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FEMTOGRAM DETECTION OF PERFLUOROCARBON TRACERS USING CAPILLARY GAS CHROMATOGRAPHY–ELECTRON-CAPTURE NEGATIVE ION CHEMICAL IONISATION MASS SPECTROMETRY

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SUMMARY

An ultrasensitive and selective method has been developed for the detection of a range of perfluorocarbon tracers suitable for long-range atmospheric studies. Following direct injection onto a capillary column the perfluorocarbons are separated and detected using mass spectrometry with electron-capture negative ion chemical ionisation (ECNICI-MS) with methane as reagent gas and selected-ion monitoring. All nine perfluorocarbons tested underwent non-dissociative resonance electron capture to form the molecular anion which was the base peak in all cases. Using this technique, detection limits (signal-to-noise ratio of 2:1) of 3 and 2 fg were obtained for perfluoromethylcyclohexane and perfluoro-1,3-dimethylcyclohexane respectively. The corresponding detection limits using a conventional electron-capture detector were 8 and 9 fg respectively. In addition to increased sensitivity, the ECNICI-MS technique allows temperature programming for the simultaneous analysis of a range of perfluorocarbons and has superior selectivity being less prone to coeluting interferences. Furthermore the method is potentially one to two orders of magnitude more sensitive than the current gas chromatography–MS methods using $^{13}\text{C}^2\text{H}_4$ tracers.

INTRODUCTION

In recent years there has been renewed interest in the movement of atmosphere and ocean masses both on a regional and global basis^{1–3}. The impetus for these studies has developed from a serious concern over the pollution derived from increasing human activity and its long term effects on climate and the global environment. Numerous computer transport models, mainly for the atmosphere, have emerged to simulate the movement of pollutants and to quantify their long-range dispersion from the source regions. However in order to test the validity of various models, tracer experiments using non-reactive and non-depositing simulants are necessary to enable the direct measurement of the transport path and concentrations along the trajectory. The requirements for such tracers have been discussed by Lovelock and Ferber⁴. Historically, however, only two classes of compound have emerged as capable of

meeting the stringent requirements for long-range tracers, namely selected perfluorocarbons and isotopically labelled methane ($^{13}\text{C}^2\text{H}_4$), the latter being characterised by a rare yet stable isotopic composition^{5,6}. Of these two groups, the perfluorocarbons have several advantages. They are commercially available at reasonable cost and can be detected at very high sensitivity by gas chromatography with electron-capture detection (GC-ECD)⁷⁻⁹. The perfluorocarbons are particularly suited to ECD since their rate constants for thermal electron attachment are close to the diffusion controlled limit of $3 \cdot 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (ref. 10). In the practical use of GC-ECD and to obtain high selectivity for the perfluorocarbons it is generally necessary to chromatographically separate and/or catalytically remove oxygen and other ubiquitous halocarbons which would otherwise interfere with the analysis^{8,9}.

An alternative approach for analysing perfluorocarbons with both high sensitivity and high selectivity is to use electron-capture negative ion chemical ionization mass spectrometry, (ECNICI-MS)^{11,12}. This technique has already been used for the ultrasensitive detection of a number of environmentally important compounds which undergo resonance capture of thermal electrons¹³⁻¹⁶. Because this technique measures absolute negative ion abundances rather than small variations in electron current superimposed on a much larger standing current it was expected that the MS technique should be 10-100 times more sensitive than the conventional electron-capture detector¹⁷. In fact Hunt and Crow¹¹ have reported experimental detection limits exceeding the theoretical limit of the electron-capture detector by a factor of ten. The general tendency of perfluorocarbons to undergo non-dissociative electron capture has been reported by Christophorou *et al.*¹⁰, and suggests that ECNICI-MS would provide a uniquely selective analytical method for the perfluorocarbons due to the formation of stable molecular negative anions. We have therefore investigated the analytical potential of ECNICI-MS for the selective detection of several currently used and candidate perfluorocarbon tracers at the low femtogram level. The results of our studies and a comparison of the relative sensitivities of ECNICI-MS and ECD for the analysis of perfluorocarbons are presented below.

EXPERIMENTAL

Materials

Perfluoro-1,2-dimethylcyclobutane, perfluoromethylcyclopentane, perfluoromethylcyclohexane, perfluoro-1,3-dimethylcyclohexane, perfluorodecalin and trichlorofluoromethane were purchased from Imperial Smelting (Bristol, U.K.) Perfluorocyclohexane was obtained from Aldrich (Gillingham, U.K.). Perfluorobicyclo[2,2,1]heptane and perfluoro-1,3,5-trimethylcyclohexane were obtained from the University of Birmingham (Birmingham, U.K.). The perfluorobicyclo[2,2,1]heptane sample was only *ca.* 50% pure, one of the major contaminants being perfluoromethylcyclohexane. Perfluoroadamantane was purchased from Sun Tech (Philadelphia, PA, U.S.A.)¹⁸.

Preparation of standards

A mixture of all the above compounds was prepared gravimetrically by successively adding approximately 50- μl quantities of each compound (except perfluoromethylcyclohexane) into a weighed glass vial (5 ml, P/N 13223, Pierce and War-

ringer, Chester, U.K.). Perfluoromethylcyclohexane was not added since it was present as an impurity in the perfluorobicyclo[2,2,1]heptane. The septum of the vial was removed and the mixture was allowed to evaporate into a room of known volume, equipped with fans for rapid mixing. After 15 min a sample was taken by opening a clean evacuated cylinder (Scotty IV, Scott Environmental Technology, Plumsteadville, PA, U.S.A.). This cylinder was then filled to 420 p.s.i.g. with high-purity nitrogen (5.5 grade, >9.995% purity, Air Products, Crewe, U.K.) that had been previously checked by GC-ECD to have no background interferences. It was estimated that the standard, nominally $5 \cdot 10^{-9}$ parts per volume, was accurate to within $\pm 20\%$. Trichlorofluoromethane was included in the mixture as an internal standard and cross-checked against the ambient background levels on a day free from industrial pollution to confirm the dilution factors during the preparation of the standard and to monitor any degradation of the standard on storage. A second standard containing only perfluoromethylcyclohexane, perfluoro-1,3-dimethylcyclohexane and trichlorofluoromethane at nominally 6 ppb* levels was prepared using the same procedure. This sample was then further diluted to nominally 0.3 ppb in another cylinder by pressurisation to 275 p.s.i.g. and was subsequently used for the determination of system detection limits.

Analysis

Analyses were performed using a Finnigan 4510 gas chromatograph-mass spectrometer fitted with a standard PPNICI option. A 50 m \times 0.2 mm I.D. fused-silica column coated with 0.33- μ m crosslinked SE-54 (Ultra Series, Option 105, Hewlett-Packard, Winnersh, U.K.) was used with 99.996% purity helium carrier gas (Air Products, Bracknell, U.K.) at 22 p.s.i.g. pressure, this corresponding to a column flow of *ca.* 1 ml min⁻¹ at 50°C. The chromatograph plumbing was changed so that the standard split/splitless injector was replaced by a low dead volume 6-port $\frac{1}{16}$ -in. Valco valve (P/N 9105, Alltech, Carnforth, U.K.) fitted with a sample loop which, allowing for the internal dead volume of the valve, enabled the injection of 30 μ l gas samples. To obtain full scan spectra a 1-ml sample loop was used. The sample loop and the $\frac{1}{16}$ -in. transfer lines to the column were heated with insulated nichrome wire to a temperature of 250°C. After injection of the sample, the oven temperature was held at -80°C using liquid nitrogen cooling for 3 min followed by temperature programming at 40°C min⁻¹ to 0°C and then at 10°C min⁻¹ to 250°C. The column was directly inserted into the source of the mass spectrometer via the transfer oven which was maintained at 260°C.

The mass spectrometer was operated in the negative ion mode using CP grade methane (BOC, Wembley, U.K.) as chemical ionization reagent gas. An ion source pressure of 0.38 Torr was employed. The source temperature was 60°C (indicated). Both the carrier and reagent gases were supplied using two-stage regulators fitted with stainless-steel diaphragms (Model 11 or 11A, Scott Environmental Technology). The instrument was routinely mass calibrated with perfluoro-tri-*n*-butylamine (FC-43). When operated in the selected-ion monitoring (SIM) mode, the total scan time for ions of interest was *ca.* 1 s.

For comparative studies, analyses were also performed on a Hewlett-Packard

* Throughout the article the American billion (10^9) is meant.

5880 gas chromatograph fitted with a ^{63}Ni electron-capture detector, operated in the constant current mode, and a 50 m \times 0.3 mm I.D. fused-silica column coated with 0.52- μm crosslinked methyl silicone (Ultra Series, Option 115, Hewlett-Packard). High-purity nitrogen (99.992%, BOC) was further purified by passage through a filter containing charcoal followed by 13X molecular sieve. The gas inlet system of the chromatograph was modified to bypass the internal plumbing by insertion of a pressure controller fitted with a stainless-steel diaphragm (Porter Model 8286, 0–30 p.s.i.g. outlet pressure, SGE, Milton Keynes, U.K.) and a low dead volume 6-port $\frac{1}{8}$ -in. valve (Valco P/N 9105, Alltech) fitted with a sample loop so as to enable the injection of 30- μl gas samples. The valve was connected directly to the column via a stainless-steel transfer line ($\frac{1}{8}$ -in. \times 0.020 in. I.D.), which was wrapped with insulated nichrome wire and maintained at 250°C to prevent adsorption of the tracers. The column was operated isothermally at -10°C with a column flow of 1 ml min^{-1} (input pressure 18 p.s.i.g.). A detector make-up flow of 40 ml min^{-1} of nitrogen was introduced via a low dead volume Tee-piece (GCUT, SGE). The detector was operated at a temperature of 330°C.

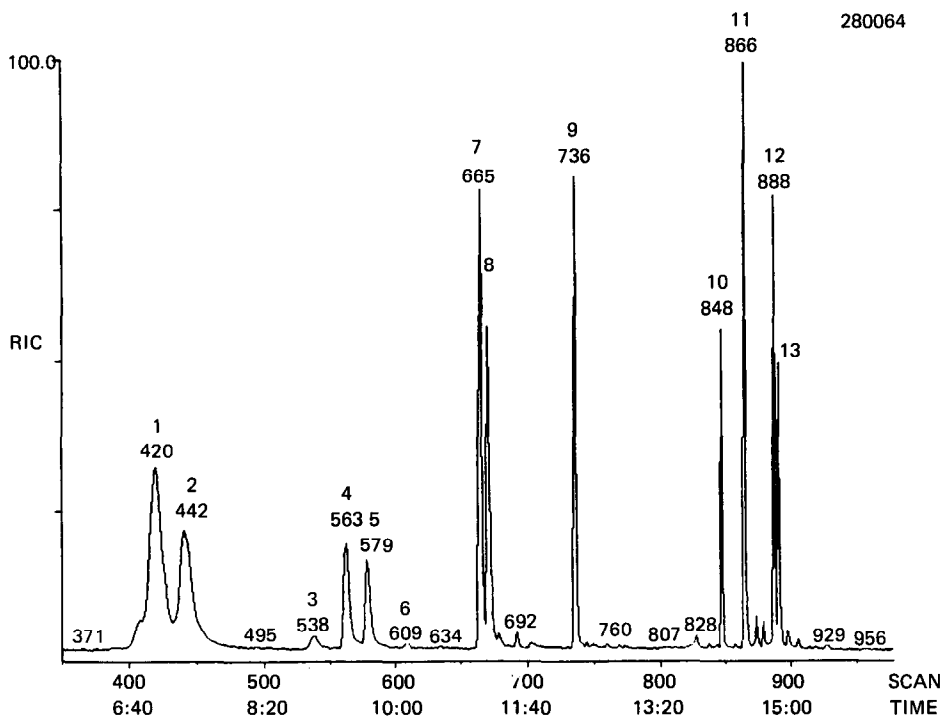


Fig. 1. Reconstructed total negative ion current chromatogram of a perfluorocarbon standard (30 μl) containing individual compounds at a nominal 5-ppb level. The term "total negative ion" refers to the molecular ions of the perfluorocarbons (*i.e.*, m/z 300, 312, 350, 400, 424, 450 and 462). Peaks: 1 = perfluorodimethylcyclobutane (2.3 pg); 2 = perfluoromethylcyclopentane (1.3 pg) and perfluorocyclohexane (2.5 pg); 3 = perfluorodimethylcyclopentane(?); 4 = perfluoroethylcyclopentane(?); 5 = perfluoromethylcyclohexane; 6 = perfluorobicyclo[2,2,1]heptane [3, 4 and 5 are impurities in the sample of 6 (2.4 pg)]; 7 and 8 = perfluoro-1,3-dimethylcyclohexane isomers (3.0 pg); 9 = perfluoro-1,3,5-trimethylcyclohexane (2.7 pg); 10 and 11 = *trans*- and *cis*-perfluorodecalin (3.1 pg); 12 and 13 = perfluoroadamantane isomers (3.0 pg).

RESULTS AND DISCUSSION

A capillary mass chromatogram of the perfluorocarbon mixture at a level of *ca.* 1–3 pg per component is shown in Fig. 1. Peak assignments were made on the basis of the full-scan mass spectra in combination with the retention times of individual components run independently. Peaks 3 and 4 in Fig. 1 are additional impurities in the perfluorobicyclo[2,2,1]heptane sample and are very tentatively assigned as perfluorodimethylcyclopentane and perfluoroethylcyclopentane respectively on the basis of full-scan spectra, which contain essentially only the molecular anion, and predicted boiling points. With the exception of perfluoromethylcyclopentane and perfluorocyclohexane, which coeluted, all other species were separated with almost baseline resolution. To separate perfluorodimethylcyclobutane from the above perfluorocarbons it proved necessary to temperature programme from an initial cryofocusing temperature of -80°C since initial studies at -60°C gave poor resolution of these low boiling species. Some band broadening of earlier eluting perfluorocarbons is still noted and is attributed to gas–solid chromatography at the low initial temperatures. Perfluoro-1,3-dimethylcyclohexane, perfluorodecalin and perfluoroadamantane were resolved into their isomers. The relative assignment of the *cis* and *trans* isomers of perfluorodecalin is made on the basis of the lower boiling point of the *trans* isomer.

The full-scan spectra of all the perfluorocarbons consisted essentially of only the M^{-} molecular ion. Fig. 2 illustrates this feature and shows the full-scan spectra for perfluoromethylcyclohexane, perfluoro-1,3,5-trimethylcyclohexane, *cis*-perfluorodecalin and perfluoroadamantane. The only other structurally significant ion present is $(\text{M} - 38)^{-}$ associated with the loss of fluorine. In the case of perfluoro-1,2-dimethylcyclobutane an additional peak (m/z 212) was present, albeit at only *ca.* 2% of the molecular ion base peak of 300. This can be attributed to the loss of carbon tetrafluoride with the formation of perfluoromethylcyclobutene. At the 2-pg level (see Fig. 1) high molecular ion counts were observed for all species with the exception of perfluorobicyclo[2,2,1]heptane. This is surprising since the corresponding chromatogram with a conventional electron-capture detector contains a much larger perfluorobicyclo[2,2,1]heptane peak. Since the molecular ion at m/z of 312 is still the base peak it is possible that either the perfluorobicyclo[2,2,1]heptane molecule or its molecular anion has undergone decomposition within the ion source to give a new species with a low cross-section for electron capture. This is consistent with the appearance of a small ion (*ca.* 20% of base peak) at m/z 100 attributable to perfluoroethylene. The larger response of the electron-capture detector could be attributed to the greater stabilisation of the molecular anion at atmospheric pressure. Perfluorobicyclo[2,2,1]heptane is therefore not recommended for use as an atmospheric tracer if ECNICI-MS is to be used as the mode of detection.

In order to determine the potential sensitivity of the negative ion MS technique a diluted standard containing 16 fg of perfluoromethylcyclohexane, and 16 fg of perfluoro-1,3-dimethylcyclohexane was analysed using SIM at the molecular ion masses of m/z 350 and 400 respectively. The results are illustrated in Fig. 3. Using a signal-to-noise criterion of 2:1 this is equivalent to a detection limit of 3 fg for perfluoromethylcyclohexane and 2 fg for each of the resolved perfluoro-1,3-dimethylcyclohexane isomers. This assumes that each isomer is detected with equal sensitivity.

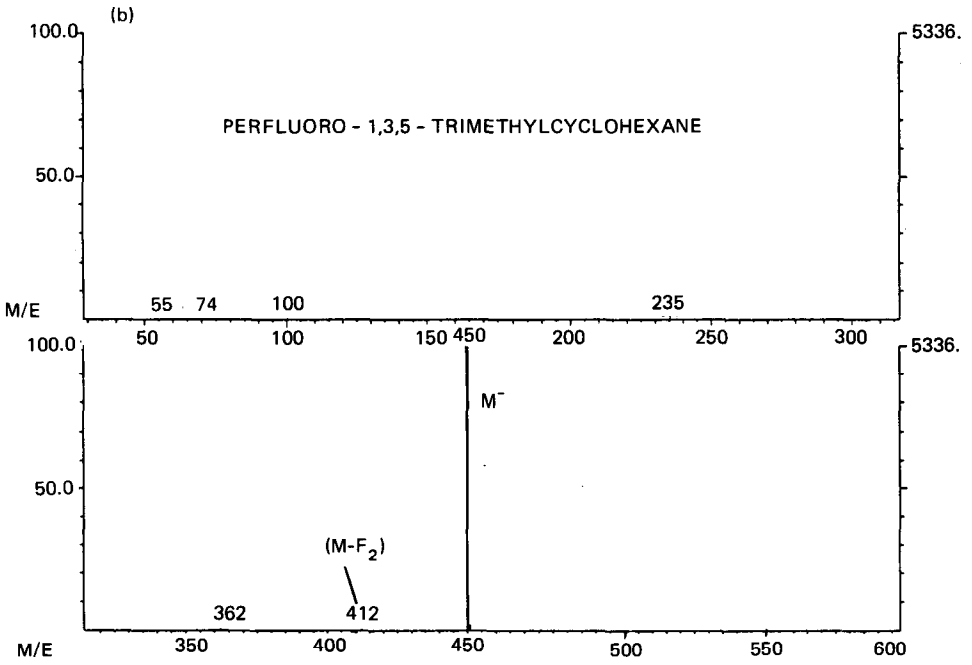
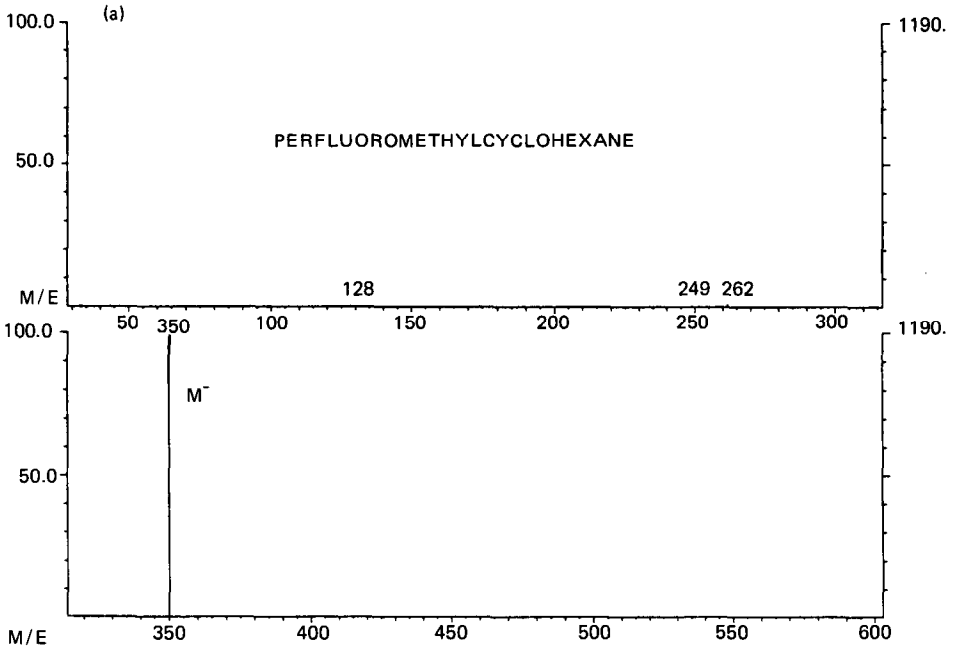


Fig. 2.

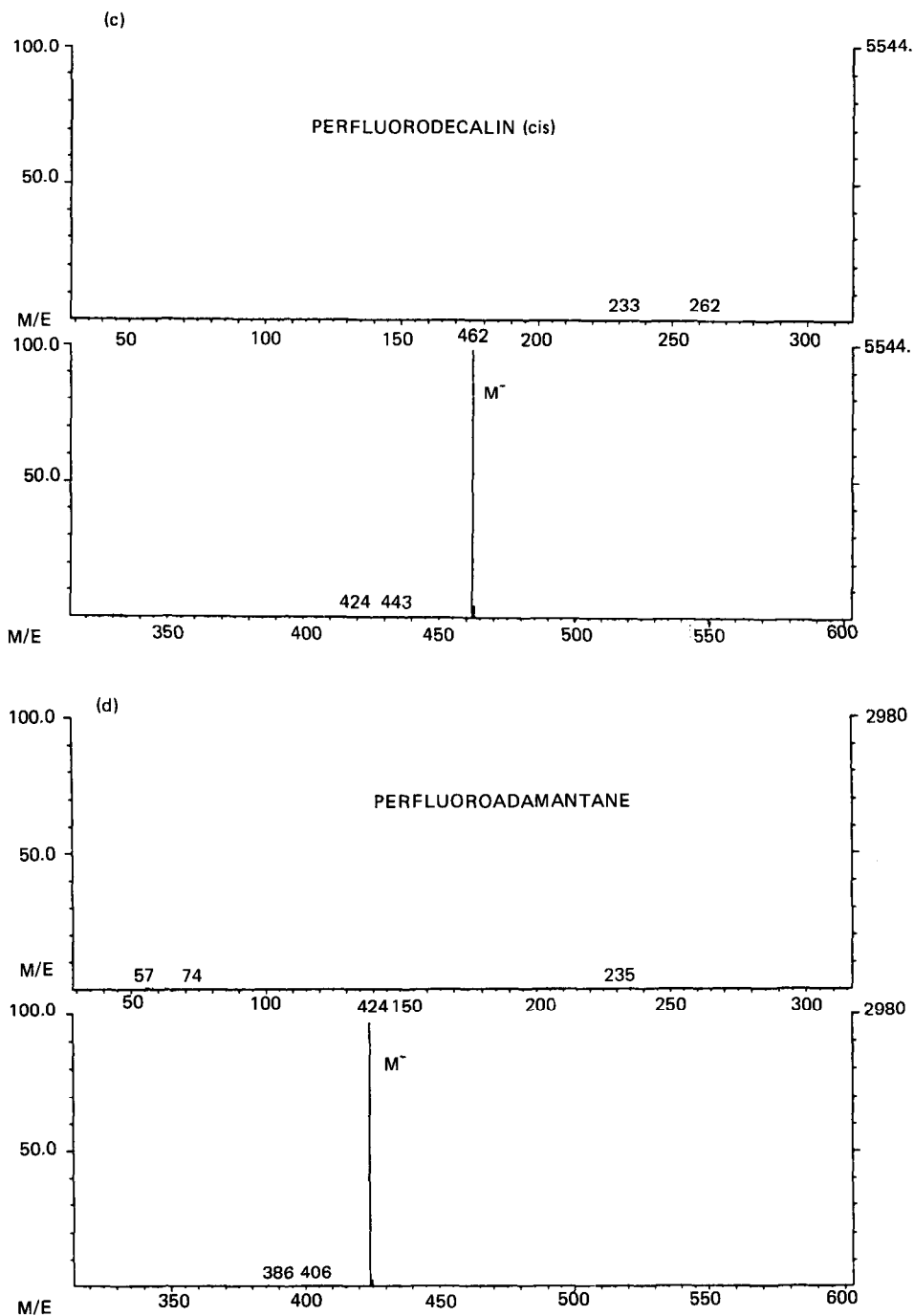


Fig. 2. ECNICI full-scan mass spectra of (a) perfluoromethylcyclohexane; (b) perfluoro-1,3,5-trimethylcyclohexane; (c) *cis*-perfluorodecalin and (d) perfluoroadamantane (isomer labelled 12 in Fig. 1). A perfluorocarbon standard (1 ml) containing individual standards at a nominal 5-ppb level was used.

These detection limits, and those determined by GC-ECD (see later), were determined by simply measuring the peak heights of the signals and comparing these with the mean levels of the noise either side of the peaks. Whilst the procedure neglects the possibility of sample adsorption at low levels we feel this is appropriate for a comparison of two detectors coupled to similar chromatographic systems. It should be noted that noise rather than signal is the limiting factor in determining the detection limit. The noise is thought to be due to general chemical background. Other than using pure gases and a crosslinked capillary column no effort was made to reduce the background. It is possible that the use of a higher source pressure could further enhance the sensitivity. This feature has been observed in our laboratory¹⁵ and by Shang-Zhi and Duffield¹³, where the higher source pressure is thought to aid collisional stabilisation of the molecular ion. Unfortunately it was not possible to test this hypothesis for the perfluorocarbons.

In order to see whether our observed detection limits were an improvement on a conventional electron-capture detector, a dilute standard containing 160 fg of perfluoromethylcyclohexane and 160 fg of perfluoro-1,3-dimethylcyclohexane was analyzed using GC-ECD. The resulting chromatogram is shown in Fig. 4. The corresponding detection limits at a signal-to-noise ratio criterion of 2:1 are 8 fg for perfluoromethylcyclohexane and 9 fg for each perfluoro-1,3-dimethylcyclohexane isomer, thereby demonstrating a significant improvement in sensitivity for the mass spectral technique. In addition to this improved sensitivity, which substantiates

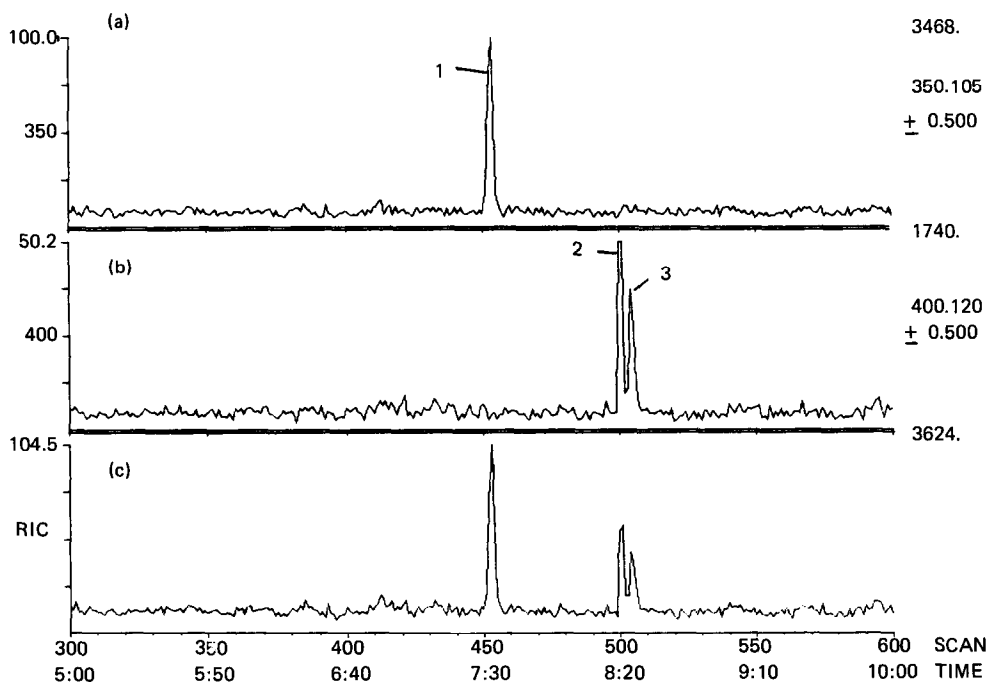


Fig. 3. Selected negative ion chromatograms for m/z 350 and 400 of a sample ($30 \mu\text{l}$) containing (a) 16 fg perfluoromethylcyclohexane (1) and (b) 16 fg perfluoro-1,3-dimethylcyclohexane (2 and 3). The lowest trace (c) is the sum of the m/z 350 and 400 ion counts.

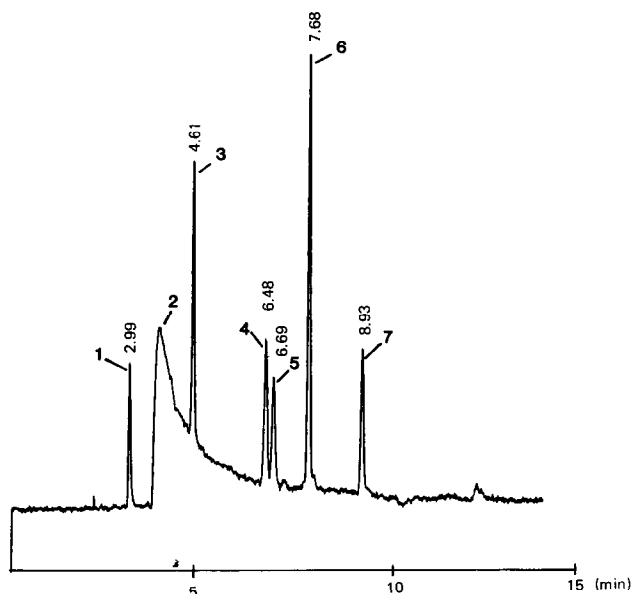


Fig. 4. ECD chromatogram for a sample (30 μ l) containing 160 fg perfluoromethylcyclohexane (3); 160 fg perfluoro-1,3-dimethylcyclohexane (4 and 5) and 57 fg trichlorofluoromethane (6). The other peaks are: 1 = oxygen; 2 = water; 7 = 1,1,2-trichlorotrifluoroethane impurity in the nitrogen gas used to prepare the calibration standard.

Hunt's earlier claims¹¹, the selectivity of the method is superior since it is less prone to excessive baseline drift with temperature necessitating column compensation.

ECNICI-MS therefore provides a very selective and extremely sensitive method for the determination of perfluorocarbon tracers. Sensitivity is in fact even greater than positive ion MS analysis of deuterated methane tracers, when due account is taken of the sample volumes involved. For example, cryogenic adsorption of the deuterated methane $^{13}\text{C}^2\text{H}_4$ from a 330 STP litre air sample is required to achieve a detection limit of $7 \cdot 10^{-16}$ STP mol m^{-3} [ca. $1.7 \cdot 10^{-17}$ cm^3 (v/v)]. The MS detection limit for a typical perfluorocarbon tracer (perfluoromethylcyclohexane) is about 3 fg [ca. $2.0 \cdot 10^{-13}$ cm^3 (v/v)]. Assuming that a sample volume of 330 STP litres of air (comparable to deuterated methane sample volume) could be similarly cryotrapped to enrich the perfluorocarbon tracer, this would yield a theoretical detection limit of ca. $6 \cdot 10^{-19}$ cm^3 (v/v). Unfortunately, the global background concentrations for several perfluorocarbon tracers are approaching $1 \cdot 10^{-15}$ cm^3 (v/v)^{7,8}, which places a practical limitation on the actual exploitation of these extreme sensitivities. This problem further reinforces the strong argument voiced by Lovelock and Ferber⁴ that some of the candidate tracers which are potentially so ideal for studies of long-range atmospheric and ocean transport be reserved where possible for this purpose. Where the candidate perfluorocarbon tracers have no appreciable background (e.g., perfluoroadamantane) then the lower detection limits can be practically exploited. The added advantage of the perfluorocarbons is that several tracers are available⁴ and there is no absolute requirement to have unique windows in the mass spectrum since the perfluorocarbons are easily resolved chromatographically.

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