An Improved Gas Chromatographic Method for the Determination of Perfluorocarbon Tracers in the Atmosphere

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Abstract

A method for the quantitative determination of perfluorocarbon tracers in atmospheric samples with a fused-silica capillary column is described. The analytical method, modifications to the gas chromatograph, improvements in the separation of the atmospheric tracer compounds, and enhancements in the sensitivity of detection are discussed. Atmospheric background concentrations of the tracers and the precision of their collection and analysis are given.

Introduction

A number of atmospheric tracer experiments have been conducted to provide empirical data to evaluate mathematical models of the atmospheric transport and dispersion of pollutants to distances as far as 3000 km from the source (1–6). These experiments involve the release of measured and controlled quantities of perfluorocarbon tracers (PFTs) into the atmosphere under well-documented meteorological conditions. The tracers are collected in adsorbent tubes that are contained in air samplers located along the anticipated tracer plume trajectory. The tracer quantities in each sample are subsequently measured by gas chromatography (GC) with electron-capture detection (ECD).

The perfluorocycloalkanes are ideal tracer compounds for the simulation of atmospheric transport and dispersion of pollutants because of their inert, nontoxic, and nondepositing properties, low atmospheric backgrounds, long atmospheric lifetimes, and limited commercial use. Their stability under high-temperature catalytic reduction allows them to be separated from interfering chlorofluorocarbons and their high electron affinities makes them particularly suitable for quantitative measurement at very low concentrations with the use of the ultrasensitive ECD.

The technology was originally developed by Lovelock and Ferber (7) who proposed the use of perfluoromethylcyclohexane (PMCH) and perfluorodimethylcyclohexane (PDCH) as meteorological tracers. A third tracer, perfluoromethylcyclopentane (PMCP), was later identified by Brookhaven National Laboratory to satisfy a requirement to provide a different tracer for each of three different release locations during a series of short-range experiments (1). Although the three tracers were used for a number of different short (<20 km) and intermediate range (1000 km) experiments (2–5), they could not be economically employed for long-range studies (>1000 km) because of their relatively high atmospheric background concentrations (3.0 fL/L).

The group from the Brookhaven National Laboratory also identified other perfluorocycloalkanes as long-range tracers: perfluoro-1,2(cis)-dimethylcyclohexane (OC-PDCH) and two unidentified isomers of perfluorotrimethyl-cyclohexane, arbitrarily named 1-PTCH and 2-PTCH. They have atmospheric background concentrations of 0.3 and less than 0.1 fL/L, respectively. Both compounds were custom synthesized and successfully used for the Across North America Tracer Experiment (ANATEX) (6), which was a near transcontinental study of transport and dispersion. Concurrent to identifying the new long-range tracers, Brookhaven National Laboratory also developed a packed-column gas chromatographic procedure to quantitatively determine all of the tracers in adsorbent-collected air samples. A more detailed description of the tracer technology has been published (6,8).

In the absence of any injections into the atmosphere, very stable daily ambient background tracer concentrations are expected. To ascertain tracer plume interceptions, stable background concentrations are essential during the tracer release experiments. However, sporadic increases in the OC-PDCH concentrations (up to 1.0 fL/L) were first observed in ambient tracer background samples collected at the Environmental Measurements Laboratory's Regional Baseline Station in Chester, New Jersey, for a laboratory intercomparsion study (8). The chromatographic scans of those samples with the elevated OC-PDCH concentrations exhibited an interference in the OC-PDCH region that was not evident in the scans of those samples with the expected background concentration. This sporadic contaminant was also observed in daily Chester samples collected over a subsequent 5-month period. All samples were collected when no tracer releases were in progress.

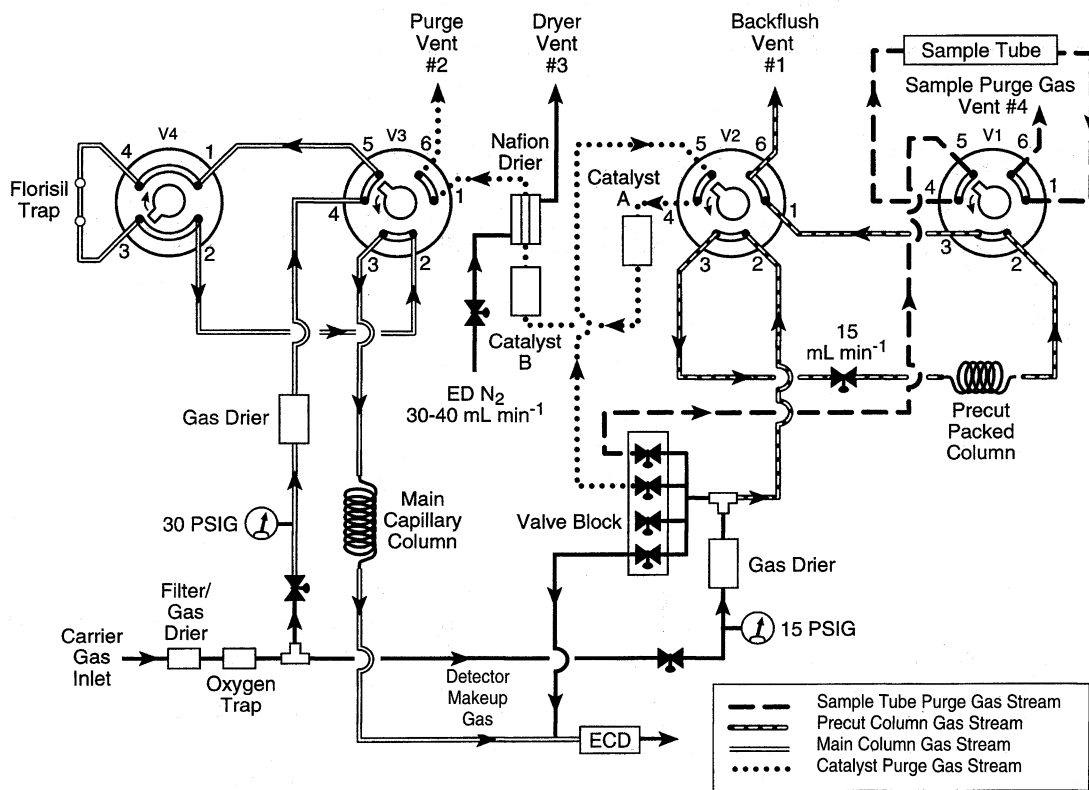Interferences associated with the packed-column separation

Figure 1. Injection into capillary column by Florisil trap and desorption with precut column backflush (Method 1).
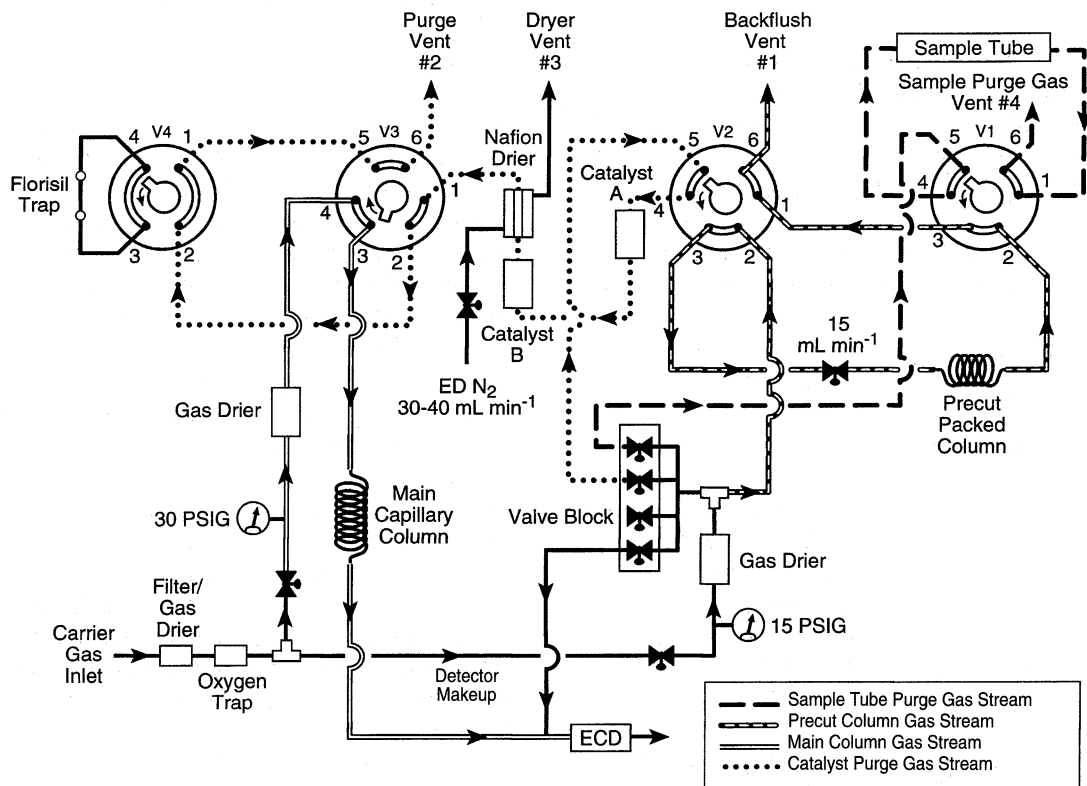

Figure 2. Pneumatics configuration of the perfluorocarbon tracer gas chromatograph. Carrier gas flow paths: chromatographic separation and detection with precut column backflush (Method 3).
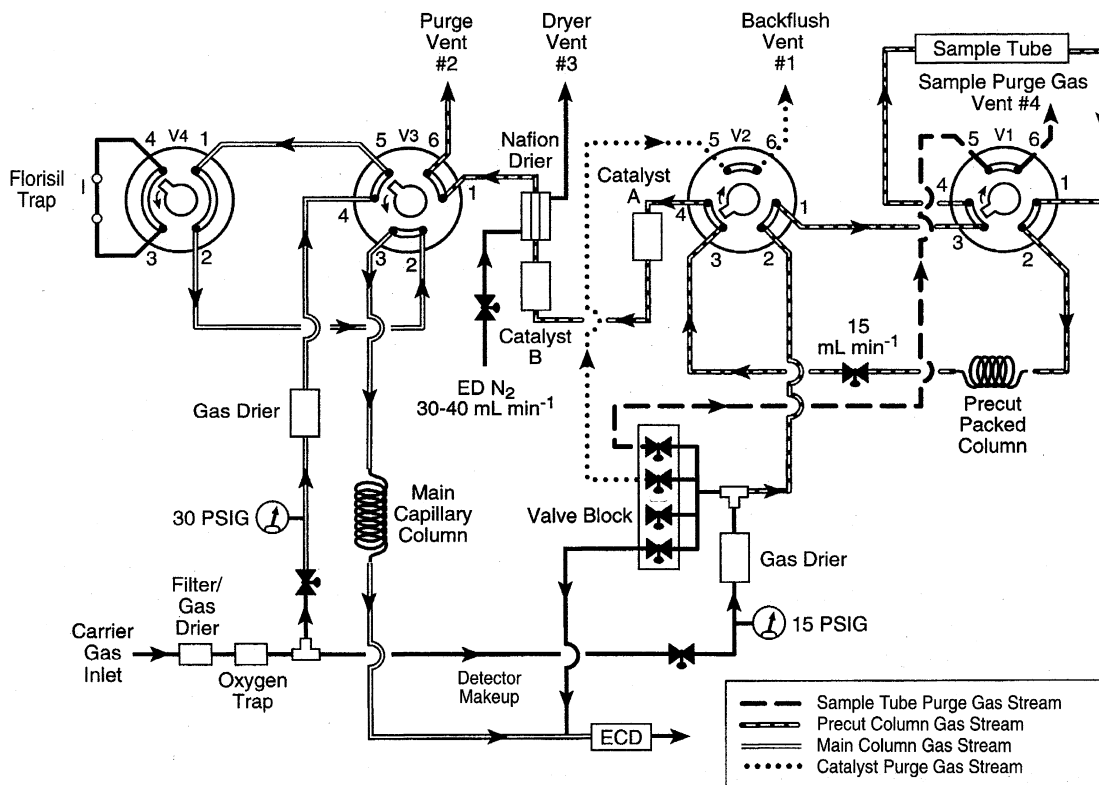
Figure 3. Desorption of sample from Ambersorb, sample purification, and venting of low boiling components to atmosphere (Method 4).
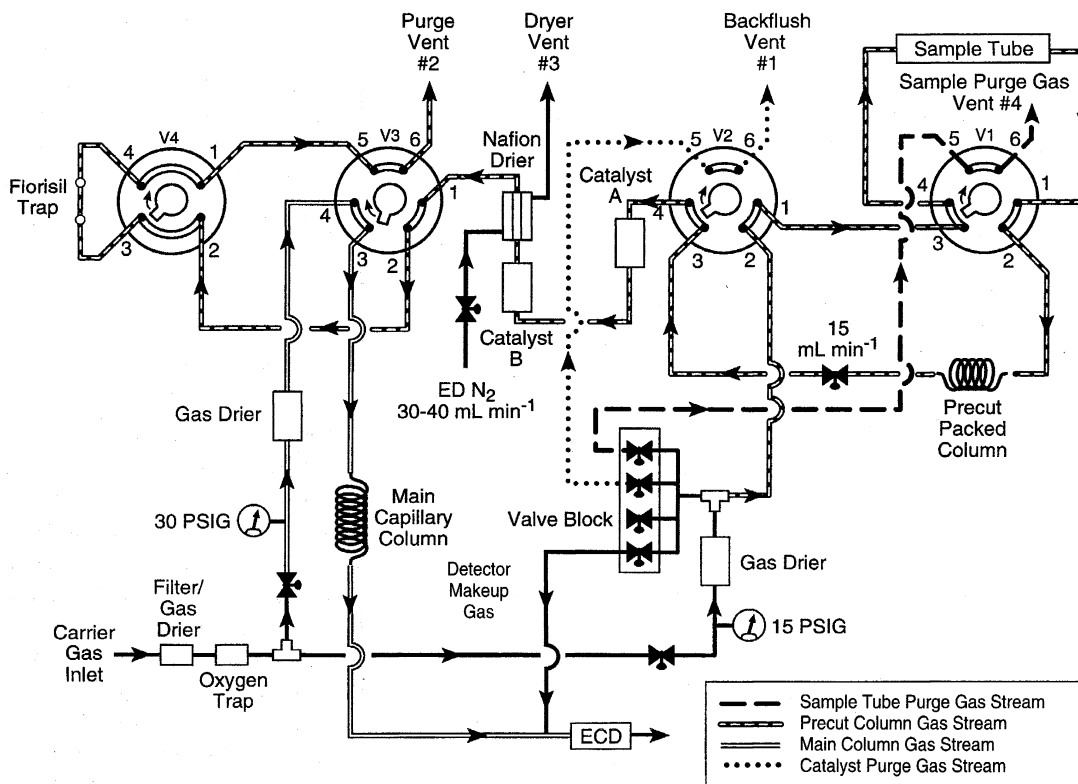

Figure 4. Adsorption of PFTs on Florisil trap (Method 5).

Table I. Gas Chromatograph Relay Assignments

Relay no.	Assignment*
1	V1, Sample valve
2	V2, Precut valve for changing the direction of the precut column carrier gas
3	V3, Flow directional valve
4	V4, Florisil trap valve
5	Desorption power relay: high heat
6	Desorption power relay: low heat
7	Programmable atmospheric tracer sampler tube/Florisil trap power routing relay
8	Auxiliary power to the precut column relay, on for high temperature and off for low temperature

Table II. Timed Relay Automation Program

Method no.	Method description	Time (min)	Relay on*	Relay off*
1	Inject PFTs into capillary column by ohmic heating of Florisil trap; backflush precut column	0.00	8	
		0.01	3,7	
		0.02	4	
		0.05	5	
		0.08	6	5
		0.40		6
		0.45		7
		2.90		4
		2.95		3
		3.00	End of Method	
3	Chromatographic separation elution, electron-capture detection of PFTs; backflush precut column	0.00	8	
		17.00	End of Method	
4	Desorb sample from Ambersorb adsorbent by ohmic heating; vent low boilers to atmosphere; purify PFTs by catalytic reduction and remove moisture	0.00		8
		0.01	3	
		0.50	2	
		0.60	1,5	
		2.50	End of Method	
5	Absorb PFTs on Florisil trap	0.05	8	
		0.70		3
		0.80	4	
		1.50		1,5
		3.90		2
		3.95		4
		4.00	End of Method	
6	Cool oven to subambient temperature, backflush precut column; equalize Florisil trap pressure to main column system pressure	0.00	8	
		1.00	3	
		1.10	4	
		1.80		4
		1.90		3
		2.00	End of Method	

* See Table I for explanation of relay numbers.

also affected the quality of the results of the PTCH analysis. Concentrations of PTCH in background ambient air samples and samples that contained released tracers at near background levels could not be accurately determined because of contaminant peaks that coeluted with 1-PTCH and 2-PTCH.

The high resolution that can be obtained with fused-silica capillary columns appeared to offer a solution for the interference problems associated with packed columns and to potentially improve the signal-to-noise ratio to significantly lower the limits of detection. In a review of the GC separations of perfluorocarbons, O'Mahoney and co-workers (9) concluded that the majority of the published methods used packed columns and that capillary columns have not been fully exploited for this purpose. Perfluorocarbon tracers and other perfluorocarbon compounds have been analyzed with alumina porous-layer open-tubular (PLOT) (10), fused-silica SE-30 (11), and fused-silica SE-54 (12) columns. PFT analysis with a 100 m × 0.32-mm i.d. alumina PLOT column was attempted under different temperature conditions and carrier gas flow rates with our modified capillary GC, but baseline separations of the PDCH isomers could not be obtained. Trial analyses were not attempted with the SE-30 and SE-54 type columns because of the extreme subambient temperatures required for the analytical methods. It was anticipated that a significant holdup would result from freezeout of the sample components in the gas switching valves and sample transfer lines located in the column oven.

In this report, a method is described for the routine purification and quantitative measurement of perfluorocarbon tracer compounds in sample tubes that contain adsorbent-collected air. The analysis was carried out by direct injection from a heated adsorbent trap into a temperature-programmed DB-Petro 100 fused-silica capillary column.

Experimental

Sample collection

Sixteen duplicate daily background air samples were collected by using programmable atmospheric tracer samplers (PATS) at the Environmental Measurements Laboratory's Chester station during late December 1993 and early January 1994. This sampler, developed specifically for perfluorocarbon tracer sampling, consisted of two sections: (a) a lid with 23 stainless steel adsorbent tubes that each contained 150 mg of Ambersorb adsorbent (Rohm and Haas, Philadelphia, PA) and a multiple-port switching valve for directing either air flow (in the sampling mode) or carrier gas and

thermal desorption current (in the analysis mode) to a selected adsorbent tube; and (*b*) a base that contained batteries, a sampling pump, and associated electronics. The system was set to collect one sample per day at a flow rate of 50 mL/min so that each sample contained quantitatively adsorbed tracers (R. Dietz, Brookhaven National Laboratory, Upton, Long Island, NY, 1996, personal communication) from 72 L of air. Details of the sampling system have been published elsewhere (2–6,8).

Modifications to the GC

The system for automated perfluorocarbon tracer analysis was a modified Varian 6000 GC (Varian Associates, Palo Alto,

CA). This analytical system comprised two major carrier gas (5% hydrogen–nitrogen) stream systems:

- an externally mounted precut column system that contained a stainless-steel column (51 cm × 3.2-mm i.d.) packed with 80/100 mesh Unibeads 2 (Alltech Associates, Deerfield, IL). It was used for preliminary separation of the perfluorocarbon tracers
- the main column system where the perfluorocarbons were separated for quantitative determination by a DB-Petro 100 fused-silica column (100 m × 0.25-mm i.d., 0.5-μm film thickness) (J&W Scientific, Folsom, CA).

In converting to a capillary system, emphasis was placed on relocating as few components as possible and optimizing resolution by minimizing dead volumes in the main column system. Both catalyst beds and the Nafion dryer were relocated from the main column system to the precut column system where components with larger internal volumes have a small effect on the preliminary PFT separations. A liquid nitrogen cooling system was installed to operate the column oven at subambient temperatures. The high temperature rotors of the gas switching valves (1.59 mm, ultralow volume) were replaced with low temperature "P" type rotors (Valco, Houston, TX). All 1.59-mm transfer lines in the main column system were replaced with 304 stainless steel tubing with a smaller internal diameter (0.762 mm). The column was directly attached to the switching valve port with a fused-silica adapter (Valco), and a packed capillary column conversion kit (Supelco Inc., Bellefonte, PA) was installed at the detector inlet located in the column oven. Since low carrier gas flows are required for the capillary column, the high flow element of the Porter gas flow controller cartridge (Varian Associates, Sunnyvale, CA) was replaced with a 0–10 mL/min type. No changes were made in the electrical circuits (R.L. Dietz and E.A. Cote, Preliminary Operating Manual Brookhaven National Laboratory Addendum to a Modified Varian Model 6000 GC, Brookhaven National Laboratory, Upton, NY, 1986, personal communication) that provided the current to heat the externally mounted precut column and Florisil trap. However, AC originally supplied by the chromatographic system for ohmic heating of the sample tube was replaced with DC from an externally located constant-current power supply. A schematic of the pneumatic system is shown in Figure 1. Carrier gas flow streams with all valves in the standby position are shown in Figure 2.

GC method

In preparation for the lid adsorbent tube analysis, the sample lid was electrically coupled to an EML Model PO-55 GC tube sequencer (N. Latner and N. Chiu, A tube sequencer for the perfluorocarbon tracer gas chromatograph, Environmental Measurements Laboratory, New York, NY, 1994, personal communication) which pro-

| Table III. Temperature Program Profile			
Method no.	Method description	Capillary column	Precut column
1	Initial temperature	–10°C	140°C
	Isothermal time	3 min	3 min
3	Initial temperature	–10°C	140°C
	Isothermal time	3 min	17 min
	Ramp rate	4°C/min	
	Temperature 2	24°C	
	Isothermal time	4.5 min	
4	Initial temperature	24°C	85°C
	Isothermal time	2.5 min	2.5 min
5	Isothermal time	2 min	None
	Ramp rate	50°C/min	50°C/min
	Temperature 3	60°C	160°C
	Isothermal time	2.28 min	3.4 min
6	Initial temperature	60°C	160°C
	Final temperature	–10°C	160°C
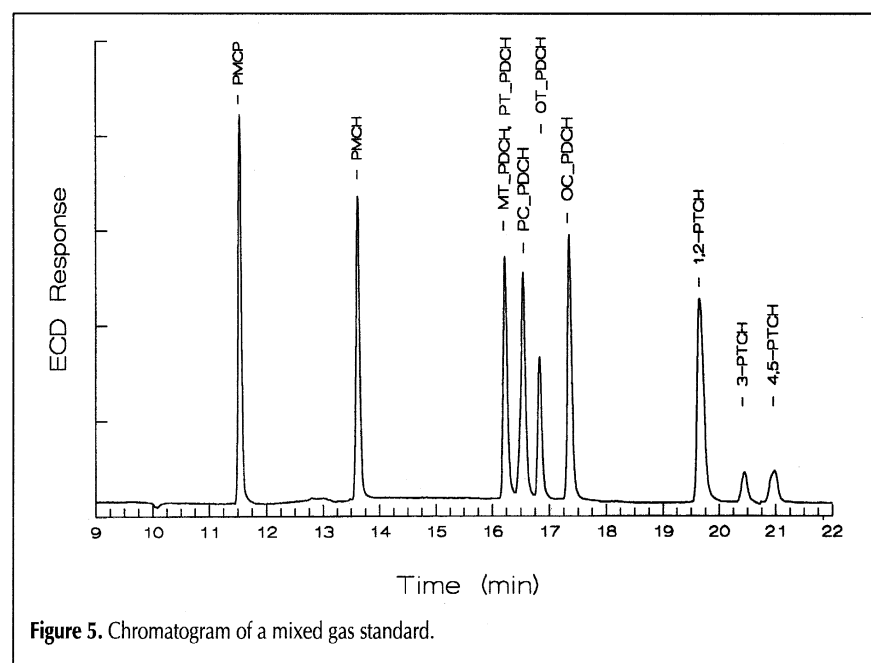
Figure 5. Chromatogram of a mixed gas standard.

vided a signal to the lid multiport valve to sequentially advance each adsorbent tube into position and trigger the start of the GC analysis sequence and data acquisition system. The analysis time between each tube (30 min) was controlled by a Micromaster Model WP6200 (Minarick Electric, Glendale, CA). Carrier gas lines (1.59-mm i.d. polyurethane) were attached to the lid from the sample valve V1 (Figure 1) to enable introduction of the desorbed sample into the analytical system.

The system was automated so that each of the 23 lid adsorbent tubes were sequentially analyzed. At the start of the analysis sequence, the lid adsorbent tube was switched into the GC sample tube purge carrier gas stream, valves V3 and V4 were energized, and the PFTs contained on the Florisil trap from the previously purified sample were injected into the capillary column by ohmic heating of the trap to 200°C (8°C/s) (Figure 1). Both valves were returned to the standby position at approximately 3 min into the run.

After the PFTs had eluted from the main column (20 min) (Figure 2), valves V1, V2, and V3 were energized, and a current of 14.25 A, which was supplied by the constant current power supply, was turned on and the lid adsorbent tube was ohmically heated to 400°C. The PFTs and impurities were quantitatively desorbed into the carrier gas stream and passed through the temperature-programmed precut column where a preliminary separation of the tracers from the impurities was made. Early eluting low-boiling impurities were vented to the atmosphere at purge vent 2 (Figure 3). The PFT fraction was allowed to proceed for further purification while the high boiling impurities were retained on the column from which they were subsequently backflushed to the atmosphere. The entire sequence was con-

trolled by column temperature programming and timed switching of the carrier gas valves. Switching valve precut times (Tables I and II) for retaining the PFT fraction were previously established from an ECD chromatogram of the column effluent at vent 2.

Precut column heating was by ohmic heating controlled by the auxiliary oven temperature control module. The surviving impurities in the eluted PFT fraction were catalytically reduced by passing through two 50.8 mm × 2.18-mm i.d. × 3.175-mm o.d. reactors that contained 20/40 mesh Royer Palladium (Strem Chemicals, Newburyport, MA) mounted in the injector blocks. Both catalyst beds are required to remove the chlorofluorocarbons that were co-collected on the Ambersorb. Moisture was removed from the carrier gas stream by a 24-cm × 1.59-mm Nafion permeation dryer (Permapure Products, Toms River, NJ). By switching V3 to standby and energizing V4, the PFTs were concentrated at room temperature on a 7.62-mm × 0.762-mm i.d. × 1.59-mm o.d. stainless steel adsorbent trap that contained 60/100 mesh Florisil (Supelco, Bellefonte, PA) (Figure 4). Data acquisition was with a PE Nelson Model 760 A/D converter and PE Nelson Model 2600 chromatography software (Perkin-Elmer, Cupertino, CA).

GC operating conditions

The entire switching valve and heating sequences described above were controlled by the chromatograph's external events capability. Relay assignments are identified in Table I. Timed relay automation programming for the switching valves, sample desorptions, and temperature program profiles for the capillary column oven and precut column was divided into five GC instrument methods. The program for each method is shown in Table II. Method 2 was not used since it is a system memory default method. Switching valve port positions and carrier gas flow paths pertaining to each method are shown in Figures 1–4. Temperature program profiles for each method are listed in Table III. The main column oven temperature was raised (60°C) during method 5 to eliminate any sample holdup in the valves and gas transfer lines located in the column oven. The carrier gas flow rate for the precut column was set at 15 mL/min, and the main column flow rate was set at 1.0 mL/min at input pressures of 15 psig (103 kPa) and 30 psig (208 kPa), respectively. Precut column gas flow (measured at purge vent 2) was set by manually energizing the precut valve (V2), flow directional valve (V3), and the Florisil trap valve (V4) (see Figure 3) and by adjusting the flow rate with an extra fine flow controller (Veriflow, Richmond, VA) located in the precut column gas stream line. Detector makeup gas, sample tube purge gas, and catalyst purge gas flow rates were each set at 15 mL/min. Extra dry nitrogen, at a flow rate of 30–40 mL/min, was used as the purge gas for the Nafion drier. Catalyst bed
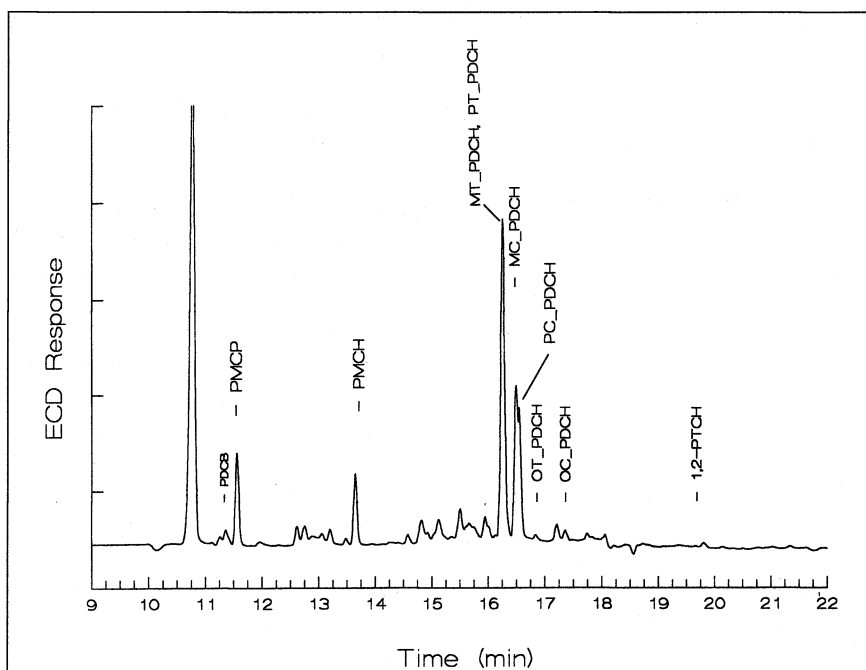

Figure 6. Chromatogram of a 72-L adsorbent-collected air sample. Peaks: 1, perfluoro-1,2 dimethylcyclobutane (PDCB); 2, perfluoromethylcyclopentane (PMCP); 3, perfluoromethylcyclohexane (PMCH); 4, perfluoro-1,3-(trans) dimethylcyclohexane (MT-PDCH); 5, perfluoro-1,3-(cis)-dimethylcyclohexane (MC-PDCH); 6, perfluoro-1,4-(trans)-dimethylcyclohexane (OT-PDCH); 9, perfluoro-1,2-(cis)-dimethylcyclohexane (OC-PDCH); and 10, perfluorotrimethycyclohexane (1, 2-PTCH, 3,4,5-PTCH).

temperatures were maintained at 220°C (injector temperatures), and the ECD (constant-current mode) temperature was 260°C.

Calibration

The system was calibrated with mixed tracer certified (±5.0%) standards (1 and 100 ppt) prepared in nitrogen by Airco (Riverton, NJ) in their Spectro Seal cylinders. A chromatogram of this standard, also used for GC calibration for the ANATEX study, is shown in Figure 5. The elution times of the PFTs, PMCP, PMCH, and the isomers of perfluorodimethylcyclohexane, perfluoro-1,3-trans-dimethylcyclohexane (MT-PDCH), perfluoro-1,4-cis-dimethylcyclohexane (PC-PDCH), perfluoro-1,4-trans-dimethylcyclohexane (PT-PDCH), OC-PDCH, and perfluoro-1,2-trans-dimethylcyclohexane (OT-PDCH), were previously determined from injection of the nearly pure compounds into the column under the previously described GC operating conditions. PT-PDCH is not evident because it coeluted with the MT-PDCH. The major PTCH isomers in the standard (68%), the unidentified and arbitrarily named 1-PTCH and 2-PTCH, were not separated. Other unidentified isomers of PTCH are labeled 3-PTCH and 4,5-PTCH.

System calibration standards that contained tracer quantities ranging from 2 to 3500 fL were prepared in triplicate by adsorption of known quantities of the tracers onto decontaminated PATS sampler lid adsorbent tubes. The desired quantity of loaded tracers was controlled by the gas flow, measured with a soap bubble spyrometer whose calibration is traceable to NIST standards, and time controlled.

Results and Discussion

A typical chromatogram obtained from the analysis of tracers adsorbed from a 24-h, 72-L ambient air sample is shown in Figure 6. The relative peak amplitudes differ from those in the standard (Figure 5) because the standard was not prepared to approximate the ambient air concentration of each component.

Two other perfluorocarbon compounds that were also identified by injection of relatively pure compounds, perfluoro-1,3-cis-dimethylcyclohexane (MC-PDCH) and perfluorodimethyl-cyclobutane (PDCB), and that were present in ambient air but not in the ANATEX standard are indicated.

Both chromatograms demonstrate the ability of the column to resolve the perfluorocarbon tracers and the effectiveness of the injection technique of thermal desorption from an adsorbent trap as evidenced by baseline separations and peak symmetries with almost no peak tailing.

Table IV shows the elution times, measured from the time of injection into the capillary column by ohmic heating of the Florisil trap, the lower limits of detection at a signal-to-noise ratio of 3:1, mean ambient background concentrations, and the precision of sampling and analysis (relative standard deviations) for each of the perfluorocarbons. Since standard calibration values for PDCB, PC-PDCH, and OT-PDCH have not been established, their lower limits of detection, concentration, and precision results have been omitted. The ambient background values reflect the mean concentrations obtained from the analyses of 16 daily 72-L duplicate samples collected during December 1993 and January 1994.

Conclusion

A capillary column system has been developed for the routine analysis of perfluorocarbon tracers in adsorbent-collected ambient air samples. Direct injection of a sample into a capillary column by rapid ohmic heating of an adsorbent trap without cryogenic concentration has been demonstrated. Perfluorocarbon tracer compounds with boiling points of less than one degree of each other have been resolved. The interferences encountered in the determination of OC-PDCH and PTCH with a packed-column system have been eliminated. However, the 1-PTCH and 2-PTCH isomers are not separated by the fused-silica capillary column. Therefore, the PTCH results reflect the

Table IV. Elution Times, Lower Limits of Detection, Mean Ambient Air Concentrations, and Precision of Sampling and Analysis

Tracer	Elution time (min)*	Limit of detection (fL)[†]	Limit of detection ratio[‡]	Ambient air conc. (fl/L)[§]	Relative standard deviation (%)[§]
PDCB	11.36	–	–	–	–
PMCP	11.56	0.15	1.3	04.15	6.0
PMCH	13.65	0.30	3.0	03.84	4.5
MT-PDCH, PT-PDCH	16.25	0.30	–	12.80	3.2
MC-PDCH	16.50	0.30	–	08.41	3.1
PC-PDCH	16.57	–	–	–	–
OT-PDCH	16.85	–	–	–	–
OC-PDCH	17.36	0.20	5.0	00.34	5.0
1, 2-PTCH	19.66	0.40	8.8	00.07	7.1

* From Florisil trap desorption.
[†] At a signal-to-noise ratio of 3:1.
[‡] Lower limit of detection of packed divided by capillary columns.
[§] For 32 samples.

ambient air concentrations of both isomers. Capillary column chromatography has improved the lower limits of detection of the PFTs up to a factor of 8 (see Table IV) over the packed-column system (6). This enhancement in the sensitivities of detection

- significantly reduces the quantity, hence the cost, of the tracer required to be released into the atmosphere to produce measurable concentrations at long distances from the source
- improves plume definition
- extends the identification of the limits of dispersion of the tracer plume

Since this procedure is also applicable to the measurement of PDCB and OT-PDCH, both perfluorocarbon compounds may be added to the library of useful tracer compounds. Identification of other peaks shown in the chromatogram of the ambient air sample (Figure 6) by GC–MS may lead to other candidate tracer compounds. Use of the newly developed fused-silica capillary columns for separation of the tracers at the aforementioned ambient temperatures coupled to reductions of analysis time will be further investigated.

Acknowledgment

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