4.2 ATMOSPHERIC TRACER TECHNOLOGY (ATT)

4.2.1 SCOPE

For over a decade EML has participated in a number of atmospheric tracer experiments designed to provide dynamic modelers with large data bases to verify, modify, or develop computer simulations of atmospheric transport and diffusion of energy-related pollutants over long distances. The tracer technology involves the release of perfluorocarbon tracers at controlled and known rates from a source(s) into the atmosphere under well-documented meteorological conditions, and measuring the tracers at very low concentrations at various distances from the release point(s).

We will present here the analytical procedure for the determination of the perfluorocarbon tracers (PFTs), perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), ortho(cis)dimethylcyclohexane (OC-PDCH), perfluorodimethylcyclohexane isomer (PDCH), and perfluorotrimethylcyclohexane (PTCH). The PFTs are quantitatively determined by gas chromatography/electron capture detection.

ATT-01

GAS CHROMATOGRAPHIC DETERMINATION OF PERFLUOROCARBON TRACERS

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APPLICATION

This procedure is applicable to tracers adsorbed on Ambersorb adsorbent contained in stainless steel tubes in the programmable atmospheric tracer sampler (PATS) lids (described in Section 2.2.4.2).

The procedure (Dietz, 1986) involves the heating of the PATS tubes (described in Section 2.2.4.2) to 400°C by resistance heating and desorbing the PFTs and ambient air impurities (halocarbons) into the carrier gas. The compounds pass through a temperature programmed precut column (heated by resistance heating) where the high boiling point impurities are retained. The low boiling point impurities and the PFTs are partially separated by the precut column. Further decontamination of the lighter impurities is accomplished by catalytic reduction using a first stage palladium catalyst maintained at 200°C and by venting the impurities to the atmosphere by proper timing of the carrier gas switching valves. A trap containing Florisil (FL) adsorbent is opened and the partially purified PFTs are adsorbed. Subsequent rapid resistance heating of the trap to 200°C injects the PFTs into the carrier gas of the main chromatographic column system. The desorbed tracers are further purified by passage through two palladium catalyst beds maintained at 200°C, and a Nafion permeation dryer. The purpose of the dryer is to remove moisture and halogenated acids produced by the catalytic reduction. The PFTs are then chromatographically separated by the main column and detected by the electron capture sensor. Details of the pneumatics configuration are shown in Figure 1.

SPECIAL GASES

1. 5% ultra high purity (UHP) (99.999%) hydrogen in UHP (99.999%) N_2 carrier gas.

2. Compressed air to operate the valve actuators.

3. UHP (99.999%) N_2.

4. Primary calibration standards consisting of a mixture of the four tracers: perfluoro-methylcyclopentane, perfluoromethylcyclohexane, ortho-(cis) perfluoro-dimethylcyclohexane (with isomers), and perfluorotrimethylcyclohexane.

   a. 1.0 µL L^{-1} of each tracer in UHP (99.999%) N_2.
   b. 10 nL L^{-1} of each tracer in UHP (99.999%) N_2.
   c. 0.1 nL L^{-1} of each tracer in UHP (99.999%) N_2.
   d. 1.0 pL L^{-1} of each tracer in UHP (99.999%) N_2.

SPECIAL APPARATUS

1. Gas chromatograph, modified Varian Vista 6000 or equivalent with Ni-63 electron capture detector and 1 mV recorder or data acquisition system.

a. Main column	15 cm x 3.2 mm: stainless steel packed with 0.1% SP-1000 on Carbopack C, 80/100 mesh.
b. Precut column	53 cm x 3.2 mm thin walled stainless steel tubing packed with Unibeads 2S, 80/100 mesh.
c. Florisil trap	11.5 cm x 1.6 mm thin walled stainless steel tubing packed with FL, 60/100 mesh.
d. Catalyst	1% palladium on polyethylenimine/SiO_2 (Royer Pd Catalyst), 20-40 mesh beads.
e. Carrier gas purifiers	activated charcoal, 13X molecular sieve and O_2 traps.

2. PATS, power control module (base).

3. Matheson Model 3800 gas regulators or equivalent.

4. Power Mate Corporation Model BPA 2086-V constant current power supply or equivalent.

5. Primeline (Soltec) two channel strip chart recorder or equivalent to monitor the PATS adsorbent tube desorption current and FL trap desorption temperature.

A. Gas chromatograph operating conditions.

Carrier gas flow	main column system - 22 cm^3 min^{-1} precut column system - 15 cm^3 min^{-1}
Catalyst temperature	200ºC (Injectors A and B)
Column temperature	main column - 160ºC precut column - temperature programmed - 80ºC to 160ºC at 160º min^{-1}
Detector temperature	200ºC
Compressed air	set at 276 kPa (40 psig) to actuate switching valves
Nitrogen	set at 207 kPa (30 psig) for PATS lid Scanivalve equalization pressure

B. Gas chromatograph relay assignments.

Relay No.	Assignment
1	V1, sample valve (SV)
2	V2, precut valve (PCV) for changing the direction of the precut column (PCC) carrier gas flow.
3	V3, flow direction valve (FDV) for loading FL trap and purging catalyst B.
4	V4, FL trap valve (FTV).
5	Desorption power - **High** heat.
6	Desorption power - **Low** heat.
7	PATS tube/FL trap power routing relay.
8	Auxiliary power to precut column (PCC) for **High** temperature. Relay **Off** for **Low** temperature.

C. Timed relay automation programming.

Method No.	Method time (min)	Analysis integrated time (min)	Relay **On**	Relay **Off**	Aux. temp. (°C) precut column)	Remarks
1	.00	.00			85	
	.01	.01	3,7	8		V3 (FDV) **On**, FL Trap relay **On**. Auxiliary power to PCC **Off**.
	.02	.02	4			V4 (FTV) **On** (FL Trap **Open**)
	.05	.05	5			**High** heat **On** FL Trap
	.08	.08	6	5		**Low** heat **On** FL Trap, **High** heat **Off**
	.35	.35	4,6			V4 (FTV), (FL Trap **Off**), heat **Off**
	.40	.40		7		FL Trap relay **Off**
	3.00	3.00				Total run time
3	.00	3.00			80	
	.01	3.01	2			V2 (PCV) **On**, PCC low **Forward**
	.10	3.10	1,5			V1 (SV) **On**, **High** heat **On**
	2.00	5.00				Total run time
4	.00	5.00	8		160	Auxiliary Power to PCC **On**
	.60	5.60		3		V3 (FDV) **Off**
	.65	5.65	4			V4 (FTV) (Trap **Open**)
	1.50	6.50		1,5		V1 (SV) **OFF**, **High** heat **Off**
	4.50	9.50		4		V4 (FTV) (Trap **Closed**)
	4.60	9.60		2		V2 (PCV) **Off** (precut Column **Back-Flush**)
	6.20	11.20				Total run time
5	.00	11.20			145	PCC in **Back-Flush**, Catalyst B purge
	.60	11.80				Total run time

D. Setting the gas chromatograph.

1. Set the 5% UHP hydrogen in UHP N_2 carrier gas pressure regulator to 690 kPa (100 psig).

2. Set the main column pressure to 276 kPa (40 psig) and adjust the main column flow to 22 cm^3 min^{-1} using a calibrated flowmeter or soap bubble spyrometer. Set the precut column pressure to 104 kPa (15 psig). This pressure should give carrier gas flows of 15 cm^3 min^{-1} at vents 1, 2, and 4.

3. Adjust the Nafion permeation dryer purge gas flow rate at vent 3 to ~ 30 cm^3 min^{-1}.

4. Input all GC operating conditions and the timed relay program for each method as specified in Section 4.2.3.3. Method 2 is not used because it is a permanent gas chromatograph memory default method.

5. Set the constant current power supply to 14-14.25 A.

E. Determination.

1. Attach the PATS lid containing the samples to the PATS base. Plug in the lid AFM connector into the base receptacle labelled **AFM Connector**.

2. Set the base sample **Duration** rotary switches to **0013** (13.0 min) and the **Sample Quantity** (number of tubes) to **24**. This sets the switching time between tubes and the number of tubes to be sequentially analyzed. The number of tubes desired is 23; however, the analysis sequence is such that the PFTs from a sample are not injected into the main column until Method 1 of the next analysis sequence. Turn the **Power Switch** of the base to **On**.

3. Plug the constant current power supply jack into the lid receptacle labelled **Power Desorption**.

4. Attach the UHP N_2 gas line to the lid connector labelled **To Equalization** and set the tank regulator pressure at 207 kPa (30 psig). Its purpose is to equalize the pressure to prevent the lid Scanivalve plates from separating. Pressurize the Scanivalve and

manually step through each of the 23 tubes by rapidly pushing the **Valve** step switch to assure that the Scanivalve plates are properly seated. Step to tube number "**00**" and leave at that tube number.

5. Pull off the lid filter at the connector labelled **To SV** and attach the polyurethane tubing purge gas outlet from V1 (SV) to this connector. Attach the V1 (SV) polyurethane tubing carrier purge gas inlet line to the lid connector labelled **To PCM**. This connects the GC carrier gas lines to the lid.

6. Turn on the constant current power supply and the two-channel strip chart recorder.

7. Turn on the compressed air, set at 276 kPa (40 psig), to operate the valve actuators.

8. To start the analysis cycle, push the PATS base **Operate** switch to **Off**, bring the **Alarm** toggle switch from **Manual** to **Multi** then back to **Manual** and finally move the **Operate** toggle switch to **Run**. Tube No. 1 will advance into position, the gas chromatograph will start and run through its automated sequence consisting of four methods.

   Method 1: The FDV (V3) and FTV (V4) valves are energized and the FL trap containing the PFTs from the previous sample is heated. The desorbed PFTs are injected into the main column system (Figure 2). The precut column is in the back-flush mode.

   Method 3: SV (V1) and PCV (V2) are energized to place the precut column carrier gas flow into the forward position. Heat is applied to the PATS sample tube to desorb the sample (Figure 3).

   Method 4: The desorbed PFTs pass through the precut column, the column is heated to 160°C at a rate of 160°C min^{-1}. V3 is placed in standby and V4 is energized to allow effluent from the precut column to flow through the FL trap where the PFTs are adsorbed (Figure 4). V1, V2, and V4 rotate to standby, forcing the precut column carrier gas path into the back-flush mode.

Method 5: The precut column temperature is lowered to 145°C with continued back-flush to elute the residual higher boiling components out of vent 1 to the atmosphere (Figure 5).

9. At the end of 13 min, the next sample tube will step into position. This sequence will continued until all 23 sample tubes have been desorbed and analyzed.

10. Record the chromatogram. A typical chromatogram of an ambient air sample containing tracers is shown in Figure 6.

11. Integrate the tracer peaks corresponding to their appropriate retention times. Apply the appropriate response factor corrections obtained from the analysis of working standards prior to the analysis of each batch of samples. Obtain the tracer volumes from the appropriate calibration curves and convert to concentrations using the sample collection volume.

12. The retention times are based upon the start of the 13-min run. The expected retention times are as follow:

Perfluoromethylcyclopentane (PMCP)	- 1.47 min
Perfluoromethylcyclohexane (PMCH)	- 2.25 min
Ortho(cis)perfluorodimethylcyclohexane (OC-PDCH)	- 3.60 min
Meta-para perfluorodimethylcyclohexane (MP-PDCH)*	- 4.17 min
Meta(cis)perfluorodimethylcyclohexane (MC-PDCH)	- 4.43 min
Para(trans)perfluorodimethylcyclohexane (PT-PDCH)	- 4.84 min
Perfluorotrimethylcyclohexane (1-PTCH)	- 9.20 min
Perfluorotrimethylcyclohexane (2-PTCH)	- 9.73 min

*Combination of the meta(trans) and para(cis) perfluorodimethylcyclohexane.

LOWER LIMIT OF DETECTION

Lower limit of detection (LLD) is defined here as that amount which gives detector response equal to three times the noise level (ACS, 1980). The LLDs are:

Perfluorocarbon	LLD (fL)
PMCP	2.7
PMCH	4.0
OC-PDCH	2.2
MP-PDCH	2.1
MC-PDCH	2.0
PT-PDCH	4.0
PTCH	3.9

DATA ACQUISITION AND REDUCTION

A. Computer hardware.

1. IBM personal computer AT with a minimum of 512 kilobytes system memory, 20 megabyte hard-disk drive, 5 1/4 inch floppy disk drive, enhanced graphics adapter card, graphics memory expansion card (64K) or equivalent.

2. IBM enhanced color display monitor offering 640 by 350 screen resolution and keyboard or an equivalent monitor and keyboard.

3. Nelson Series 760 intelligent A/D interface box or equivalent.

4. Citizen Model MSP-20 printer or equivalent.

5. Standard IEEE-488 (GPIB) cable.

6. Dysan 5 1/4 inch high-capacity, 96 TPI floppy diskettes or industry equivalent.

B. Computer software.

1. Nelson Analytical Corp. Model 2600 chromatography software package. Other software vendors provide equivalent packages.

2. Nelson Analytical Corp. Model 2660 peak summary tables software (optional).

3. Nelson Analytical Corp. Model 2670 batch reprocessing software (optional).

C. General procedure.

The electron capture detector (ECD) signal from the Vista 6000 gas chromatograph is monitored in real time by the Nelson intelligent interface offering 20 bit precision. The interface digitizes the detector signal and stores the values in its memory. When the data are available in the interface and the operating program is the 2600 software ACQUIRE on the IBM AT, the data is transmitted to the computer according to the METGEN method. The software detects peaks, determines their baselines, integrates these peaks, and then calculates the component concentrations. Three data files are created for each sample. They are distinguished by their file extensions: .PTS, .HDR, and .ATB. In the .PTS file, raw chromatographic mV data are saved in binary form, while in the .HDR file, parameters for sample identification pertaining to that raw data are stored in ASCII form. The peak heights and/or peak areas obtained from integration, as determined by the method, are stored in the .ATB file. Baselines different than those specified in the method may be drawn using the software's timed events capability. The values from the reintegration may be overwritten in the .ATB file. A schematic of the data acquisition and data reduction system is shown in Figure 7.

CALIBRATION

A. Standards preparation.

Presented here is a procedure for the preparation of PFT standards for both instrument calibration and daily working standards. The daily standards are analyzed prior to the analysis of a batch of samples to determine response factor corrections resulting from changes in electron-capture sensitivity. This method is applicable to PATS lids (described in Section 2.2.4.2).

B. Special apparatus.

1. Matheson Model 3800 gas pressure regulator or industry equivalent.

2. Nupro Model SS-4BMG gas flow regulating valve or industry equivalent. **Caution**: Low concentrations of tracer material could be adsorbed with other type valves.

3. A complete PATS unit consisting of a base (PCM) and a baked-out lid (AFM).

4. Teledyne-Hastings-Raydist Model HBM-1A bubble spyrometer or industry equivalent, NIST traceable.

5. A 1A cylinder containing 1 fL L^{-1} each of PMCP, PMCH, OC-PDCH and PTCH in UHP N_2.

C. Sample preparation.

1. Plug the battery charger into the port labelled **Chg.Jack** and a jumper in the receptacle labelled **Analysis**. The purpose of the jumper is to disable the sampling pump. Set the thumbwheel switches to the following settings:

   a. **Set Time/Alarm**: set to the appropriate time of day.

   b. **Duration**: set to the time in minutes desired for each tube to remain in line position.

c. **Sample Quantity**: set to 24. The sample quantity (23 in this instance) must always be set for one more tube than is physically present on a lid.

d. **Day Select**: place to the **On** position for the appropriate day of the week.

2. Plug the lid connector into the base receptacle marked **AFM Connector** and turn the **Power Switch** of the base to the **On** position.

3. Set the Matheson purity N_2 tank pressure to 207 kPa (30 psig) and attach the 3.2 mm polyurethane tubing line from the cylinder to the equalization inlet port labelled **To Equalization** on the lid. Open the N_2 supply to pressurize the Scanivalve and manually cycle through each of the 23 tubes. This is done by a rapid push of the **Valve** step switch. Make sure that the LCD display indicates that tube "**00**" is in line after this is completed.

4. Attach the 3.2 mm polyurethane tubing from V2 of the standard gas flow control system (Figure 8) to the lid port labelled **To SV**.

5. Set the pressure of the standard cylinder containing the PFTs to 207 kPa (30 psig). Slowly open the regulator valve (V1) to permit tracer gases to flow into the PATS lid through the Nupro Flow Control Valve (V2).

6. Connect the 3.2 mm polyurethane tubing from the outlet of the lid labelled **To PCM** to a calibrated flowmeter and adjust V2 to obtain 50 cm^3 min^{-1}.

7. Remove the calibrated flowmeter and replace with the bubble spyrometer.

8. Using a stopwatch, time a soap bubble to travel from 0 to the 100 cm^3 marks. Record the time and convert minutes and seconds to a pure minute time frame.

9. The quotient of 100 and the time is the flow rate of a mixed tracer gas.

10. If the flow rate is <49.0 or above 51.0 cm^3 min^{-1}, fine adjust the needle valve to obtain ~ 50 cm^3 min^{-1}.

11. Repeat Step 8 at least four times. The precision of the average of the four measurements should be within 2%.

12. Disconnect the tubing from the outlet of the lid to the bubble spyrometer.

13. To load daily working standards, set the **Duration** to **0002** (2 min) to load 100 fL of tracers onto each tube.

14. A signal must be given to inform the PATS logic to start the time sequence that indexes the first tube into position. To start the sequence push the **Operate** toggle switch to **Off**, move the **Alarm** toggle switch from **Manual** to **Multi** to **Manual** and finally push the **Operate** switch to **Run**.

15. The first tube will switch into line and 100 cm^3 of PFT gas will flow through the tube over a 2-min period. At the end of the 2-min period, the next tube will switch into position. This cycle will continue for 23 tubes. The actual volume of each PFT adsorbed on each tube is calculated by multiplying the average of the four measurements of flow rate obtained from Step 11 by time and by the value of the standard of each tracer affixed to the standard (fL).

$$\text{Volume of PFT added} = \sum_{i=1}^{n} f_i \; / \; n \times \text{fL standard} \times \text{time}$$

where f_i is the value of the ith flow measurement in $cm^3\ min^{-1}$.

16. After tube "**00**" appears on the tube LCD, push the **Operate** switch to **Off** and shut all cylinder valves.

17. Disconnect all tubing and place a 1/2 hole septum over the lid inlet and outlet ports.

18. Disconnect the lid plug from the base and remove the entire lid from the base.

19. For preparing standards up to 5 x 10^6 fL, the same loading procedure is followed by using the appropriate standard for the desired range of tracer quantities and setting the flow rate and time. The PATS base time setting may be increased during a run so that by extending the time, increased tracer quantities may be loaded from one adsorbent tube to the next. For constructing a calibration curve, the standards are prepared in triplicate. Data (peak height or area) obtained from the analysis of the standards in

the 10^2 to 10^6 fL range are fitted by a 6th-order polynomial. A linear fit is applied below 100 fL.

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Private Communication (1986)

Subcommittee on Environmental Analytical Chemistry, American Chemical Society (ACS), Committee on Environmental Improvement (1980)
"Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry"
Anal. Chem., 52, 2242-2248 (1980)

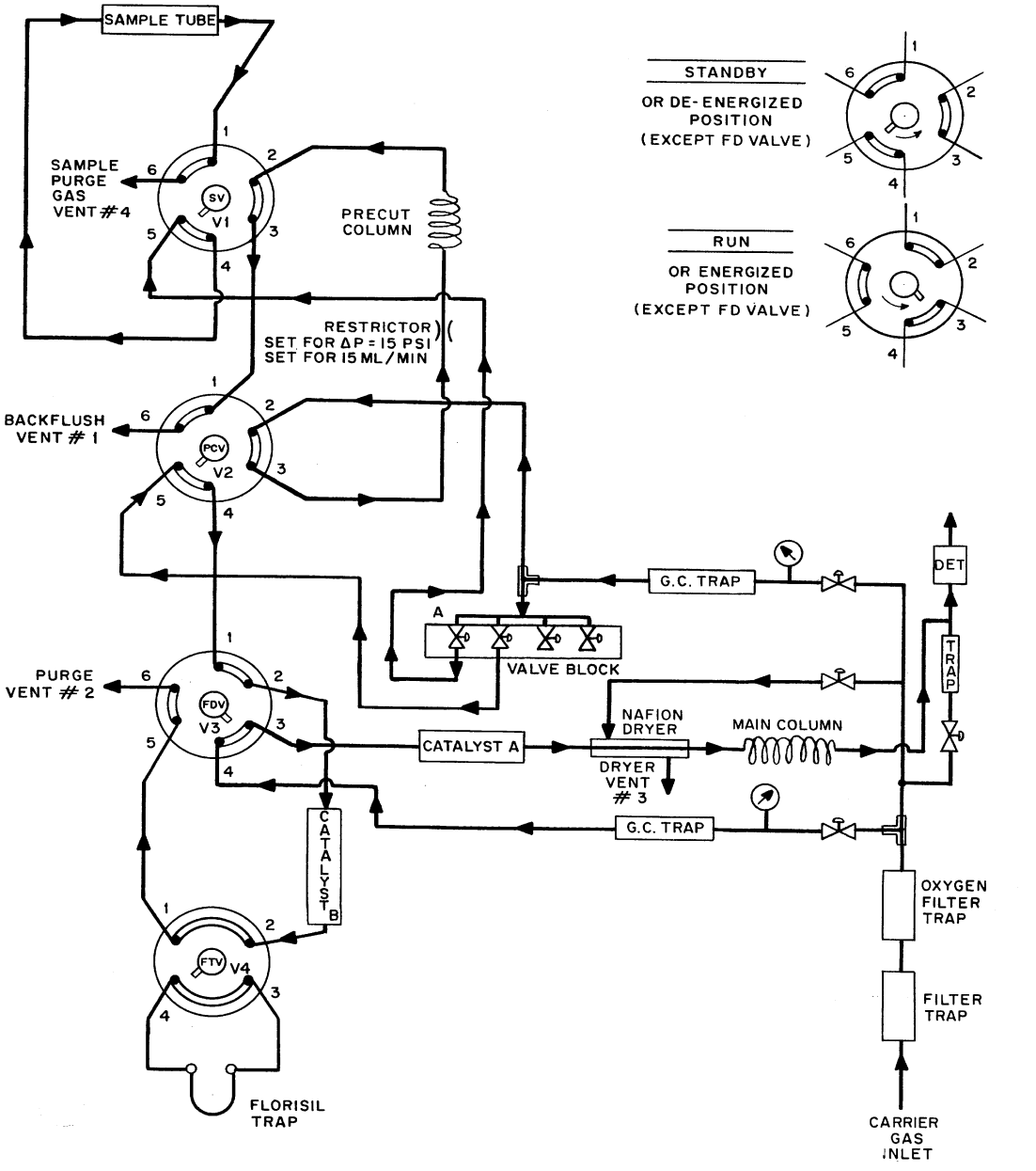


Figure 1. Pneumatics configuration of the perfluorocarbon tracer gas chromatograph.

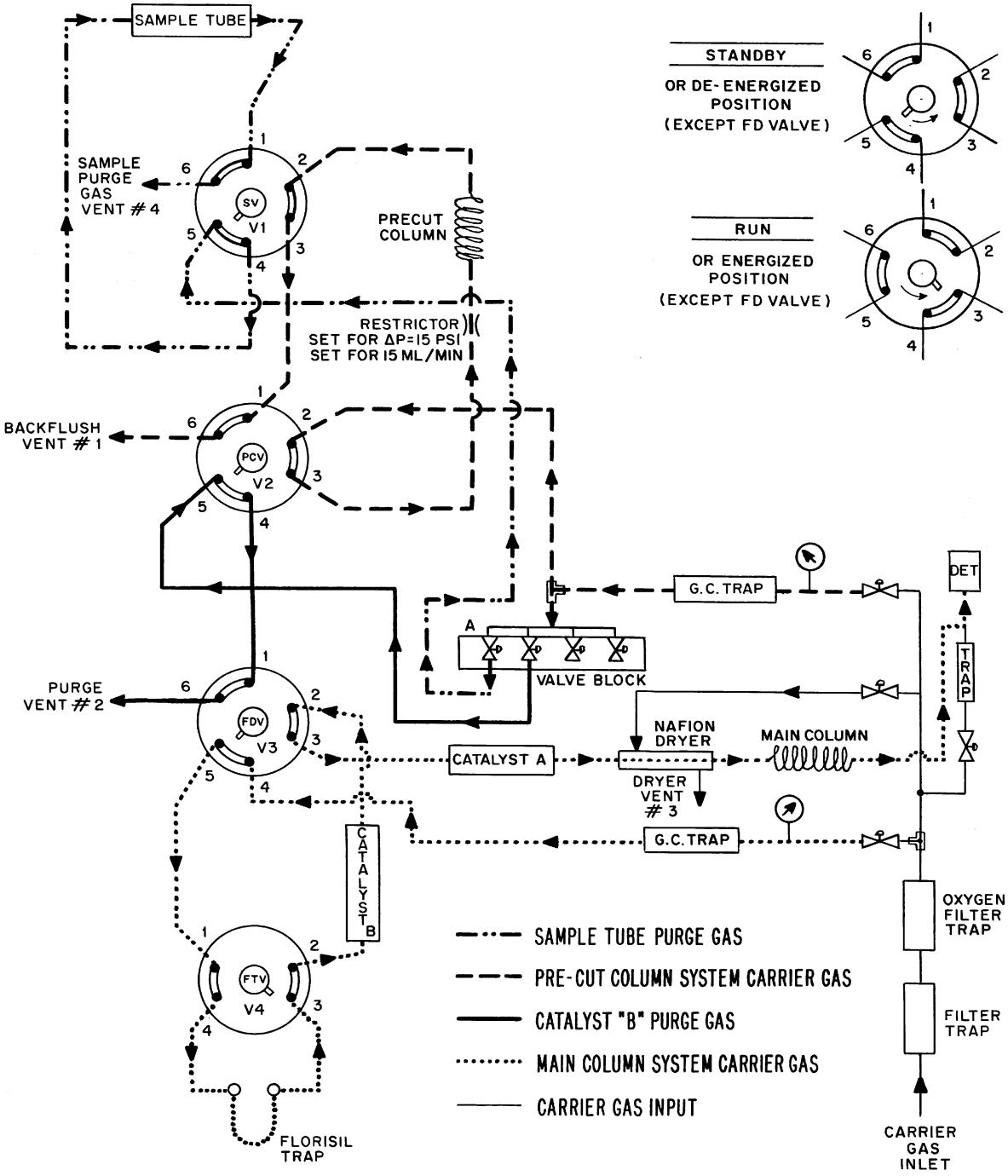


Figure 2. Method 1: carrier gas flow paths - Florisil trap desorption.

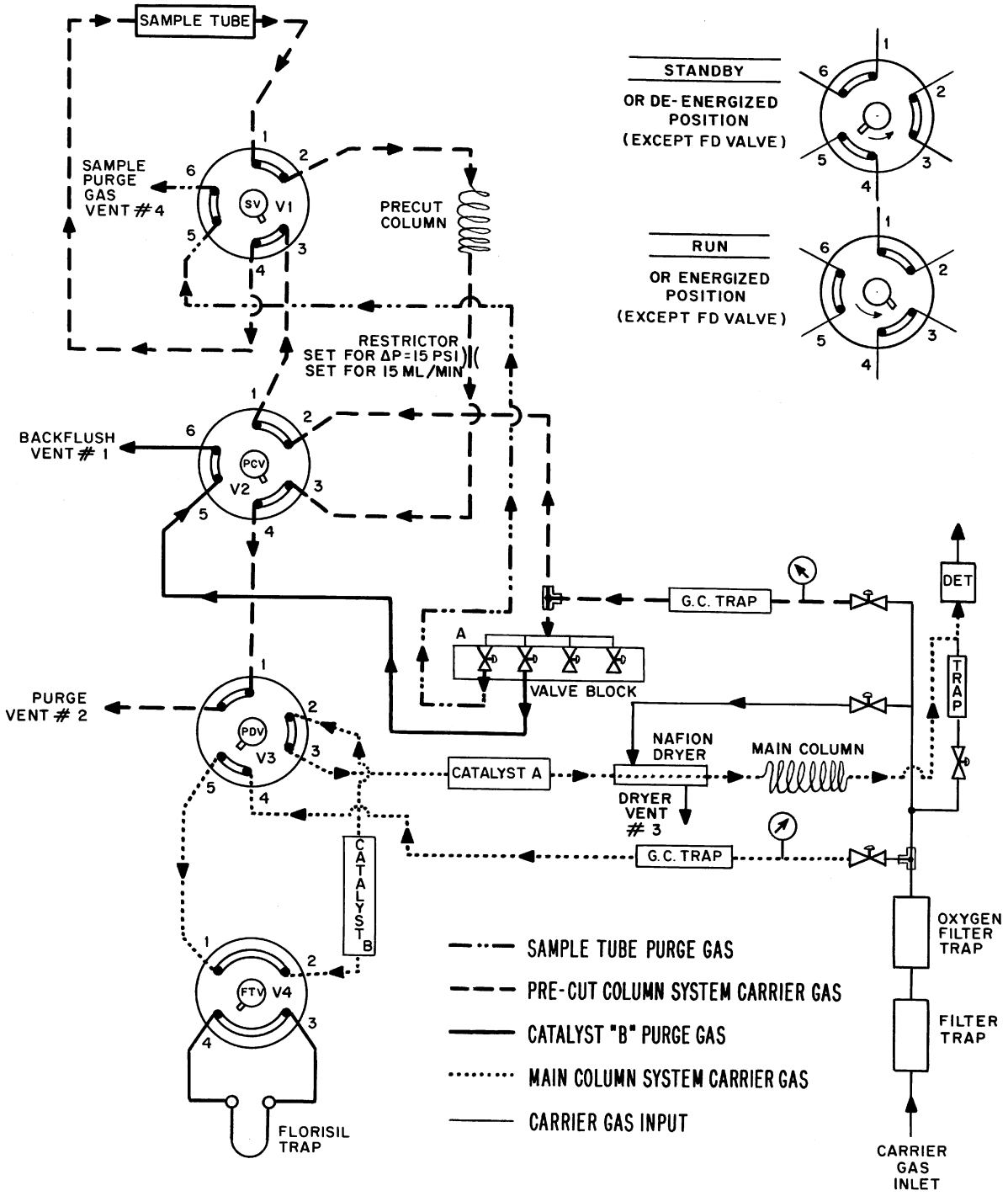


Figure 3. Method 3: carrier gas flow paths - PATS sample adsorption.

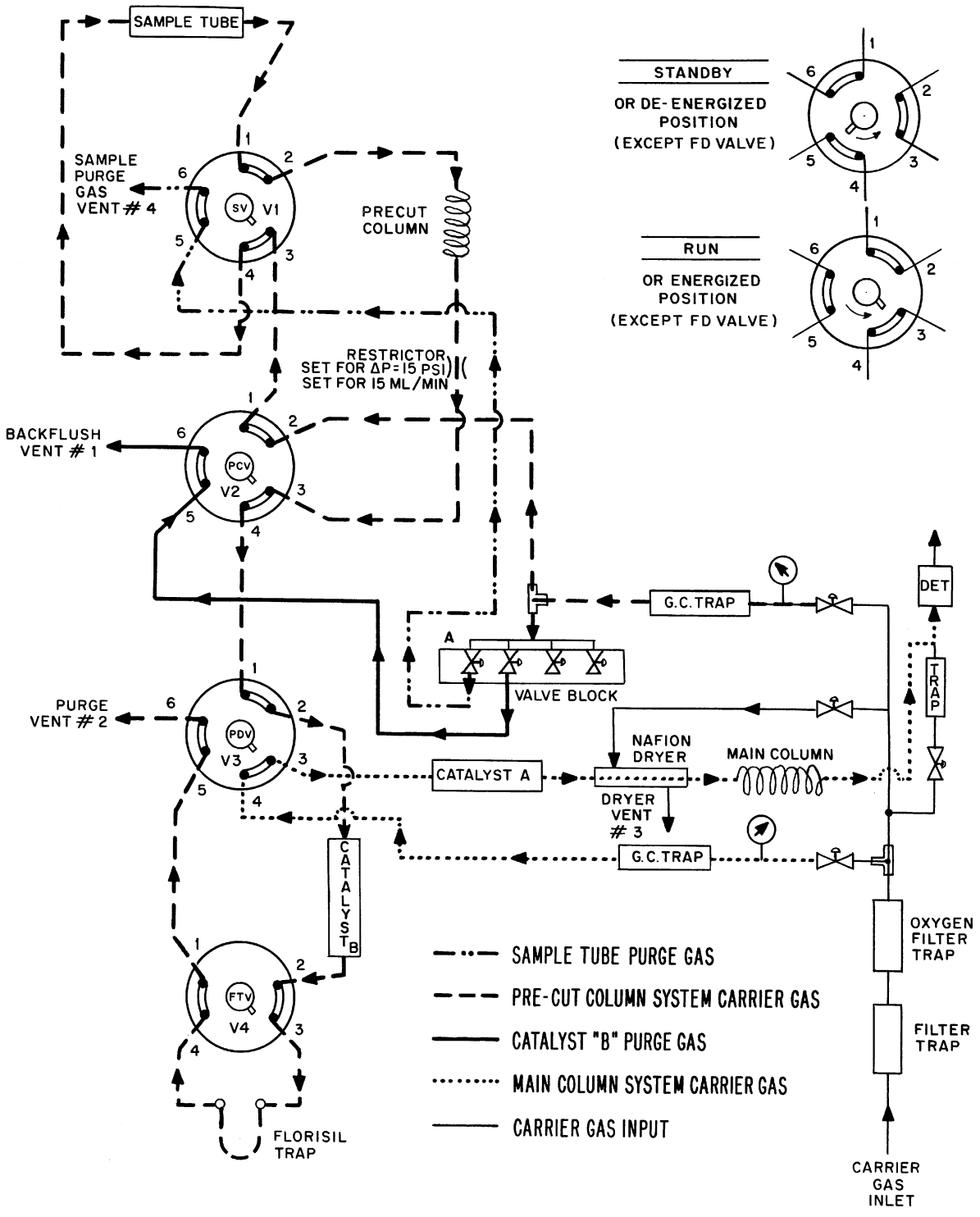


Figure 4. Method 4: carrier gas flow paths - absorption of PFTs on Florisil trap.

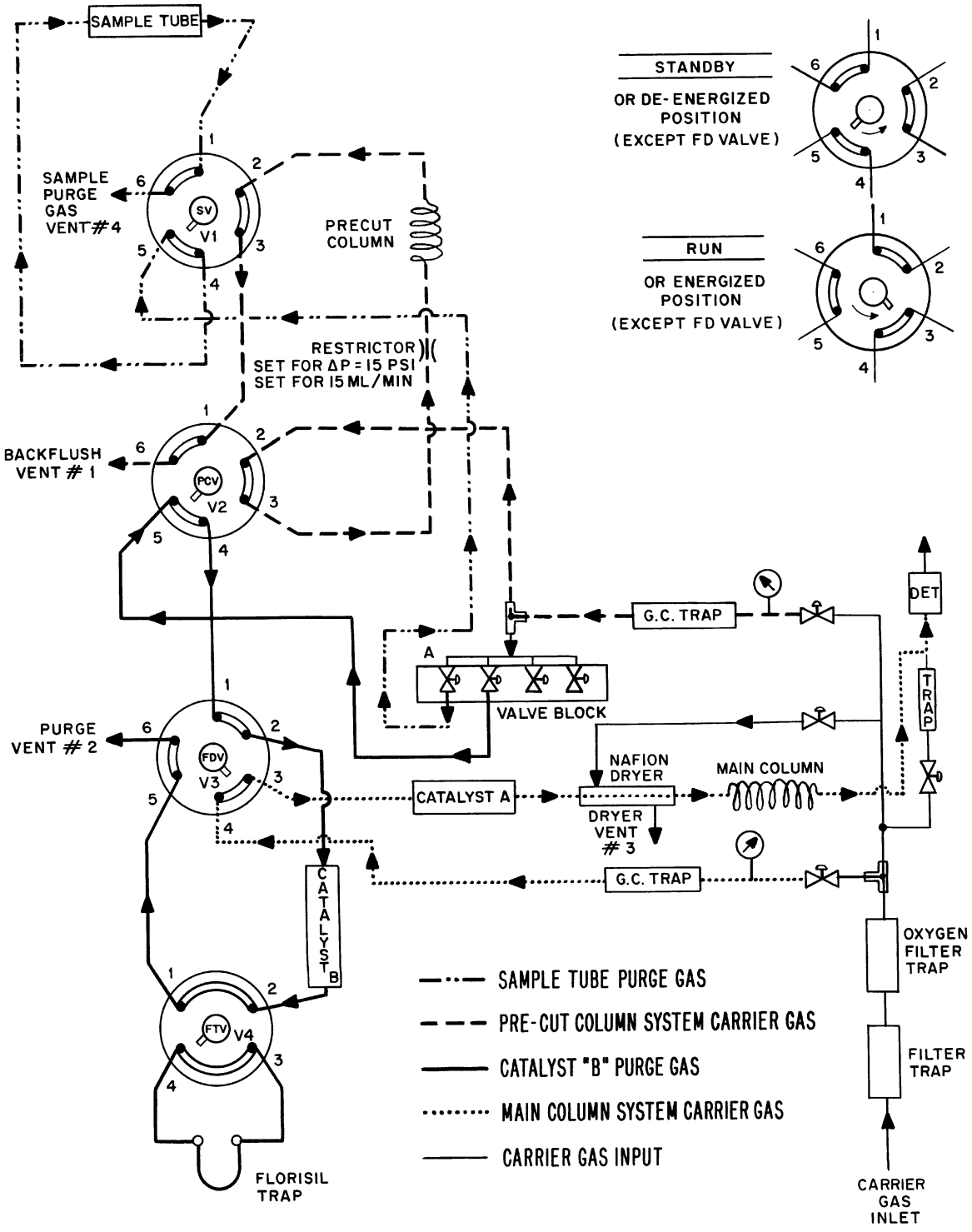
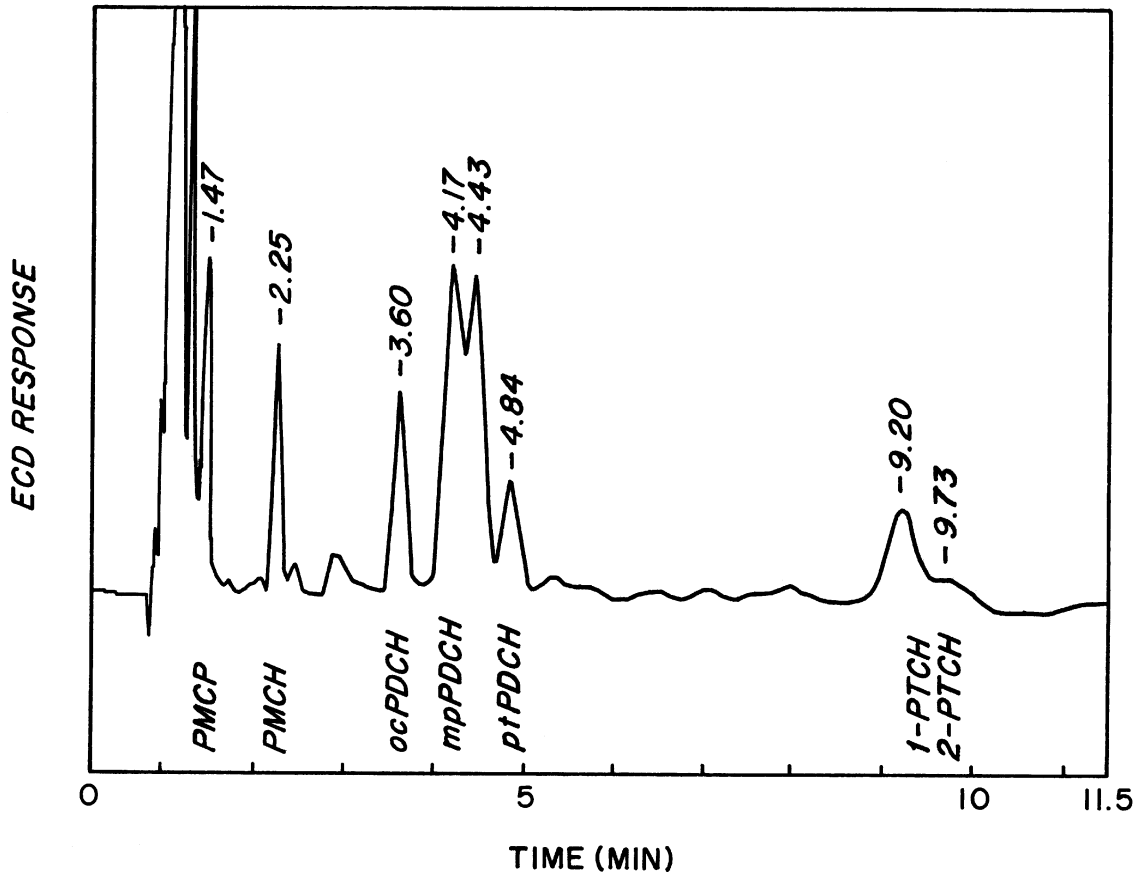


Figure 5. Method 5: carrier gas flow paths - precut column back-flush.

Figure 6. Chromatogram of a 72 L ambient air sample containing perfluorocarbon tracers.



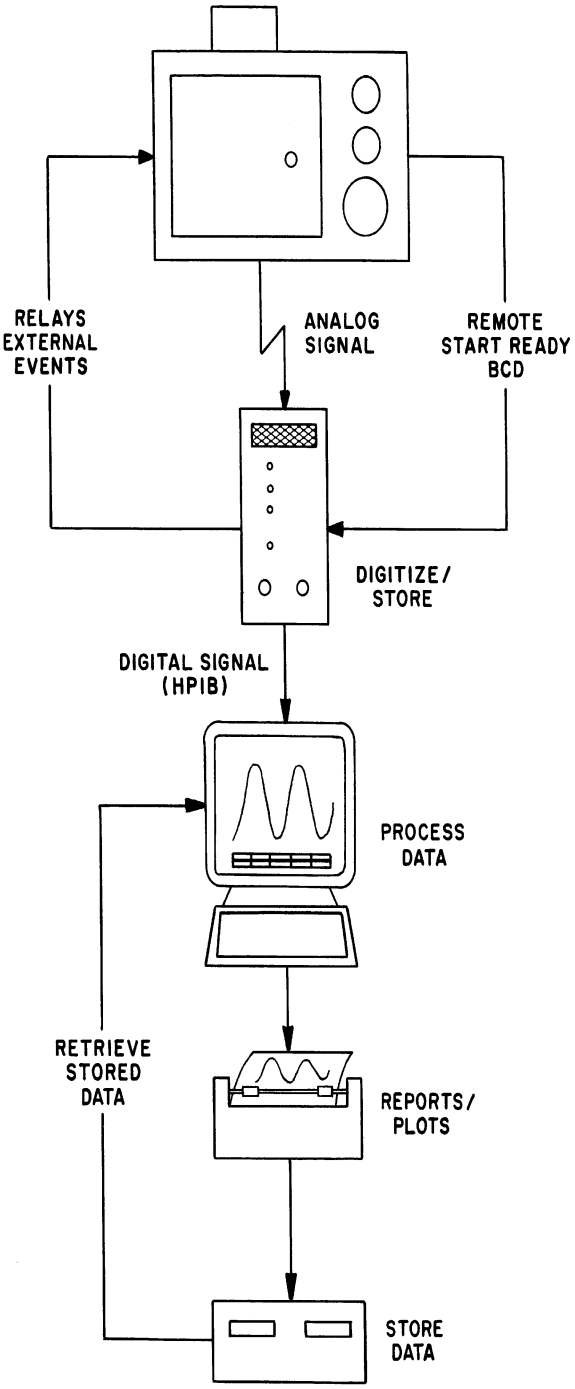


Figure 7. Schematic diagram of the data acquisition and data reduction system.

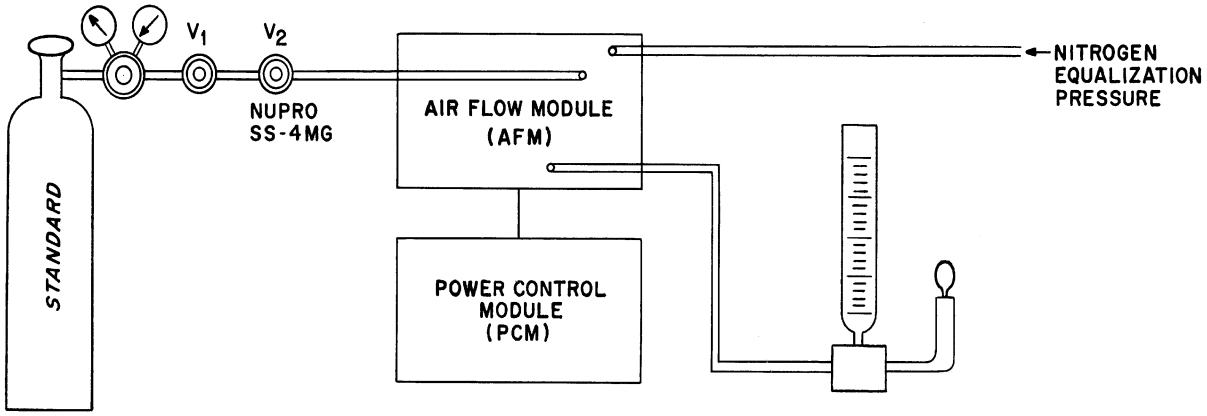


Figure 8. PFT standard sample preparation system.