UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 21 1996

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

George E. Dials, Manager
Carlsbad Area Office
Department of Energy
P.O. Box 3090
Carlsbad, New Mexico 88221

Dear Mr. Dials:

This letter provides written response to a request by DOE in our September 19, 1995 meeting to use Fourier Transform Infrared Spectroscopy (FTIRS) for headspace gas sampling analysis, and follows up verbal approval at the September meeting for DOE to use the FTIRS to characterize headspace samples. Additionally, this letter notifies you that the FTIRS method has been accepted as a SW-846 draft method.

It is our position that the Carlsbad Area Office (CAO) has adequately demonstrated that FTIRS is acceptable for the analysis of drum headspace VOCs. Our approval for use of FTIRS for the analysis of drum headspace VOCs is contingent upon the CAO incorporating the requirements in the draft FTIRS method and report (INEL-95/0332, September 19, 1995), as presented and discussed at our September meeting, into the "Transuranic Waste Characterization Quality Assurance Program Plan" (QAPP), DOE/CAO-94-1010, Revision 0. These requirements include the use of multivariant techniques [e.g., partial least squares (PLS)], use of blanks, field reference standards, demonstration of compliance with appropriate QAPP quality assurance objectives and participation in the CAO performance demonstration program as specified in the QAPP. The QAPP must be revised and implemented at the DOE generator/storage sites prior to using FTIRS for the analysis of drum headspace VOCs.

Mr. Barry Lesnik, EPA-OSW Organics Method Development Manager, has been working with Dr. Michael Connolly, Idaho National Engineering Laboratory FTIRS principal investigator, to get this method approved for incorporation into the EPA SW-846 methods manual. The draft FTIR method and INEL-95/0332 report have undergone extensive review by the OSW and has been approved as an EPA SW-846 draft method. This draft method has been assigned an EPA SW-846 method number of 8450, and will be included in the next proposed update to EPA SW-846. Copies of the draft EPA Method 8450 will be sent to the CAO when available.

If you have any questions or require additional information, please contact Chris Rhyne of my staff at (703) 308-8658

Sincerely Yours,

for Elizabeth A. Cotsworth

Michael Shapiro, Director
Office of Solid Waste

cc: David Neleigh, Region 6
Barry Lesnik, EMRAD
Chris Rhyne

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FAX TRANSMITTAL # of pages ▶ 1
To Craig Snider
Dept./Agency US DOE
From Chris Rhyne
Phone # 703 308 8658

NOTE REGARDING ATTACHED FTIRS METHOD

The following is the current copy of the Fourier Transform Infrared Spectroscopy (FTIRS) Method. This is the method that was approved by the EPA for use in the WIPP Program. The attached copies are from the Quality Assurance Program Plan, Interim Change, and the Methods Manual as Method 430.7, respectively.

TRANSURANIC WASTE CHARACTERIZATION QUALITY ASSURANCE PROGRAM PLAN

INTERIM CHANGE

HEADSPACE GAS VOLATILE ORGANIC COMPOUND AND METHANE ANALYSIS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

This interim change is being provided to participants in the Transuranic (TRU) Waste Characterization Program (the Program) to allow implementation of headspace gas analysis by Fourier Transform Infrared Spectroscopy (FTIRS) prior to approval of Revision 1.0 of the *Transuranic Waste Characterization Quality Assurance Program Plan* (QAPP). This change describes applicable revisions to the QAPP in order to perform headspace gas analysis by FTIRS. All other QAPP requirements not addressed in this interim change still apply. A procedure that details the implementation of FTIRS analysis is included as Appendix A.

FTIRS is a rapid and cost-efficient method for the analysis of headspace gas and can be used as part of an on-line integrated sampling/analysis system or with the SUMMA canister based sampling methods described in the QAPP. The procedure included in Appendix A describes the on-line integrated sampling/analysis approach. If SUMMA canister sampling methods are used, the applicable procedure(s) (Procedure 110.1 through 110.4) found in the *Transuranic Waste Characterization Sampling and Analysis Methods Manual* (Methods Manual) must be followed.

Training Requirements and Certifications

FTIRS Technical Supervisors must possess a B.S. degree, or equivalent experience, and 1 year of applicable experience. FTIRS Operators must possess applicable training and demonstrated expertise. The definitions for technical supervisors and operators can be found in Table 1-4 of the QAPP.

Performance Demonstration Program Participation

On-line integrated sampling/analysis systems must participate in the Headspace Gas Performance Demonstration Program (PDP). This participation shall be at the same frequency as laboratories (semi-annual). For mobile systems, participation shall be semi-annual regardless of the operating location of the system. Currently, the *Performance Demonstration Program Plan for the Analysis of Simulated Headspace Gases for the Transuranic Waste Characterization Program* (Gas PDP Plan) does not address FTIRS analysis. However provisions for FTIRS will be added during the next revision. Participants who wish to use FTIRS must contact the Carlsbad Area Office and state their intent to participate along with any unique sample volume or pressure requirements. Until the appropriate revisions are made to the

Gas PDP Plan, FTIRS results will be considered in accordance with Sections 6.1.5.4 and 6.1.5.5 of that document, "Special Scoring" and "Canister or Analyte Disqualification."

On-line Batch Definition

For the purpose of operating an on-line integrated headspace gas sampling/analysis system, samples shall be collected and analyzed in on-line batches. An on-line batch is defined as the number of headspace gas samples that are collected and analyzed within a 12-hour period using the same on-line integrated sampling/analysis system.

Data Review, Validation, and Verification Requirements

All data review, validation, and verification requirements outlined in Section 3.1 of the QAPP applicable to sampling or analytical batches also apply to on-line batches.

On-line Quality Control Samples

For on-line integrated sampling/analysis systems, the sampling batch and analytical batch quality control (QC) samples are combined as on-line batch QC samples as follows:

- The on-line blank replaces the equipment blank and the laboratory blank.
- The on-line control sample replaces the field reference standard and the laboratory control sample.
- The on-line duplicate replaces the field duplicate and the laboratory duplicate.

A separate field blank must still be collected and analyzed for each on-line batch. However, if the results of a field blank collected through the sampling manifold meet the acceptance criterion, a separate on-line blank need not be collected or analyzed.

Method Detection Limit Calculation

For headspace gas analysis using FTIRS, the method detection limit (MDL) is defined as follows:

$$MDL = 3s \quad (1)$$

where s is the standard deviation. Initially, a minimum of seven samples of ambient air or hydrocarbon and carbon-dioxide (CO_2) free dry air or nitrogen must be used to establish the MDLs. MDLs should be constantly updated using the results of the on-line control sample.

Sample Handling and Custody Requirements

For headspace gas samples collected and transferred to the analytical instruments on-line, the chain-of-custody (COC) and sample handling requirements outlined in Section 6.0 of the QAPP associated with discrete field samples do not apply. However, controls must be in place to document the source of all samples, including QC samples, and ensure on-line sample handling conditions are adequate to maintain sample quality and integrity. These controls must be described in Standard Operating Procedures (SOPs) or other appropriate site-specific documentation.

Sampling Equipment

The same sampling heads and sampling manifold described in the QAPP and the Methods Manual may be used for on-line integrated sampling/analysis systems, with the following modifications:

- $ Only one port for the attachment of a SUMMA canister is needed.
- $ Hydrocarbon and CO_2-free dry air or nitrogen must be used for purging of the manifold and the collection of blanks. Helium and compressed zero air must not be used.
- $ The manifold, sample transfer system, and analytical system must be kept dry.
- $ The manifold must be configured so that on-line batch QC samples are collected through the sampling head, the entire manifold, and the sample transfer system.

Analytical Requirements

Quality Assurance Objectives: For on-line integrated sampling/analysis systems, precision shall be assessed by analyzing on-line duplicates and replicate analysis of on-line control samples. Accuracy shall be assessed by analyzing PDP blind audit samples and on-line control samples. MDLs for FTIRS shall be expressed in parts per million by volume (ppmv) and shall be determined as shown in Equation (1). The quality assurance objectives (QAOs) for FTIRS analysis (and for on-line integrated FTIRS sampling/analysis system operation) are shown in Table 1.

Methods Requirements: For FTIRS qualitative and quantitative analysis, a multivariate analysis technique is required because of the multiple frequencies and high degree of spectral overlap required to determine each analyte. Partial least squares (PLS) is one multivariate analysis technique that may be used. Other multivariate analysis techniques may also be used and sites shall specify the technique(s) used in SOPs.

PLS is a spectral decomposition method which is trained or calibrated by a large set of known spectra that must be acquired. A set of factors is generated as a result of the PLS

TABLE 1

Gas Volatile Organic Compounds Target Analyte List and Quality Assurance Objectives for FTIRS

Compound	CAS Number	Precision[a] (%RSD or RPD)	Accuracy[a] (%R)	MDL (ppmv)	PRQL (ppmv)	Completeness (percent)
Benzene	71-43-2	#25	70-130	5	10	90
Bromoform	75-25-2	#25	70-130	5	10	90
Carbon tetrachloride	56-23-5	#25	70-130	5	10	90
Chlorobenzene	108-90-7	#25	70-130	5	10	90
Chloroform	67-66-3	#25	70-130	5	10	90
Cyclohexane	110-87-7	#25	70-130	5	10	90
1,1-Dichloroethane	75-34-3	#25	70-130	5	10	90
1,2-Dichloroethane	107-06-2	#25	70-130	5	10	90
1,1-Dichloroethylene	75-35-4	#25	70-130	5	10	90
cis-1,2-Dichloroethylene	156-59-2	#25	70-130	5	10	90
Ethyl benzene	100-41-4	#25	70-130	10	20	90
Ethyl ether	60-29-7	#25	70-130	5	10	90
Formaldehyde[b]	50-00-0	#25	70-130	-	10	90
Hydrazine[c]	302-01-2	#25	70-130	-	10	90
Methane	74-82-8	#25	70-130	0.05[d]	0.1[d]	90
Methylene chloride	75-09-2	#25	70-130	5	10	90
1,1,2,2-Tetrachloroethane	79-34-5	#25	70-130	5	10	90
Tetrachloroethylene	127-18-4	#25	70-130	5	10	90
Toluene	108-88-3	#25	70-130	5	10	90
1,1,1-Trichloroethane	71-55-6	#25	70-130	5	10	90
Trichloroethylene	79-01-6	#25	70-130	5	10	90
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	#25	70-130	5	10	90
1,2,4-Trimethylbenzene	95-63-6	#25	70-130	5	10	90
1,3,5-Trimethylbenzene	108-67-8	#25	70-130	5	10	90
m-Xylene	108-38-3	#25	70-130	5	10	90
o-Xylene	95-47-6	#25	70-130	5	10	90
p-Xylene	106-42-3	#25	70-130	5	10	90
Acetone	67-64-1	#25	70-130	50	100	90
Butanol	71-36-3	#25	70-130	50	100	90
Methanol	67-56-1	#25	70-130	50	100	90
Methyl ethyl ketone	78-93-3	#25	70-130	50	100	90
Methyl isobutyl ketone	108-10-1	#25	70-130	50	100	90

%RSD = Percent relative standard deviation
RPD = Relative percent difference
%R = Percent recovery
MDL = Method detection limit (maximum permissible value) based on 1 m sample cell
PRQL = Program required quantitation limit

[a]Criteria apply to PRQL concentrations.
[b]Required only for homogenous solids and soil/gravel from Los Alamos National Laboratory.
[c]Required only for homogenous solids and soil/gravel from Oak Ridge National Laboratory and Savannah River Site.
[d]Volume percent.

training/calibration step. These factors describe the analyte of interest and all of the potential interferences that are included in the calibration set. PLS, and its application to FTIRS analysis, is explained more fully in the procedure (Appendix A).

Quality Control: QC samples, frequency, and acceptance criteria for FTIRS are presented in Table 2. Individual headspace gas samples shall serve as duplicates. Blanks shall be hydrocarbon and $C0_2$-free dry air or nitrogen. Blanks must be analyzed daily before analysis of any samples and at least once per analytical batch or on-line batch. Laboratory control samples or on-line control samples must contain at least 10 of the target analytes included in Table 1.

For comparison purposes, one sample per analytical batch or on-line batch must be analyzed by GC/MS. For on-line integrated sampling/analysis systems, this will involve the collection of a sample in a SUMMA canister. The results of this comparison sample shall be acceptable if the relative percent difference (RPD) between the FTIRS results and the GC/MS results is less than or equal to 25.

Instrument Testing, Inspection, and Maintenance Requirements: FTIRS equipment and materials must meet all of the requirements specified in the procedure (Appendix A). The sample cell must be of a path length that will allow the MDLs to be met. The sampling head(s) and manifold must meet all of the requirements found in Section 7.0 of the QAPP, with revisions as discussed in the "Sampling Equipment" section of this interim change.

Instrument Calibration and Frequency: The FTIR spectrometer is calibrated using a relatively large set of training/calibration spectra and the multivariate analysis technique algorithm. The initial set of calibration spectra must consist of a minimum of two pure component spectra of the analyte(s) of interest, two pure component spectra of each suspected interference, and additional spectra which demonstrate background components such as water or carbon dioxide. Independent multivariate analysis technique methods for each analyte of interest are preferred so that the optimum spectral region for each analyte is used to minimize the effects of interferences and widely different sample compositions. The control sample serves as the continuing calibration check for FTIRS. Table 3 summarizes the FTIRS calibration requirements.

It is possible to transfer the multivariate analysis technique calibrations from one instrument to another, with some limitations. The transfer can be easily accomplished if the instrumentation is essentially identical, processing of the interferogram is performed with the same apodization

TABLE 2

Summary of Quality Control Samples and Frequencies for Gas Volatile Organic Compounds Analysis by FTIRS

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
Method performance samples	Seven (7) samples initially and four (4) semiannually	Meet Table 1 QAOs	Repeat until acceptable
Laboratory duplicates or on-line duplicates	One (1) per analytical batch, or, one (1) per on-line batch	RPD # 25[b]	Nonconformance if RPD > 25
Laboratory blanks or on-line blanks	Daily prior to sample analysis, or, one (1) per on-line batch for FTIRS	Analyte concentrations < PRQL	Nonconformance if analyte concentrations > PRQL
Laboratory control samples or on-line control samples	One (1) per analytical batch, or, one (1) per on-line batch	70-130 %R	Nonconformance if %R < 70 or > 130
GC/MS comparison sample	One (1) per analytical batch, or, one (1) per on-line batch	RPD # 25[b]	Nonconformance if RPD > 25
Blind audit samples	Samples and frequency controlled by the Gas PDP Plan	Specified in the Gas PDP Plan	Specified in the Gas PDP Plan

[a]Corrective Action when QC samples do not meet the acceptance criteria; Nonconformance procedures are outlined in Section 2.1.2.1 of the QAPP

[b]Applies only to concentrations greater than the PRQLs listed in Table 1.

MDL = Method detection limit
PDP = Performance Demonstration Program
QAO = Quality assurance objective
%R = Percent recovery
RPD = Relative percent difference

TABLE 3

Summary of Calibration Requirements for Gas Volatile Organic Compounds Analysis by FTIRS

Technique	Procedure	Frequency of Procedure	Acceptance Criteria
FTIRS	Initial calibration spectra for analyte components, interferences, and background components.	Initially and as needed	Meets PLS (or other appropriate multivariate technique) requirements
	Continuing calibration	Every 12 hours, or, once per on-line batch	%R of 70-130 for 10 analytes in laboratory control samples, or, on-line control sample

PLS = Partial least squares
%R = Percent recovery

function, wavelength/frequency accuracy is verified, the same detector is used for calibration and analysis, and the sample spectra are recorded at the same temperature as the calibration spectra. It is possible to use different detectors, however, the linear range may be somewhat shorter for certain analytes so verification of the linear range may be necessary.

Data Management: All organic analyte concentrations shall be quantified using a linear regression equation or an appropriate multivariate analysis technique. If spectral residuals are still prevalent after dilution, the presence of an unmodeled interferant(s), or tentatively identified compounds (TICs), is likely. To determine the identity of a new interference, contributions to the original spectrum from compounds found in the sample must be subtracted from the original sample spectrum. The resulting spectrum can then be interpreted for functional groups and compound identifications. A library search must be performed to determine the five most likely compounds contributing to the interference. If the interference is prevalent in multiple samples within a batch (i.e., 20 percent), a SUMMA canister sample must be collected and analyzed by GC/MS to confirm the unknown compound identity. TICs are added to the analyte list if they occur at the frequency specified in the QAPP and appear in 40 CFR Part 264, Appendix IX.

For on-line integrated sampling/analysis systems, the sampling batch and analytical batch data reports are combined. All other data reporting requirements included in the QAPP (Section 12.6) still apply.

References

DOE 1995a. *Transuranic Waste Characterization Quality Assurance Program Plan*. CAO-94-1010, Current Revision, Carlsbad, New Mexico, Carlsbad Area Office, U.S. Department of Energy.

DOE 1995b. *Transuranic Waste Characterization Sampling and Analysis Methods Manual*. DOE/WIPP-91-043, Current Revision, Carlsbad, New Mexico, Carlsbad Area Office, U.S. Department of Energy.

APPENDIX A

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AND METHANE IN HEADSPACE GAS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

PROCEDURE 430.7

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AND METHANE IN HEADSPACE GAS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

1.0 Scope and Application

1.1 This procedure is intended for the automated determination of the volatile organic compounds (VOCs) and methane listed in Table 1 in gaseous samples by Fourier Transform Infrared Spectroscopy (FTIRS). The information concerning the analytes of interest and the potential interferences must be available prior to setting up and standardizing the method for use. Because of this, the procedure is considered to be an application dependent method that has widespread and varied potential for use in headspace gas or gas analysis.

1.2 The procedure was originally developed for the determination of VOCs and methane in the headspace of waste drums containing transuranic (TRU) waste for the Department of Energy (DOE). The analytes listed in Table 1 and interferences listed in Table 2 were determined to be pertinent to this particular application. Table 1 also lists the quality assurance objectives (QAOs) for this procedure. All performance data presented in this method were generated during the original method development effort for these analytes.

1.3 The procedure was developed as a turn-key analytical system operating with minimal operator input. All components are commercially available and complete systems can also be purchased (e.g., Applied Automation and Bomem divisions of Hartmann and Braun for hardware and applications; Galactic Industries for quantitative analysis software).

1.4 This procedure may be used for on-line integrated sampling/analysis or for analysis of samples collected in SUMMA® canisters. If SUMMA® canisters are used, the sampling procedures described in Procedure 110.1 through 110.4 of this Methods Manual must be used. The EPA has not determined the stability of alcohols and ketones when stored in pressurized or subambient SUMMA® canisters. It is anticipated that no adverse problems will be encountered with these types of VOCs when stored in SUMMA® canisters due to the concentration levels at which these VOCs are expected to be found. This procedure includes the on-line integrated sampling steps and the FTIRS analysis method. This procedure must be implemented with a site-specific standard operating procedure (SOP).

1.5 This procedure is restricted to use by or under the supervision of analysts experienced in sampling and analysis of gas samples and in the operation and interpretation of FTIRS.

1.6 For the purposes of the TRU Waste Characterization Program, samples are to be analyzed in analytical batches or on-line batches. An analytical batch is defined as a suite of samples that is processed as a unit, using the same analytical method, within a specific time period. An analytical batch can be up to 20 samples (excluding laboratory QC samples), all of which must be received by the laboratory within 14 days of the validated time of sample receipt (VTSR) of the first sample in the batch. An on-line

Gas Volatile Organic Compounds and Methane Target Analyte List and Quality Assurance Objectives

Compound	CAS Number	Precision[a] (%RSD or RPD)	Accuracy[a] (%R)	MDL[b] (ppmv*m)	PRQL[b] (ppmv)	Completeness (percent)	Spectral Region (cm^{-1})
Benzene	71-43-2	≤25	70-130	5	10	90	670-712
Bromoform	75-25-2	≤25	70-130	5	10	90	1120-1170
Carbon tetrachloride	56-23-5	≤25	70-130	5	10	90	734-824
Chlorobenzene	108-90-7	≤25	70-130	5	10	90	672-775, 988-1150
Chloroform	67-66-3	≤25	70-130	5	10	90	731-806, 1181-1255
Cyclohexane	110-87-7	≤25	70-130	5	10	90	2825-2987
1,1-Dichloroethane	75-34-3	≤25	70-130	5	10	90	1022-1106
1,2-Dichloroethane	107-06-2	≤25	70-130	5	10	90	700-750, 1203-1556
1,1-Dichloroethylene	75-35-4	≤25	70-130	5	10	90	744-912, 1049-1169
cis-1,2-Dichloroethylene	156-59-2	≤25	70-130	5	10	90	827-882, 1255-1324
Ethyl benzene	100-41-4	≤25	70-130	10	20	90	680-830, 3005-3140
Ethyl ether	60-29-7	≤25	70-130	5	10	90	1020-1255
Formaldehyde[c]	50-00-0	≤25	70-130	-	10	90	--
Hydrazine[d]	302-01-2	≤25	70-130	-	10	90	--
Methane	74-82-8	≤25	70-130	0.05[e]	0.1 [e]	90	1291-1310, 3000-3026
Methylene chloride	75-09-2	≤25	70-130	5	10	90	714-784, 1237-1296
1,1,2,2-Tetrachloroethane	79-34-5	≤25	70-130	5	10	90	690-845
Tetrachloroethylene	127-18-4	≤25	70-130	5	10	90	870-940
Toluene	108-88-3	≤25	70-130	5	10	90	672-872
1,1,1-Trichloroethane	71-55-6	≤25	70-130	5	10	90	675-756, 1041-1137
Trichloroethylene	79-01-6	≤25	70-130	5	10	90	907-968, 817-865

TABLE 1

Gas Volatile Organic Compounds and Methane Target Analyte List and Quality Assurance Objectives (Continued)

Compound	CAS Number	Precision[a] (%RSD or RPD)	Accuracy[a] (%R)	MDL[b] (ppmv*m)	PRQL[b] (ppmv)	Completeness (percent)	Spectral Retion (cm^{-1})
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	≤25	70-130	5	10	90	996-1240
1,2,4-Trimethylbenzene	95-63-6	≤25	70-130	5	10	90	774-882
1,3,5-Trimethylbenzene	108-67-8	≤25	70-130	5	10	90	811-860
m-Xylene	108-38-3	≤25	70-130	5	10	90	730-810
o-Xylene	95-47-6	≤25	70-130	5	10	90	700-773
p-Xylene	106-42-3	≤25	70-130	5	10	90	710-840
Acetone	67-64-1	≤25	70-130	50	100	90	1160-1262
Butanol	71-36-3	≤25	70-130	50	100	90	906-1156
Methanol	67-56-1	≤25	70-130	50	100	90	935-1100
Methyl ethyl ketone	78-93-3	≤25	70-130	50	100	90	1035-1240, 1290-1400
Methyl isobutyl ketone	108-10-1	≤25	70-130	50	100	90	1070-1407

%RSD = Percent relative standard deviation
RPD = Relative percent difference
%R = Percent recovery
MDL = Method detection limit (maximum permissible value) based on 1 m sample cell
PRQL = Program required quantitation limit

[a] Criteria apply to PRQL concentrations.
[b] Values in ppmv m at 640 Torr based on original development work using 20 centimeter cell.
[c] Required only for homogenous solids and soil/gravel from Los Alamos National laboratory (no FTIR Data available).
[d] Required only for homogenous solids and soil/gravel from Oak Ridge National Laboratory and Savannah River Site.
[e] Volume percent.

TABLE 2

Interferences and/or Secondary Analytes

Compound	Spectral Region(cm^{-1})	Factors	DL[a]
Carbon Dioxide	2250-2318	7	31
Ammonia	895-1000	10	0.6
Trimethylamine	2675-2860	14	0.6
Carbon Monoxide	2024-2142	6	0.6
Nitrous Oxide	1220-1334, 2140-2224	30	2.4
Hydrocarbons	2800-3000	18	5.4

[a]Estimated detection limits in ppmv*m based on original development work.

batch is defined as the number of samples collected and analyzed within a 12-hour period using the same on-line integrated sampling/analysis system. If using an integrated, on-line sampling/analysis system, the on-line batch QC samples serve as combined sampling batch/analytical batch QC samples.

2.0 Summary of Method

2.1 The FTIRS methodology for the determination of VOCs and methane in headspace samples is based upon absorption spectroscopy in the mid infrared region (200-4000 cm^{-1}). Most molecules with a dipole moment have the ability to absorb mid infrared radiation. Each molecule that absorbs infrared radiation typically has an absorption spectrum that is unique to that molecule and the spectrum can be used to qualitatively identify the compound. The absorbance is also linearly related to the concentration of that molecule making quantitative analysis possible as well. The gaseous sample is aspirated in to an evacuated cell mounted on an FTIR spectrometer and the infrared (IR) spectrum is recorded. Due to the large number of analytes required for analysis of headspace samples, a very high degree of spectral overlap is expected and multiple frequencies are required to determine each analyte. All of the components of interest are identified and quantitated from each spectrum using a multivariate analysis technique algorithm. Partial least squares (PLS) is one such multivariate analysis technique, but the analyst may choose another appropriate technique. The multivariate analysis technique chosen must be specified in site SOPs.

2.2 The standardization process for the multivariate analysis technique includes collecting a library of spectra in the appropriate concentration range for all of the

analytes and interferences. More than one spectrum is required for each analyte and all spectra should be recorded under the same physical conditions as those to be used to analyze the field samples. Individual multivariate analysis technique methods for each analyte are used so that the optimum spectral regions can always be used for each analyte. The entire library of spectra for the particular application is used in each multivariate analysis technique calibration/standardization.

2.3 Since the absorbtivity is a constant for a given molecule at a given IR frequency, it is possible to have precalibrated methods that can be transferred from instrument to instrument, with some limitations. Once the multivariate analysis technique calibration/standardization for a particular application is established, it may be transferable to other instruments used to perform the same analysis as long as the physical parameters (e.g., temperature and pressure) under which the sample spectra are obtained remain the same. Optimally, when transferring the methods to other instruments, the hardware for all of the instruments should be as similar as possible, although this may not always be absolutely necessary. Spectral abnormalities due to a particular instrument can often be accommodated by adding blank spectra to the calibration set.

3.0 Interferences

3.1 Carbon dioxide (CO_2) and water are the primary interferences in field samples. Other interferences may exist based upon the nature and source of the gas sample to be analyzed. In most cases, every analyte of interest is interfered with by other analytes of interest, matrix components (e.g., CO_2 and water), or both. Table 1 and Table 2 list the analytes and interferences, with their respective best quantitative spectral regions.

3.2 Because spectra of all of the analytes and known interferences are included in the PLS calibration/standardization and because spectral overlaps are generally always present, true interferences for this method consist of any compound that absorbs IR light in the spectral region of interest for a particular analyte but is not present in the calibration set. Once identified, spectra of the new interference can be added to the calibration set and previously recorded spectra reanalyzed with the new calibration/standardization.

3.3 Another type of interference may be due to concentrations of either the analyte or an interferant that exceed the linear absorbance range of the method. The extent of the linear range will depend upon the detector used, the nature of the analyte absorption band, the resolution of the instrument, and the mathematical functions used in the conversion of the interferogram to the single beam spectrum. In this case, the interference can often be overcome by including spectra of the component(s) through the entire concentration range that is expected. The multivariate analysis technique algorithm will define factors to identify and deal with the nonlinearities. In some cases, this may require the addition of multiple spectra to the calibration set to define factors not only for the component with the wide concentration range but also low concentration components that are affected by the high concentration component.

3.4 Additional apparent interferences may also be due to slight changes in the wavelength (frequency) accuracy. This type of interference is usually most evident for analytes with very narrow absorption bands relative to the resolution at which the spectra were recorded. The frequency accuracy of the instrument should be verified to minimize this problem.

3.5 Contamination can occur whenever high-concentration and low-concentration samples are analyzed sequentially. A blank of hydrocarbon and CO_2-free dry air or nitrogen should be analyzed between the analysis of a high-concentration sample and a low-concentration sample. In addition, contamination may be introduced if the sampling manifold is not cleaned properly between samples.

3.6 The use of non-Teflon plastic coatings, non-Teflon thread sealants, or flow controllers with rubber components should be avoided.

4.0 Safety

4.1 This procedure may involve the use of hazardous materials, operations, and equipment. It is the responsibility of whoever uses this procedure to consult appropriate site personnel concerning health and safety issues and establish appropriate health and safety practices. Consideration should be given to safety concerns regarding chemical and radiation exposure. Training regarding proper storage, usage, and disposal of chemicals is recommended.

4.2 Many of the VOCs analyzed for or otherwise used in this method are known health hazards and may be flammable. Handling of neat solvents, condensates, or other standards should be done with appropriate personal protective equipment. Proper ventilation should be provided and these materials should be kept away from heat, sparks, and open flame. All samples will exit the FTIRS system via the vacuum pump so the outlet of the pump should be fitted with an appropriate trap to capture the exiting VOCs. The trap should be handled as hazardous waste.

4.3 If samples are to be obtained from radioactively contaminated containers, the inlet to the sampling manifold should be fitted with an appropriate particulate filter to prevent contamination of the system components. This trap should be handled as radioactive until it can be surveyed. If contaminated, it should be disposed of as radioactive waste.

4.4 The gas sample cell and all other gas sampling manifold components will be heated to at least 110EC. Precautions must be taken to avoid burns.

5.0 Apparatus and Materials

5.1 Sampling Manifold

An example of the sampling manifold is shown in Figure 1. The manifold consists of the following components:

5.1.1 1/4 in. chromatographic grade stainless steel tubing with fittings rated for operation pressures of < 0.1 to > 1400 mm Hg.

5.1.2 Pneumatic or solenoid valves controlled by the data station and capable of operation from < 0.1 to > 1400 mm Hg. Valves E1-E8 in Figure 1 are electronically controlled. M2-M4 are manual valves or regulators. The manual values may be replaced with electronically controlled valves.

5.1.3 250 mL passivated stainless steel SUMMA® canisters.

5.1.4 Vacuum pump capable of evacuating the manifold and IR sample cell to < 100 um Hg.

5.1.5 Generator or other source of hydrocarbon, and CO_2-free dry air or nitrogen.

5.1.6 Port/connection for the introduction of gas standards for calibration and quality control.

5.1.7 Port/connection for the collection of samples in SUMMA® canisters.

5.1.8 Heat tape, insulation, thermocouples, and controller (i.e. Omega 10 channel) capable of maintaining the sampling manifold and other transport lines at 110EC or higher. (The actual temperature must be consistent to " 2EC for standards, reference material, blanks, and samples.)

5.1.9 Pressure transducer capable of recording pressures from < 0.1 to > 1400 mm Hg.

5.2 FTIR Spectrometer

5.2.1 Interferometer: Interferometer with all components of the optical system capable of operation from 550-4000 cm^{-1}. Zinc selenide (ZnSe) windows with an antireflective coating are recommended for strength to resist the stress of the vacuum and to resist degradation from water. The interferometer should have user selectable resolution with a maximum resolution of at least 1 cm^{-1}. Actual choice of resolution used for a particular analysis will depend upon multiple factors including the number and nature of the analytes to be determined. Lower resolutions may have the advantage of slightly increasing the signal-to-noise ratio, thereby increasing the precision and possibly lowering the detection limits. Ultimately the choice of resolution will be up to the analyst and any resolution will be acceptable if the QAOs for accuracy and precision listed in Table 1 can be met.

5.2.2 Optical Bench: To assure stability of the instrument, the optical bench should be purged with hydrocarbon and CO_2-free dry air or nitrogen. An alternative would be to seal the optical bench and fill it with an appropriate hydrocarbon-, CO_2-, and water-free gas.

5.2.3 Sample Cell: Selection of the sample cell pathlength is dependent upon the expected analyte concentration range and the necessary detection limits for the particular application. For the analysis of TRU waste drum headspace, a 20 cm or 1 m pathlength is suggested. The choice depends upon the laboratory's ability to achieve the required detection limits.

5.2.4 Detector: Two detectors are commonly used with FTIRS, a mercury cadmium telluride (MCT) or a deuterated triglycine sulfate (DTGS). The DTGS detector's response is very linear but is less sensitive than the MCT. The response of the MCT detector is often not as linear but can be electronically linearized or software manipulated. The MCT detector must be cooled with liquid nitrogen (LN_2) (which can be problematic when working inside a glovebox) or thermo electric cooled.

5.2.5 Data System: A data system that controls all of the functions of the sampling manifold (if using an on-line integrated sampling/analysis system), operation of the FTIRS and is capable of data collection and software data reduction.

6.0 Reagents

6.1 Reference/Blank Gas:

Source of hydrocarbon and CO_2-free dry air or nitrogen (e.g., cylinder or generator).

6.2 Stock Standards:

Stock calibration gas standards of all analytes listed in Table 1 must be purchased commercially (Scott Speciality Gases or equivalent). The standards must be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Alternatively, analytical facilities may prepare stock standards and document the analyte concentrations in these standards on analytical equipment that has been calibrated using traceable and certified reference materials. Documentation shall be based on at least three analyses with the concentration being reported as the mean " one standard deviation. All gas standards must be replaced after 12 months if comparison with check standards indicates a problem.

7.0 Sample Collection, Preservation, and Handling

7.1 Since sample collection and handling is performed with the automated sampling manifold and is associated with the analysis step, the actual sampling technique will be discussed in detail in Section 8.0. Preservation, handling, and chain-of-custody requirements for discreet field samples do not directly apply to this automated on-line sampling and analysis technique. However, controls must be in place to ensure the integrity of the sample and the data associated with that sample. This also applies to the quality control (QC) samples.

7.2 If samples are collected in SUMMA® canisters before analysis, they must be collected using the sampling procedures described in Procedure 110.1 through 110.4 of this Methods Manual. Sample canisters must be stored at room temperature and holding times cannot exceed 28 days. In addition, all sample handling and chain-of-custody procedures described in Section 6.0 of the *Transuranic Waste Characterization Quality Assurance Program Plan* (QAPP) (DOE 1995b) must be followed.

8.0 Procedure

8.1 Recommended FTIRS System Operating Conditions

Optical System:	550-4000 cm^{-1}
IR windows:	ZnSe, with antireflective coating
Resolution:	1 cm^{-1}
Sample Cell:	20 cm or 1 meter
Sampling manifold and transfer lines:	110EC or higher ("2EC)

8.2 Detector Options

Two detectors are available for use with the FTIRS, a mercury cadmium telluride (MCT) or a deuterated triglycine sulfate (DTGS). The DTGS is less sensitive than the MCT detector, however the DTGS's response is very linear. The MCT detector

can be linearized electronically or software manipulated to meet requirements. A disadvantage of the MCT detector is that it must be cooled which presents a problem when working with radioactive samples in certain locations (e.g., suspect radiation zones).

8.3 Performance Testing

8.3.1 The stability of the FTIRS instruments used to develop this method is very good. Because of this stability, signal-to-noise and wavelength/frequency accuracy checks are only required on a monthly basis (see Table 3) to verify that the optical characteristics are still within the performance window defined for the optical and detector configuration used.

8.3.2 At the beginning of each 12-hour analysis period or each shift, a single beam spectrum of hydrocarbon and CO_2-free dry air or nitrogen is recorded as the reference spectrum for calculating the absorbance spectra for the samples. These spectra can also be archived and used for the long term evaluation of source intensity and contamination of the optical components in the system.

8.4 Calibration

Qualitative and quantitative determinations at multiple frequencies are complex and necessarily require multivariate analysis techniques, among the best of which is PLS. This discussion references PLS, but other appropriate multivariate analysis techniques may also be used. The chosen multivariate analysis technique must be specified in the site SOP.

PLS is a spectral decomposition method which is calibrated/standardized using a relatively large set of calibration spectra. The calibration set consists of spectra containing the analyte of interest and spectra containing all of the interferences and background effects which need to be modeled. Because of the large number of analytes to be determined, the set of calibration spectra should, at a minimum, consist of two pure component spectra of the analyte(s) of interest, two pure component spectra of each suspected interference, and some spectra which demonstrate the range of background components such as water and CO_2. If very wide or high concentrations are suspected, nonlinear effects (i.e., which can be modeled by linear equations such

TABLE 3
Summary of FTIRS Calibration Requirements
for Gas Volatile Organic Compound and Methane Analysis

Technique	Procedure	Frequency of Procedure	Acceptance Criteria
FTIRS	Frequency Validation	Monthly	Within performance window
	Signal to noise testing	Monthly	Within performance window
	Initial calibration spectra for analyte components, interferences, and background components	Initially and as needed	Meets PLS (or other appropriate multivariate technique) requirements

Continuing calibration	Once per on-line batch	%R of 70-130 for 10 analytes in on-line control sample

%D = Percent difference
PLS = Partial least squares
%RSD = Percent relative standard deviation

as $y = ax^2 + bx + c$) can be modeled by the PLS algorithm by the addition of spectra to the calibration spectra which adequately demonstrate the effect. Similarly, if high concentrations and nonlinear effects of an interferant cause problems with an analyte of interest, spectra which demonstrate the range of this problem can be added to the calibration set. Multicomponent spectra can also be used for calibration if the concentration of the analytes vary independently of each other. The result of the PLS calibration is a set of factors which qualitatively and quantitatively describe the analyte of interest and all of the potential interferences that were included in the calibration set. Independent PLS methods for each analyte of interest are preferred so that the optimum spectral regions can be used for that analyte. The use of the optimum spectral region for each analyte helps to minimize the effects of interferences and widely different sample compositions.

Commercially available software is used for the PLS predictions. Different packages may require slightly different methodologies for the actual steps associated with calibration and prediction. Consult the software manual for specific instructions. The PLS-1 algorithm as described in Halland and Thomas (1988) is preferred and was the basis of the commercial software used to develop these methods. A separate PLS method is generated for each analyte. The change provided is derived from the experience with the add-on application PLSplus for Grams/386 acquired from Galactic Industries Corporation.

8.4.1 Collect a library of analyte and interference spectra from known concentration standards of the components as described in the sections below.

8.4.2 Once the library of calibration spectra has been obtained, the calibration file containing the file names of all samples to be used in the PLS training set and concentration of the analyte in each spectrum is generated.

8.4.3 The optimum wavelength region for each analyte method is selected from examination of the raw analyte spectrum and the correlation spectrum for that analyte. The correlation spectrum is calculated as a development aid in the PLSplus package. Optimum wavelength regions for the analytes in the TRU waste drum application are listed in Table 1.

8.4.4 Once the optimum wavelength region has been selected, the PLS-1 model is calculated and the optimum number of factors for the model determined from the predicted residual error sum of squares (PRESS) via a across-validation calculation.

$$PRESS = \sum_{i=1}^{n} (C_i - \hat{C}_i)^2 \quad (1)$$

where

i = the training set spectrum number
C_i = the true concentration
$_i$ = the concentration predicted from the model

The number of PLS factors required to minimize the PRESS is often the optimum number of factors for the PLS calibration. The optimum number of PLS factors can also be determined from the cross-validation calculation via a F-test. Consult the software users manual for additional details on factor selection.

8.5 Reference Spectrum Collection

8.5.1 Close valves E1, E2, E3, E4, and E6. Open valves E5, E7, and E8.

8.5.2 Evacuate to < 100 um Hg, then close valves E7 and E8.

8.5.3 Leak check the manifold. A loss of vacuum < 1 um Hg/second is acceptable. If > 1 um Hg/second, repeat steps 8.4.1 through 8.4.3.

8.5.4 Open valve E2 and wait for pressure to stabilize, then close valves E2 and E5.

8.5.5 Record IR spectrum as a single beam (reference) spectrum.

8.6 Calibration or Check Standard Collection

8.6.1 Close valves E1, E2, E3, E4, and E6. Open valves E5, E7, and E8.

8.6.2 Evacuate to < 100 um Hg, then close E7 and E8.

8.6.3 Leak check the manifold. A loss of vacuum < 1 um Hg/second is acceptable. If > 1 um Hg/second, repeat steps 8.6.1 through 8.6.3.

8.6.4 Open valve E2 and wait for pressure to stabilize, then close valves E2 and E5 and record the cell pressure.

8.6.5 Record IR spectrum and ratio to reference spectrum recorded as described in 8.5 to obtain the absorbance spectrum.

8.7 Blank Sample Collection

8.7.1 Close valves E1, E2, E3, E4, and E6. Open valves E5, E7, and E8.

8.7.2 Evacuate to < 100 um Hg, then close E7 and E8.

8.7.3 Leak check the manifold. A loss of vacuum < 1 um Hg/second is acceptable. If > 1 um Hg/second, repeat steps 8.7.1 through 8.7.3.

8.7.4 Open valve E2 and wait for pressure to stabilize, then close valves E2 and E5 and record the cell pressure.

8.7.5 Record IR spectrum and ratio to reference spectrum recorded as described in 8.5 to obtain the absorbance spectrum.

8.7.6 Analyze spectrum using the PLS (or other multivariate analysis technique) methods generated in 8.4.

8.8 Sample Analysis

8.8.1 Close valves E1, E2, E3, E4, and E6. Open valves E5, E7, and E8.

8.8.2 Evacuate to < 100 um Hg, then close valves E7 and E8.

8.8.3 Leak check the manifold. A loss of vacuum < 1 um Hg/second is acceptable. If > 1 um Hg/second, repeat steps 8.8.1 through 8.8.3.

8.8.4 Open E1 and wait for pressure to stabilize, then close E1 and E5 and record the cell pressure.

8.8.5 Record the IR spectrum and ratio to reference spectrum recorded as described in 8.5 to obtain the absorbance spectrum.

8.8.6 Analyze spectrum using the PLS (or other multivariate analysis technique) methods generated in 8.4.

8.8.7 If dilution is required as determined from the spectral residuals from the spectral analysis of 8.8.6, open valve E7 until the desired dilution is reached and record the pressure.

8.8.8 Close valve E7 and open E6 to back fill with air to atmospheric pressure and repeat step 8.8.5.

8.8.9 For duplicate analysis of the same sample, open valve E5 and repeat steps 8.8.4 through 8.8.8.

8.9 Replicate Sample Collection in SUMMA®**Canister**

For replicate sample collection in to a SUMMA® canister for independent verification using GC/MS, the following steps must be used.

8.9.1 Prior to 8.8.1, attach an evacuated SUMMA® canister to the port below valve E4. M4 is the manual valve on the canister.

8.9.2 Close valves E1, E2, E3, and E6. Open valves E4, E5, E7, and E8.

8.9.3 Evacuate to < 100 um Hg, then close valves E7 and E8.

8.9.4 Leak check the manifold. A loss of vacuum < 1 um Hg/second is acceptable. If > 1 um Hg/second, repeat steps 8.9.2 through 8.9.4.

8.9.5 Prompt the operator to open M4.

8.9.6 Open valves E1 and E4 and wait for pressure to stabilize. Record the pressure, prompt the operator to close M4, and close valves E1, E4, and E5.

8.9.7 Record the IR spectrum and ratio to reference spectrum recorded as described in 8.5 to obtain the absorbance spectrum.

8.9.8 Analyze spectrum using the PLS (or other multivariate analysis technique) methods generated in 8.4.

8.9.9 If dilution is required as determined from the spectral residuals from the spectral analysis of 8.9.6, open valve E7 until the desired dilution is reached and record the pressure.

8.9.10 Close valve E7 and open E6 to back fill with air to atmospheric pressure and repeat 8.9.7

9.0 Calculations

This discussion references PLS, but other appropriate multivariate analysis techniques may also be used. The chosen multivariate analysis technique must be specified in the site SOP.

The PLS-1 algorithm as described is used for identification and quantitation of the analytes of interest. Because this PLS analysis is available in commercially available software packages, these calculations are detailed in Reference 1. Also refer to the vendor software manual.

9.1 Spectral Residuals

Spectral residuals are also calculated by the vendor software, however, because of their potential usefulness a brief description is given here. Spectral residuals can be used to identify analytical problems attributed to unknown interferences, excessive analyte or interferant concentration, or abnormal backgrounds. Spectral residuals for an individual sample are defined as the sum of the squares of the difference between the sample spectrum, $>_j$, and the reconstructed spectrum predicted by the PLS method, a_j.

$$R_s^2 = \mathrm{R_s} \sum_{j=1}^{n} (a_j - \hat{a}_i)^2$$

Spectral residuals from the PLS calibration/training set are defined as:

$$R_c^2 = \sum_{j=1}^{m} \sum_{j=1}^{n} (a_j - \hat{a}_i)^2$$

where

m = the number of spectra in the calibration set
n = the number of points used from each spectrum

The F-ratio is then calculated as follows:

$$F = \frac{m^* R_s^2}{R_c^2}$$

when the probability is greater than 0.99 that R_s^2 is different from R_c^2, then the result is flagged as a possible outlier.

Potential problems with the analysis of waste drum headspace by FTIRS and PLS are flagged by statistically significant spectral residuals. The spectral residual is the sum of squares of the differences between the PLS predicted sample spectrum and the actual sample spectrum. High spectral residuals can be associated with one of the following situations: a) signal-to-noise ratios significantly less than the noise on the calibration spectra, b) unmodeled background functions, c) concentrations of the analyte or a modeled interferant that cause the absorbance to be outside of the modeled range, and d) interferences that were not in the calibration set. Solutions to situations a and b would be to first collect a new reference spectrum (ratio spectrum for the absorbance calculations). If the analysis of a blank air sample still indicates that a problem exists, spectra to model the background can be added to the PLS calibration as described above. If situation c occurs, simple dilution of the sample is appropriate or, if the situations warrants, the PLS calibration set can be altered as described previously. The initial response to situation d would be to dilute the sample to minimize the effects of the interference. If the high spectral residuals are still prevalent after the dilution, an unmodeled interferant (i.e., tentatively identified compound [TIC]) is likely present. To determine the identity of a new interference, contributions to the original spectrum from compounds found in the sample must be subtracted from the original sample spectrum. The resulting spectrum can then be interpreted for functional groups and possible compound identifications. A library search is performed to determine the five most likely compounds contributing to the interference. If the problem with an interference is prevalent in multiple samples within an on-line batch, a SUMMA canister sample must be collected and analyzed by GC/MS to confirm the unknown compound identity. Once determined, IR spectra of the interference can be collected, added to the calibration set, the PLS calibration rerun, and the stored sample spectra reanalyzed, if appropriate or necessary. A new method for the interfering compound must be added to the standard analysis routine if it appears in more than 20 percent of all samples.

9.2 Pressure Correction

The calibration and quantitation with the PLS methods assumes a constant pressure which is normally the local atmospheric pressure (P_{norm}). Samples may be collected at pressures slightly different pressures than P_{norm} or a sample may be diluted and the PLS predicted concentrations (C_{pred}) must be corrected for the actual sample pressure (P_{samp})

$$C_{actual} = C_{pred} \frac{P_{norm}}{P_{samp}}$$

10.0 Quality Control

10.1 Each facility that uses this procedure is required to operate a formal quality control program. The facility must retain records to document the quality of the data generated. Each facility must have SOPs documenting and describing activities involved in utilizing

this procedure. Specific quality control practices will include, but are not limited to, the analysis of quality control samples. The types of quality control samples, their associated frequency of analysis, acceptance criteria, and corrective action required if samples do not meet the acceptance criteria, is summarized in Table 4. SOPs must address requirements for preparing blanks, duplicates, and control samples. If using an on-line integrated sampling/analysis system, all QC samples must be collected through the entire sampling/transfer manifold.

10.2 All facilities using this procedure must demonstrate acceptable performance prior to the analysis of actual samples. Demonstration of acceptable performance will be achieved by analyzing method performance samples (Table 4). These samples can be either commercially purchased or laboratory prepared, and must contain at least 10 analytes listed in Table 1 at concentrations appropriate (2-5 times the PRQLs) to meet the quality assurance objectives specified in Table 1. The analysis of seven samples must meet the criteria specified for precision, accuracy and MDL in Table 1. Demonstration of acceptable method and analyst performance must be repeated (by analyzing four samples) at a minimum of every six months. Method performance should be conducted over a period of several days to account for long term variability. Precision will be determined as follows:

TABLE 4

Summary of Quality Control Samples and Frequencies for Gas Volatile Organic Compounds Analysis by FTIRS

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
Method performance samples	Seven (7) samples initially and four (4) semiannually	Meet Table 1 QAOs	Repeat until acceptable
Laboratory duplicates or on-line duplicates	One (1) per analytical batch or on-line batch	RPD # 25[b]	Nonconformance if RPD > 25
Laboratory blanks or on-line blanks	One (1) per analytical batch or on-line batch	Analyte concentrations < PRQL	Nonconformance if analyte concentrations > PRQL
Laboratory control samples or on-line control samples	One (1) per analytical batch or on-line batch	70-130 %R	Nonconformance if %R < 70 or > 130
GC/MS comparison sample	One (1) per analytical batch, or, one (1) per on-line batch	RPD # 25[b]	Nonconformance if RPD > 25
Blind audit samples	Samples and frequency controlled by the Gas PDP Plan	Specified in the Gas PDP Plan	Specified in the Gas PDP Plan

[a]Corrective Action when QC samples do not meet the acceptance criteria; Nonconformance procedures are outlined in Section 2.1.2.1 of the QAPP.

[b]Applies only to concentrations greater than the PRQLs listed in Table 1.

MDL = Method detection limit
PDP = Performance Demonstration Program
QAO = Quality assurance objective
%R = Percent recovery
RPD = Relative percent difference

- For duplicate measurements, the precision expressed as the relative percent difference (RPD) is calculated as

$$RPD = \frac{\overline{C_1 + C_2}}{2} * 100$$

where

C_1 and C_2 = two values obtained by analyzing the duplicate samples
C_1 = larger of the two observed values

- For three or more replicate measurements, the precision expressed as the percent relative standard deviation (%RSD) is calculated as

$$\%RSD = \frac{s}{\bar{y}} * 100$$

where

s = standard deviation
y = mean of replicate analyses

- The standard deviation (**s**) is defined as

$$s = \sqrt{\sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{n - 1}}$$

where

y_i = measured value of the i^{th} replicate sample analysis measurement
n = number of replicate analyses

Accuracy will be determined as the percent recovery (%R) as follows:

$$\%R = \frac{C_m}{C_{srm}} * 100$$

where

C_m = measured concentration
C_{srm} = true concentration

MDL will be determined as follows:

$$MDL = 3s \quad (10)$$

where
s = standard deviation

Initially, a minimum of seven samples of ambient air must be used to establish the MDLs. MDLs should be constantly updated using the results of the on-line control sample.

Initial estimates of the detection limit can also be obtained from the calibration statistics. One of the statistics that can be used to evaluate the calibration is the standard error of calibration (SEC).

$$SEC = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{n - 1}}$$

where $\hat{y}_i$ = the predicted concentration in calibration standard *i*
y_i = the true concentration
n = the number of standards in the training set

Three times the SEC is a reasonable first estimate of the detection limit as it includes errors for all potential interferences for that component that are in the calibration set.

10.3 The facility must analyze blanks at the frequency specified in Table 4. The same procedure used to prepare and analyze field samples will be used to prepare and analyze the laboratory blanks or on-line blanks. A blank is run to verify that the sampling manifold is clean and that a reference single-beam spectrum for that shift is appropriate. If using an on-line integrated sampling/analysis system, if the results of a field blank collected through the sampling manifold meets the acceptance criterion, a separate on-line blank need not be collected or analyzed. Additional blanks should be run if sample carryover is suspected. Blank results are acceptable if the concentration of target analytes is less than the PRQL for each compound. Corrective action must be implemented if blanks exceed this level.

10.4 The laboratory must analyze individual field samples in duplicate at a frequency specified in Table 4. Duplicate results will be considered acceptable if the RPD is # 25 percent. RPD is determined by Equation 6. Duplicates which do not meet these criteria must be flagged.

10.5 The laboratory must analyze laboratory control samples (LCS) or on-line control samples at the frequency specified in Table 4. Commercially purchased gas standards will be used to prepare control samples. The gas standard used to prepare control samples must be independent of those used for initial instrument calibration. Controls must contain 10 analytes listed in Table 1 at concentrations in the linear calibration range of the FTIRS system. If more than one standard is used, they should be of different analyte combinations and/or concentration ranges. Control sample results will be considered acceptable if the %R is 70 to 130 percent of the known value. %R is determined by Equation 9. If the results are outside of this range, then the source of the error must be determined, and any problems corrected. It is also recommended that the data from the analysis of the control sample be used to track not only the precision and accuracy, but to maintain a current tabulation of appropriate detection limits.

10.6 For comparison purposes, one sample per analytical batch or on-line batch must be analyzed by GC/MS. For on-line integrated sampling/analysis systems, this will involve the collection of a sample in a SUMMA canister. The results of this comparison shall be

acceptable if the RPD between the FTIRS results and the GC/MS results is less than or equal to 25.

10.7 All suspect data will automatically be reported with qualifiers. The decision to dilute the sample for additional analysis is based upon either an excessive concentration or a statistically significant spectral residual. Spectral residuals can be indicative of unmodeled spectral interferences or concentrations of either the analyte or a modeled interference that cause nonlinear absorbances which have not been included in the multivariate analysis technique calibration model. Flags will indicate if the dilution was triggered by high concentration of the analyte, was the result of a spectral residual, or both. If a spectral residual and/or high concentration is noted in the diluted sample spectrum, a second flag will be set. Only those analytes which were flagged in the original analysis will be requantitated in the second analysis and the detection limits appropriately adjusted for the dilution.

10.8 The laboratory is required to analyze blind audit samples. These audit samples are part of the Performance Demonstration Program. Details of this program as related to FTIRS will be added to the *Performance Demonstration Program Plan for the Analysis of Simulated Headspace Gases for the Transuranic Waste Characterization Program* (Gas PDP Plan) (DOE 1995a) during the next revision. Until that time, participants who wish to use FTIRS must notify the Carlsbad Area Office of their intent along with any unique sample volume and pressure requirements. FTIRS results will be considered in accordance with Sections 6.1.5.4 and 6.1.5.5 of the Gas PDP Plan, "Special Scoring" and "Canister or Analyte Disqualification."

11.0 Method Performance

11.1 The data listed in Table 5 summarizes the analyses of commercial standards containing the 10 VOCs listed over several months. This table also includes the results from GC method analysis. The precision of the FTIRS analysis is typically < "10 percent and within the 25 percent requirement. The accuracy appears to have a negative bias but is within the 30 percent requirement. The detection limits were calculated from the deviations in the analyses of these standards.

12.0 References

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DOE 1995a. *Performance Demonstration Program Plan for the Analysis of Simulated Headspace Gases for the Transuranic Waste Characterization Program.* CAO-95-1076, Current Revision, Carlsbad, New Mexico, Carlsbad Area Office, U.S. Department of Energy.

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TABLE 5

Method Performance

COMPOUND	True(dry)	True(wet)	GC(dry)[a]	GC(wet)[b]	FTIRS(dry)[c]	FTIRS(wet)[d]
Carbon Tetrachloride	96.3	101	99	100	86	90
1,1-Dichloroethene	98.9	102	107	115	92	94
1,1-Dichloroethane	96.9	101	109	111	87	90
Freon 113	95.5	97	97	106	84	85
Methylene Chloride	97.6	98	98	107	79	80
Toluene	96.7	102	86	89	86	90
1,1,1-Trichloroethane	97.3	100	110	101	96	95
Trichloroethene	100.3	99	91	101	83	85
Methane	99.5	985	nd	nd	100	1053
Methanol	96.2	107	72	47	49	57

Replicates may have been collected on different days.

nd = Not detected

[a]Based on seven replicates.
[b]Based on four replicates.
[c]Based on 40 replicates.
[d]Based on 45 replicates.