

PERFLUOROCARBON TRACER TECHNOLOGY

R.N. DIETZ

1 INTRODUCTION

Whether we want to know how air pollutants are dispersed and diluted as they travel hundreds to thousands of kilometers across the countryside, how cooled nighttime mountain air flows down into the valleys, how air leaks into buildings, or gases or liquids escape from containments, there is a significant role for the technology of tagging and tracing.

Tagging, in these cases, is the process of adding a particular gas, a tracer, to the substance or system to be traced, and then quantitatively detecting or tracing its presence with a variety of sampling and analysis tools. Subsequently, models are used to quantify or to make inferences as to the physical and perhaps chemical nature of the processes governing the particular application.

One of the problems facing the research community is the effect of pollutant sources on local and long-range receptor sites. Regardless of the nature of the pollutant emissions, that is, their physical and chemical interaction with the environment as well as their consequence on human health, the prevailing factors in source-receptor evaluations are the direction of transport of pollutants after they leave the source, how they are dispersed as the pollutants are carried downwind and, ultimately, what will be the diluted concentrations at various distant sites due to dispersion alone.

These processes of atmospheric transport, dispersion, and dilution are complex in different ways depending upon the scales of atmospheric transport (see Table 1). For some time, physical models have been applied to the forecasting of trajectories and dispersion and the prediction of downwind concentrations. Traditionally, model verification has been accomplished through the use of pollutant air quality data and other tracers-of-opportunity such as the anthropogenic use of halocarbons or through the intentional release of conservative tracers.

Such tracers can be either gases or particles, the latter not truly being conservative since they can be scavenged by rain and dry deposited on scales of transport other than short-range. For long-range transport, the required properties of conservative gaseous tracers (see Table 2) are met by a family of perfluorocarbon tracers (PFTs), which are the focus of this presentation.

TABLE 1

Atmospheric transport, dispersion and dilution

1. Scales of atmospheric transport
 - Short-range (up to 10 km) --- coastal, urban, fumigation
 - Long-range (up to 500 to 1500 km) --- acid rain precursors, storms
 - Continental (>2000 km) --- climate and weather
 - Complex terrain (up to 15 km) --- mountains, valleys
2. Modeling long-range transport (up to 1000 km)
 - Trajectories
 - Dispersion
 - Concentration predictions
3. Experimental model verification
 - By use of air quality data and tracers-of-opportunity
 - By use of intentionally released conservative tracers

TABLE 2

Conservative gaseous tracers

1. Properties
 - Non-depositing
 - Non-scavenged
 - Non-reactive
 - Low atmospheric background
 - Limited industrial use
 - Sensitive detectable
2. Perfluorocarbon tracers (PFTs)
 - PDCB (P^a - dimethylcyclobutane)
 - PMCP (P - methylcyclopentane)
 - PMCH (P - methylcyclohexane)
 - PDCH (P - dimethylcyclohexane)

^aP as in PDCB means "perfluoro"

Descriptions of the use of other familiar gaseous conservative tracers, for example, sulfur hexafluoride (SF₆), halocarbons, and deuterated methanes (refs. 1-2), will only be briefly covered. The four PFTs listed in Table 2, which are in the generic family of perfluoroalkylcycloalkanes, have been used in a number of tracer experiments, some of which will be described later.

Table 3 lists the units for reporting atmospheric tracer concentrations, since a variety of these may have been used in the figures or may be mentioned in the course of this presentation. Convention would have us use pL/L and fL/L.

The purpose of this presentation, as outlined in Table 4, is to describe the perfluorocarbon tracer technology developments at Brookhaven, including the latest identified as well as available PFTs and air sampling and analysis tools, to demonstrate their utility in a number of different atmospheric tracer experiments as well as in other applications, and to provide food-for-thought

TABLE 3

Units for atmospheric PFT concentrations

1. Parts-per-trillion
 - ppt
 - $\times 10^{-12}$
 - pp10¹²
 - nL/m³ (nanoliters/cubic meter)^a
 - pL/L (picoliters/liter)^a
2. Parts-per-quadrillion
 - ppq
 - $\times 10^{-15}$
 - pp10¹⁵
 - pL/m³
 - fL/L (femtoliters/liter)^a

^anano (10⁻⁹), pico (10⁻¹²), femto (10⁻¹⁵)

TABLE 4

Outline of perfluorocarbon tracer technology presentation

1. Introduction
2. Description and design of PFT technology
 - 2.1 PFT identification and availability
 - 2.2 Air samplers
 - 2.3 Vertical atmospheric sampling cables
 - 2.4 Analysis tools
3. Applications of PFT technology
 - 3.1 Atmospheric tracer experiments
 - 3.2 Building air infiltration and indoor air quality
 - 3.3 Potential new applications
4. Conclusions

on new ways in which the PFTs can be applied in other research objectives. All of the important tools will be described, but emphasis will be given to work that has not previously been given in detail and to the latest developments in the technology.

2 DESCRIPTION AND DESIGN OF PFT TECHNOLOGY

The complete system for performing long range atmospheric transport and dispersion experiments consists of the PFTs, the air samplers, and the analytical methodology.

As will be shown shortly, availability and cost of PFTs are two key factors for consideration in the design of any long-range tracer experiment. In addition, the equipment for automatically and routinely releasing the tracer must be considered.

Air samplers are used for routine collection by adsorption, using both programmable and passive samplers, located both on the ground and aloft. The

platforms for vertical samples consist of programmable or miniature sampling tubes in aircraft, balloon-supported vertical sampling cables with pumps on the ground, and passive samplers connected to tethered balloon cables.

Analyses are performed routinely on adsorbent-based samplers returned to the laboratory and also in real-time in the field using a dual-trap analyzer, which can be mounted in aircraft.

First proposed to the U.S. National Oceanic and Atmospheric Administration (NOAA) nearly a decade ago by James Lovelock (ref. 3), an intensive reduction to practice has already been implemented by the U.S. Department of Energy (DOE) at its Brookhaven National Laboratory (BNL) and Environmental Measurements Laboratory (EML) facilities and by NOAA's Air Resources Laboratory in terms of quantitatively and, more or less, routinely releasing, collecting, and automatically analyzing PFT air samples.

Before describing the PFT technology in detail, it will be useful to look at a simplified picture of how the tracers are analyzed in order to understand the advantages of the PFTs over other types of gaseous tracers. The PFTs are analyzed by gas chromatography which is shown in a simplified schematic in Fig. 1. The constituents in an air sample are thermally desorbed from the sample tube and are injected into the carrier gas stream via the sample valve. Before entering the chromatographic column, all the components will be present as a slug (see the square wave in Fig. 1a). After passing through the column, the constituents will be physically separated to an extent which depends on the nature and conditions of the column. However, as shown in Table 5, the atmosphere contains many compounds whose concentrations exceed those of the PFTs and which are detectable in the electron capture detector (ECD) used to measure the PFTs. Included are O_2 , nitrogen oxides, chlorofluorocarbons (Freons), SF_6 , and others, each of which could interfere with the early eluting PFTs (Fig. 1b). As will be described later, physical means (e.g., sampling onto an adsorbent with subsequent purging) removes most of the oxygen and some of the Freons, but a catalyst bed operating at about $200^\circ C$ (Fig. 2) is needed to destroy many of the remaining interfering compounds so that the surviving PFTs can be detected (Fig. 1c). The importance of the catalyst bed should not be underestimated in the successful determination of the PFTs.

Referring back to Table 2 then, it is the physical and chemical inertness of the PFTs that not only prevents their loss in the atmosphere but also helps in their separation and analysis from the less-stable interfering compounds and makes them biologically inactive; thus they are perfectly safe to use (ref. 1). Because of their low solubility in H_2O and moderate vapor pressure they are not readily scavenged nor deposited in the atmosphere, but, unlike SF_6 , their vapor pressures are low enough to allow them to be readily sampled onto solid adsorbents. Their limited industrial use not only results in a low

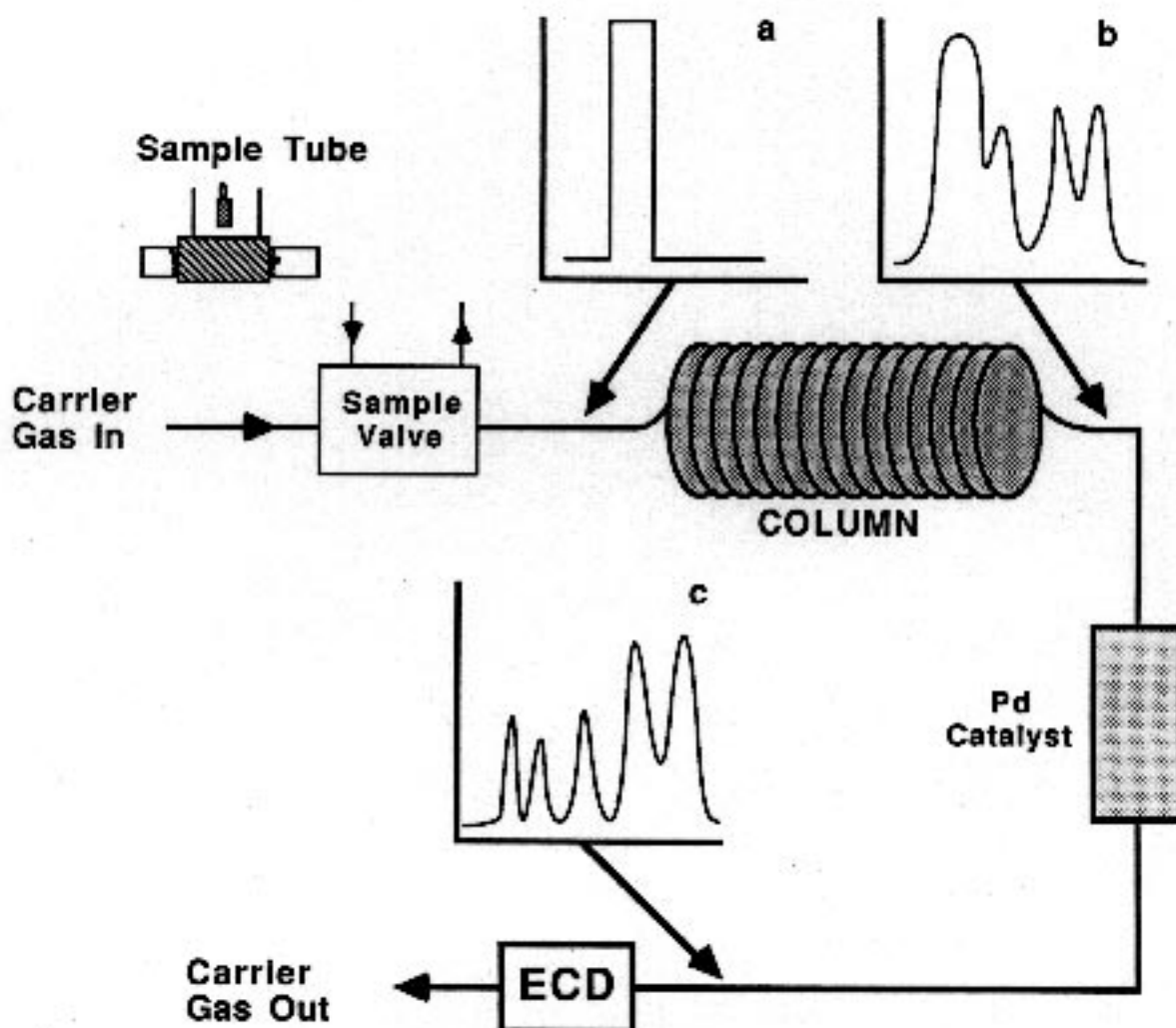


Fig. 1. Simplified schematic of a gas chromatograph (GC) system showing the function of the sample valve, the GC column, and the palladium (Pd) catalyst bed prior to electron capture detection (ECD). (a) Sample. (b) Interfering compounds and PFTs. (c) PFTs alone.

ambient background concentration but also precludes the possibility of numerous higher local concentrations which might confuse atmospheric tracer experimental results.

Lastly, the high affinity of PFTs for their reaction with electrons makes them some of the most sensitive compounds for detection on the ECD, which is a small (0.1 to 0.2 mL) reaction chamber containing an electron source. The cloud of electrons in the chamber is periodically collected, producing a current. When tracer molecules enter the cell, the reacted electrons can not be collected; this resulting reduction in current is a measure of the PFT concentration.

TABLE 5
Some components in the atmosphere

| Gas | Rural Concentration, pp 10 ¹² | Formula | Concentration Range |
|-------------------------------|---|---------------------------------|------------------------|
| Nitrogen | 780,900,000,000 | N ₂ | % |
| Oxygen | 209,500,000,000 | O ₂ | |
| Argon | 9,300,000,000 | A | |
| Carbon dioxide | 335,000,000 | CO ₂ | ppm |
| Methane | 1,480,000 | CH ₄ | |
| Nitrous oxide | 315,000 | N ₂ O | ppb |
| Ozone | 35,000 | O ₃ | |
| Nitrogen oxides | 3,000 | NO, NO ₂ | |
| Methyl chloride | 630 | CH ₃ Cl | ppt |
| Freon 12 | 305 | CCl ₂ F ₂ | |
| Freon 11 | 186 | CCl ₃ F | |
| Carbon tetrachloride | 135 | CCl ₄ | |
| Chloroform | 20 | CHCl ₃ | |
| Sulfur hexafluoride | 0.85 | SF ₆ | |
| Bromotrifluoromethane (F13B1) | 0.75 | CBrF ₃ | |
| Perfluorodimethylcyclohexane | 0.022 | C ₈ F ₁₆ | ppq |
| Perfluoromethylcyclohexane | 0.0045 | C ₇ F ₁₄ | |
| Perfluoromethylcyclopentane | 0.0032 | C ₆ F ₁₂ | |
| Perfluorodimethylcyclobutane | 0.00034 | C ₆ F ₁₂ | sub-ppq |
| Deuterated methane | 0.00030 ^a | CD ₄ | |
| Deuterated methane | 0.00001 ^a | ¹³ CD ₄ | |

^aCurrent limits of detection; actual background estimated at <0.000001pp10¹².

2.1 PFT identification and availability

Since many researchers have used a variety of gaseous tracers other than the PFTs (refs. 1-2), a comparison of the properties and costs of their use in long-range atmospheric tracer experiments will be made in order to demonstrate the cost-advantages of the PFTs. Also presented will be analyses of ambient air samples for currently-used PFTs to demonstrate background levels, analyses of the manufacturers' PFT samples to determine purity and to identify various isomers, examples of new tracers to be used in up-coming continental-scale tracer experiments, and lastly, a brief description of future potential tracers.

The physical properties of a few of the important compounds previously used as tracers are shown in Table 6. The tracers are listed in decreasing order with respect to the cost of the quantity released, which is based on the ability to detect the tracer concentration above its ambient background level. Many of these tracers are liquids at room temperature and must be released by either atomization or vaporization followed by dilution to prevent condensation until the vapors are sufficiently diluted below the ambient dew point

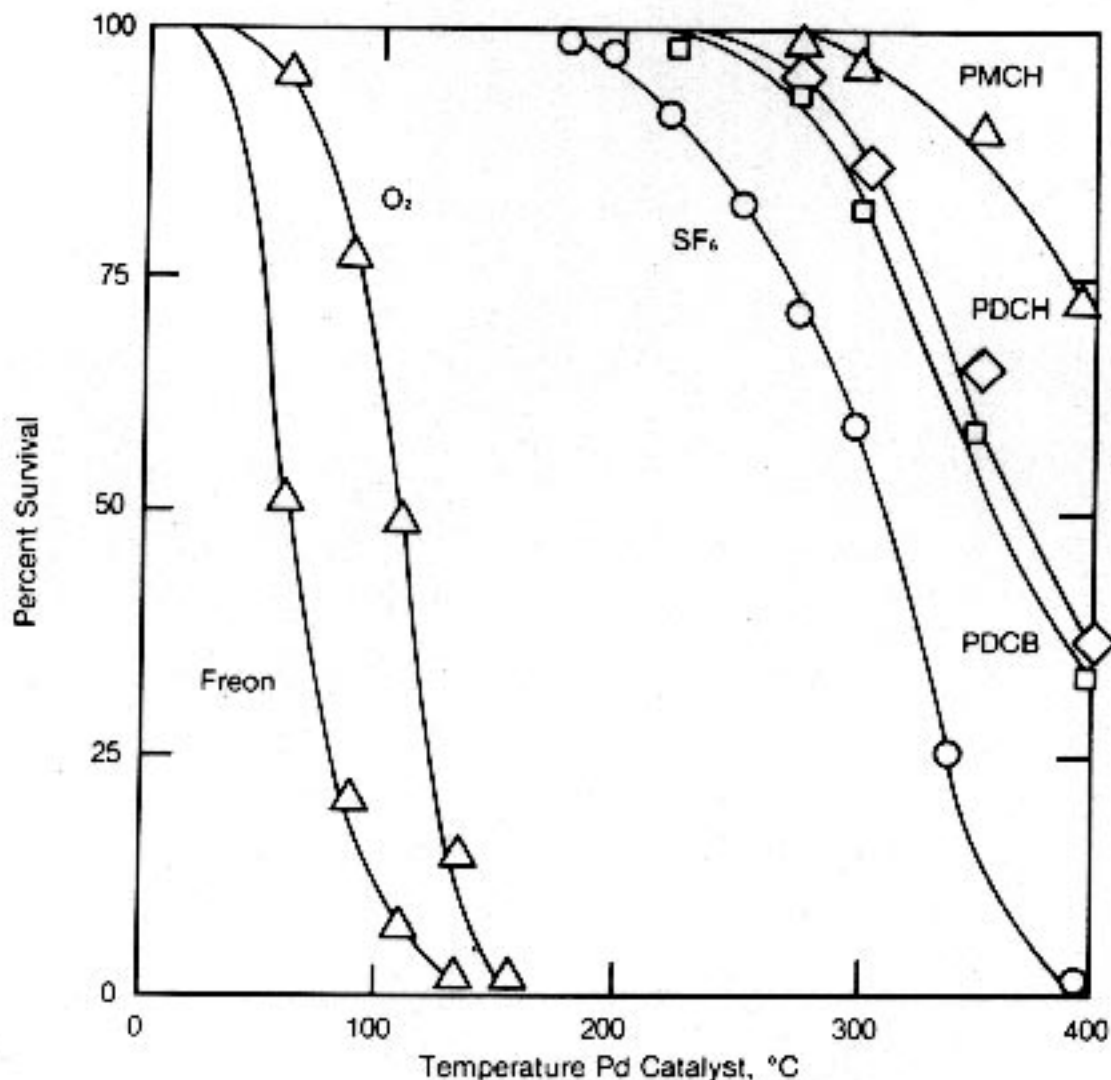


Fig. 2. Effect of catalyst bed temperature on destruction of PFTs and interfering compounds such as O₂ and Freons (chlorofluorocarbons).

TABLE 6

Properties of some gaseous conservative tracers

| Symbol | Formula | Molecular weight | Phase at 20°C | Boiling point, °C | Supplied form |
|-------------------------------|---------------------------------|------------------|---------------|-------------------|---------------|
| SF ₆ | SF ₆ | 146 | gas | -64 | liquefied gas |
| F13B1 | CBrF ₃ | 149 | gas | -58 | liquefied gas |
| PDCH ^a | C ₈ F ₁₆ | 400 | liquid | 102 | liquid |
| F12B2 | CBr ₂ F ₂ | 210 | liquid | 25 | liquid |
| PMCH ^a | C ₇ F ₁₄ | 350 | liquid | 76 | liquid |
| PDCB ^a | C ₆ F ₁₂ | 300 | liquid | 45 | liquid |
| CD ₄ | CD ₄ | 20 | gas | -160 | gas |
| ¹³ CD ₄ | ¹³ CD ₄ | 21 | gas | -160 | gas |
| α-PDCH ^a | C ₈ F ₁₆ | 400 | liquid | 102 | liquid |

^aThe chemical names for these four PFTs are given in Table 8.

concentration. Thus the release apparatus is somewhat more complex than for the liquefied gaseous tracers such as SF₆ and F13B1. Descriptions of the tracer release equipment as well as the calculations to be made to estimate the release quantities have been summarized elsewhere (ref. 1). An alternative technique for the release of liquefied gases such as SF₆ was based on the release of the liquid through fuel burner nozzles (ref. 4).

The relative tracer costs for plume centerline detection of tracer at 100 times background concentrations were shown in Table 7. Even though PFTs cost

TABLE 7

Relative gaseous conservative tracer costs

Distance: 100 km

Desired Concentration: 100 times background at centerline

Release time: 3 hours

| Symbol | Formula | Ambient conc., fL/L ^a | Cost \$/kg | Released qty., kg | Relative ^d tracer cost, 1000 \$ |
|-------------------------------|---------------------------------|----------------------------------|------------|-------------------|--|
| SF ₆ | SF ₆ | 2000 ^b | 10 | 2320 | 23.2 |
| F13B1 | CBrF ₃ | 750 | 15 | 887 | 13.3 |
| PDCH | C ₈ F ₁₆ | 22 | 120 | 70 | 8.4 |
| F12B2 | CBr ₂ F ₂ | <20 | 30 | <33 | <1.0 |
| PMCH | C ₇ F ₁₄ | 4.5 | 100 | 12.5 | 1.2 |
| PDCB | C ₆ F ₁₂ | 0.34 | 500 | 0.81 | 0.41 |
| CD ₄ | CD ₄ | 0.60 ^c | 3000 | 0.095 | 0.29 |
| ¹³ CD ₄ | ¹³ CD ₄ | 0.02 ^c | 50000 | 0.0033 | 0.17 |
| ocPDCH | C ₈ F ₁₆ | 0.3 | 220 | 0.95 | 0.21 |

^a1000 fL/L equals pL/L or 1 part-per-trillion.

^bNear-urban SF₆ is 2000 fL/L or more in many locations because of significant use; tropospheric background is 850 fL/L.

^cValues for deuterated methanes represent current limits of detection (S/N=2) for a 1 m³ air sample; actual backgrounds are about 0.0005 fL/L.

^dCost is for required release quantity and does not reflect the cost of the analyses.

10 to 50 times that of SF₆, the significantly lower background concentrations mean less material needs to be released. Thus, for PMCH, the relative tracer cost is more than 10-fold less than if SF₆ or F13B1 had been used in a given tracer experiment, for a savings of about \$10,000 to \$20,000. Of course, for a 1000-km experiment, the savings would be an order of magnitude higher. For the last PFT, the ortho(cis) isomer of PDCH, the cost would be another factor of 6 lower. Only the deuterated methanes have comparable tracer costs, but their analytical costs are substantially higher, perhaps more than an order of

magnitude (ref. 2). In addition to their lower costs, the family of useful PFTs has the potential to grow to 10 to 12 tracers sampled and analyzed on the same equipment.

(1) Previously used PFTs. Two example chromatograms of the analysis of 14.5- and 3.8-L ambient air samples are shown in Fig. 3. Specific details on the sampling and analysis technique will be described later. Briefly it consisted of pulling the air through tubes packed with a solid, charcoal-like adsorbent which was then thermally desorbed into the gas chromatograph. The identification of the PDCB, PMCP, and PMCH peaks as well as the group of peaks representing the PDCH isomers had been previously determined (ref. 2). The definitions of the symbols for each of the named peaks are given in Table 8.

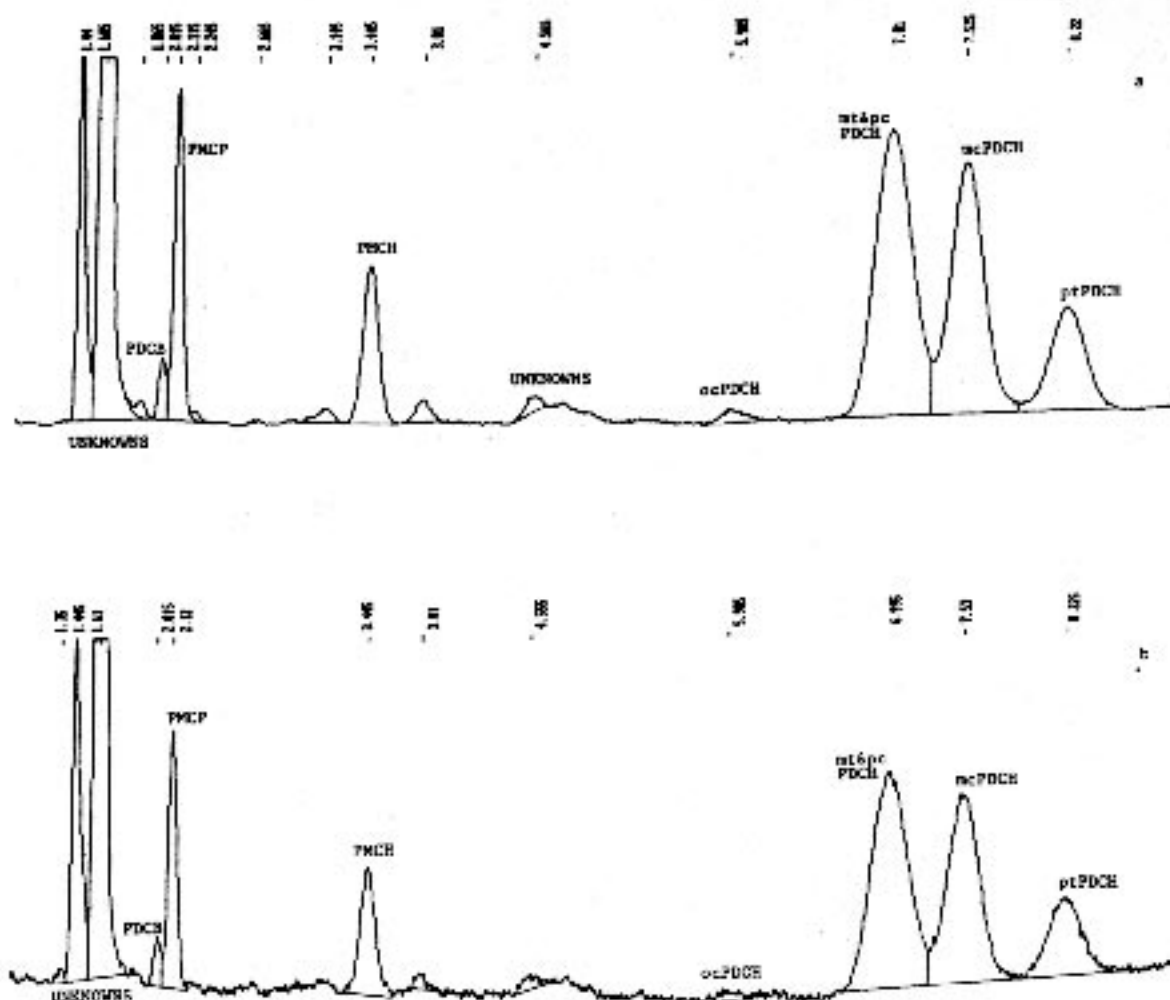


Fig. 3. Chromatograms of adsorbent-collected ambient air samples analyzed on a 6-foot (1.8-m) by 0.093-inch (2.36-mm) ID, 0.1% SP 1000 on Carbopack C (Supelco) column at 140°C with 22 mL/min of 5% H₂ in N₂ (a) 14.5-L air sample. (b) 3.8-L air sample.

TABLE 8

Identification of current and potential PFT components

| No. | Symbol | Name(perfluoro-) | Elution ^a time,min | Ambient air conc., fl/l |
|-----|--------|---|----------------------------------|----------------------------|
| 1 | PDCB | dimethylcyclobutane | 1.26 | 0.34 ± 0.01 |
| 2 | PMCP | methylcyclopentane | 1.32 | 3.22 ± 0.03 |
| 3 | PMCH | methylcyclohexane | 2.08 | 4.46 ± 0.05 |
| 4 | ocPDCH | ortho ^b (cis)-DCH ^d | 3.43 | 0.3 ± 0.1 |
| 5 | mtPDCH | meta(trans)-DCH | 3.97 | 7.7 |
| 6 | pcPDCH | para(cis)-DCH | 4.04 | 2.2 |
| 7 | PECH | ethylcyclohexane | 4.12 | <2 |
| 8 | otPDCH | ortho(trans)-DCH | 4.16 | 0.2 |
| 9 | mcPDCH | meta(cis)-DCH | 4.24 | 8.2 |
| 10 | ptPDCH | para(trans)-DCH | 4.62 | 3.4 ± 1 |
| 11 | 1 PI | 1-indane | 4.53 | ? |
| 12 | 2 PI | 2-indane | 5.99 | ? |
| 13 | 1 PTCH | 1-trimethylcyclohexane | 8.98 | 0.07 |
| 14 | 2 PTCH | 2-trimethylcyclohexane | 9.50 | <0.03 |

^aMid-point of tracer peak in gas chromatogram at conditions given in Fig. 3, but with column at 160°C.

^bortho, meta, and para mean the 1,2-, 1,3-, and 1,4-isomers.

^ccis and trans mean the alkyl groups (e.g., methyl) are on the same or opposite sides, respectively, of the molecular plane.

^dDCH represents dimethylcyclohexane.

By collecting and analyzing ambient air samples of about 0.5 to 14.5 L in volume and plotting tracer quantity versus air sample volume as shown in Fig. 4, it was possible to determine the ambient air concentrations of each of the PFTs as listed in Table 8. The standard deviations on the concentrations do not reflect the uncertainty in the calibration gas standards which is another ±5%.

The actual determination of which isomers of PDCH were represented by the peaks in Fig. 3 at retention times of about 6 to 8 minutes (the numbers at the top of the figure) was only recently resolved. The elution order for the isomers of the hydrocarbon, dimethylcyclohexane (DCH), was previously determined by gas chromatography on a graphitized carbon support (ref. 5). The seven isomers of DCH (the cis and trans of each of the ortho, meta, and para isomers plus the 1,1-isomer) were available as relatively pure hydrocarbons. These were analyzed on the same support used in our PFT gas chromatograph, confirming the elution order found in ref. 5.

Starting with pure quantities of the ortho-, meta-, and para-xylenes as well as ethyl benzene, the catalytic (cobalt trifluoride) fluorination by the PFT manufacturer (ISC Chemicals Limited, Avonmouth, Bristol, Great Britain) yielded the perfluorinated versions. Subsequent analysis by thermal conductivity gas chromatography gave the chromatograms shown in Fig. 5 and the PDCH compositions shown in Table 9. Thus, starting with pure ortho-xylene, the resultant product is only 84.4% ortho-PDCH, 46.4% as the cis isomer and 38.0% as the trans

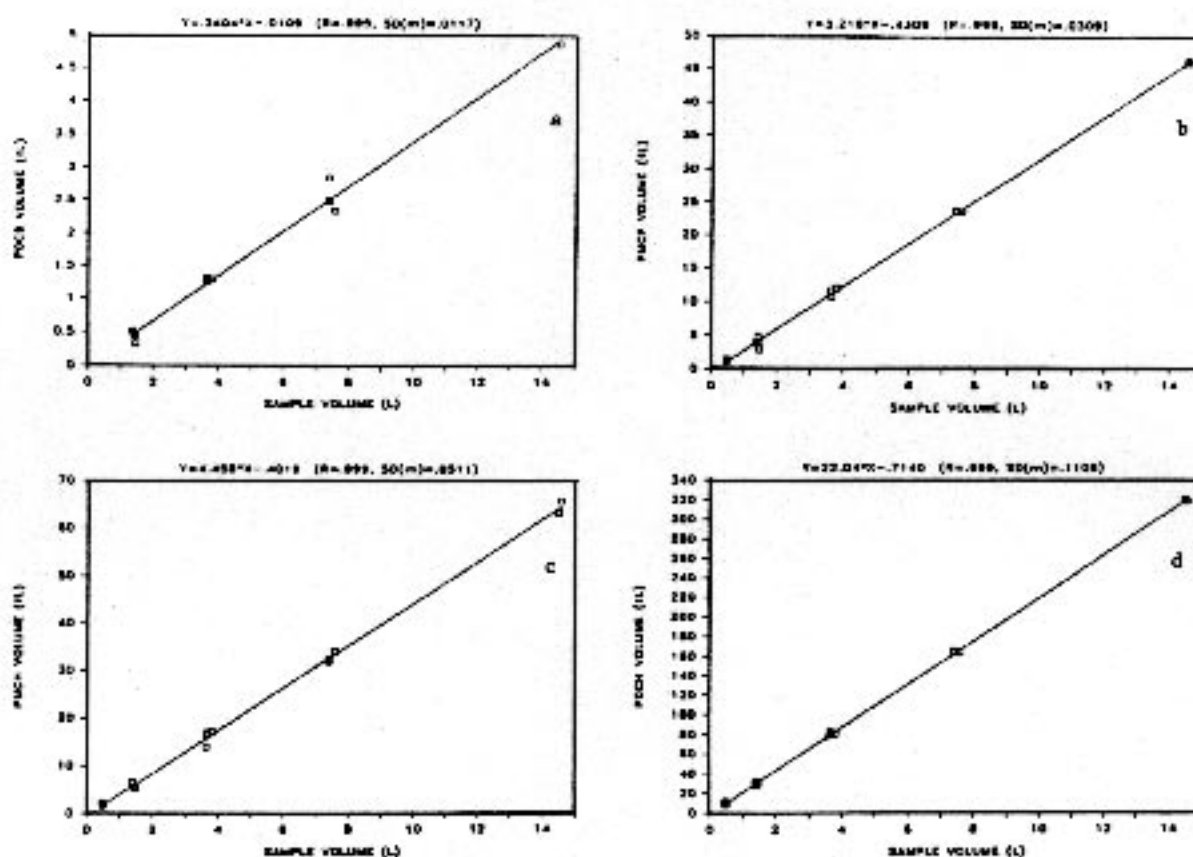


Fig. 4. Quantity of four PFTs found in the ambient air for samples ranging from 0.5 to 14.5 L. The slope of the line representing PFT quantity (fL) versus air sample volume (L) is the background ambient air concentration (fL/L). See Table 8 for tracer names. (a) PDCB. (b) PMCP. (c) PMCH. (d) PDCH is the total of all isomers.

isomer. The purities of the resultant meta- and para-PDCH, which were only 83.1 and 91.8%, respectively, as shown in Table 9, were computed by an iterative procedure since not all of the isomers are separately resolved. In fact, as shown in Fig. 5, only ocPDCH (the first peak) and ptPDCH (the last peak) are clearly resolved. The mt- and pc-PDCHs are nearly coincident as are the ot- and mc-PDCHs. In addition, the PECH is right between the two meta-PDCH peaks.

Referring back to the ambient air chromatograms of Fig. 3, it was now possible to identify the PDCH isomers in the last four peaks, which have been appropriately labelled. The ambient air concentration of each of the six PDCH isomers listed in Table 8 was computed as follows. The ocPDCH concentration was determined directly because it was separately resolved. Then the otPDCH was computed assuming the same ratio as in the manufactured ortho-PDCH (Table 9) which was then subtracted from the next-to-the-last peak to leave the ambient concentration of the mcPDCH. Note that the peak in Fig. 3 was only labelled as mcPDCH because the otPDCH was trivial (compare the ocPDCH peak).

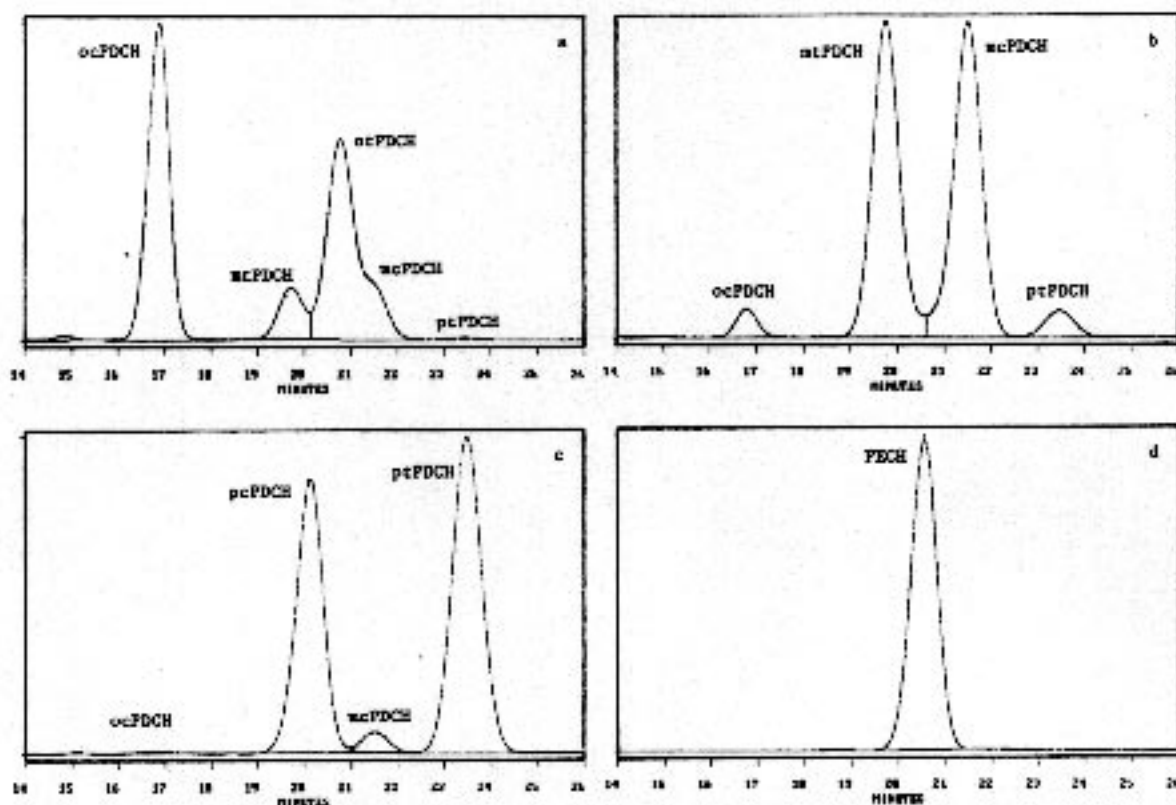


Fig. 5. Identification of the relative elution order of the isomers of PDCH as well as the location of PECH (see Table 8 for tracer names). (a) ortho-PDCH. (b) meta-PDCH. (c) para-PDCH. (d) PECH.

TABLE 9

Composition^a of PDCH isomers, percent (mol)

| Component | Ortho-PDCH | Meta-PDCH | Para-PDCH |
|----------------|------------|-----------|-----------|
| PMCH | 2.4 | 1.0 | - |
| ocPDCH | 46.4 | 3.1 | 0.1 |
| mtPDCH | 6.6 | 38.7 | 3.8 |
| pcPDCH | 0.3 | 4.1 | 36.7 |
| otPDCH | 38.0 | 2.6 | 0.1 |
| mcPDCH | 5.6 | 44.4 | 4.2 |
| ptPDCH | 0.4 | 6.1 | 55.1 |
| Totals | 99.5 | 100.0 | 100.0 |
| Primary | | | |
| cis and trans: | 84.4 | 83.1 | 91.8 |

^aAnalyzed by thermal conductivity (TC)GC which, unlike the ECD, gives the same response for each isomer.

Similarly, the ptPDCH was directly determined (it stands alone), and the computed pcPDCH was then subtracted from the combined mt- and pc-PDCH to yield the mtPDCH.

The resultant ambient air concentrations for each of the PDCH isomers are only good estimates because the relative response of the ECD to each of the isomers is not the same. The ECD was originally calibrated with the meta-PDCH, which is the predominant isomer in the ambient air at 15.9 of the 22.0 fL/L total (see the slope from Fig. 4d) or 72%; thus the meta-PDCH concentrations should be reasonably accurate. A preliminary evaluation of their ECD response showed that only the ptPDCH, the last peak, had a significantly lower response, indicating that its ambient concentration might be higher. Further laboratory studies will be conducted to accurately determine this important variable of ECD response.

From the ambient chromatograms in Fig. 3 and the known concentrations of each PFT (Table 8), it is possible to see that the limits of chromatographic detection range from 0.2 fL for PDCB and PMCP, and 1 fL for PMCH and α -PDCH, to about 1.5 fL for ptPDCH.

(ii) New and future PFTs. There are two basic processes that have been used commercially for the production of PFTs, here restricted to the family of perfluoroalkylcycloalkanes because they have the maximum response to the ECD. Other perfluoroalkanes and other perfluorocarbons are two or more orders-of-magnitude poorer in detection capability (ref. 1). The one process already mentioned, cobalt trifluoride catalyzed fluorination, is available from ISC Chemicals Limited in England. The purity of their tracers has been from 85 to 99%, with a limited amount of the other existing and identified PFTs as impurities, generally less than 1%. This can be important in a tracer experiment if the PFT being released has a 1% impurity of another also being released. Of course, correction can be made based on the analyses of the impurities in the released PFTs, but that correction becomes more significant as the number of tracers used in any one experiment increases. Fortunately, ISC has been able to keep the purity of the PFTs they supply quite high for these applications. All of the PFTs in Table 8 with the exception of No. 1, PDCB, are supplied by ISC.

The other process for making PFTs is the dimerization of perfluoroalkenes at high pressures (up to 3000 atmospheres) and moderate temperatures (400°C). Originally patented by E.I. duPont in Wilmington, Delaware, more than 19 years ago, the technique was used at one time to make the PDCB. They abandoned the technology more than five years ago and other small companies can now produce a number of the dimerization products, generally perfluorodialkylcyclobutanes, but at costs up to ten times or more those of the PFTs from ISC. However, the PDCB is a potential continental scale tracer because it has the highest ECD response of any of the PFTs and has a low ambient concentration. Recently, the Flora Corporation in North Carolina has indicated an interest in supplying tracers made by this process.

Beginning in January 1987, a major tracer experiment, ANATEX (Across North America Tracer Experiment), will involve the release of two new PFTs never before intentionally released. This three-month-long experiment requires background concentrations to be less than 0.4 fL/L at a tracer cost of less than \$200/kg if the total tracer cost is to be less than \$500,000 for daily average PFT concentrations no higher than 10 times background. One tracer meeting that need was the *o*-PDCH which can be supplied by ISC.

A number of alternative compounds were suggested to ISC, one being perfluorotrimethylcyclohexane (PTCH) and another, perfluoroindane (PI). A mixture of these two new tracers plus four of the earlier PFTs was analyzed as shown by the chromatogram in Fig. 6a, which showed the elution of the 1 PI (at 4.5 min) and seven isomers of PTCH at 6.3 to 11.2 min. The two major isomers of PTCH were arbitrarily named. Ultimately they will be identified to locate potential

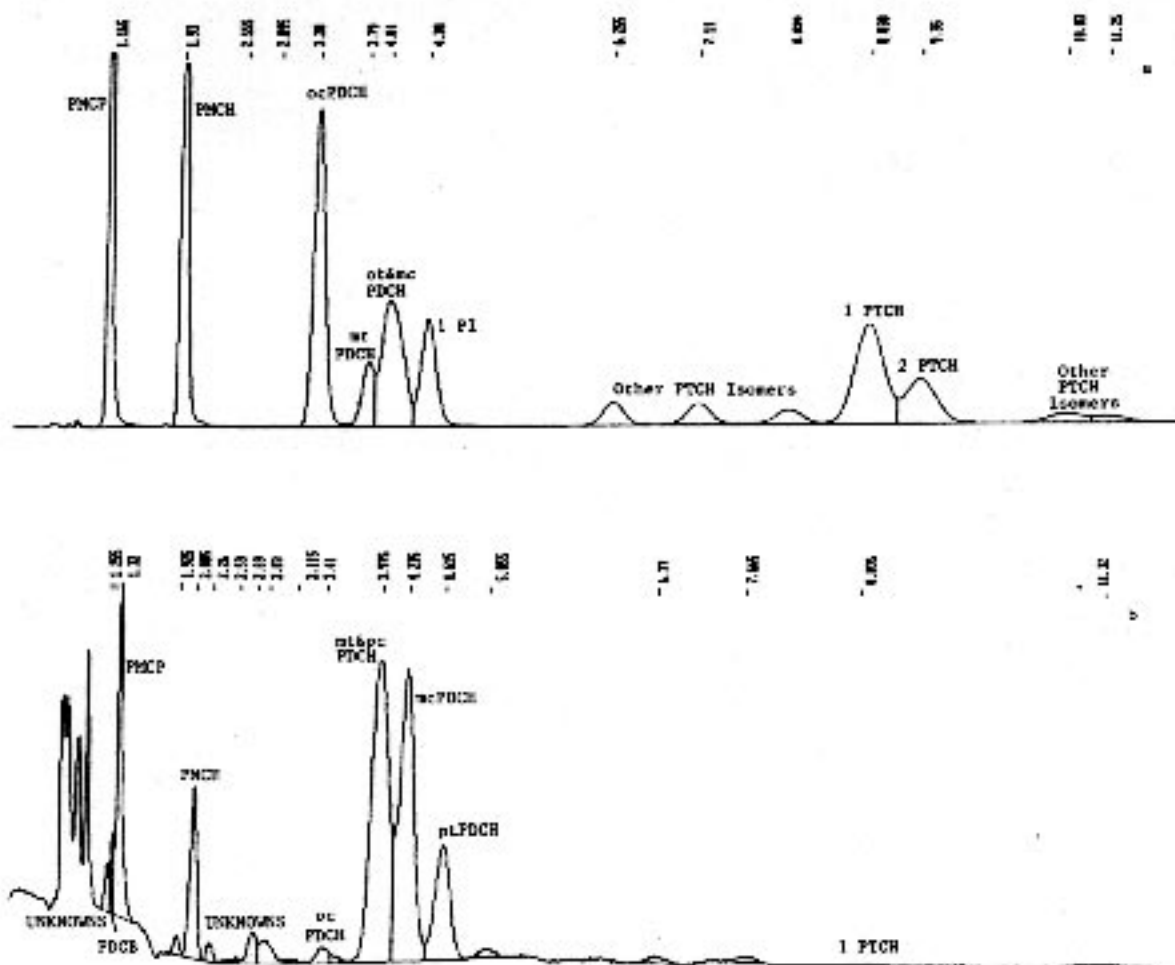


Fig. 6. Chromatograms of (a) about equimolar standard of PMCP, PMCH, *o*-PDCH, *m*-PDCH, PI and PTCH, and (b) about 50-L of ambient air, but with the column of Fig. 3 at 160°C.

future tracer types. The retention or elution time of all the PFTs at the 160°C column temperature are shown in Table 8.

A 50-L ambient air sample was analyzed under the same GC conditions. The normal PDCH isomer distribution was attained as shown in Fig. 6b. Note that the 1 PI in the standard had the same elution time as the ptPDCH in the air sample. This alone would preclude PI as a continental-scale tracer because the background ptPDCH would interfere. But it was also determined that the PI was sensitive to catalyst destruction depending upon its operating condition and cleanliness. Thus PI was temporarily abandoned as a tracer pending further research on alternative catalysts.

In Fig. 6b, it is difficult to see if any PTCH exists in the ambient air. It certainly would appear to be less than the ocPDCH level. Fig. 7 shows an expansion of that chromatogram in two regions. The early region shows that the PDCB is still separated from the PMCP. The late region shows that at the 1 PTCH elution time, the very small peak would correspond to an ambient air concentration of about 0.07 fL/L, which would make it a viable continental-scale tracer.



Fig. 7. Expansion of Fig. 6b (a) Early region showing resolution of PDCB and PMCP. (b) Late region indicating the detection of negligible quantity of PTCH in ambient air.

(111) Summary of PFT investigation. It was shown that the family of PFTs can be uniquely detected on a single analysis of an air sample by a special gas chromatograph to be described in detail later. Table 10 lists the currently usable PFTs, their limits of detection, and the principal supplier. There is a good likelihood that additional research into fluorination of alkylcycloalkenes

TABLE 10
Currently usable PFTs^a

| No. | Tracer | Limit of detection, fL |
|-----|--------|------------------------|
| 1 | PDCB | 0.2 |
| 2 | PMCP | 0.2 |
| 3 | PMCH | 0.9 |
| 4 | o-PDCH | 1.0 |
| 5 | m-PDCH | 4 ^b |
| 6 | p-PDCH | 1.5 |
| 7 | PTCH | 3.5 |

^aAll PFTs supplied by ISC Chemicals Ltd. (England) except PDCB, which is available in small quantities elsewhere.

^bDetermined by difference.

and the dimerization of perfluoroalkylcyclobutanes will lead to a much larger family of useful PFTs.

2.2 Air samplers

The PFTs can be collected as whole air samples using conventional means such as bags, bottles, syringes, etc. (ref. 1). However, the PFTs can be adsorbed onto the surface of carbon steel surfaces and, of course, they are soluble in fluoroelastomers (e.g., Viton), silicone rubber, and fluoropolymers (e.g., Teflon) so these materials should be avoided. We have found that polyolefins, polyurethane, and nylon are quite compatible, as are stainless steel and specially treated aluminum (ref. 1).

Like almost all hydrocarbons, PFTs readily adsorb onto charcoal-like materials. Unlike most hydrocarbons, however, the PFTs are thermally stable to quite high temperatures in the absence of any reducing catalysts, thus permitting thermal recovery for subsequent analysis. Based on these considerations, two adsorbent samplers were designed and built.

(i) Programmable PFT sampler. This was developed by Dietz at Brookhaven and commercially manufactured for NOAA by Gilian Instrument Corporation as the Brookhaven Atmospheric Tracer Sampler (BATS). The entire unit shown in Fig. 8a measures just 14 x 10 x 8 inches and weighs 7 kg. The lid contains 23 sampling tubes, each containing 150 mg of 20-50 mesh type 347 Ambersorb (Rohm and Haas Co.) which can retain all the PFTs in more than 30 L of air. Internal batteries provide power for up to one month of unattended operation of all the

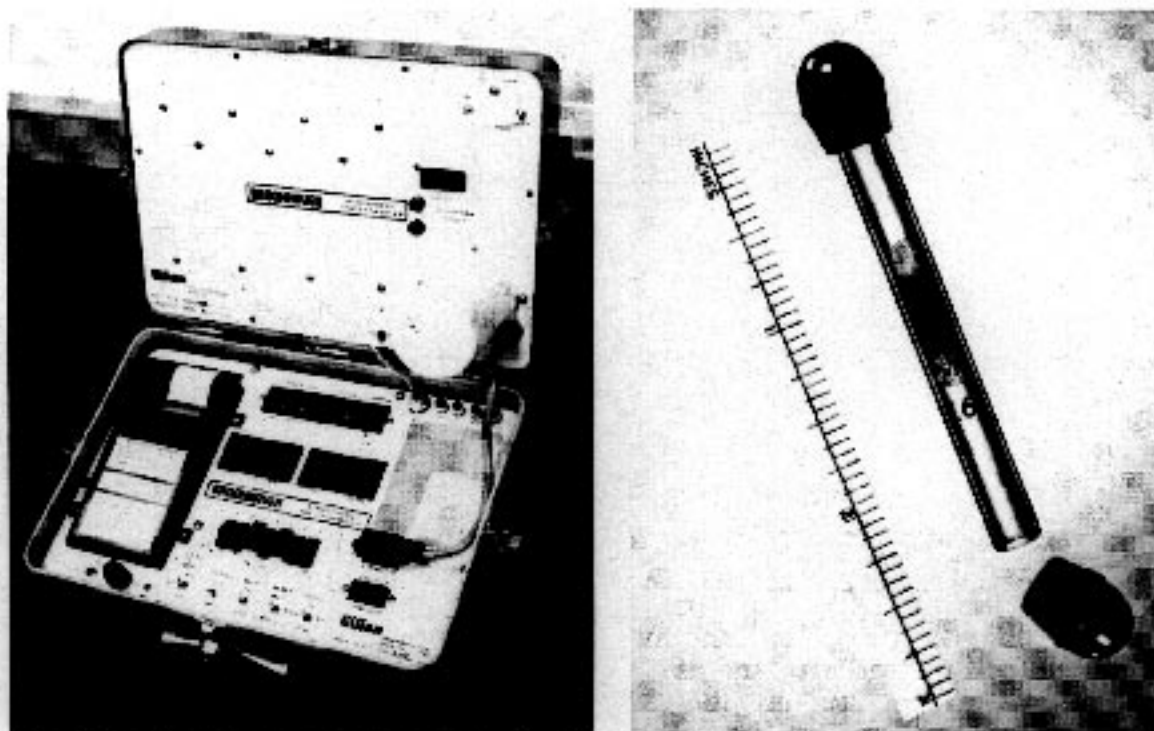


Fig. 8. Two PFT adsorbent samplers. (a) The programmable Brookhaven Atmospheric Tracer Sampler (BATS). (b) The passive capillary adsorption tube sampler (CATS).

automatic sampling and recording features. In the laboratory, sample recovery was accomplished by direct ohmic heating of the adsorption tube to 400°C, with the PFTs being purged from the BATS tube through an automated ECD-GC system, analyzing all 23 tubes in about 3 h (ref. 6).

The ability to collect variable volume air samples with good precision is indicated by the results shown in Fig. 4 for samples collected on a BATS. However, since their first commercial production in 1980, they have been used in no less than seven major atmospheric tracer experiments and numerous other field projects. The major weak points found in the instrument were the pump and the paper tape printer. In preparation for ANATEX, all of the BATS bases are having an EML-developed pump (ref. 7) called TAPS (tethered air pump system) installed and, in the BATS lids, a solid state memory device which can be read directly into a computer. These modified BATS units should have a substantially improved reliability.

A new prototype BATS base is under development to provide both computerized control of all the sampling functions as well as real-time determination of the pumping rate based on a patented pump and pressure and temperature measurements across a computer-selectable orifice.

(11) Passive PFT sampler. Originally developed as a means to measure the indoor PFT concentration during the determination of air infiltration and air exchange rates in homes and buildings using miniature PFT permeation sources (refs. 8-9), the passive sampler has also been used in atmospheric tracer studies (ref. 10).

In its first configuration, one end of the sampler contained a 1-mm capillary tube and so was coined the Capillary Adsorption Tube Sampler (CATS). The present configuration of a CATS is shown in Fig. 8b. The passive sampler, which is made from 6 mm OD by 4 mm ID glass tubing exactly 2.5 inches (6.4 cm) long, contains 64 mg of Ambersorb 347. Sampling occurs by the process of Fickian diffusion when one cap is removed as shown. From the depth to the bed (2.76 cm), the cross-sectional area (0.126 cm^2), and the empirically derived diffusion coefficients of the PFTs in air, it was determined that the CATS sampled at a rate equivalent to about 200 mL of air per day for PMCH.

Numerous comparisons with the BATS and the CATS have shown that they determine the PFT concentration to within the same precision of about $\pm 5\%$. A special rack was built to sequentially desorb 23 CATS for GC analysis in much the same way that the 23 tubes in the BATS lid were automatically stepped (ref. 9) for analysis.

2.3 Vertical atmospherizing sampling cables (VASC)

Although aircraft platforms with real-time analyzers or with high-flow-rate sample collection systems can provide useful pictures of the plume aloft, in certain complex terrain studies, for example, near mountains and valleys and especially at nighttime, the well-defined directions of the valley flows lend themselves to be monitored with balloon-borne vertical sampling devices for the vertical definition of the transport and dispersion of pollutants.

Several types of balloon-borne systems have been designed and used in the ASCOT (Atmospheric Studies of Complex Terrain) program in which tracers, including SF_6 , heavy methanes, and perfluorocarbons, were measured in air samples collected to a height of 500 m above the ground (refs. 11-12). Traditionally, these systems have used tethered balloons, from 5 to 100 m^3 in volume, to suspend whole air sampling packages such as plastic bags with pumps and automated syringes at several altitudes along the cable or to collect sequential whole air samples over time and space as the balloon is moved from the ground to its maximum altitude.

In this section, a brief description will be given of two novel balloon-borne VASCs - a multitube, ground-based cable (VASC-I) with multiple sampling pumps and a single-tube, multi-level adsorbent sampler cable (VASC-II) with a single pump on the ground. Each was carefully designed by considering all aspects of the flow of a compressible fluid (air) through long tubing,

computing the pressure drop by taking into account laminar and, where necessary, turbulent flow friction effects, the effect of gravity since the air was being pulled down a vertical column, the impact of density changes due to changes in altitude as an air parcel moves down the cable as well as effects of expansion and contraction when the air flow is controlled by a capillary tube or a sub-miniature orifice plate - a small hole in a nearly flat plate such as a small hole drilled through the wall of the tubing cable. Laboratory validation tests conducted on the models used to compute flows at various pressures through tubing (Fig. 9a) and orifice holes (Fig. 9b) showed good agreement between measured points and computed curves. Also taken into account were the characteristics of the vacuum pumps used to pull the air through the cables. Matching the total flow rate and the pressure drop of the cable to the pump capacity required multiple, step-wise computations from the top of the cable to the pump at the bottom.

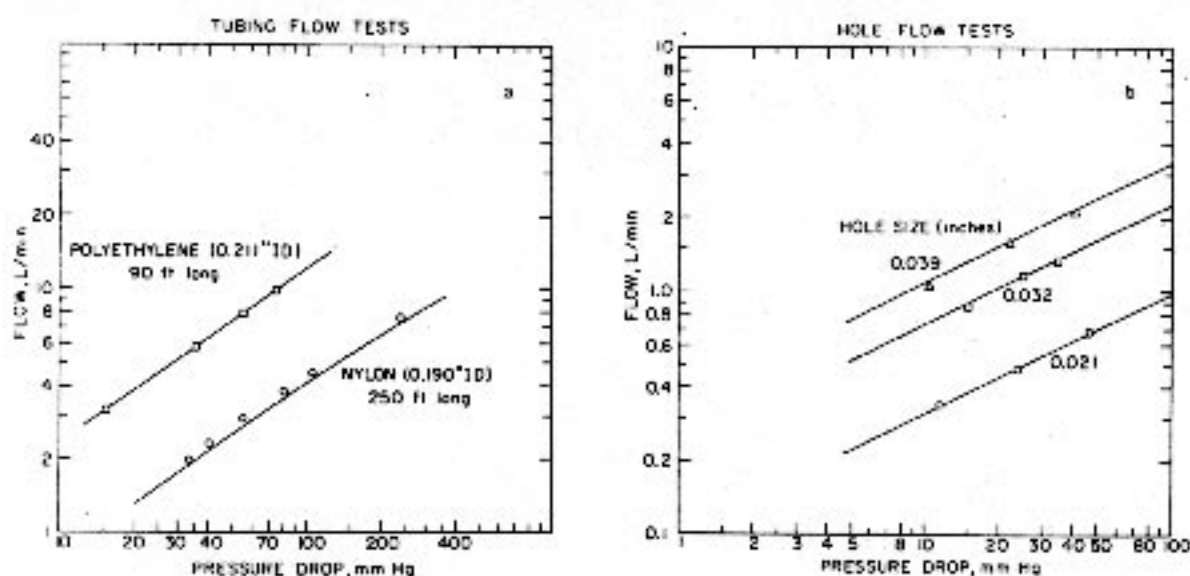


Fig. 9. Flow versus pressure drop tests for the validation of the model used in the design of the vertical atmospheric sampling cables (VASCs). (a) Flow through long plastic tubes. (b) Orifice plate model for flow through holes drilled in a plastic tube wall.

The process consisted of assuming an orifice dimension and orifice flow rate at the uppermost sampling location. Using the barometric pressure at that altitude, the required pressure inside the cable necessary to cause that flow was computed. Then, using that flow rate and the dimensions of the vertical tubing cable, the pressure inside the cable at the next sampling location was computed. From that pressure and the ambient pressure at that new location, the dimension of the next orifice was computed assuming an orifice flow rate equal to that of the first. This process was repeated, adding the flow from subsequent sampling locations to the total cable flow when calculating the

cable tubing pressure drop from position to position. At the end of the cable on the ground, the final total flow rate and inside tubing pressure had to meet the design flow rate versus pressure characteristics of the pump. The iterative solution was repeated until those characteristics were met.

(i) VASC-I. Four separate 1/4-inch OD polyethylene sampling cables were bundled together in a braided Kevlar sheath (Cortland Line Company) and suspended from a 100-m³ balloon tethered for an altitude of 1600 ft above the ground (ref. 12). The cable was designed at Brookhaven to sample four separate 400-ft layers from 0-400 ft up to 1200-1600 ft as shown in Fig. 10. Each cable

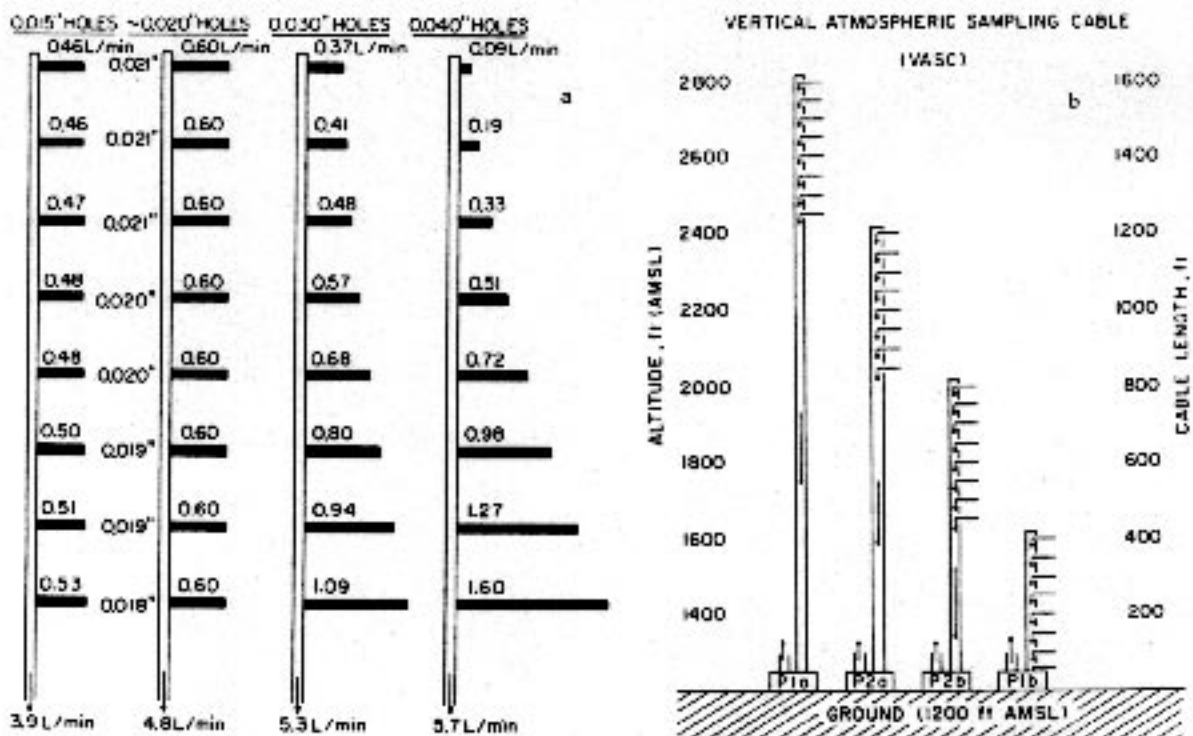


Fig. 10. Design of the vertical atmospheric sampling cable I (VASC-I). (a) Calculated effect of hole diameter on flow through 8 holes spaced 50-feet (15.2-m) apart for the four hole diameters shown. (b) Conceptual schematic of VASC-I.

had eight intake holes at 50-ft intervals over the designated sampling span. Fig. 10a showed that it was necessary to select an orifice diameter of about 0.020-inches (0.50-mm), varying slightly from top to bottom to have a uniform flow rate into each hole of 0.60 L/min for a total flow rate of 4.8 L/min at the pump. If the hole size had been 0.040-inches (1.0-mm), it was shown that the sampling would have been biased to the lowest portion of the sampling zone. Pumps on the ground continuously pull air through each of the four cables to air sampling devices on the ground, certainly a significant attribute.

(ii) VASC-II. A major disadvantage of VASC-I was its more than 18-kg weight requiring the large 100-m³ balloon and gasoline-powered winch. For sampling in complex terrain where access to sampling sites for the tethering of vertical cables is limited, a much lighter cable was desired. In addition, because flow in complex terrain is usually more variable near the ground, it was desired to have a greater number of sampling locations in the lower region of the cable.

The final design consisted of a 500-m-long polypropylene tubing, 0.062-in. (1.6-mm) ID by 0.010 in. (0.25-mm) wall, with 15 orifices located 50-m apart from 500 m down to 200 m and then decreasing to only 10 m apart near the ground. The orifice lengths (Fig. 11a) were individually sized using the flow model to allow the air to be sampled at closer intervals near the ground, but at the same flow rate, about 4.5 ml/min, through each sampling tube at every altitude. Each orifice was designed to be equipped with a CATS passive sampler of the type described earlier, but used in an active mode. Flow through each sampling tube was accomplished with a single small pumping station on the ground, pulling a total of 67.5 ml/min at about 0.5 atm vacuum. The whole cable, with 15 samplers, weighed just 0.6 kg, which, together with an airsonde for altitude and temperature requirements, was readily supported by a 5-m³ balloon (Fig. 11b).

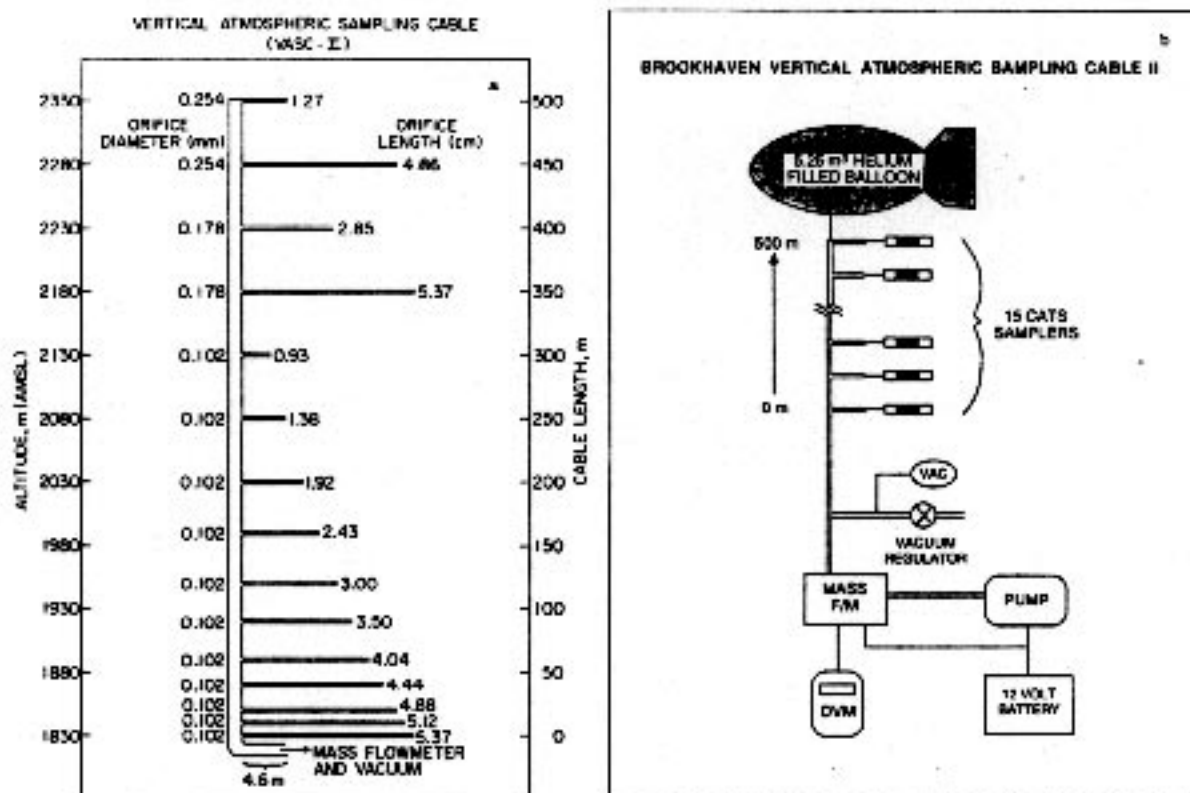


Fig. 11. Design of the vertical atmospheric sampling cable II (VASC-II). (a) Schematic of computed orifice dimensions necessary to achieve the same flow through each sampler. (b) Balloon and pumping system.

Each orifice was cut to the proper length (not a trivial task to prevent closing of the holes) and its effective diameter was computed using the flow model. Each of the measured tube diameters from individual flow measurements was larger than the manufacturer's claimed value (Table 11). After installation on the cable, the diameters were again determined by measuring the individual flow while pumping on the entire cable. The agreement on- and off-cable was excellent.

TABLE 11
VASC-II Calibration of orifice diameters

| Sampler height | -----Orifice diameter (mil) ^a ----- | | |
|----------------|--|-----------|----------|
| | Claimed | Off cable | On cable |
| 500 | 10 | 11.66 | 11.52 |
| 450 | 10 | 11.33 | 11.39 |
| 400 | 7 | 7.84 | 7.88 |
| 350 | 7 | 7.96 | 8.06 |
| 300 | 4 | 5.09 | 5.17 |
| 250 | 4 | 5.13 | 5.17 |
| 200 | 4 | 5.22 | 5.26 |
| 160 | 4 | 5.29 | 5.33 |
| 120 | 4 | 5.22 | 5.31 |
| 90 | 4 | 5.43 | 5.49 |
| 60 | 4 | 5.37 | 5.39 |
| 40 | 4 | 5.11 | 5.20 |
| 20 | 4 | 5.31 | 5.37 |
| 10 | 4 | 5.30 | 5.29 |
| 0 | 4 | 5.42 | 5.46 |

^aA mil is 0.001-in or 0.025-mm.

The advantages of VASC-II were its low weight, multiple (15) sampling positions, and the fact that the sample did not flow through the cable. However, a disadvantage compared to VASC-I was that the sampling was not truly continuous. An integrated 0.5-L sample could be obtained in just 2 h, sufficient to measure down to the ambient background of PMCP and PMCH. But it requires about 1 h to replace the CATS before sampling can begin again.

2.4 Analysis tools

For application to long-range tracing, the principal PFT analyzers are the laboratory gas chromatograph system for the analysis of samples collected on the programmable and passive samplers and a real-time dual-trap analyzer for in-the-field collection and analysis of PFTs.

Another analyzer which continuously responds to electron capturing tracers by combusting the oxygen with hydrogen over a catalyst bed, will respond to PFTs. But its detection capability is limited to about 1 to 30 pL/L (parts-per-trillion) and is generally not economically useful (considering

tracer costs) beyond 100 km. Details of the operation of this continuous analyzer have been presented earlier (refs. 13-14) and will not be discussed here.

(i) The laboratory gas chromatograph system. The system is comprised of the gas chromatograph (GC), the data handling devices, gas standards, and the PFT adsorbent samplers, the latter of which have already been described. The use of the system requires a temperature-controlled room and an uninterruptable power supply capable of supporting the data handling system during brief power failures. The GC has internal battery backup for its microprocessor.

The operation of the GC can first be given in a simple overview. Whether from programmable or passive samplers, the sample is automatically thermally desorbed and passed through a Pd catalyst bed, permeation dryer, and a pre-cut column before being re-concentrated on an in situ trap. The trap prevents the collection of unwanted low molecular weight constituents, the pre-cut column prevents the passage of unwanted high molecular weight constituents, and the dryer removes moisture from the ambient samples. After thermally desorbing the trap, the PFTs are separated in the main column after passing through another Pd catalyst bed and detected in the ECD.

The current configuration of the GC system (Fig. 12) was used to produce the chromatograms shown in Fig. 6. Two processes occur during a single cycle, analysis of a previously collected sample and the loading of a new sample onto the trap. At the start of the cycle, the FD valve goes on as well as the Florasil trap valve (FS). Note that all the valves are shown in their "off" position; "on" means the FS valve rotor turns 90 degrees and the others, 60 degrees. Thus, when heat is applied to the FS trap, the adsorbed PFTs are flushed out through catalyst bed "A," catalyst bed "B," the dryer, the main column, and the detector (ECD). As shown by the chromatogram in Fig. 6, the entire process for the last PTCH isomer to elute is under 12 min; the cycle time was set for 12 min.

However, during this time, another sample tube is desorbed, processed, and collected on the trap. For the first 3 min, the sample tube is purged of oxygen by the carrier gas (5% H₂ in N₂). Then both the PC and SV are turned on and heat is applied to the sample tube to sweep the PFTs into the pre-cut column, a 22-in. (56 cm) by 0.113-in. (2.9 mm) thin-walled stainless steel column packed with Unibeads 2S (Alltech) at 85°C. The unknown, early-eluting interfering compounds will flow out of purge vent #2. Just before the first PFT elutes from the pre-cut column, the FD valve is turned off and the FS trap is opened. This allows the PFTs to be collected in the Florasil trap as they leave the pre-cut column, which is ohmically heated to a higher temperature. When the last PFT component has entered the trap, all the valves go to their

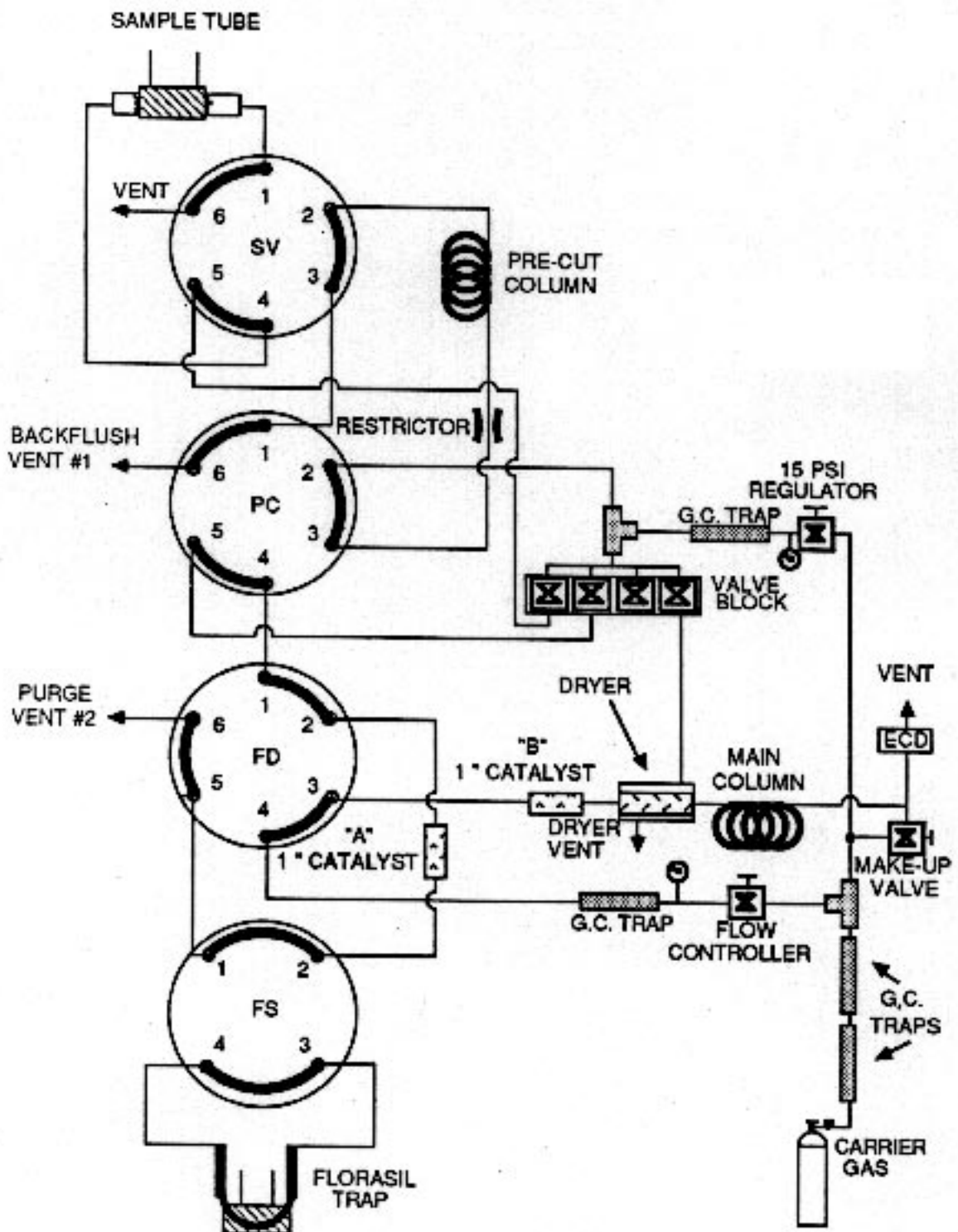


Fig. 12. Schematic of the laboratory GC plumbing. (SV) Sample valve. (PC) Pre-cut column backflush valve. (FD) Flow direction valve to isolate the chromatography occurring in the main column from the loading of the next sample. (FS) Florasil trap valve. All valves are shown in their "off" position.

off position (at 9.6 min), which allows the pre-cut column to be backflushed at the higher temperature for more than 2 min to eliminate any heavy components.

The pre-cut column system prevents components lighter than the first PFT from seeing the catalyst bed "A" or from entering the trap. Components heavier than the last PFT selected for analysis are also precluded. By tailoring the pre-cut column temperatures, the PFT "window" can be increased or decreased at either the beginning or the end.

As mentioned earlier, the catalyst is important in removing interfering compounds. With this system, the PFT sample passes once through catalyst bed "A" on its way into the trap, once again upon recovery from the trap, and once through catalyst bed "B." This assures a good cleanup of the sample.

The data handling system is a basic Nelson Analytical 3000 Chromatography system with an IBM PC/AT, an ink-jet printer, the Series 860 A/D converters, and the Nelson 2600 Chromatography Software, set up in the laboratory as shown in Fig. 13. Other appropriate software and hardware complete the system.

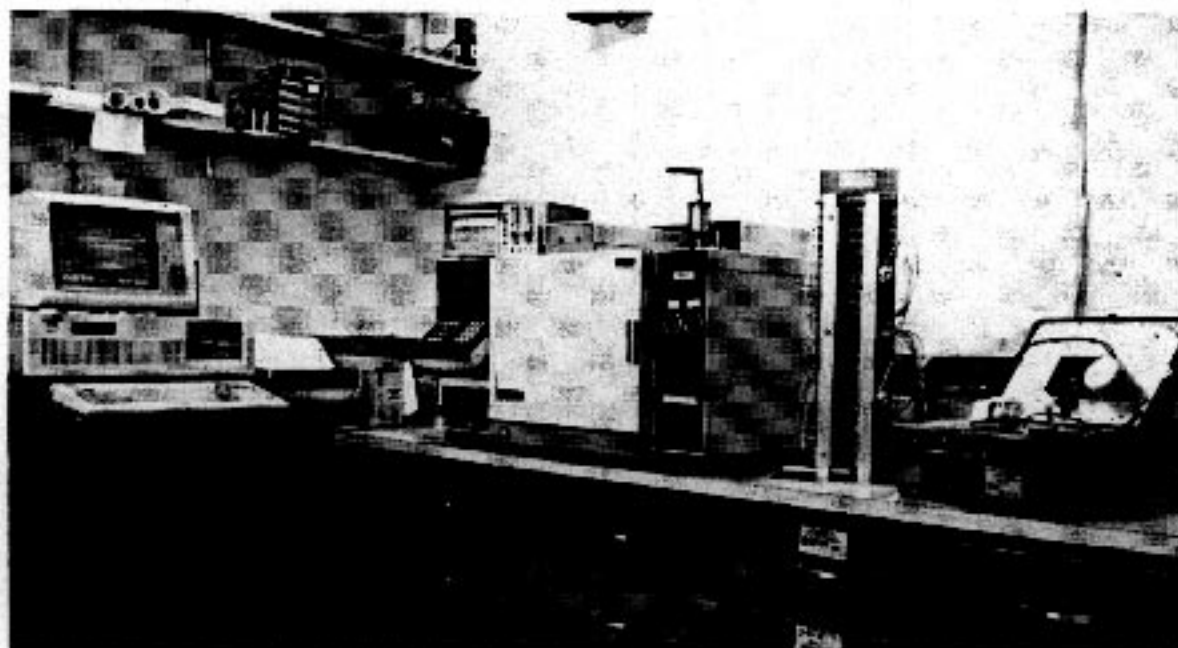


Fig. 13. Gas chromatograph laboratory system. The IBM PC/AT is on the left followed by the printer, the Nelson A/D converter, the GC with recorder on top, the CATS desorption rack, and a BATS.

which currently handles three GCs for the analysis of PFTs. Once a data collection method has been stored in the A/D box, the computer can be used for other operations, such as checking previous data for proper peak integration, while the A/D box stores the current analysis output. The system data storage is sized such that chromatograms for up to 25 to 35 analyses can be stored on one floppy disk, thus accommodating an entire BATS lid or CATS rack.

Gas standards for calibrating the GC have been prepared in-house as well as commercially (Airco Industrial Gases, Riverton, New Jersey) in their Spectro Seal aluminum cylinders in the working range of 1 pp 10^8 , 1 pp 10^{10} , and 1 pp 10^{12} . Brookhaven prepared primary standards in the range of 100 to 1000 pp 10^6 in He using pressure-volume techniques, which were corroborated by analyzing on a thermal conductivity detector (TCD) GC. The working range cylinders were then prepared by pressure-dilution in steps of 100-fold using ultrapure air (BNL standards) or nitrogen (Airco standards). Airco has prepared the cylinder standards on a very large manifold accommodating up to 24 cylinders. Thus they can make one large batch of a PFT standard to be distributed in cylinders to many users of the PFT technology such that every one has the same working standards.

BNL has prepared working standards containing different mixtures of PFTs-- one containing PDCB, PMCH, and m-PDCH and another containing PMCH and m-PDCH. Airco had previously prepared one set of standards containing PMCP, PMCH, and m-PDCH. They are currently preparing a large batch of another set containing PMCP, PMCH, o-PDCH, p-PDCH, and PTCH.

The working standards are corroborated by comparing them to dynamically prepared PFT mixtures by passing nitrogen at a measured flowrate over temperature-controlled, gravimetrically calibrated PFT sources which were originally developed to conveniently tag homes when performing air infiltration measurements (ref. 12).

Sampling of either of the standards, working or dynamic, is accomplished by passing a set flow rate of the PFT standard through a BATS tube or CATS for a known period of time and then analyzing on the GC system. Using preset flow restrictors to deliver 50 mL/min of the gas standard at tank pressure, a one-minute sample of the 1 pp 10^{12} standard would contain just 50 fL of each tracer. By increasing the standard loading time automatically, using a BATS base to increment the time, and by switching to the higher working standards once a 30- to 50-min sample of two decades lower had been loaded, it is readily easy to prepare sample tubes containing PFTs from 50 to 10^7 fL (the latter is 20 min of 1 pp 10^8 at 50 mL/min). Since the standards can readily be loaded onto CATS tubes, boxes of such samplers are routinely stored and used in the laboratory for calibrations about two to three times daily.

A complete calibration curve can be run using the prepared standards, but in two modes as shown in Fig. 14. Normally, as the quantity of tracer analyzed

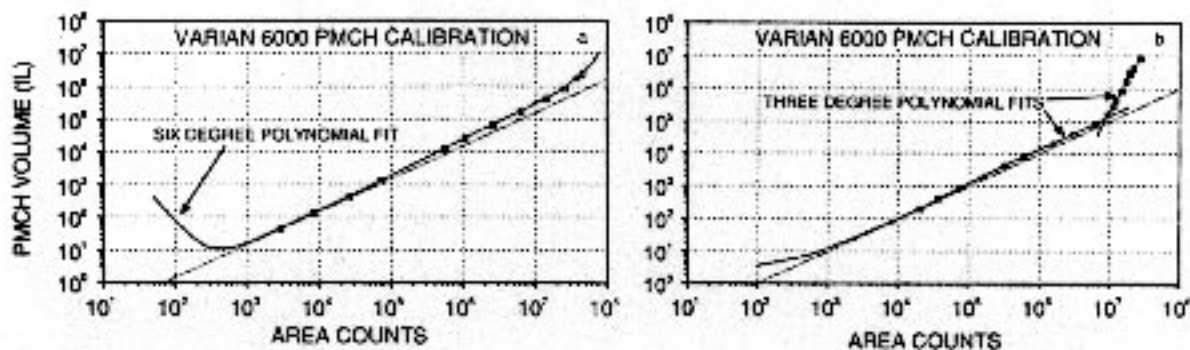


Fig. 14. PMCH calibration data obtained and correlated in two ways. (a) The electrometer gain was decreased 10-fold above 10^5 fL. (b) The gain was not reduced and the overload region was separately fitted.

increases, the electrometer gain is reduced an order-of-magnitude when its output nears 1 volt, the Nelson system voltage input limit. By multiplying the range 10 areas by 10, the tracer volume versus peak area data continue on a smooth curve above the range 1 overload point which, for PMCH, occurs at about 10^5 fL. It is apparent from Fig. 14a that the data in the region up to about 10^3 fL (1 pL) falls on the unity slope line. But from 10^3 to 10^4 fL, the curve displaces to a new unity slope line before starting to curve again at the overload of the PFT-electron reaction in the ECD which occurs at about 5×10^5 fL. This data is best fitted by a 6-order polynomial with a usual tracer quantity prediction of about $\pm 4\%$ or better. Below 50 fL (the limit of the usual low end of the calibration), the polynomial deviated markedly from the unity line which is what is used in that region. Five femtoliter standards (1 min of 1 pp 10^{12} at 5 mL/min) confirmed the linearity.

The alternative approach which is currently the favored method is shown in Fig. 14b. The electrometer range is not changed at the range 1 overload. Although the peak heights do not increase above 1 volt (the Nelson A/D cutoff), the areas increase, because the peaks are broadening, but at a higher quantity-per-unit area rate. A third-order polynomial was fitted to the data below the 1 volt overload (clearly evident at about 10^5 fL of PMCH), and another above that level. The precision of this approach appears to be as good as the former, but here there is no concern for guessing which electrometer range should be used when analyzing unknown samples.

Remembering that the limit-of-detection for PMCH was about 1 fL, the dynamic range would appear to be about seven orders-of-magnitude. However, the GC has a memory of about 0.01 percent of the previous sample when analyzing the next, which then decreases at a slower rate upon subsequent analyses of lower concentration samples.

(ii) Dual-trap analyzer. The peak PFT concentration typically encountered in long-range tracer experiments range from 1 to 5 pL/L at 100 km downwind to about 100 to 400 fL/L at 800 km downwind. These concentrations can easily be measured with BATS located both on the ground and in aircraft. The expense of an aircraft platform, however, mandates that the sampling occur where the plume is actually located. Thus, the need exists for a real-time PFT analyzer.

In the late 1970s, Lovelock, under a contract to NOAA, built a prototype instrument which was subsequently modified at Brookhaven. The unit consisted of two adsorbent traps, packed with the same material used in the BATS and CATS, and an in situ ECD chromatograph. While one trap was sampling at 1 L/min for 5 min, the other was heated to recover and analyze the collected PFTs. Since the traps reversed position every 5 min, no tracer was lost.

A new version of this real-time analyzer was built in 1983 for the fall CAPTEX experiment. Improvements allowed the separation of 3 PFTs in a 4-min chromatogram of a 4-min air sample collected at the rate of 1 L/min. The unit was able to see down to the ambient levels of PMCP and PMCH, indicative of the limit of detection of about 10 fL (ref. 15).

3 APPLICATIONS OF PFT TECHNOLOGY

The ultra sensitive detection of the PFTs through the use of some simple and inexpensive field tools as well as with sophisticated laboratory analyzers has lead to an extensive number of applications.

The principal supporter of the development of the technology has been the U.S. Department of Energy (DOE) because of its application in long-range atmospheric tracing (Table 12). Another DOE office has been funding the

TABLE 12

Supporters of PFT tracer technology

U.S. Department of Energy

- long-range and complex terrain atmospheric transport
- building infiltration and ventilation

Utilities

- oil leak detection from urban buried high-voltage cables
- air infiltration, weatherization and indoor air quality in homes and buildings
- leak detection in boiler and condenser tubes
- integrity of nuclear facilities, both safeguards and emissions

Oil and Gas Industries

- geophysical exploration
- leak detection in storage and pipe transport
- process flow measurements

Federal, State and Local Agencies

- indoor air quality and air infiltration
- atmospheric and oceanic transport and dispersion
- detection of tagged explosives

development of the passive PFT source and sampling device for the inexpensive determination of air leakage rates in homes and buildings.

In the last two years, the utility industry has expressed interest in using the technology to detect oil leaks from underground high voltage transmission cables. The industry costs for finding such leaks each year can run to \$1 million for just one major city. Utilities supplying gas for home heating and cooking are concerned about the magnitude of pollutant emissions from various appliances and the increase in pollutant concentrations that might arise as customers attempt to conserve energy by reducing the leakage of heated air in the wintertime through weatherization efforts which reduce air infiltration and exfiltration. The PFT technology can quantify the energy savings of weatherization and can pinpoint and quantify the source of the various pollutants found in the home as well as provide a model for predicting the consequences of weatherization on the indoor pollutant levels. Concepts have been considered for detecting, quantifying and locating leaks in power plant condenser tubes and systems, but no active work is currently taking place.

Despite the apparent oil glut in the world economy today, the oil and gas industry is actively involved with the search for new sources of these natural resources and applying new technology in attempts to improve the yields from existing oil and gas fields. Understanding the geophysical characteristics of these petroleum reservoirs through the application of radioactive tracers has been occurring for more than 15 years, but recently the PFT technology has been applied because the PFT quantity required for the same signal-to-noise would cost at least two orders-of-magnitude less, saving nearly one hundred thousand dollars in just one experimental field measurement.

Other groups of federal, state, and local agencies have been supporting the use of PFTs for quantifying and locating the sources of radon contamination in homes and demonstrating the applicability of various mitigating strategies, for studying other indoor pollutants (it is always necessary to know the air leakage rate into the building), for determining the effectiveness of air handling equipment in commercial buildings, for atmospheric and oceanic transport studies on all scales, and for the detection of tagged explosives in clandestine bombs at airport environments. This latter research has been more-or-less ongoing since 1972. By attaching PFT vapors to blasting caps during their manufacture, the PFT technology has been demonstrated to have sufficient sensitivity to detect a tagged bomb in a suitcase on a conveyor belt, on a plane, or secreted into a building.

3.1 Atmospheric tracer experiments

Table 13 provides an outline of the atmospheric tracer field experiments in which PFT technology has been used.

Some details on the results will be presented during the lecture.

TABLE 13
Atmospheric tracer experiments using PFT technology

| No. | Name | Date | Scale of transport | PFTs used | PFT sampling used |
|-----|---|--------------------------|-------------------------|--------------------|--|
| 1 | Multitracer atmos. exper.-Idaho (ref. 16) | April 1977 | 100 km | PDCB, PMCH, m-PDCH | Prototype (PT) adsorbent sampler, bags and bottles, PT Dual-trap |
| 2 | Long-range atmos. demo.-Oklahoma (ref.6) | July 1980 | 600 km | PMCH, m-PDCH | 60 BATS, modified dual-trap (MDT), bags |
| 3 | ASCOT 80 and ASCOT 81 (ref.12, 17) | Sept. 1980 Sept. 1981 | Complex terrain (15 km) | PMCH, m-PDCH | 60 BATS, MDT, bags, WASC-I |
| 4 | Mini-CAPTEX 82 | 1982 | 10 km | PMCH | 5 BATS, CATS, MDT |
| 5 | CAPTEX 82 | Sept. 1982 | 800 km | PMCH | 60 BATS, CATS |
| 6 | CAPTEX 83 (ref. 18) | Sept. 1983 | 1200 km | PMCH | 80 BATS, New dual-trap (NDT) |
| 7 | ASCOT 84 | Sept. 1984 | Complex terrain (25 km) | PMCP, PMCH, m-PDCH | 80 BATS, CATS, WASC-II |
| 8 | METREX (ref. 10) | Nov. 1983- Dec. 1984 | Urban (15 km) | PMCP, PMCH, m-PDCH | 3 BATS, 93 CATS sites |
| 9 | SCCCAMP | Sept. 1985 | Coastal (200 km) | PMCP, PMCH, m-PDCH | 30 BATS, CATS |
| 10 | AMATEX | Jan. 1987 | 3000 km | o-PDCH, PTCH | 75 BATS, CATS, MDT |

3.2 Building air infiltration and indoor air quality

Structures, from the smallest homes to the largest types of commercial buildings, are very rarely capable of being modeled as single, well-mixed zones, but rather are comprised of multiple zones each of which may be considered as well-mixed if care is given in the partitioning. Thus, tracer techniques for measuring air infiltration rates into each zone as well as the air exchange rates between zones must be able to provide multiple tracers, one for each physically distinct building zone, and the means to simply determine each of those tracers from a single air sample collected in each zone.

The passive sampler (CATS) provides the means to measure the indoor air concentration of PFTs. Miniature PFT permeation-type sources (ref. 9) can

provide the tracer source. With up to seven PFTs now capable of being sampled and analyzed, each of up to seven zones in a home can be separately tagged.

By measuring the concentration of a pollutant in each zone of the house with a separate sampling device, for example, the passive Palmes tube is used for NO_2 , it is possible to compute the source strength of the pollutant in each zone. For NO_2 , if the source was found to be a positive value in the kitchen and about zero in all other zones, then the source might likely be the unvented gas range. If, however, a positive source term was computed in another zone as well, for example, a bedroom, then the NO_2 source might be from a leak in the flue duct from the home heating device. Such results have indeed been found and corrective action was initiated on the basis of this work. A summary of results in 30 homes will be shown.

The penetration of radon in homes is another important area where multiple PFT technology can identify the location of the source (usually the basement or crawl space) and the magnitude of the source. Studies on developing mitigating strategies based in part on the application of the PFT technology are underway.

3.3 Potential new applications

A two year research project has just been initiated with the Electric Power Research Institute (EPRI) in the U.S. to demonstrate the potential of detecting oil leaks in underground high voltage cables. By dissolving just 0.1% by weight of a PFT into the oil, which would increment the cost of the oil about 5 to 10%, it is projected that the PFT samplers will be able to pin-point and quantify the magnitude of oil leaks as low as 1 L/h, more than one order-of-magnitude better than prevailing methods, and be able to make that determination remotely whereas the other approaches require an attempt to physically measure the leak-induced low oil flow rate which requires removing the cable from service.

In another technique, the geophysical study of oil and gas movement two to three thousand meters under the North Sea are underway, but the samples have yet to be analyzed. The application of SF_6 , another tracer, to gas movement 2500 m below the North Slope, Alaska, oil field was successful.

4 CONCLUSIONS

The PFT technology, consisting of the tracers, the samplers, and the analyzers, comprise a system which, because of its sub-femto-liter per liter detection capability for multiple tracers, has significantly advanced the ability to perform long-range and continental-scale atmospheric transport experiments. The data obtained from such studies will provide a valuable resource for modelers.

The break through in the passive PFT source and sampler has established the technique on a world-wide basis as the most economical and yet perhaps the most powerful multitracer technique for studying air flow patterns in multizoned homes and buildings.

The technology appears to be applicable to other transport and dispersion problems such as underground gas and oil movement as well as the numerous leak detection problems.

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