CHROM. 13,191

CALIBRATION METHOD FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF HALOCARBONS IN ATMOSPHERIC SAMPLES USING PERMEATION TUBES AND AN ELECTRON-CAPTURE DETECTOR

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SUMMARY

A method for calibrating the electron-capture detector for the analysis of halocarbons in atmospheric samples is presented. Permeation tubes are used as primary standards. The precision is evaluated under different operating conditions, and a standard deviation of 5 % was the optimal. The difficulty of determining halocarbons present at very different concentrations is discussed.

INTRODUCTION

The accurate determination of halocarbons in the atmosphere became extremely important after Molina and Rowland[1] had concluded that these compounds destroy the stratospheric ozone layer. Their hypothesis is based on the assumption that halocarbons of anthropogenic origin (in particular CCl_2F_2 and CCl_3F) accumulate in the troposphere and reach the stratosphere after several years. An accuracy of a few percent is then necessary in order to follow the increase in atmospheric concentration with time, or to reveal the presence of any possible tropospheric sink. However, at present, the discrepancy among inter-laboratory comparative results is of the order of 30 % in many instances[2].

This discrepancy can be attributed to the lack of reliable sources of known concentrations of halocarbons rather than to the well known difficulties connected with the routine use of the electron-capture detector (ECD). In this paper, a calibration method based on the coupling of permeation tubes with the ECD is described.

Permeation tubes, introduced by O'Keeffe and Ortman[3], have been employed as primary standards for the analysis of a number of atmospheric polluntants[4-9], and were first used by Singh and co-workers for the measurement of halocarbons in air samples[10,11]. The advantage of the use of permeation tubes over other calibration methods, such as static or dynamic dilution, is in that calibration is referred directly to gravimetric measurements, independent of the operator and ancillary techniques used.
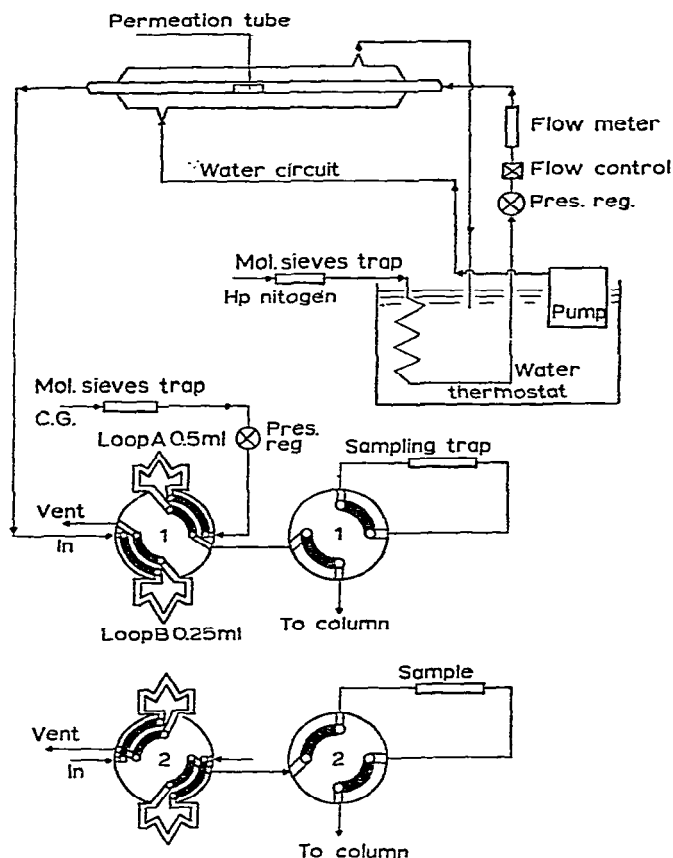
Fig. 1. Schematic diagram of the apparatus for the calibration and analysis of halocarbons in atmospheric samples. C.G. = Carrier gas.

EXPERIMENTAL

The apparatus used, shown schematically in Fig. 1, is designed to inject the calibration mixture following the same procedure as used for air sample injection, *i.e.*, trapping at $-78°C$ on an adsorbent (Carbopack B) and injection by the heat-stripping technique[12].

A water thermostat kept at $25 \pm 0.1°C$ feeds a double-walled glass holder, in the inner space of which are placed permeation tubes. High-purity nitrogen, further purified through a molecular sieves trap kept at $-78°C$ (dry-ice and acetone slush) flows continously through the glass holder. The flow-rate can be varied in the range 10–150 ml/min. The two sample loops were calibrated by mercury weighing and allow the injection of 0.25 and 0.50 ml.

The calibration mixture is sampled through one of the two loops and the contents of the loop can be transferred into the trap kept at $-78°C$. This step can be repeated as many times as is required to obtain different amounts of various halocarbons according to the range of concentration needed. The contents of the trap are

then injected into the column through the zero-volume valve system (Valco Model 2-2274, 2-2278) by means of the heat-stripping technique. Alternatively, the contents of the loop can be injected directly into the column. When real samples have to be injected into the column, the trap used for calibration is replaced by the trap where air was sampled. In this way, the same procedure is followed for both calibration and the actual halocarbon mixture.

The gas chromatographic (GC) system is also equipped with a standard syringe injector. A Dani 3600 gas chromatograph equipped with a ^{63}Ni frequency-modulated ECD (Dani 68/30) is used. The detector is kept at 220°C and fed with an additional carrier gas flow-rate of 30 ml/min. High-purity nitrogen further purified as described above is used as the carrier gas.

The GC column, a 3 m × 2 mm I.D. glass column packed with Carbopack B (80–100 mesh), coated with 0.5% SP 1000 (Supelco, Bellefonte, PA, U.S.A.), and with the other conditions used have been described previously[12]. Only the temperature programme was modified and simplified, without affecting the overall separation (5 min at 40°C and then programmed at 6°C/min up to 230°C).

All permeation tubes are made of FEP Teflon (DuPont) and are sealed with stainless-steel spheres or glass plugs. Their dimensions and wall thickness (0.3, 0.9 and 3.0 mm) vary according to the permeation rate. The permeation tubes were calibrated by weighing them twice a week. Two to six weeks are required before a constant permeation rate is reached.

RESULTS AND DISCUSSION

Calibration of permeation tubes

The loss of weight with time for permeation tubes containing different halocarbons is shown in Fig. 2. The experimental points reported are those obtained only after linearity has been obtained. It can be seen that at least 15 days are needed after preparation before the graph becomes linear. However, after linearity has been reached, the permeation tubes behave as expected. The errors involved in the measurements do not exceed the thickness of the points on the graph. The lifetime of permeation tubes depends on the permeation rates of the individual halocarbons, which differ according to the nature of the compounds and the geometrical characteristics of the tube, such as thickness and surface area. In this way the slope of the graphs is not related to the physical characteristics of the individual compounds but represents the effect of all of the parameters involved.

Calibration graphs

Calibration graphs for various halocarbons are shown in Fig. 3. The most important feature of the graphs is that the more sensitive the detector, the less linear is its response to increasing concentration. This is perhaps the main disadvantage in the use of the ECD in the analysis of atmospheric samples of halcarbons. In fact, owing to the differences in the response factors and the mixing ratios, it is almost impossible to determine different halocarbons within the same sample. The example offered by F-11 and F-21 is one of best to illustrate the situation. F-11 is one of the most abundant halocarbons and the ECD is extremely sensitive to it, whereas F-21 is often present in ultra-trace concentrations and the detector shows a response that
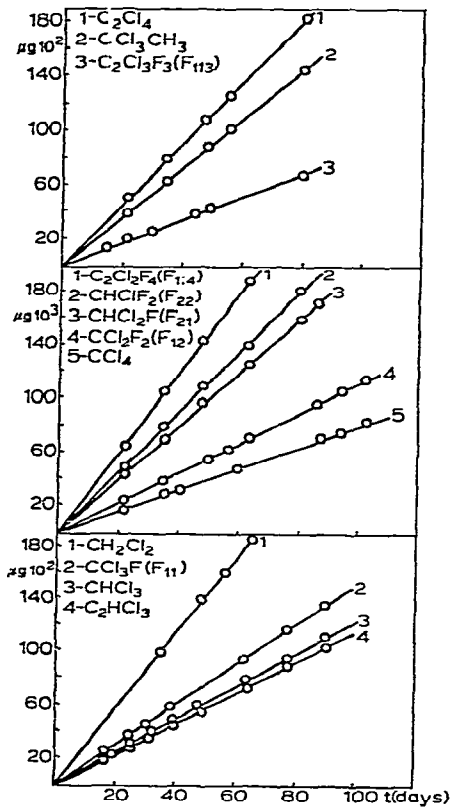
Fig. 2. Loss of weight with time of permeation tubes for various halocarbons.
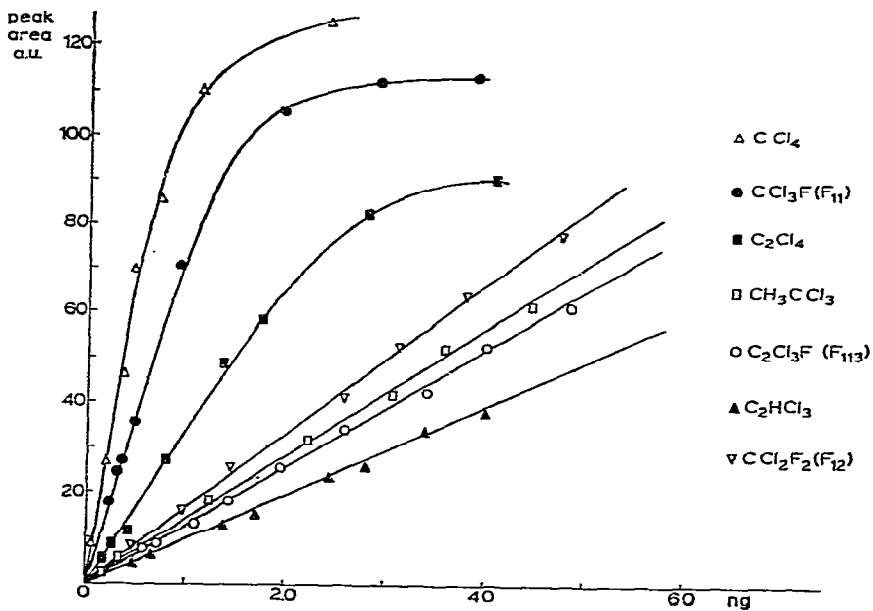

Fig. 3. Calibration graphs for several halocarbons.

is about 70 times lower. This means that unless very peculiar concentrations of the two compounds occur, the difference in peak areas between F-11 and F-21 is of the order of $7 \cdot 10^3$. This difference makes impossible the simultaneous determination of the two halocarbons in the same sample.

In Table I the volume range for a good quantitative evaluation of several halocarbons determined by the detector response, atmospheric abundance and linearity of calibration graphs is reported. Of course, the data are necessarily approximate and refer to the analytical procedure and detector used in our laboratory, but they should be of general interest. In order to have a linear response for CCl_4 the sample volume should not exceed 1.0 l. With such a volume of air F-11, F-12, F-113, 1,1,1-trichloroethane and tetrachloroethylene can be determined. In order to determine F-21, trichloroethylene and other possible minor components a larger volume of air should be sampled.

TABLE I

MINIMAL AND MAXIMAL SAMPLE VOLUMES FOR THE ANALYSIS OF SOME HALO-CARBONS DIFFERING IN ATMOSPHERIC MIXING RATIOS AND DETECTOR RESPONSES

Compound	Average concentration range in the atmosphere (ppt)	Maximal sample volume for linearity (l)	Minimal sample volume for detection (l)
F-12 (CCl_2F_2)	200–1000	10–2	$8 \cdot 10^{-3}$–$1.6 \cdot 10^{-3}$
F-11 (CCl_3F)	70–300	3–0.7	$6 \cdot 10^{-4}$–$1.4 \cdot 10^{-4}$
CCl_4	100–180	1–0.6	$4 \cdot 10^{-4}$–$2.2 \cdot 10^{-4}$
$C_2H_3Cl_3$	80–130	14–9	$8 \cdot 10^{-3}$–$5 \cdot 10^{-3}$
C_2HCl_3	5–20	100–56	1.7–0.4
F-21 ($CHCl_2F$)	0.5–90	100–22	18–$9 \cdot 10^{-2}$
C_2Cl_4	20–40	17–8	$2 \cdot 10^{-3}$–$9 \cdot 10^{-3}$
F-113 ($C_2Cl_3F_3$)	5–20	100–39	$6 \cdot 10^{-2}$–$1.5 \cdot 10^{-2}$

Reproducibility of calibration

Calibration was carried out with particular care for F-21, because we are particularly interested in measuring this compound with a high degree of accuracy. Two different calibration graphs were constructed by (a) conditioning the ECD and the entire GC system for 1 week, then establishing the calibration graph in one working day; (b) obtaining calibration points on different days, with the detector turned off and the additional carrier gas flow to the detector stopped between different calibration experiments, the column flow-rate being maintained instead. Calibration runs were executed 2 h after the entire system had been re-set.

The obvious aim of such double procedure was to show the influence of the operating conditions has they occur in a typical monitoring programme.

In Fig. 4 the results obtained with procedure (a) are shown for F-21. The errors for the single points are shown by vertical bars. The errors on the abscissa are assumed to be smaller than the thickness of the points on the graph. An average standard deviation of 5% along the entire graph was found. In Fig. 4 the top abscissa indicates the actual amount of F-21 injected (nanograms) and the lower abscissa the corre-
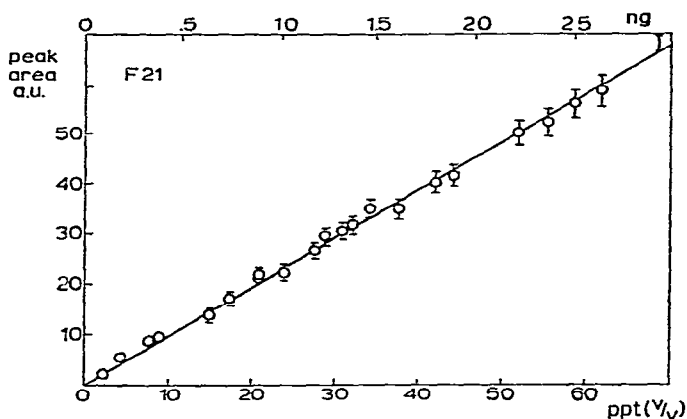
Fig. 4. Calibration for F-21 carried out in one working day.

sponding concentration (ppt*) referred to a 10-1 air sample. This is usually the volume of air trapped in our sampling system for the analysis of F-21.

Fig. 5 shows the data points obtained during a calibration programme during 2 weeks. As expected, the data are more scattered than in Fig. 4, with a standard deviation of 20%. It is our opinion that such a value is more significant for checking the precision of the analytical method. However, the conditions found with procedure (a) are certainly met if a calibration run is made immediately before and after the elution of the actual air sample. It should be noted that the calibration run is made by injecting the standard mixture and eluting it following the temperature programme for the actual air sample.
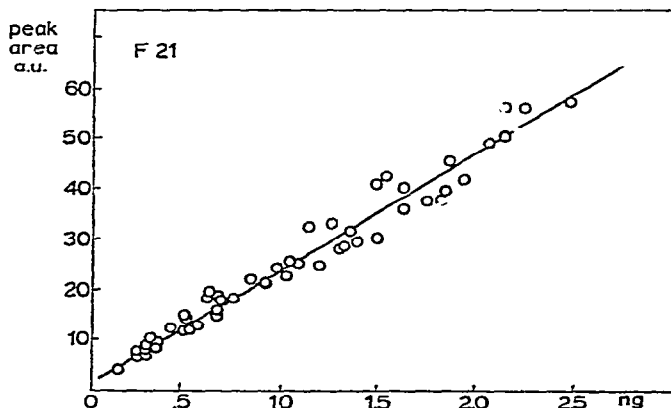

Fig. 5. Calibration for F-21 carried out in 1 week turning on and off the detector.

The most interesting feature of Figs. 4 and 5 is that the graphs are linear over the entire range examined. This is due to the circumstance that the concentrations hypothesized for F-21 in the troposphere are not high.

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* Throughout this article, the American trillion (10^{12}) is meant.

In conclusion, the following statements can be made about the use of the ECD as a quantitative detector for the analysis of atmospheric samples for halocarbons. The overall method can have good precision, with a standard deviation of about 5%, if permeation tubes are used as reference standards.

The method has some disadvantages owing to the non-specificity of the ECD and to the high background that might occur as a result of other compounds present in the atmosphere. Also, the determination of halocarbons with greatly different abundances and detector responses within the same air sample is difficult. The mass spectrometer used in mass fragmentography is more specific and the linearity of the response is much higher[13], so that it is to be preferred if F-11 and F-21 have to be determined in the same air sample.

ACKNOWLEDGEMENTS

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