concentration.

[c] Integrated absorbance of combined FT-IR scans which occur at or above the chromatogram peak half-height.

[d] Regression analysis carried out at four concentration levels. Each level analyzed in duplicate. Chromatographic conditions are stated in Sec. 7.3.

[e] Subject to interference from co-eluting compounds.


Start
7.1 Sample preparation prior to GC/FT-IR analysis.
7.2 Optional Gel Permeation Cleanup of extracts.
7.3 Initial Calibration; recommended GC/FT-IR conditions.
7.4 Check detector centerburst intensity.
7.5 Column Interface Sensitivity.
A
A
7.6 Adjust interferometer drive air pressure.
7.7 MCT Detector; centerburst intensity <75% plot max of Section 7.4.
Yes
No
7.7 Replace Source.
7.8 Frequency Calibration.
7.9 Determine min. identifiable quantities of analyte of interest.
7.9.1 Prepare plot of lightpipe T vs. MCT centerburst intensity.
B
B
7.10.1 Analyze extracts using conditions of Section 7.3.
7.10.2 GC/FT-IR identification; compare analyte IR spectrum; report.
7.10.3 Retention Time; compare RRT of analyte with standard.
7.10.4 Report compound class if no library match is found.
7.10.5 Quantitation desired.
7.10.6 Quantitation by integrated absorbance?
Yes
7.10.6 Standard calibration curve of conc. vs. integrated IR absorbance.
No
7.10.7 Standard calibration curve of conc. vs. max. IR band intensity.
7.10.8 Is GC Detector used in tandem with FT-IR detector?
Yes
7.10.8 Supplemental GC Detector Technique.
No
Stop

4.4 MISCELLANEOUS SCREENING METHODS

The following methods are included in this section:

Method 3810:	Headspace
Method 3820:	Hexadecane Extraction and Screening of Purgeable Organics
Method 4010:	Screening for Pentachlorophenol by Immunoassay
Method 8275:	Thermal Chromatography/Mass Spectrometry (TC/MS) for Screening Semivolatile Organic Compounds

METHOD 3810

HEADSPACE

1.0 SCOPE AND APPLICATION

1.1 Method 3810 was formerly Method 5020 in the second edition of this manual.

1.2 Method 3810 is a static headspace technique for extracting volatile organic compounds from samples. It is a simple method that allows large numbers of samples to be screened in a relatively short period of time. It is ideal for screening samples prior to using the purge-and-trap method. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The method works best for compounds with boiling points of less than 125°C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.3 Due to the variability of this method, this procedure is recommended for use only as a screening procedure for other, more accurate determinative methods (Methods 8010, 8015, 8020, 8030, and 8240).

2.0 SUMMARY OF METHOD

2.1 The sample is collected in sealed glass containers and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gas-tight syringe for screening analysis using the conditions specified in one of the GC or GC/MS determinative methods (8010, 8015, 8020, 8030, or 8240).

3.0 INTERFERENCES

3.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 105°C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific determinative method for appropriate apparatus and materials.

4.2 Vials: 125-mL Hypo-Vials (Pierce Chemical Co., #12995, or equivalent), four each.

4.3 Septa: Tuf-Bond (Pierce #12720 or equivalent).

4.4 Seals: Aluminum (Pierce #13214l or equivalent).

4.5 Crimper: Hand (Pierce #13212 or equivalent).

4.6 Syringe: 5-mL, gas-tight with shutoff valve and chromatographic needles.

4.7 Microsyringe: 250- or 500-uL.

4.8 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

5.0 REAGENTS

5.1 Refer to the specific determinative method and Method 8000 for preparation of calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Gas chromatographic conditions and Calibration: Refer to the specific determinative method for GC operating conditions and to Method 8000, Section 7.4, for calibration procedures.

7.2 Sample preparation:

7.2.1 Place 10.0 g of a well-mixed waste sample into each of two separate 125-mL septum-seal vials.

7.2.2 Dose one sample vial through the septum with 200 uL of a 50 ng/uL calibration standard containing the compounds of interest. Label this "1-ppm spike."

7.2.3 Dose a separate (empty) 125-mL septum seal vial with 200 uL of the same 50 ng/uL calibration standard. Label this "1-ppm standard."

7.2.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90°C water bath for 1 hr. Store the remaining sample vial at 4.0°C for possible future analysis.

7.3 Sample analysis:

7.3.1 While maintaining the vials at 90°C, withdraw 2 mL of the headspace gas with a gas-tight syringe and analyze by direct injection into a GC. The GC should be operated using the same GC conditions listed in the method being screened (8010, 8015, 8020, 8030, or 8240).

7.3.2 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2 times the background. Record retention times (RT) and peak areas of compounds of interest.

7.3.3 Analyze the 1-ppm spiked sample in the same manner. Record RTs and peak areas.

7.3.4 Analyze the undosed sample as in Paragraph 7.3.3.

7.3.5 Use the results obtained to determine if the sample requires dilution or methanolic extraction as indicated in Method 5030.

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 ug/g of sample, then the sensitivity of the instrument should be increased.

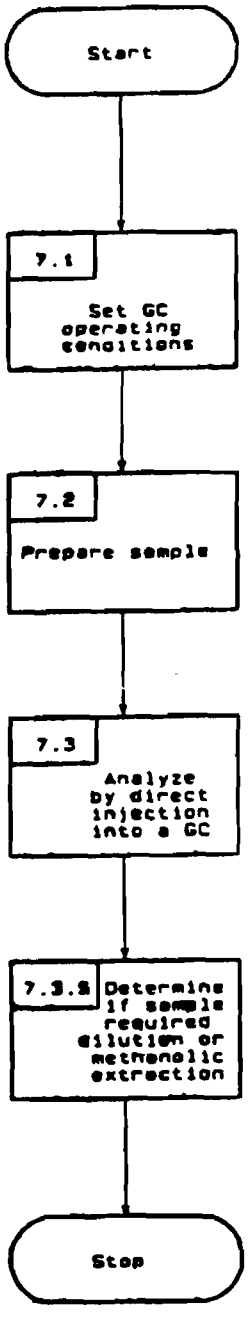
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Hachenberg, H. and A. Schmidt, Gas Chromatographic Headspace Analysis, Philadelphia: Hayden & Sons Inc., 1979.

2. Friant, S.L. and I.H. Suffet, "Interactive Effects of Temperature, Salt Concentration and pH on Headspace Analysis for Isolating Volatile Trace Organics in Aqueous Environmental Samples," Anal. Chem. 51, 2167-2172, 1979.


Start
7.1
Set GC operating conditions
7.2
Prepare sample
7.3
Analyze by direct injection into a GC
7.3.5
Determine if sample required dilution or methanolic extraction
Stop

METHOD 3820

HEXADECANE EXTRACTION AND SCREENING OF PURGEABLE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 This method is a screening procedure for use with purge-and-trap GC or GC/MS. The results of this analysis are purely qualitative and should not be used as an alternative to more detailed and accurate quantitation methods.

2.0 SUMMARY OF METHOD

2.1 An aliquot of sample is extracted with hexadecane and then analyzed by GC/FID. The results of this analysis will indicate whether the sample requires dilution or methanolic extraction prior to purge-and-trap GC or GC/MS analysis.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware. All these materials must be routinely demonstrated to be free from contaminants by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from sample to sample depending upon the nature and diversity of the water being sampled.

3.2 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20x less sensitive than aromatics and haloethanes approximately 10x less sensitive. Low-molecular-weight, water-soluble solvents (e.g., alcohols and ketones) will not extract from the water, and therefore will not be detected by GC/FID.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.0001 gm.

4.2 Gas Chromatograph: An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder (or equivalent). A data system is recommended for measuring peak heights and/or peak areas.

4.2.1 Detector: Flame ionization (FID).

4.2.2 GC column: 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100/120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min and held at 280°C for 10 min.

4.3 Centrifuge: Capable of accommodating 50-mL glass tubes.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Volumetric flasks: 10- and 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.6 Centrifuge tubes: 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.7 Pasteur pipets: Disposable.

4.8 Bottles: Teflon-sealed screw-cap.

5.0 REAGENTS

5.1 Hexadecane and methanol: Pesticide quality or equivalent.

5.2 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of each parameter of interest.

5.3 Stock standard solutions (1.00 ug/uL): Stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in methanol in a 10-mL volumetric flask and dilute to volume (larger volumes may be used at the convenience of the analyst). If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially available stock standards may be used if they are certified by the manufacturer.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. These standards should be checked frequently for signs of degradation or evaporation.

5.4 Standard mixture #1: Standard mixture #1 should contain benzene, toluene, ethyl benzene, and xylene. Prepare a stock solution containing these compounds as described in Paragraph 5.3 and then prepare a working standard (through dilution) in which the concentration of each compound in the standard is 100 ng/uL in methanol.

5.5 Standard mixture #2: Standard mixture #2 should contain n-nonane and n-dodecane. Prepare a stock solution containing these compounds as described in Paragraph 5.3. Dilute the stock standard with methanol so that the concentration of each compound is 100 ng/uL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 Water:

7.1.1.1 Allow the contents of the 40-mL sample vial to come to room temperature. Quickly transfer the contents of the 40-mL vial to a 50-mL volumetric flask. Immediately add 2.0 mL of hexadecane, cap the flask, and shake the contents vigorously for 1 min. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

7.1.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0-mL GC vial. If an emulsion is present after shaking the sample, break it by:

1. pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or

2. transferring the emulsion to a centrifuge tube and centrifuging for several min.

7.1.2 Standards:

7.1.2.1 Add 200 uL of the working standard mixtures #1 and #2 to separate 40-mL portions of reagent water. Follow the instructions in Sections 7.1.1.1 and 7.1.1.2 with the immediate addition of 2.0 mL of hexadecane.

7.1.3 Sediment/Soil:

7.1.3.1 Add approximately 10 g of sample (wet weight) to 40 mL of reagent water in a 50-mL centrifuge tube. Cap and shake vigorously for 1 min. Centrifuge the sample briefly. Quickly transfer the supernatant water to a 50-mL volumetric flask.

7.1.3.2 Follow the instructions given in Sections 7.1.1.1 and 7.1.1.2, starting with the addition of 2.0 mL of hexadecane.

7.2 Analysis:

7.2.1 Calibration:

7.2.1.1 External standard calibration: The GC/FID must be calibrated each 12-hour shift for half of full-scale response when injecting 1-5 uL of each extracted standard mixture #1 and #2 (Paragraphs 5.4 and 5.5).

7.2.2 **GC/FID analysis:** Inject the same volume of hexadecane extract for the sample under investigation as was used to perform the external standard calibration. The GC conditions used for the standards analysis must also be the same as those used to analyze the samples.

7.2.3 **Interpretation of the GC/FID chromatograms:** There are two options for interpretation of the GC/FID results.

7.2.3.1 Option A: The standard mixture #1 is used to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge-and-trap if the sample is a water. If the sample is a sediment/soil, use this information to determine which GC/MS purge-and-trap method (low- or high-level) should be used. If aromatics are absent from the sample or obscured by higher concentrations of other purgeables, use Option B.

7.2.3.2 Option B: The response of standard mixture #2 is used to determine which purge-and-trap method should be used for analyzing a sample. All purgeables of interest have retention times less than the n-dodecane retention time. A dilution factor (Paragraph 7.2.4.1.3) may be calculated for water samples, and an X factor (Paragraph 7.2.4.2.3) for soil/sediment samples, to determine whether the low- or high-level purge-and-trap procedure should be used.

7.2.4 Analytical decision point:

7.2.4.1 Water samples: Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.1.1 If no peaks are noted, analyze a 5-mL water sample by the purge-and-trap method.

7.2.4.1.2 If peaks are present prior to the n-dodecane peak and aromatics are distinguishable, follow Option A (Paragraph 7.2.3.1).

7.2.4.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, Option B should be used as follows: If all peaks (prior to n-dodecane) are <3% of the n-nonane, analyze 5 mL of water sample by the purge-and-trap method. If any peak is >3% of the n-nonane, measure the area of the major peak and calculate the necessary dilution factor as follows:

$$\text{dilution factor} = 50 \times \frac{\text{area of major peak in sample}}{\text{peak area of n-nonane}}$$

The water sample should be diluted using the calculated factor just prior to purge-and-trap GC or GC/MS analysis.

7.2.4.2 **Soil/sediment samples:** Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.2.1 If no peaks are noted, analyze a 5-g sample by the low-level purge-and-trap procedure.

7.2.4.2.2 If peaks are present prior to the n-dodecane and aromatics are distinguishable, follow Option A using the concentration information given in Table 1 to determine whether to analyze the sample by a low- or high-level purge-and-trap technique.

7.2.4.2.3 If peaks are present prior to n-dodecane but aromatics are absent or indistinguishable, use Option B. Calculate an X factor for the sample using the following equation:

$$X \text{ factor} = \frac{\text{area of major peak in sample}}{\text{area of n-nonane}}$$

Use the information provided in Table 1 to determine how the sample should be handled for GC/MS analysis.

7.2.4.2.4 If a high-level method is indicated, the information provided in Table 2 can be used to determine the volume of methanol extract to add to 5 mL of reagent water for analysis (see Methods 5030 and 8240 for methanolic extraction procedure).

8.0 QUALITY CONTROL

8.1 It is recommended that a reagent blank be analyzed by this screening procedure to ensure that no laboratory contamination exists. A blank should be performed for each set of samples undergoing extraction and screening.

9.0 METHOD PERFORMANCE

9.1 No data available.

10.0 REFERENCES

1. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

TABLE 1. DETERMINATION OF GC/MS PURGE-AND-TRAP METHOD

X Factor	Approximate Concentration Range [a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

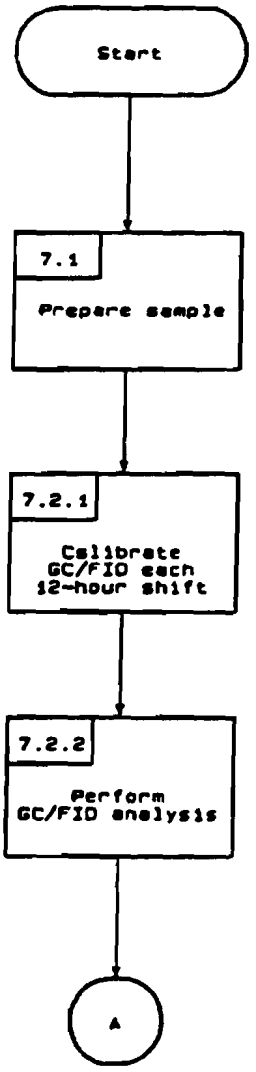
TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOIL/SEDIMENTS

X Factor	Approximate Concentration Range [a]	Volume of Methanol Extract [b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 uL of 1/50 dilution [c]

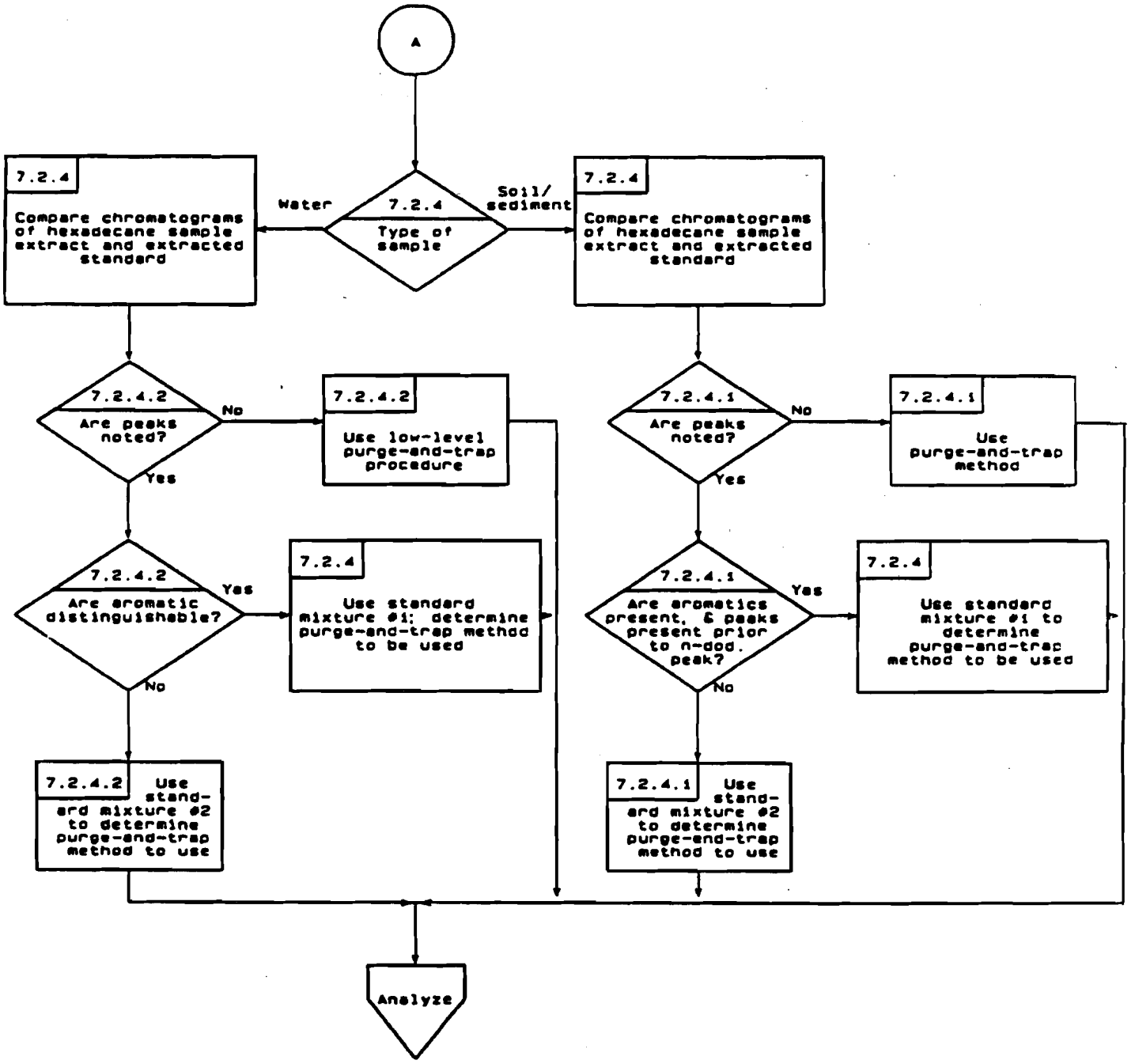
[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less than 100 uL, additional methanol should be added to maintain the constant 100-uL volume.

[c] Dilute an aliquot of the methanol extract and then take 100 uL for analysis.


Start
7.1
Prepare sample
7.2.1
Calibrate GC/FID each 12-hour shift
7.2.2
Perform GC/FID analysis
A

HEXADECANE EXTRACTION AND SCREENING OF PURGEABLE ORGANICS
(Continued)



METHOD 4010

SCREENING FOR PENTACHLOROPHENOL BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4010 is a procedure for screening solids such as soils, sludges, and aqueous media such as waste water and leachates for pentachlorophenol (PCP) (CAS Registry 87-86-5).

1.2 Method 4010 is recommended for screening samples to determine whether PCP is likely to be present at concentrations above 0.5 mg/Kg for solids or 0.005 mg/L for aqueous samples. Method 4010 provides an estimate for the concentration of PCP by comparison with a standard.

1.3 Using the test kits from which this method was developed, 95 % of aqueous samples containing 2 ppb or less of PCPs will produce a negative result in the 5 ppb test configuration. Also, 95 % of soil samples containing 125 ppb or less of PCBs will produce a negative result in the 500 ppb test configuration.

1.4 In cases where the exact concentration of PCP is required, additional techniques (i.e., gas chromatography (Method 8040) or gas chromatography/mass spectrometry (Method 8270)) should be used.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed. In general, the method is performed using a water sample or an extract of a soil sample. Sample and an enzyme conjugate reagent are added to immobilized antibody. The enzyme conjugate "competes" with PCP present in the sample for binding to immobilized anti-PCP antibody. The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standard(s) simultaneously.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for PCP. The test kit used in preparation of this method was evaluated for interferences. Table 1 provides the concentration of compounds found to give a false positive test at the indicated concentration.

3.2 Other compounds have been tested for cross reactivity with PCP, and have been demonstrated to not interfere with the specific kit tested. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.3 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

4.1 PENTA RISc Test Kits (EnSys, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

5.1 Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance indicated in Tables 2-3.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4010 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 This method has been applied to a series of groundwater, process water, and wastewater samples from industries which use PCP, and the results compared with GC/MS determination of PCP (Method 8270). These results are provided in Table 2. These results represent determinations by two laboratories.

9.2 This method has been applied to a series of soils from industries which use PCP and the results compared with GC/MS determination of PCP via Method 8270. These results are provided in Table 3. These results represent determinations by two laboratories.

10.0 REFERENCES

1. J.P. Mapes, K.D. McKenzie, L.R. McClelland, S. Movassaghi, R.A. Reddy, R.L. Allen, and S.B. Friedman, "Rapid, On-Site Screening Test for Pentachlorophenol in Soil and Water - PENTA-RISc™", Ensys Inc., Research Triangle Park, NC 27709

2. J.P. Mapes, K.D. McKenzie, L.R. McClelland, S. Movassaghi, R.A. Reddy, R.L. Allen, and S.B. Friedman, "PENTA-RISc™ - An On-Site Immunoassay for Pentachlorophenol in Soil", Bull. Environ. Contam. Toxicol., 49:334-341, 1992.

3. PENTA-RISc™ Instructions for Use, Ensys Inc.

Table 1 Cross Reactivity for PCP[a]		
Compound	Concentration (mg/Kg) in Soil to Cause a False Positive for PCP at 0.5 mg/Kg	Concentration (μg/L) in Water to Cause a False Positive for PCP at 5 μg/L
2,6-Dichlorophenol	700	600
2,4,6-Trichlorophenol	16	100
2,4,5-Trichlorophenol	100	500
2,3,4-Trichlorophenol	400	600
2,3,5,6-Tetrachlorophenol	1.2	7
Tetrachlorohydroquinone	500	>1500

[a] for PENTA RISc Test Kit (EnSys, Inc.)

Table 2
Comparison of Immunoassay[a] with GC/MS
Water Matrix

Sample Type	Screening Results (ppm)							Concentration measured by GC/MS	Does screening test agree with GC/MS determination?
	0.005	0.05	0.1	0.5	1	5	50		
groundwater					>	>	<	3.5	no
			>	<				0.35	yes
	>	<						<0.1	yes
						>	<	8.2	yes
					>	<		2.6	yes
					>	<		2.9	yes
process water	>	>	<	<				0.21	no
	>	>	>	<				0.17	yes
			>	<				0.12	yes
wastewater		>	>	<	<			0.6	no
					>	<		1.4	yes
	>	>	<					<0.1	yes
			>	<				0.17	yes
run-off	>	>	<					<0.1	yes
	>	<						0.034	yes
		>			<			0.098	yes
		>			<			0.084	yes
		>			<			0.066	yes
						>		2.1	no
		>			<			0.073	yes
		>			<			0.026	no
	>	<						0.006	yes
					>			0.169	no
		>			<			0.239	yes
					>			0.190	no
					>			0.114	no
			>			<		0.346	yes
						>		1.1	yes
						>		19	yes
					>		<	4.3	yes

> = screening test indicates that the sample concentration is greater than the test concentration

< = screening test indicates that the sample concentration is less than the test concentration

[a] for PENTA RISc Test Kit (EnSys, Inc.)

Table 3
Comparison of Immunoassay[a] with GC/MS
Soil Matrix

Screening Results (ppm)			Concentration measured by GC/MS	Does screening test agree with GC/MS determination?
0.5	5	50		
>	>	>	1100	yes
>	>	<	88	no
<	<	<	0.31	yes
<	<	<	0.72	no
>	>	>	315	yes
	<	<	1.5	yes
>	>	<	6.4	yes
>	>	<	9	yes
>	<	<	1.9	yes
>	>	>	46	no
>	<	<	<1	yes
>	>	<	21	yes
>	<	<	3.3	yes
>	>	<	4	no
>	>	<	11	yes
>	>	<	18	yes
>	>	<	33	yes
>	>	>	54	yes
>	>	>	65	yes
>	>	>	74	yes
>	>	>	83	yes
>	<	<	1.1	yes
>	>	<	14.3	yes
<	<	<	<1	yes
<	<	<	<1	yes
<	<	<	<1	yes
>	<	<	3.9	yes
<	<	<	<1	yes
>	<	<	1.4	yes
>	>	>	48	no
<	<	<	<1	yes
>	>	>	142	yes
>	>	<	108	no

Table 3 Continued				
Screening Results (ppm)			Concentration measured by GC/MS	Does screening test agree with GC/MS determination?
0.5	5	50		
>	>	>	117	yes
>	>	>	56	yes
>	<	<	2.5	yes
>	>	<	3.5	no
>	>	>	143	yes
<	<	<	nd	yes
<	<	<	0.02	yes
>	<	<	5	yes

> = screening test indicates that the sample concentration is greater than the test concentration

< = screening test indicates that the sample concentration is less than the test concentration

[a] for PENTA RISc Test Kit (EnSys, Inc.)

METHOD 8275

THERMAL CHROMATOGRAPHY/MASS SPECTROMETRY (TC/MS) FOR SCREENING SEMIVOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Method 8275 is a screening technique that may be used for the qualitative identification of semivolatile organic compounds in extracts prepared from nonaqueous solid wastes and soils. It is not intended for use as a rigorous quantitative method. Direct injection of a sample may be used in limited applications. The following analytes can be qualitatively determined by this method:

Compound Name	CAS No.[a]
2-Chlorophenol	95-57-8
4-Methylphenol	106-44-5
2,4-Dichlorophenol	120-83-2
Naphthalene	91-20-3
4-Chloro-3-methylphenol	59-50-7
1-Chloronaphthalene	90-13-1
2,4-Dinitrotoluene	121-14-2
Fluorene	86-73-7
Diphenylamine	122-39-4
Hexachlorobenzene	118-74-1
Dibenzothiophene	132-65-0
Phenanthrene	85-01-8
Carbazole	86-74-8
Aldrin	309-00-2
Pyrene	129-00-0
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8

[a] Chemical Abstract Services Registry Number.

1.2 Method 8275 can be used to qualitatively identify most neutral, acidic, and basic organic compounds that can be thermally desorbed from a sample, and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A portion of the sample (0.010-0.100 g) is weighed into a sample crucible. The crucible is placed in a pyrocell and heated. The compounds desorbed from the sample are detected using a flame ionization detector (FID). The FID response is used to calculate the optimal amount of sample needed for mass spectrometry. A second sample is desorbed and the compounds are condensed on the head of a fused silica capillary column. The column is heated using a temperature program, and the effluent from the column is introduced into the mass spectrometer.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever low-level samples are analyzed after high-level samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of an empty (clean) crucible to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Thermal Chromatograph (TC) System

4.1.1 Thermal chromatograph™, Ruska Laboratories, or equivalent.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID), 1 µm film thickness, silicone-coated, fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Flame Ionization detector (FID).

4.2 Mass Spectrometer (MS) system

4.2.1 Mass Spectrometer - Capable of scanning from 35 to 500 amu every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

4.2.2 TC/MS interface - Any GC-to-MS interface producing acceptable calibration data in the concentration range of interest may be used.

4.2.3 Data System - A computer must be interfaced to the mass spectrometer. The data system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass (or group of masses) and that can plot such ion abundances versus time or scan number. This type of plot is defined as an extracted ion chromatogram (EIC). Software must also be available that allows for integration of the abundances in, and EIC between, specified time or scan-number limits.

4.3 Tools and equipment

4.3.1 Fused quartz spatula.

4.3.2 Fused quartz incinerator ladle.

4.3.3 Metal forceps for sample crucible.

4.3.4 Sample crucible storage dishes.

4.3.5 Porous fused quartz sample crucibles with lids.

4.3.6 Sample crucible cleaning incinerator.

4.3.7 Cooling rack.

4.3.8 Microbalance, 1 g capacity, 0.000001 g sensitivity, Mettler Model M-3 or equivalent.

4.4 Vials - 10 mL, glass with Teflon lined screw-caps or crimp tops.

4.5 Volumetric flasks, Class A - 10 mL to 1000 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

5.2 Solvents

5.2.1 Methanol, CH_3OH - Pesticide grade or equivalent.

5.2.2 Acetone, CH_3COCH_3 - Pesticide grade or equivalent.

5.2.3 Toluene, $C_6H_5CH_3$ - Pesticide grade or equivalent.

5.2.4 Methylene chloride, CH_2Cl_2 - Pesticide grade or equivalent.

5.2.5 Carbon disulfide, CS_2 - Pesticide grade or equivalent.

5.2.6 Hexane, C_6H_{14} - Pesticide grade or equivalent.

5.2.7 Other suitable solvents - Pesticide grade or equivalent.

5.3 Stock Standard solutions - Standard solutions may be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by weighing about 0.01 g of pure material. Dissolve the material in pesticide quality acetone, or

other suitable solvent, and dilute to 10 mL in a volumetric flask. Larger volumes may be used at the convenience of the analyst.

5.3.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at -10°C to -20°C or less and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially prior to use in preparation of calibration standards.

5.3.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal Standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Sec. 7 are met. Dissolve about 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride, so that the final solvent is approximately 20/80 (V/V) carbon disulfide/methylene chloride. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. Prior to each analysis, deposit about 10 μL of the internal standard onto the sample in the crucible. Store internal standard solutions at 4°C or less before, and between, use.

5.5 Calibration standards - Prepare calibration standards within the working range of the TC/MS system. Each standard should contain each analyte or interest (e.g. some or all of the compounds listed in Sec. 1.1 may be included). Each aliquot of calibration standard should be spiked with internal standards prior to analysis. Stock solutions should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly, and stored at 4°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Crucible Preparation

7.1.1 Turn on the incinerator and let it heat for at least 10 minutes. The bore of the incinerator should be glowing red.

7.1.2 Load the sample crucible and lid into the incinerator ladle and insert into the incinerator bore. Leave in the incinerator for 5 minutes, then remove and place on the cooling rack.

7.1.3 Allow the crucibles and lids to cool for five minutes before placing them in the storage dishes.

CAUTION: Do not touch the crucibles with your fingers. This can result in a serious burn, as well as contamination of the crucible. Always handle the sample crucibles and lids with forceps and tools specified.

7.1.4 All sample crucibles and lids required for the number of analyses planned should be cleaned and placed in the storage dishes ready for use.

7.2 Sample Preparation and Loading

7.2.1 The analyst should take care in selecting a sample for analysis, since the sample size is generally limited to 0.100 g or less. This implies that the sample should be mixed as thoroughly as possible before taking an aliquot. Because the sample size is limited, the analyst may wish to analyze several aliquots for determination.

7.2.2 The sample should be mixed or ground such that a 0.010 to 0.100 g aliquot can be removed. Remove one sample crucible from the storage dish and place it on the microbalance. Establish the tare weight. Remove the sample crucible from the balance with the forceps and place it on a clean surface.

7.2.3 Load an amount of sample into the sample crucible using the fused quartz spatula. Place the assembly on the microbalance and determine the weight of the sample. For severely contaminated samples, less than 0.010 g will suffice, while 0.050-0.100 g is needed for low concentrations of contaminants. Place the crucible lid on the crucible; the sample is now ready for analysis.

7.3 FID Analysis

7.3.1 Load the sample into the TC. Hold the sample at 30°C for 2 minutes followed by linear temperature programmed heating to 260°C at 30°C/minute. Follow the temperature program with an isothermal heating period of 10 minutes at 260°C, followed by cooling back to 30°C. The total analysis cycle time is 24.2 minutes

7.3.2 Monitor the FID response in real time during analysis, and note the highest response in millivolts (mV). Use this information to determine the proper weight of sample needed for combined thermal extraction/gas chromatography/mass spectrometry.

7.4 Thermal Extraction/GC/MS

7.4.1 Prepare a calibration curve using a clean crucible and lid by spiking the compounds of interest at five concentrations into the crucible and applying the internal standards to the crucible lid. Analyze these standards and establish response factors at different concentrations.

7.4.2 Weigh out the amount of fresh sample that will provide approximately 1000 to 3000 mv response. For example, if 0.010 g of sample gives an FID response of 500 mv, then 0.020 to 0.060 g (0.040 g ± 50 %)

should be used. If 0.100 g gives 8000 mv, then 0.025 g ± 50 % should be used.

7.4.3 After weighing out the sample into the crucible, deposit the internal standards (10 μL) onto the sample. Load the crucible into the pyrocell, using the same temperature program in Sec. 7.3.1. Hold the capillary at 5°C during this time to focus the released semivolatiles (the intermediate trap is held at 330°C to pass all compounds onto the column). Maintain the splitter zone at 310°C, and the GC/MS transfer line at 285°C. After the isothermal heating period is complete, temperature program the column from 5°C to 285°C at 10°C/minute and hold at 285°C for 5 minutes. Acquire data during the entire run time.

7.4.4 If the response for any quantitation ion exceeds the initial calibration curve range of the TC/MS system, a smaller sample should be analyzed.

7.5 Data Interpretation

7.5.1 Qualitative Analysis

7.5.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.5.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.5.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.5.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.5.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributing by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be within 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting. Data system library reduction programs can sometimes create these discrepancies.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 Table 1 presents method performance data, generated using spiked soil samples. Method performance data in an aqueous matrix are not available.

10.0 REFERENCES

1. Zumberge, J.E., C. Sutton, R.D. Worden, T. Junk, T.R. Irvin, C.B. Henry, V. Shirley, and E.B. Overton, "Determination of Semi-Volatile Organic Pollutants in Soils by Thermal Chromatography-Mass Spectrometry (TC/MS): an Assessment for Field Analysis," in preparation.

TABLE 1
METHOD PERFORMANCE, SOIL MATRIX

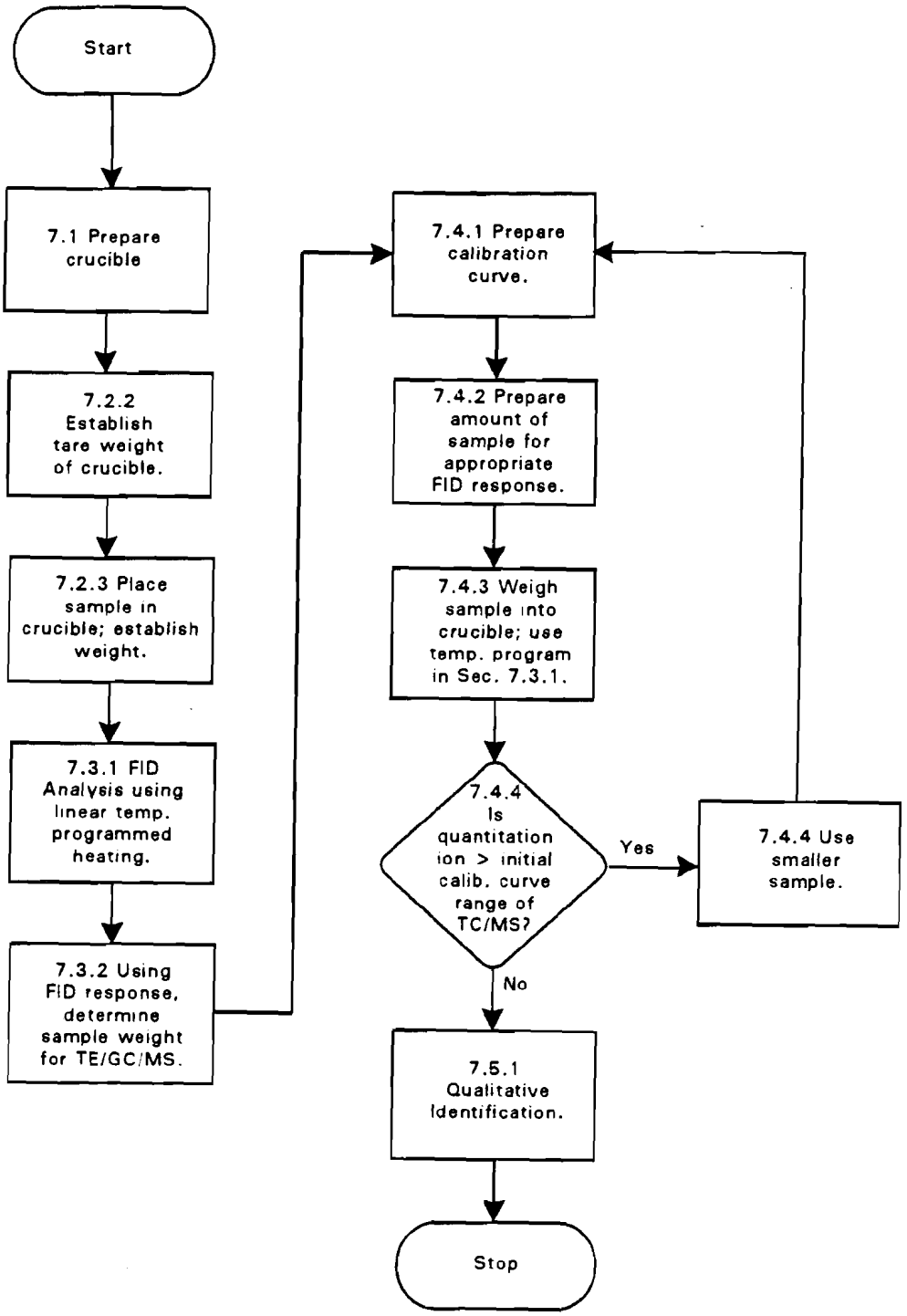
Analyte	Average % Recovery[a]			Mean Recovery
	Clay	Silt	Subsoil	
2-Chlorophenol	30	22	2	18
4-Methylphenol	10	77	7	31
2,4-Dichlorophenol	23	20	26	23
Naphthalene	77	120	63	87
4-Chloro-3-methyl-phenol	9	12	9	10
1-Chloronaphthalene	96	103	70	90
2,4-Dinitrotoluene	7	10	10	9
Fluorene	9	25	19	18
Diphenylamine	5	6	6	6
Hexachlorobenzene	68	64	80	71
Dibenzothiophene	20	35	50	35
Phenanthrene	11	31	40	24
Carbazole	4	8	9	7
Aldrin	3	19	15	12
Pyrene	7	19	20	15
Benzo(k)fluoranthene	4	9	11	8
Benzo(a)pyrene	4	8	11	8

[a] Percent theoretical recovery based upon linearity of injections deposited on the crucible lid (slope and y-intercept). Average of 9 replicates (~10 mg soil spiked with 50 ppm of analyte); 3 different instruments at 3 different laboratories.

TABLE 2
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
2-Chlorophenol	128	64,130
4-Methylphenol	107	107,108,77,79,90
2,4-Dichlorophenol	162	164,98
Naphthalene	128	129,127
4-Chloro-3-methyl-phenol	107	144,142
1-Chloronaphthalene	162	127,164
2,4-Dinitrotoluene	165	63,89
Fluorene	166	165,167
Diphenylamine	169	168,167
Hexachlorobenzene	284	142,249
Phenanthrene	178	179,176
Aldrin	66	263,220
Pyrene	202	200,203
Benzo(k)fluoranthene	252	253,125
Benzo(a)pyrene	252	253,125

METHOD 8275
THERMAL CHROMATOGRAPHY/MASS SPECTROMETRY (TC/MS) FOR SCREENING SEMIVOLATILE ORGANIC COMPOUNDS



APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

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