# QUANTITATIVE ANALYSIS OF CHLOROFLUOROCARBONS

# ABSOLUTE CALIBRATION OF THE ELECTRON-CAPTURE DETECTOR

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SUMMARY

For the absolute calibration of the chromatographic system (graphitized thermal carbon black column + electron-capture detector, ECD) primary standards at the ppb* level are generated using permeation tubes and a recording electro-microbalance determines dynamically the weight loss of the permeation device situated continuously in a flow of pure nitrogen. The relative error of the permeation rate determines the absolute precision of the calibration (7 % for $CFCl_3$).

The response of the ECD in the constant-current, pulse-modulated frequency and the d.c. modes of operation was studied for $CF_2Cl_2$, $CFCl_3$, $CH_3CCl_3$, $CCl_4$, $CHCl_3$, $CH_3Cl$, $CHFCl_2$ and a large linear dynamic range was observed in both instances. The sensitivity limit was determined for each compound. A hypercoulometric response was observed for $CFCl_3$ with the fixed frequency pulsed detector.

INTRODUCTION

Since the original work of Molina and Rowland[1], a number of investigators have developed models describing the interaction of anthropogenic halocarbons with stratospheric ozone, through a catalytic destruction process with excess of chlorine.

Better analytical precision and absolute accuracy are now needed[2], however, in order to be able to predict the exact mecanisms of interaction and to reveal the extent to which natural sinks can remove halocarbons from the lower atmosphere. Therefore, Rasmussen and co-workers[3-5] conducted inter-laboratory comparisons in order to interpret the trace data accumulated over several years and to evaluate the degree of agreement or disagreement between data supplied by different laboratories.

Recently Lovelock and co-workers[2,6] have used the electron-capture detector (ECD) as a secondary standard, using a pre-determined value for the rate constant of the reaction between electrons and the halocarbons. An exponential dilution

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* Throughout this article the American billion ($10^9$) and trillion ($10^{12}$) are meant; ppb and ppt are by volume.

chamber was used to prepare accurate standards in the concentration range from 1 to 0.1 ppb. The results confirmed the validity of the coulometric calculations within within 5% for CFCl₃ (ref. 2).

In most laboratories, however, quantitative analysis is accomplished by reference to standards prepared by static dilution of either pure materials or commercially prepared standards at the 10 ppm level[7-13]. Using this calibration technique, the absolute accuracy obtained for $CFCl_3$ and $CF_2Cl_2$ concentrations is 10%[7].

Schmeltekopf *et al.*[14] have developed a dynamic dilution technique. Reference standards prepared by static dilution were further diluted in a flow system with six stages of turbulent mixing. Calibration mixtures ($CFCl_3$ in nitrogen) were crosschecked against mixtures obtained by passing nitrogen over a permeation tube calibrated gravimetrically in conjunction with an exponential dilution flask and against the static dilution technique. The agreement observed between calculated and measured concentrations was about 10%.

Although the permeation tube technique is a simple and accurate method of generating primary standards of low concentration[15-19] in air pollution studies, only Singh and co-workers[20,21] have used it to prepare halocarbon primary standards.

In this work, quantitative analysis of halocarbons is effected by the generation of primary standards at the ppb level by the permeation tube technique, and in the analytical procedure itself on-line trapping enrichment is used. The absolute precision of the method is improved by a dynamic gravimetric determination of the weight loss of the permeation tubes.

EXPERIMENTAL

*Analytical procedure*

A Varian 3700 gas chromatograph (Varian, Palo Alto, CA, U.S.A.) equipped with an ECD operated continuously at 300°C was used. The gas injection valve was an eight-port automatic rotating valve (Carlo Erba, Milan, Italy). The carrier gas (highpurity nitrogen) was passed through a purifier which reduced the oxygen and water levels to less than 1 ppm (Dow gas purifier; Varian) and an activated charcoal filter.

With the Varian detector cell (8 mCi ⁶³Ni) we used either the instrument electronics[22] operated in the constant-current, pulse-modulated frequency mode or a simpler electronic system with a constant voltage supply (10 V in the d.c. operation mode). The anode was then connected to a constant-voltage power supply (Model 6102 A, Hewlett-Packard, Palo Alto, CA, U.S.A.) and the cathode to the electrometer (Model 417K, Keithley, Cleveland, OH, U.S.A.). The standing current in d.c. operation mode was $2.3 \cdot 10^{-9}$ A.

For some experiments the detector was operated in fixed-frequency pulsed mode and a pulse generator (Model 214 A, Hewlett-Packard) providing pulses of constant frequency (pulse period 250 $\mu$sec, pulse width 2.5 $\mu$sec, voltage 20 V) was connected to the anode of the detector cell. The above pulse specifications are optimal operating conditions of the detector cell providing the highest detector signal for a given amount of sample injected. Then, the standing current was $1.3 \cdot 10^{-9}$ A.

Computer data acquisition was achieved with a digital voltmeter (LM 1604, Solartron, Schlumberger, Bagneux, France) as analogue to digital coverter, and the chromatographic signal was collected by the computer (21 MX, Hewlett-Packard)

with a precision of four decimal digits. The noise level calculated by computer program was equal to the standard deviation of the base line random fluctuations; it was $2 \cdot 10^{-12}$ A in the d.c. and fixed-frequency pulsed mode and $10^{-3}$ kHz in the constant-current, pulsed-frequency mode.

The analytical column (length 2 m, O.D. 1/8 in.) was packed with graphitized thermal carbon black (GTCB) (Carbopack CHT, 12 m²/g; Supelco, Bellefonte, PA, U.S.A.). The thermal carbon black, which had been graphitized at 3000°C, was purified at 1000°C under a flow of hydrogen. It has been shown that GTCB either uncoated[23] or modified with small amounts of liquid stationary phase[24] can separate with good selectivity the main halocarbons. In Table I are given the absolute retention times, the experimental conditions being the same as in Fig. 1. These data show that on pure GTCB, $CH_3Cl$ is well resolved from $CHF_2Cl$, and $CHFCl_2$ from $CH_3I$. Thus, the uncoated adsorbent was selected for this work in order to obtain good reproducibility in quantitative analysis with no stationary phase bleeding, which provides for the best conditions for sensitive detection.

TABLE I

RETENTION TIMES OF HALOCARBONS ON A GTCB COLUMN

Experimental conditions as in Fig. 1.

| Compound | Retention times (sec) | Compound | Retention times (sec) |
|---|---|---|---|
| $CH_3Cl$ | 210 | $CH_3$–$CHCl_2$ | 655 |
| $CHF_2Cl$ | 225 | $CHCl_3$ | 700 |
| $CH_3Br$ | 270 | $CH_2Br_2$ | 745 |
| $CF_2Cl_2$ | 310 | $CF_2Cl$–$CFCl_2$ | 780 |
| $CHFCl_2$ | 370 | $CH_2Cl$–$CH_2Cl$ | 790 |
| $CH_2Cl_2$ | 420 | $CH_3$–$CCl_3$ | 865 |
| $CH_3I$ | 425 | $CCl_4$ | 910 |
| $CF_3$–$CFCl_2$ | 490 | $CHCl$=$CCl_2$ | 1175 |
| $CFCl_3$ | 565 | $CCl_2$=$CCl_2$ | 1695 |
| $CCl_2$=$CH_2$ | 615 | | |

The sampling technique is basically the same as that described by Bruner et al.[24]: the air sample (sample volume ranging from 20 ml to several litres) is trapped on an inert adsorbent (GTCB, Carbopack B, 90 m²/g) kept in dry-ice. Air is driven into the trap by a pump placed downstream of it, and air cannot be polluted by the pump.

The halocarbons are released from the trap by heating it at 200°C and are concentrated as a narrow pulse at the head of the analytical column cooled at −60°C. The analysis with on-line trapping enrichment is achieved in situ as the trap (length 10 cm, O.D. 1/4 in.) is always connected to the injection rotating valve in place of the sampling loop during each step: sampling, injection, regeneration at 200°C.

Fig. 1 shows the analysis of (a) a 100-ml and (b) a 500-ml sample of atmospheric air from the Palaiseau Plateau (20 km south-west of Paris). With the sampling technique described and the analytical conditions used, oxygen is eluted from the column at −60°C and does not interfere with the elution of the lighter halocarbons on the GTCB column. The zero on the time scale in Fig. 1 corresponds to the time
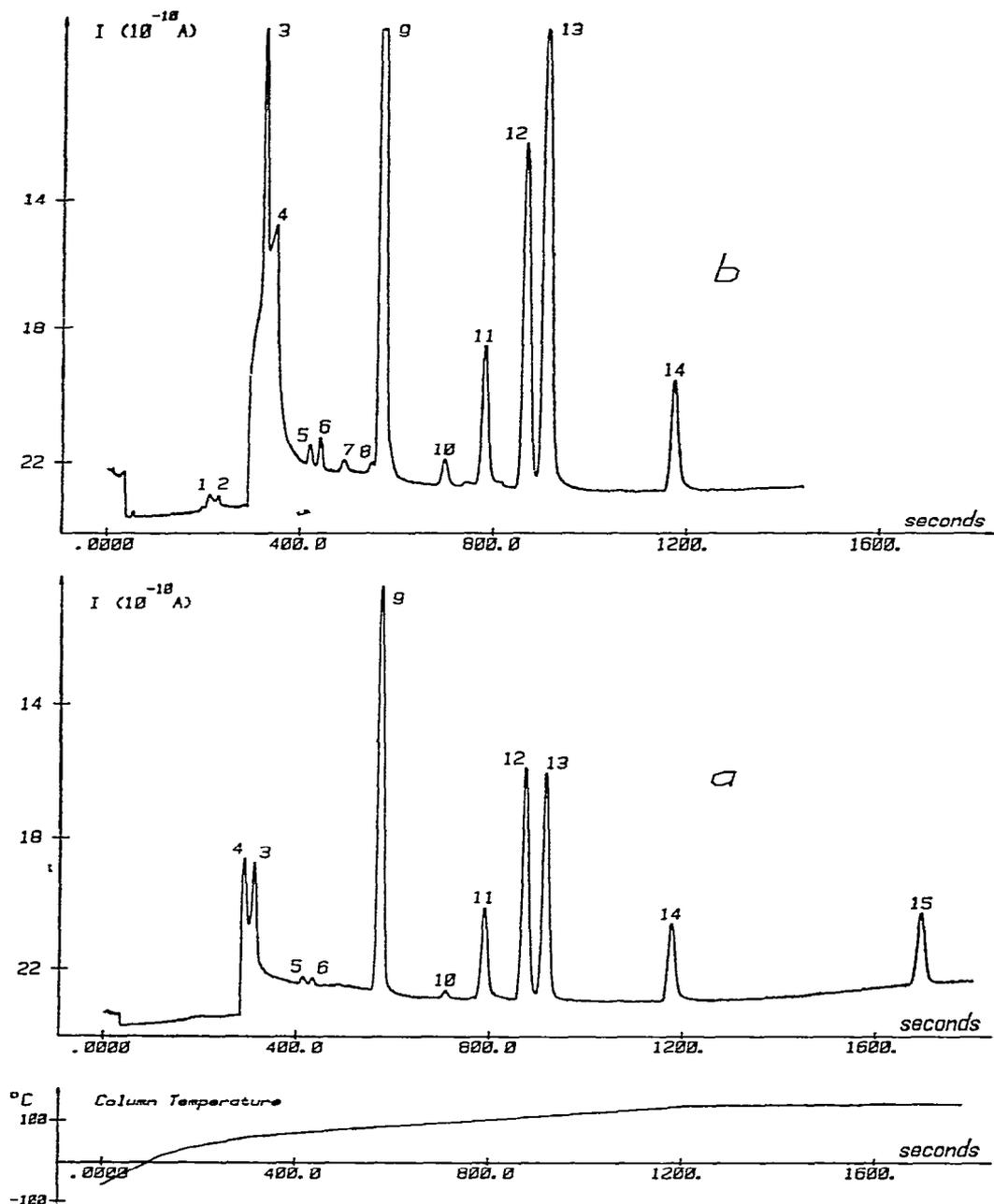
Fig. 1. Analysis of atmospheric air from Palaiseau Plateau: (a) 100 ml; (b) 500 ml. Peaks: 1 = $CH_3Cl$ (650 ppt); 2 = $CHF_2Cl$; 3 = $CF_2Cl_2$ (300 ppt); 4 = $H_2O$; 5 = unknown; 6 = unknown; 7 = $CF_3$–$CFCl_2$; 8 = unknown; 9 = $CFCl_3$ (210 ppt); 10 = $CHCl_3$ (20 ppt); 11 = $CF_2Cl$–$CFCl_2$; 12 = $CH_3$–$CCl_3$ (240 ppt); 13 = $CCl_4$ (100 ppt); 14 = $CHCl=CCl_2$; 15 = $CCl_2=CCl_2$. Nitrogen flow-rate: 17.3 ml/min (S.T.P.). Temperature: dynamic equilibrium from −60°C to 60°C (0–300 sec). Linear temperature programme from 60°C to 160°C at 5°C/min. Carbopack CHT column, length 2 m. ECD temperature: 300°C. d.c. mode of operation.

when the temperature control at −60°C is stopped and the column temperature is raised dynamically to 60°C.

The enrichment procedure on an inert adsorbent could, in principle, be used for on-field sample collection, the analysis of the trapped sample being achieved later, in the laboratory. However, the adsorbent in the trap itself adsorbs halocarbons from ambient air during storage if proper leak-proof stopping is not provided. We have observed that metal–metal Swagelok-type fittings are not convenient for this type of application and do not completely seal the traps. The halocarbons which have a large diffusion coefficient in air diffuse through microchannels along these fittings. For example, we have conducted blank analyses on a series of traps 2 days after they had been regenerated by heating under a stream of pure nitrogen at 250°C. The analyses revealed the presence of $CF_2Cl_2$, $CFCl_3$, $CCl_4$, $CH_3CCl_3$ and $C_2HCl_3$.

The only procedure we found to be valid for field sample collection is to connect the trap to two bellows seal valves (Nupro, Cleveland, OH, U.S.A.) using ultra-vacuum fittings (Cajon, Cleveland, OH, U.S.A.). Blank analyses carried out after storage of a regenerated trap for 3 months did not show the presence of any adsorbed halocarbons.

*Calibration procedure*

The generation of primary standards at the parts per billion level is effected by using the technique of permeation tubes[15–19]. A recording electro-microbalance (Model 1000; Cahn, Cerritos, CA, U.S.A.) is used for the dynamic determination[17] of the weight loss, $W'$, of the permeation device placed in a stream of pure nitrogen with a flow-rate $D_1$ (Fig. 2). A dynamic dilution stage (ratio $D_2/D_3$) is used to obtain standards in the 0.5–10 ppb range. The electro-microbalance has been specially adapted to work at slightly higher pressures than atmospheric ($\Delta p = 0$–500 g/cm²), by placing a tightening ring holding the glass bell on its support. All glassy parts designed in our laboratory are connected with special leak-tight O-rings (Rodaviss, SAV, Paris, France).
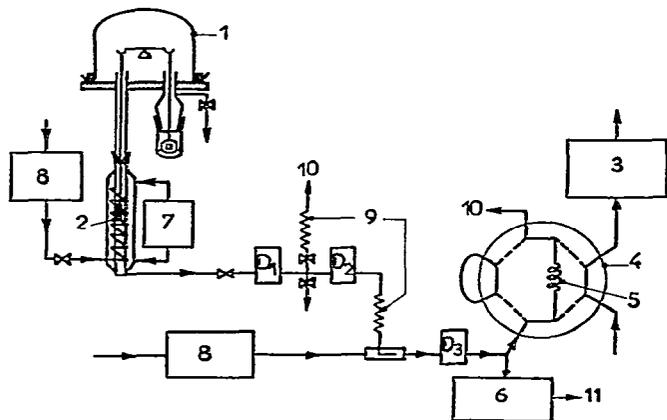


Fig. 2. Schematic diagram of the gas chromatograph calibration system. 1 = Recording electro-balance; 2 = permeation tube; 3 = gas chromatograph; 4 = sampling injection valve; 5 = sampling loop; 6 = quartz pressure gauge; 7 = thermostated bath; 8 = pure nitrogen controlled flow; 9 = pressure drops; 10 = leak; 11 = vacuum reference. Ranges of mass flow meters: $D_1$ 0–500, $D_2$ 0–50 and $D_3$ 0–1000 ml/min.

The precision of the weight loss, $W'$, determination is $1 \times 10^{-8}$ g/min. It could be improved by specially controlling the temperature of the whole electrobalance device. In order to reduce the ambient temperature fluctuations, which are the main limitation to improving the precision of $W'$, the entire electrobalance is enclosed in a case of large thermal inertia.

The geometry of the permeation device (PTFE cylinder tube or micro-bottle with a PTFE septum) and the permeation temperature, controlled to within $\pm 0.1°C$ with a thermostated circulating water-bath (Haake, Berlin, G.F.R.) are chosen for each compound studied such that the permeation rate is between $10^{-7}$ and $10^{-6}$ g/min. In Table II are listed the geometry of the permeation devices used, the surface area available for permeation and the permeation temperature.

TABLE II

PERMEATION RATE, $W'$, AND ABSOLUTE PRECISION OF CALIBRATION

| Compound | Permeation device | PTFE permeation thickness (mm) | PTFE permeation surface area (cm²) | Permeation temperature (°C) | W' (µg/min) | Absolute precision of calibration (%) |
|---|---|---|---|---|---|---|
| $CH_3Cl$ | Micro-bottle | 0.5 | 0.30 | 20 | 0.28 | 5 |
| $CHFCl_2$ | Micro-bottle | 0.5 | 0.15 | 35 | 0.20 | 6 |
| $CF_2Cl_2$ | Micro-bottle | 1 | 0.15 | 20 | 0.49 | 3 |
| $CHCl_3$ | PTFE cylinder | 0.5 | 10.0 | 20 | 0.50 | 3 |
| $CH_3–CCl_3$ | PTFE cylinder | 0.5 | 9.0 | 35 | 0.12 | 9 |
| $CCl_4$ | PTFE cylinder | 0.5 | 6.5 | 30 | 0.20 | 6 |
| $CFCl_3$ | Micro-bottle | 0.5 | 0.60 | 20 | 0.15 | 7 |

$D_1$, $D_2$ and $D_3$, the flow-rates (S.T.P.) of the dynamic dilution stage, are measured with 1% accuracy using mass-flow meters (Brooks-Emerson, Hatfield, PA, U.S.A.).

The concentration of the primary standard, $c$ (in parts by volume), is given by the equation

$$c = W' \cdot \frac{D_2}{D_1 D_3} \cdot \frac{22400}{M} \cdot \frac{273}{293} \tag{1}$$

where $M$ is the molecular weight of the compound studied and the amount injected, $m$, on to the head of the analytical column is given by

$$m = W' \cdot \frac{D_2}{D_1 D_3} \cdot V_B \cdot \frac{293}{T_B} \cdot \frac{P_B}{760} \tag{2}$$

where $V_B$ is the sample loop volume, $P_B$ its pressure and $T_B$ its temperature. A quartz gauge (Texas Instruments, Bedford, Great Britain) referenced to vacuum (Fig. 2) measures $P_B$ with an accuracy of 0.01%. $T_B$ is measured with a mercury thermometer to $\pm 0.1°C$.

The sample loop volume is calculated from the difference ($\Delta t$) between the retention times of oxygen samples injected with a syringe in the carrier gas circuit

before the sample rotating valve (Fig. 2) when the valve is either in the direct mode or rotated in the injection mode:

$$V_B = \Delta t D_c \cdot \frac{T_B}{293} \cdot \frac{760}{P_i} \qquad (3)$$

where $D_c$ is the column outlet flow-rate at S.T.P. and $P_i$ is the inlet carrier gas pressure, measured with the quartz gauge referenced to vacuum. With the procedure described, $V_B$ is measured with an accuracy of 1.5% with a 95% confidence interval as the relative errors in $\Delta t$, determined by computer data acquisition, and in the flow-rate, $D_c$, are 1%.

The relative error in $m$ and thus the absolute precision of our calibration method for a given confidence interval is obtained by convolution of the distribution curve errors made when measuring the independent parameters of eqn. 2. The absolute precision of the calibration method for a 95% confidence interval is given in Table II for each compound studied. The main contribution to the relative error in mass injection is the relative error in $W'$, the permeation rate. The precision of the calibration can be improved either by increasing $W'$ (this is not always possible, because for strong electron-capturing species such as $CFCl_3$ a second dynamic stage would be necessary, with a corresponding loss of precision) or by increasing the precision of the electrobalance by placing the balance itself in a thermostated oven.

## RESULTS

*Absolute calibration with constant-current, pulse-modulated frequency mode of operation*
Absolute calibration of the chromatographic system was carried out with the instrument electronics and the ECD operated in constant-current, pulse-modulated frequency mode. In this mode, the detector response is a linear function of peak area[22,25]. For all compounds examined so far, $CCl_4$ and $CHCl_3$ (Fig. 3a), $CH_3Cl$ and $CHFCl_2$ (Fig. 3b) and $CFCl_3$ (Fig. 4b) the calibration graphs are straight lines passing through the origin, except for the compounds with low response coefficients such as $CH_3Cl$ and $CHFCl_2$. This cannot be explained by the presence of these compounds as impurities in nitrogen, the diluent gas, as a zero response is obtained with injections of pure nitrogen. However, when small amounts of $CHCl_3$ and $CHFCl_2$ are injected, the noise level causes errors in peak area determinations and because the number of experimental points is limited great uncertainty occurs in these calibration graphs near the origin.

In Table III are reported the slope of the calibration graph, $\alpha$, the 95% confidence interval error in its determination and the detection limit for each compound studied, calculated for the analysis of a 100-ml air sample. The detection limit is calculated for a signal-to-noise ratio of 2.

*Fixed-frequency pulsed mode of operation. ECD response for $CFCl_3$*
For an ECD operated with the fixed-frequency pulsed sampling mode, the following relationship is valid[26] for the peak area:

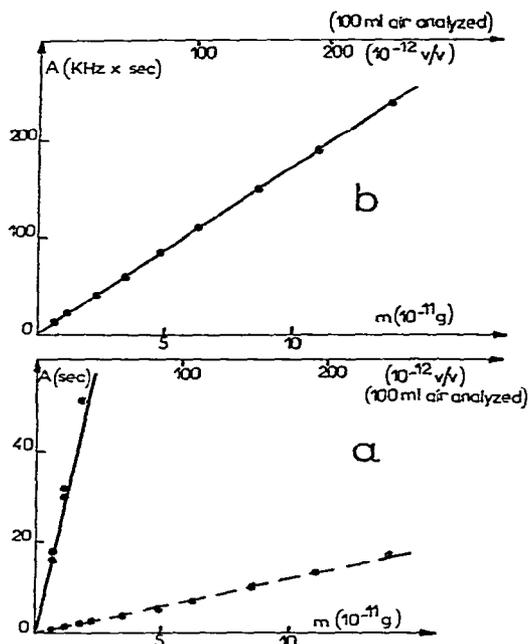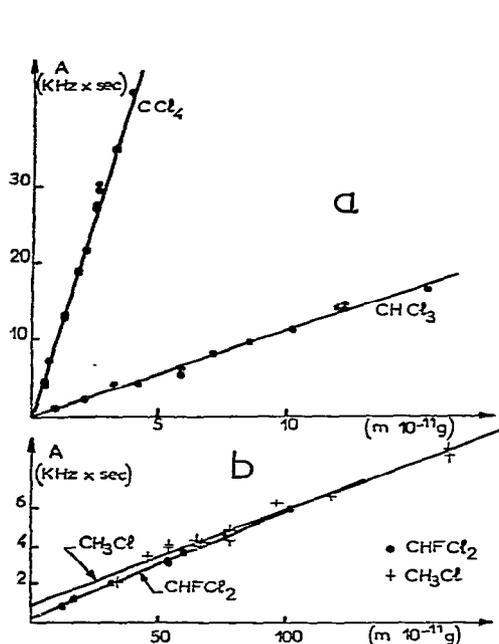$$A = \int_{t_1}^{t_2} \frac{I_0 - I}{I} \cdot dt = \frac{Km}{D_d M} = \alpha m \qquad (4)$$

Fig. 3. Calibration graphs for constant-current, pulse-modulated frequency mode of operation.

Fig. 4. Comparison of calibration graphs for CFCl₃ with three ECD modes of operation: (a) fixed-frequency pulsed mode of operation (full line) and d.c. mode of operation (dotted line); (b) constant-current, pulse-modulated frequency mode of operation. $10^{-12}$ v/v ppt (by volume).

where $I_o$ is the standing current, $I$ the detector current in the presence of capturing species, $D_d$ the flow-rate in the detector and $K$ is the electron-capture coefficient. The transformed peak area, $A$, is calculated by a computer program from the digital data for the chromatogram stored by the computer.

The electron-capture coefficient calculated from the detector response to the

## TABLE III

### SLOPE OF THE CALIBRATION GRAPH, α, AND DETECTION LIMIT IN CONSTANT-CURRENT, PULSE-MODULATED FREQUENCY ECD MODE OF OPERATION

| Compound | $\alpha$ $(kHz \cdot sec/g \times 10^{12})$ * | Detection limit for 100 ml (S.T.P.) air sample (ppt) |
|---|---|---|
| CH₃Cl | 0.49 $(\Delta = 0.04)$ | 60 |
| CHFCl₂ | 0.54 $(\Delta = 0.02)$ | 20 |
| CHCl₃ | 10.9 $(\Delta = 0.06)$ | 1.5 |
| CCl₄ | 109 $(\Delta = 0.4)$ | 0.15 |
| CFCl₃ | 175 $(\Delta = 0.2)$ | 0.08 |

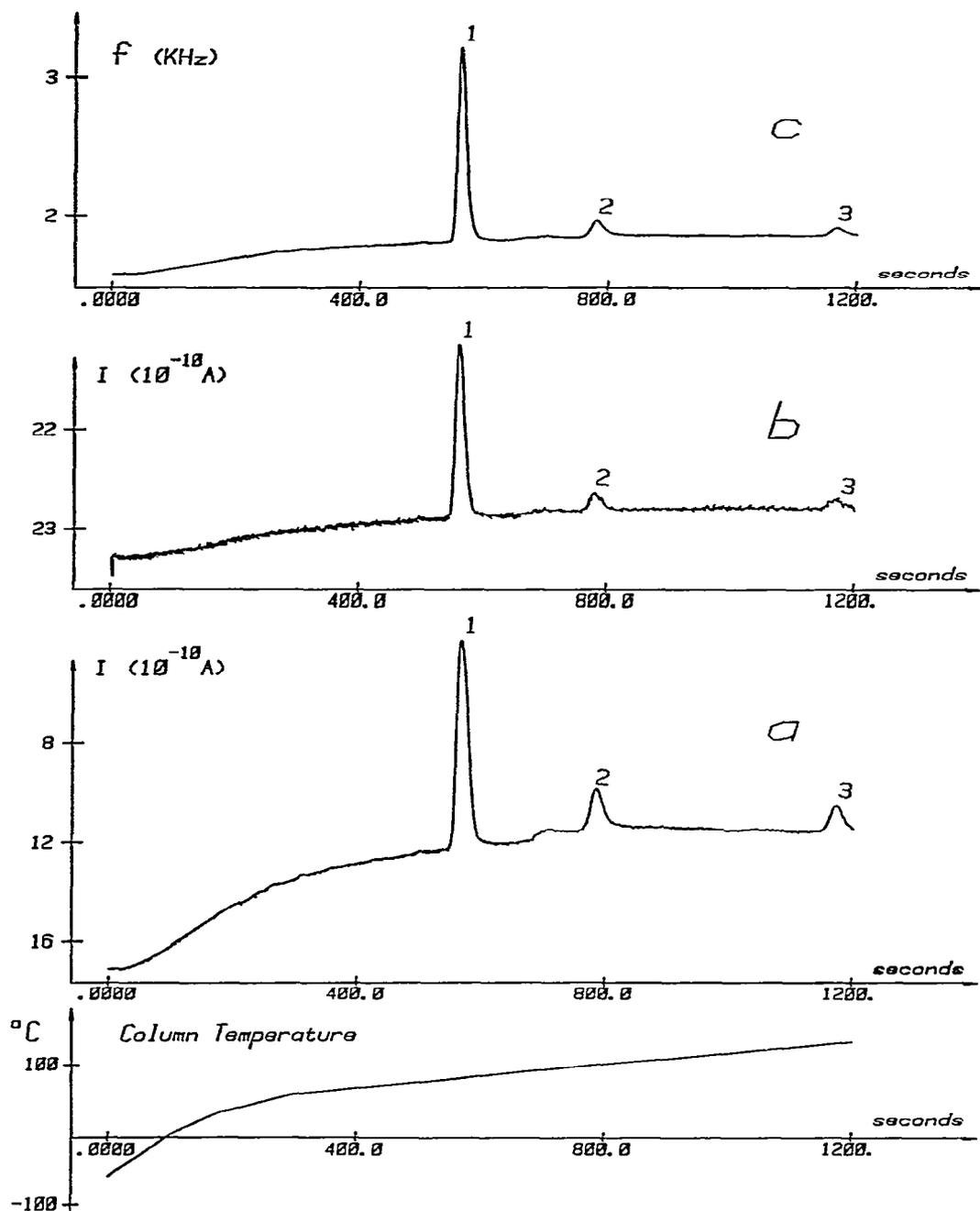* The error, $\Delta$, in the determination of $\alpha$ is calculated for a 95% confidence interval.

Fig. 5. Comparison of detector responses for CFCl₃. Mass injected: 12·10⁻¹² g. Sample loop volume: 2.47 ml. Concentration of primary standard generated in nitrogen: 0.82 ppt (by volume). Experimental conditions as in Fig. 1. Peaks: 1 = CFCl₃; 2 = CF₂Cl–CFCl₂; 3 = CHCl = CCl₂. (a) Fixed-frequency pulsed mode of operation; (b) d.c. mode of operation; (c) constant-current, pulse-modulated frequency mode of operation.

lowest $CFCl_3$ mass that could be injected $(5 \cdot 10^{-12}$ g$)$ (Fig. 4a) is $187 \cdot 10^{12}$ cm$^3$/mole. This corresponds to an ionization efficiency of 440%, which is determined assuming that each molecule reacts with only one electron.

Thus, with the detector cell used, having a highly asymmetric configuration[22], the response for $CFCl_3$ is hypercoulometric when the detector at 300°C is operated in the fixed-frequency pulsed mode, each molecule reacting with more than four electrons. Several examples of anomalous response with hypercoulometry have been studied by Aue and Kapila[27] that cannot be explained with the classical theory of electron-capture detection.

Fig. 5a shows that in the fixed-frequency pulsed mode the detector is already saturated with a mass of $12 \cdot 10^{-12}$ g of $CFCl_3$ injected, and its response corresponds to a 63% reduction in the standing current, $I_o = 1.3 \cdot 10^{-9}$ A, with the detector at 300°C and a nitrogen flow-rate of 34 ml/min. $CF_2Cl-CFCl_2$ (peak 2) and $CHCl=CCl_2$ (peak 3) are carrier gas impurities concentrated at the column head with $CFCl_3$ when the column oven is cooled to $-60°C$. These impurities are not present in pure nitrogen itself, but appear because of pollution arising in the flow controller placed ahead of the column. The carrier gas is then mainly polluted with $CF_2Cl-CFCl_2$.

In order to calibrate the detector operated in fixed-frequency pulsed mode, a mass in the range $0.5 \cdot 10^{-12}$–$5 \cdot 10^{-12}$ g should be injected (Fig. 4). This cannot be achieved with the dynamic dilution system described in Fig. 2 and another dilution stage is necessary, with a corresponding decrease in the absolute precision in the concentration of the primary standard generated.

The detection limit for $CFCl_3$ calculated for a signal-to-noise ratio of 2 (noise level $2 \cdot 10^{-12}$ A) with the detector operated in the fixed-frequency pulsed mode is
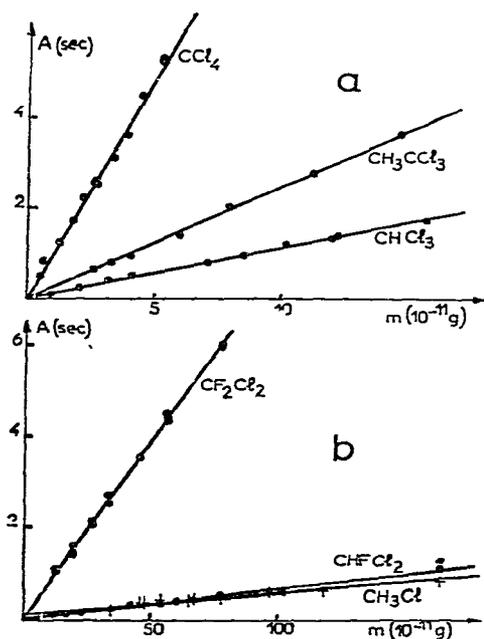


Fig. 6. Calibration graphs for d.c. mode of operation.

$0.5 \cdot 10^{-13}$ g, equal to that observed with the instrument electronics (constant-current, pulse-modulated frequency mode of operation).

Because of experimental difficulties in calibrating the chromatographic system with accuracy, an anomalous hypercoulometric response for $CFCl_3$, a high baseline drift when column temperature is increased dynamically from $-60°C$ to $60°C$ (Fig. 5a) and the well known narrow dynamic linear range achieved, air sampling analysis of halocarbons was not carried out with this mode of operation.

*d.c. mode of operation*

To calibrate the detector in the d.c. mode of operation, the same relationship as in the fixed-frequency pulsed mode was used (eqn. 4), as Wentworth and Chen[28] pointed out that the form of this equation is probably correct, but $K$ will be different in the d.c. and pulsed modes. The transformed peak area, $A$, is a linear function of the amount injected for all compounds examined: $CFCl_3$ (Fig. 4a); $CHCl_3$, $CH_3CCl_3$ and $CCl_4$ (Fig. 6a); and $CF_2Cl_2$, $CH_3Cl$ and $CHFCl_2$ (Fig. 6b). The straight lines all pass through the origin, except that for $CH_3Cl$. As previously, this can be explained by the limited number of experimental points near the origin and because of difficulties in peak-area measurements with the small masses injected, as $CH_3Cl$ gives a low response in the ECD.

Table IV lists the slope, $\alpha$, of the calibration straight lines, the 95% confidence interval error, $\Delta$, in the determination and the detection limit for a 100-ml (S.T.P.) air sample. From $\alpha$ are deduced the electron-capture coefficient, $K$, and the ionization efficiency of strong electron absorbers.

The d.c. mode was run at 10 V throughout the study. This voltage will not

TABLE IV

ELECTRON-CAPTURE COEFFICIENT, $K$, IONIZATION EFFICIENCY, SLOPE OF THE CALIBRATION GRAPH, $\alpha$, AND DETECTION LIMIT IN d.c. ECD MODE OF OPERATION

Standing current, $I_0 = 2.3 \cdot 10^{-9}$ A; detector temperature, 300°C; detector flow-rate, 34 ml/min.

| Compound | $K$ $(cm^3/mole \times 10^9)$ | Ionization efficiency (%) | $\alpha$ $(sec/g \times 10^9)$ * | Detection limit for 100 (STP) air sample (ppt) |
|----------|------|------------|------|-----------|
| $CH_3Cl$ | 12 | — | 0.42 ($\Delta = 0.04$) | 150 |
| $CHFCl_2$ | 35 | — | 0.60 ($\Delta = 0.04$) | 50 |
| $CF_2Cl_2$ | 528 | 2.2 | 7.7 ($\Delta = 0.2$) | 3 |
| $CHCl_3$ | 705 | 3.0 | 10.4 ($\Delta = 0.2$) | 5 |
| $CH_3CCl_3$ | 1860 | 7.8 | 24.6 ($\Delta = 0.2$) | 3 |
| $CCl_4$ | 8450 | 35.6 | 97.0 ($\Delta = 4$) | 0.5 |
| $CFCl_3$ | 9260 | 39.0 | 119 ($\Delta = 2$) | 0.4 |

* The error, $\Delta$, in the determination of $\alpha$ is calculated for a 95% confidence interval.
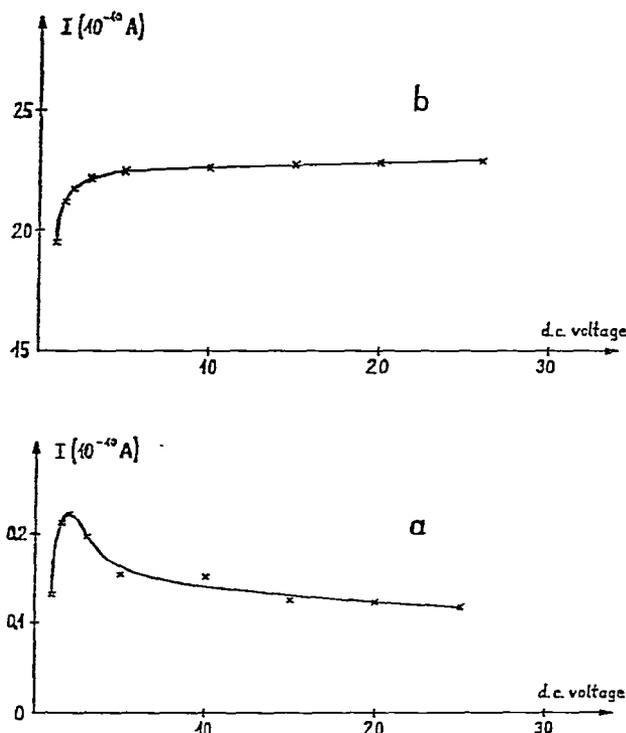
Fig. 7. (a) d.c. response profile for $CFCl_3$. Mass injected: $0.5 \cdot 10^{-12}$ g. (b) Dependence of standing current on d.c. voltage.

provide the maximal sensitivity, as shown in Fig. 7, where the response profile as a function of voltage is given for a $0.5 \cdot 10^{-12}$ –g mass of $CFCl_3$ injected. The optimal response is attained at a d.c. voltage of 2 V.

In order to obtain a good stability of response in routine analysis, we did not carry out the experiments at a low d.c. voltage as the response profiles and thus the optimal d.c. voltages are very sensitive to the amount injected, the nature of the compounds studied and column bleeding, as shown by Aue and Kapila[27].

The data reported in Table IV are therefore valid only for the actual experimental conditions used, and the detection limits could be improved in the d.c. mode of operation by optimizing the voltage for each compound studied. With $CFCl_3$ a detection limit 30% lower would be achieved with a d.c. voltage of 2 V, as shown in Fig. 7.

The detection limit is calculated for a signal-to-noise ratio of 2 (noise level $2 \cdot 10^{-12}$ A) for a 100-ml (S.T.P.) air sample injected. However, a much larger (10 times or more) volume can be trapped on the adsorbent kept in dry-ice if it is lower than the breakthrough volume of the compound to be analysed[23]. This procedure could be used to analyse $CH_3Cl$ or $CHFCl_2$ as the detection limit for a 100-ml (S.T.P.) sample is large. Saturation of the detector will then be attained for $CFCl_3$ and $CF_2Cl_2$ with an air sample volume larger than 200 ml (S.T.P.), considering their large response and the concentration measured in the atmosphere (Fig. 4 for $CFCl_3$).

Fig. 1b shows that CH$_3$Cl (concentration 650 ppt) can be analysed in 500 ml of air.

## DISCUSSION

ECD calibration has shown that both the d.c. and the constant-current pulse-modulated modes of operation can be used for the routine analysis of air samples for trace levels of halocarbons because of the large linear dynamic range observed in both modes. In this work, the analyses of actual air samples have been carried out in the d.c. mode of operation. Because of the larger response and the narrow dynamic linear range in the fixed-frequency pulsed mode, we could not use this detection mode in routine analysis (difficulties in calibrating the system, large baseline drift, interference between CF$_2$Cl$_2$ and H$_2$O peaks).

In spite of its lower sensitivity (the detection limit is 3–5 times larger than in the constant-current, pulse-modulated frequency mode, with the actual experimental conditions and 10 V d.c.), the d.c. mode of operation was preferred because of easier control of the standing current and thus of accidental detector pollution, which is always possible. To operate under the optimal conditions with the instrument electronics, the detector had to be regenerated periodically with a stream of hydrogen at 450°C, as indicated by the manufacturer, although the standing current did not reveal any special pollution. This problem was recently outlined by Miller and Grimsrud[29]. As this procedure might alter the detector performance and response in the long term, we choose to work in the d.c. mode. The calculation of the transformed peak area was not a serious problem as all analyses are performed with computer data acquisition.

In Table V are summarized the results obtained in analysing air samples provided by Rasmussen and Khalil[5] for inter-laboratory comparison measurements. Fig. 8 shows typical chromatograms obtained in the analysis of 50-ml samples of mixtures A and B.

For CF$_2$Cl$_2$ the concentration measured is close to Rasmussen and Khalil's values, with a difference of 5% for sample A and 4% for sample B. Agreement with the average value obtained by the independent laboratories lies in the same error range (1% for sample A and 6% for sample B). These results agree with the error interval given for the absolute precision of the calibration method for CF$_2$Cl$_2$ (Table II: 3% absolute precision for a 95% confidence interval).

For CFCl$_3$ the difference between our result for mixture A and the value given by Rasmussen and Khalil is 10%; it is only 4% between our result and the reported average obtained by the independent laboratories. This again is in agreement with the absolute precision of 7% at the 95% confidence interval reported in Table II.

With mixture B, which is more dilute, larger deviations are observed: 18% from Rasmussen and Khalil's value and 13% from the average value obtained by the independent laboratories. These deviations can be explained by the fact that on the column used for the separation, CFCl$_3$ interferes with an unknown component present only in the bottle mixture B (cf., Fig. 8b) but not in the canister containing mixture A (Fig. 8a) or in ambient air (Fig. 1), and difficulties in measuring precisely its peak area arise.

The agreement with the results of independent laboratories is excellent, con-

TABLE V

INTER-LABORATORY COMPARISON RESULTS

| *Result* | $CF_2Cl_2$ *(ppt)* | | $CFCl_3$ *(ppt)* | |
|----------|----------|----------|----------|----------|
|          | *Sample A* | *Sample B* | *Sample A* | *Sample B* |
| Our laboratory | 282 | 104 | 158 | 54 |
| Mean independent analysis[5] | 279 | 110 | 162 | 62 |
| Submitted analysis by Rasmussen and Khalil[5] | 298 | 100 | 174 | 65 |

sidering the different approaches used for analysing the air samples and calibrating the instrument. This shows that the accuracy of the results of Freon and halocarbon analyses carried out in these laboratories can be treated with great confidence.

This work shows also that the permeation tube technique with dynamic gravimetric determination of the permeation rate is an accurate method for generating
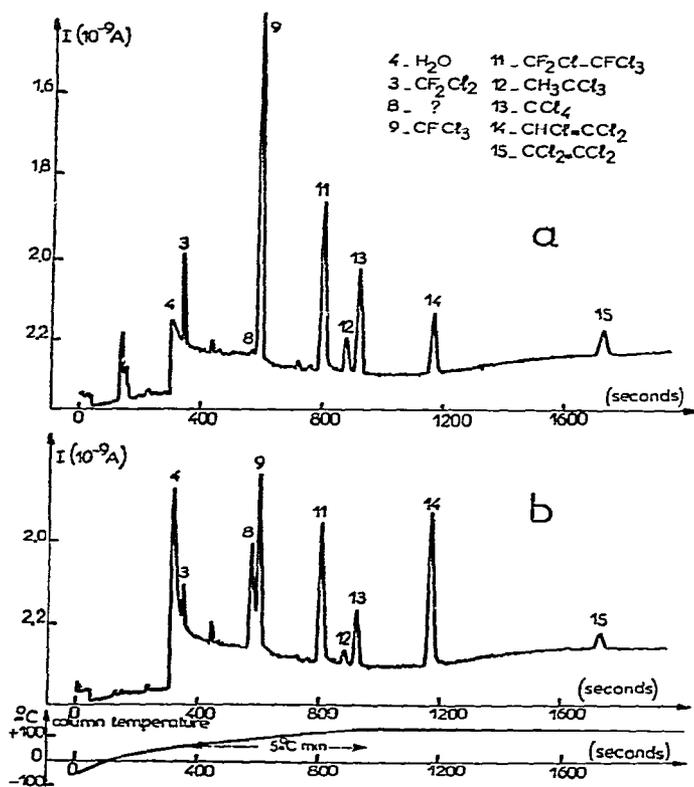


Fig. 8. Results for air samples from inter-laboratory comparison analyses. (a) Sample A, 50 ml; (b) sample B, 50 ml. Experimental conditions as in Fig. 1. Linear temperature programme from 60°C to 140°C at 5°C/min.

traces of halocarbons at the ppb level (absolute precision 5-7%). Calibration of the instrument can be carried out with the injection of a few millilitres of sample, whereas the air analysis itself is carried out with 20 ml or more of sample.

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REFERENCES

1 M. J. Molina and F. S. Rowland, *Nature* (London), 249 (1974) 810.
2 J. E. Lovelock and A. J. Watson, *J. Chromatogr.*, 158 (1978) 123.
3 R. A. Rasmussen and D. Pierotti, *Geophys. Res. Lett.*, 5 (1978) 353.
4 R. A. Rasmussen, *Atmos. Environ.*, 12 (1978) 2505.
5 R. A. Rasmussen and M. A. K. Khalil, *Atmos. Environ.*, in press.
6 D. H. Pack, J. E. Lovelock, G. Cotton and C. Curthoys, *Atmos. Environ.*, 11 (1977) 329.
7 E. Robinson, R. A. Rasmussen, J. Krasnec, D. Pierotti and M. Jakubovic, *Atmos. Environ.*, 11 (1977) 215.
8 P. W. Krey, R. J. Lagomarsino and L. E. Toonkel, *J. Geophys. Res.*, 82 (1977) 1753.
9 J. F. Vedder, B. J. Tyson, R. B. Brewer, C. A. Boitnott and E. C. Y. Inn, *Geophys. Res. Lett.*, 5 (1978) 33
10 D. R. Cronn and D. E. Harsch, *Anal. Lett.*, 12 (1979) 1489.
11 F. J. Sandalls and D. B. Hatton, *Atmos. Environ.*, 11 (1977) 321.
12 S. A. Penkett, K. A. Brice, R. G. Derwent and A. E. J. Eggleton, *Atmos. Environ.*, 13 (1979) 1011.
13 M. De Bortoli and E. Pecchio, *Atmos. Environ.*, 13 (1979) 883.
14 A. L. Schmeltekopf, P. D. Goldan, W. R. Henderson, W. J. Harrop, T. L. Thompson, F. C. Fehsenfeld, H. I. Schiff, P. J. Crutzen, I. S. A. Isaksen and E. E. Ferguson, *Geophys. Res. Lett.*, 2 (1975) 393.
15 A. E. O'Keefe and G. C. Ortman, *Anal. Chem.*, 38 (1966) 760.
16 F. P. Scaringelli, A. E. O'Keefe, E. Rosenberg and J. P. Bell, *Anal. Chem.*, 42 (1979) 871.
17 L. J. Purdue and R. J. Thompson, *Anal. Chem.*, 44 (1972) 1034.
18 B. E. Saltzman, W. R. Burg and G. Ramaswamy, *Environ. Sci. Technol.*, 5 (1971) 1121.
19 W. R. Burg, S. R. Birch, J. E. Cuddeback and B. E. Saltzman, *Environ. Sci. Technol.*, 10 (1976) 1233.
20 H. B. Singh, L. Salas, D. Lillian, R. R. Arnts and A. Appleby, *Environ. Sci. Technol.*, 11 (1977) 511.
21 H. B. Singh, L. J. Salas, H. Shigeishi and E. Scribner, *Science*, 203 (1979) 899.
22 P. L. Patterson, *J. Chromatogr.*, 134 (1977) 25.
23 C. Vidal-Madjar, M. F. Gonnord, F. Benchah and G. Guiochon, *J. Chromatogr. Sci.*, 16 (1978) 190.
24 F. Bruner, G. Bertoni and G. Crescentini, *J. Chromatogr.*, 167 (1978) 399.
25 R. J. Maggs, P. L. Joynes, A. J. Davies and J. E. Lovelock, *Anal. Chem.*, 43 (1971) 1966.
26 W. E. Wentworth, E. Chen and J. E. Lovelock, *J. Phys. Chem.*, 70 (1966) 445.
27 W. A. Aue and S. Kapila, *J. Chromatogr.*, 188 (1980) 1.
28 W. E. Wentworth and E. Chen, *J. Gas Chromatogr.*, 5 (1967) 170.
29 D. A. Miller and E. P. Grimsrud, *J. Chromatogr.*, 190 (1980) 133.