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GAS CHROMATOGRAPHIC DETERMINATION OF ULTRA-TRACE AMOUNTS OF HALOGEN-CONTAINING HYDROCARBONS IN THE ATMOSPHERE

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SUMMARY

Ultra-trace amounts of some chlorofluoromethanes in the atmosphere were determined by means of gas chromatography with an electron-capture detector. Carbon adsorbents (Carbochromes) were used for concentration and analysis.

INTRODUCTION

It has been widely believed during the last decade that the ozone content in the stratosphere may decrease as a result of photochemical reactions involving certain components whose concentration may grow due to anthropogenic factors. For instance, such highly stable compounds as trichlorofluoromethane, CFCl_3 (Freon 11) and dichlorodifluoromethane, CF_2Cl_2 (Freon 12), dissociate under the effect of ultraviolet radiation in the stratosphere and yield nascent chlorine which readily reacts with ozone^{1,2}. Other organic chlorine derivatives are also susceptible to photolysis. The ozone layer is crucial to the stratospheric heat balance and its destruction may lead to serious changes in meteorology. Information on the content of these compounds at different points of the globe provides insight into the variation in the ozone concentration.

The traces of volatile halogen-containing hydrocarbons in the atmosphere were first reported by Lovelock³ in 1971. Since that time numerous investigations have dealt with the measurement of the atmospheric concentrations of these substances¹⁻¹¹. The techniques employed were either gas chromatography (GC) with the electron-capture detector or gas chromatography-mass spectrometry. The content of halocarbons in the atmosphere is as low as a few parts per billion. Since the detectors available lack sufficient sensitivity for direct determination, the trace compounds require pre-concentration. Compression¹² and the use of solid adsorbents^{10,13,14} were suggested for this purpose. High-sensitivity detectors and special devices for sample injection have recently made it possible to determine atmospheric halocarbons by direct analysis of air⁷⁻⁹.

The present paper reports measurements of the concentrations of certain chlo-

rofluoromethanes in the atmosphere over the Pacific ocean. The compounds were pre-concentrated on an adsorbent and then desorbed into the chromatographic column.

EXPERIMENTAL

The analysis involved a Tsvet-6 chromatograph with an electron-capture detector. The detector electron source was ^{63}Ni . The sensitivity limits with regard to Freon 11 and 12 were 0.01 and 0.1 ppb respectively, the reproducibility on measurements being $\pm 10\%$. The concentration of the halocarbons was accomplished by two methods. The first employed a special accumulative attachment to the UKP-63 chro-

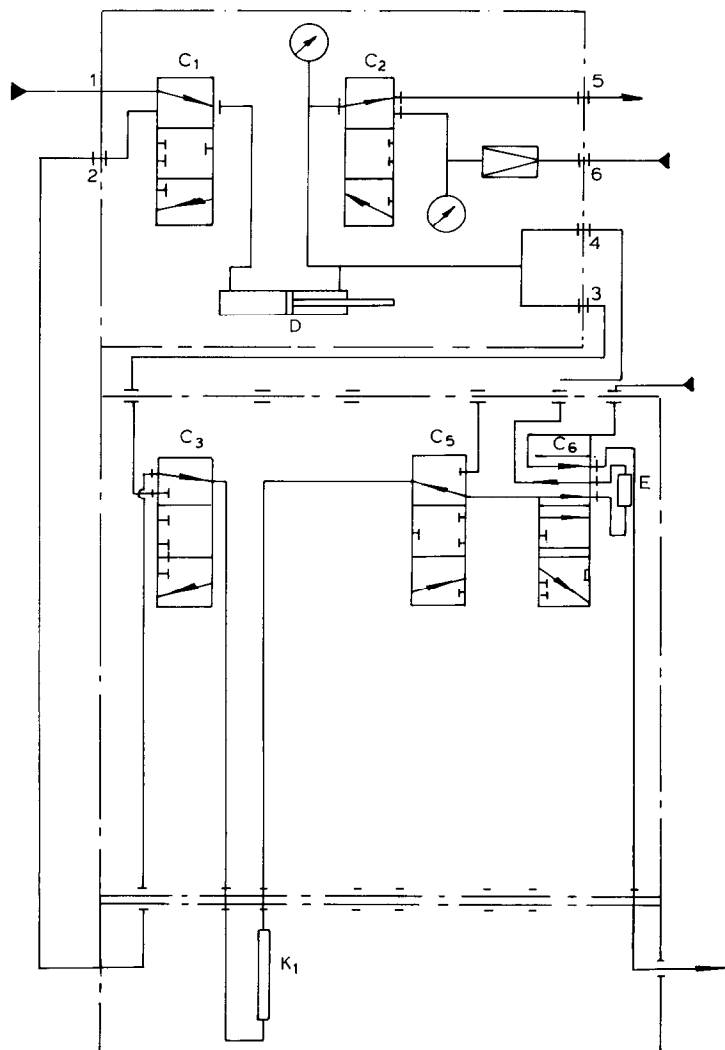


Fig. 1. Schematic of the gas concentrator.

matograph (Fig. 1). The mixture under analysis (800 ml) is fed into a delivery device (D) and then through a system of cocks (C_1 and C_3) into a column (K) packed with an adsorbent pre-evacuated to 10^{-2} Torr at 280°C for 1 h. The adsorption takes place at room temperature, desorption upon rapid heating of the column to 250°C . After 10–15 min at this temperature the mixture is passed into an evacuated trap (E) and then to the chromatograph.

In the second method, 100 ml air were fed directly into the adsorbent column by means of a gas-tight syringe. The desorption occurs as described above. Steel columns (250×3 mm I.D.) were used for the pre-concentration step.

Absorbents for the concentration step

Since halocarbon traces are to be determined in moist air, the materials for the concentration step were sought among non-specific hydrophobic heat-resistant carbon adsorbents, namely Carbochrome C (initial channel black modified by pyrocarbon¹⁵), graphitized channel black and PSKT activated carbon (prepared from SKT activated coal by washing out the ash and modification by pyrocarbon¹⁶). Adsorption on these adsorbents, whose surface consists of pure carbon, occurs by non-specific dispersion interaction¹⁷; their characteristics are given in Table I.

TABLE I
ADSORBENTS FOR THE CONCENTRATION STEP

Sample	Functional groups (mequiv./g)			Pore volume (cm^3/g)	Specific surface area, S (m^2/g)	Strength, (% of broken granules)
	OH	COOH	C=O			
Graphitized channel black	0	0	0	—	112	60
Carbochrome C	0	0	0	—	80	1.5
Ash-free SKT coal	19.6	9.3	10.3	0.6	1000	—
PSKT coal	0	0	0	0.4	860	—

Adsorbents and columns for GC

Packed glass columns (250×3 mm I.D.) were used. The temperature of the column was 40°C , and of the detector 250°C ; the carrier gas (nitrogen) velocity was 40 ml/min.

The adsorbents tested were Carbochrome B (initial thermal black modified by pyrocarbon¹⁸) having a specific surface area of $6 \text{ m}^2/\text{g}$, Carbochrome B modified by polysiloxane PMS-100, FS-16, by polyethylene glycol (M.W. 15,000) and Apiezon L (modifier content 0.05 and $0.5 \text{ mg}/\text{m}^2$) and Chromatone with 15% PEG-115 and 15% SE-30.

Calibration and preparation of standards

The chromatograph was calibrated with respect to each substance. The standards of different concentrations were prepared by injecting $10 \mu\text{l}$ of each component into 2-l Pyrex glass cylinders equipped with devices for dilution and sampling.

TABLE II

RETENTION VOLUMES (ml/g) OF SOME HALOCARBONS ON CARBON ADSORBENTS AT 50°C

Adsorbent	CF_2Cl_2	$CDCl_3$	$CHCl_3$	CCl_4
Carbochrome C	62	83	320	524
Graphitized channel black*	84	112	446	700
PSKT coal*	684	907	3600	5670

* Extrapolated data.

The samples were then diluted quantitatively in pure air. Peak area vs. concentration curves were plotted for each component.

RESULTS AND DISCUSSION

The quantitative analysis of halocarbon traces requires their adsorption from air, as well as the subsequent desorption from the adsorbent, be as complete as possible. Table II gives the retention volumes of some halocarbons on carbon adsorbents. It is seen that the adsorbents possess high capacities with regard to chlorofluoromethanes.

An optimum adsorbent for concentrating halocarbons should also enable efficient desorption. Figs. 2 and 3 present chromatograms of a mixture of chlorofluoromethanes after the first and the second desorption from PSKT carbon and Carbochrome C at 250°C. One heating suffices to remove all the adsorbate from Carbochrome C; with PSKT coal, whose microporous structure brings about its unique adsorption properties, efficient desorption evidently requires even higher temperatures. Therefore the adsorbents chosen for the concentration step were graphitized

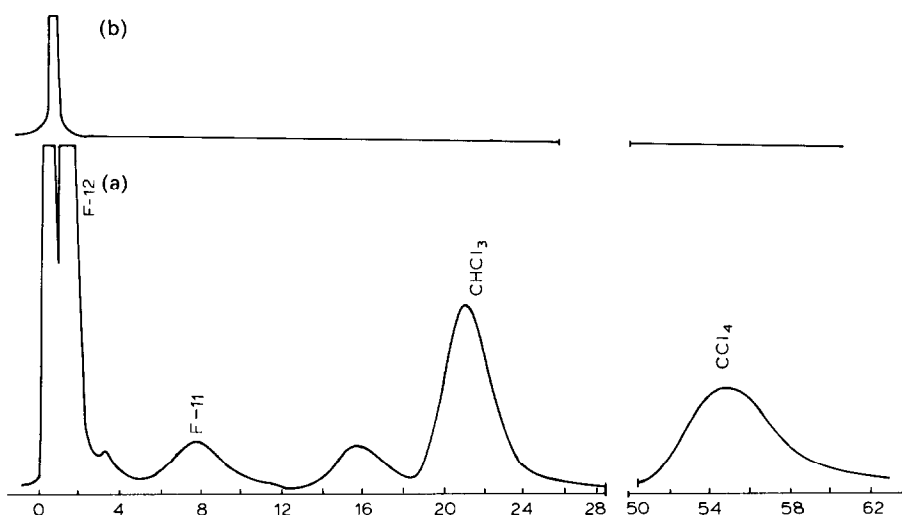


Fig. 2. Chromatograms of air samples after the first (a) and second desorption (b) at 250°C. The adsorbent for concentration was Carbochrome C; that for GC analysis was Carbochrome B. Column temperature: 40°C. Detector temperature: 230°C. Carrier gas (N_2) velocity: 40 ml/min.

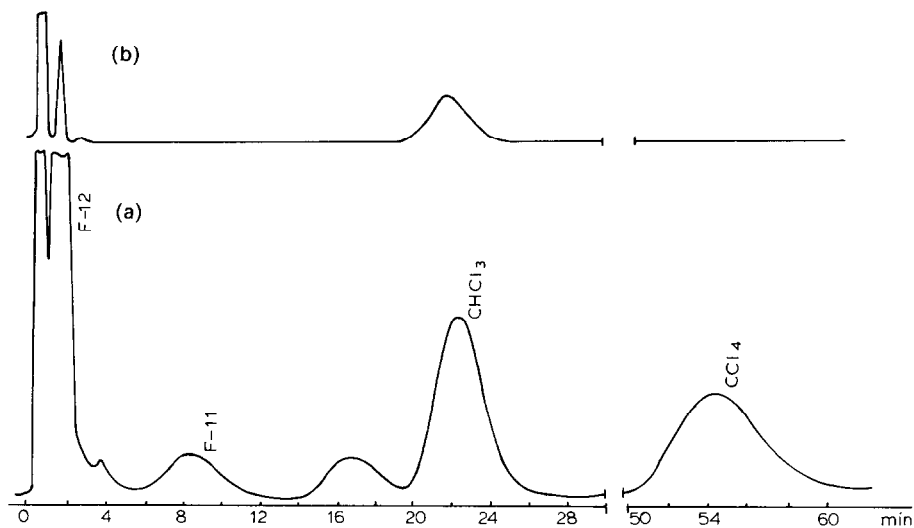


Fig. 3. Chromatograms of air samples after the first (a) and second desorption (b) at 250°C. Concentration adsorbent: PSKT carbon. Other conditions as in Fig. 2.

channel black and Carbochrome C, whose adsorption properties are similar. The latter material, however, forms much stronger granules than the former.

In the analysis of halocarbons it is important to use selective adsorbents enabling complete separation. Table III presents relative retention volumes of some halocarbons on Carbochrome B (initial and modified) and Chromatone with 15% PEG-115 and SE-30. It is seen that a small amount of the modifier on the Carbochrome surface does not affect the separation selectivity. On the other hand, such treatment gives rise to shorter retention times and, accordingly, shorter analysis times. Fig. 4 shows a chromatogram of chlorofluoromethanes on Carbochrome B and on the same adsorbent modified by 0.05 mg/m² FS-16. Use of SE-30 on Chromatone results in the separation of almost all chlorofluoromethanes but not of dichlorofluoromethane from air. A higher amount (0.5 mg/m²) of the modifier changes the selectivity of Carbochrome with respect to chlorofluorocarbons: the elution order of chloroform and carbon tetrachloride is reversed due to a strong specific interaction between the highly polar chloroform molecules and the surface functional groups of

TABLE III
RELATIVE RETENTION VOLUMES, $V_{\text{CHCl}_3}/V_{\text{CCl}_4}$

Chromatone			Carbochrome B modified by							
SE-30	PEG-115	Initial	Apiezon L		PMS-100		FS-16		PEG-115	
			0.05 mg/m ²	0.5 mg/m ²	0.05 mg/m ²	0.5 mg/m ²	0.05 mg/m ²	0.5 mg/m ²	0.05 mg/m ²	0.5 mg/m ²
0.6	2.0	0.6	0.51	0.56	0.44	0.46	0.4	0.46	0.46	1.37

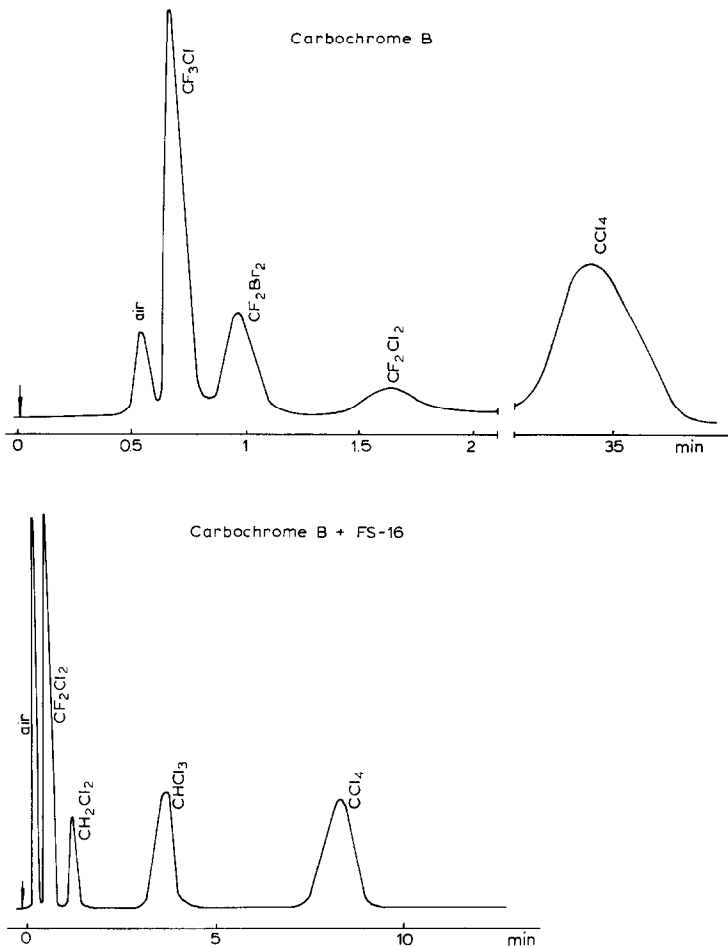


Fig. 4. Chromatogram of a mixture of halocarbons on Carbochrome B and on Carbochrome B modified by 0.05 mg/m² of a polysiloxane liquid, FS-16. Chromatographic conditions as in Fig. 2.

the modified adsorbent. Therefore, in the GC analysis of air samples we employed Carbochromes modified by a small amount (0.05 mg/m²) of non-polar or mildly polar liquids.

Analysis of halocarbons in the atmosphere

To obtain data on large scale distribution processes of minor pollutants in the troposphere we have studied the spatial distribution of Freon-11 and methylchloroform over the ocean. The results demonstrate the differences in distribution of F-11 and methylchloroform between the northern and southern hemispheres, and enable an evaluation of the residence time of methylchloroform in the atmosphere.

The atmospheric concentrations of F-11 and methylchloroform were measured during the XXVI cruise of the research vessel "Academician Korolev" (December 1979–February 1980). The region covered was the northern and southern parts of the Pacific ocean which allowed us to obtain the latitudinal distribution of the concen-

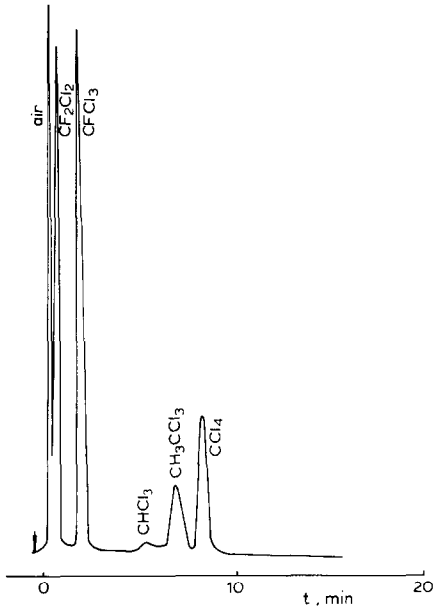


Fig. 5. Chromatogram of an air sample. The adsorbent for concentration was Carbochrome C; that for GC analysis was Carbochrome B + FS-16. Other conditions as in Fig. 2.

trations of the gases in the atmosphere over the ocean. Fig. 5 presents a typical chromatogram of an air sample.

The results given in Figs. 6 and 7 show that a latitudinal gradient in the atmospheric concentration was observed for F-11 and methylchloroform. Thus, the maximum F-11 concentrations were observed in the northern Pacific and reached 190 ppt, and the minimum ones, in the southern part, approached 140 ppt. The difference

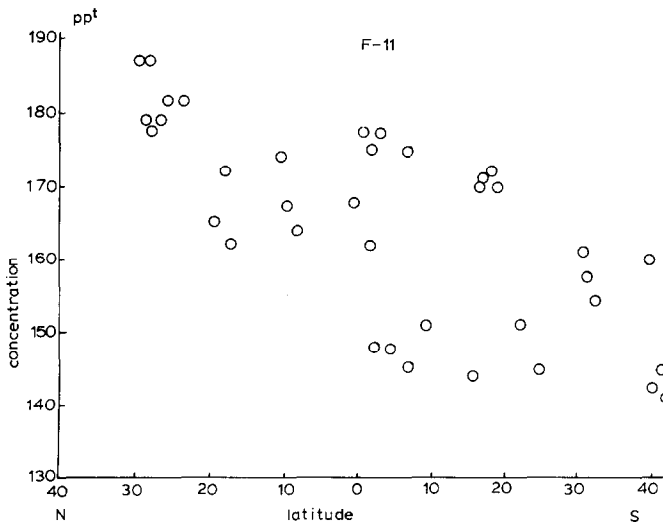


Fig. 6. Latitudinal distribution of F-11 concentration in the near-water layer of the atmosphere above the Pacific ocean.

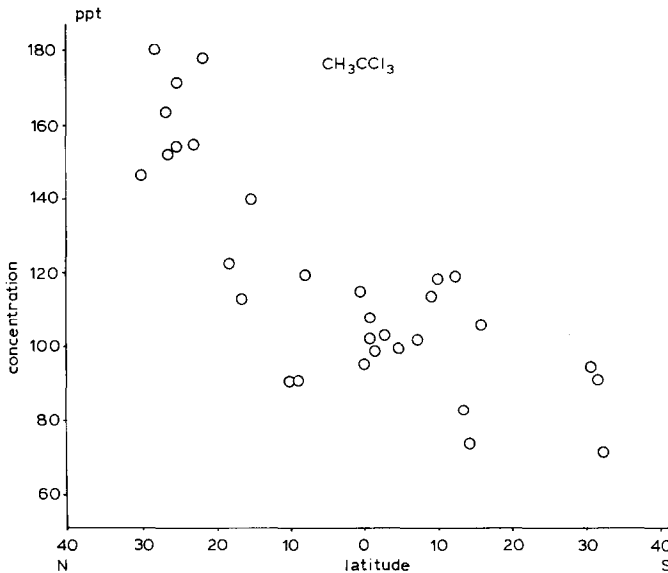


Fig. 7. Latitudinal distribution of CH_3CCl_3 concentration in the near-water layer of the atmosphere above the Pacific ocean.

in concentration of methylchloroform is even more significant: maximum concentrations as large as 180 ppt and minimum ones close to 70 ppt were observed in the northern and southern Pacific, respectively.

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REFERENCES

- 1 M. I. Molina and F. S. Rowland, *Nature (London)*, 249 (1974) 810.
- 2 R. J. Cicerone, R. S. Stolarski and S. Walter, *Science*, 185 (1974) 1165.
- 3 J. E. Lovelock, *Nature (London)*, 230 (1971) 379.
- 4 J. E. Lovelock, R. S. Maggs and R. S. Wade, *Nature (London)*, 241 (1973) 194.
- 5 J. E. Lovelock, *Nature (London)*, 252 (1974) 292.
- 6 J. E. Lovelock, *Nature (London)*, 256 (1975) 193.
- 7 N. E. Hestler, E. K. Stephens and O. C. Taylor, *J. Air. Pollut. Contr. Ass.*, 24 (1974) 591.
- 8 L. Zafonte, N. E. Hestler, E. R. Stephens and O. Taylor, *Atmos. Environ.*, 9 (1975) 1007.
- 9 E. P. Grimsrud and R. A. Rasmussen, *Atmos. Environ.*, 9 (1975) 1010.
- 10 R. A. Rasmussen, D. E. Harsch, P. H. Scwany, J. P. Krasnes and D. K. Cronn, *J. Air Pollut. Contr. Ass.*, 27 (1977) 579.
- 11 J. W. Russell and L. A. Shadoff, *J. Chromatogr.*, 134 (1977) 375.
- 12 L. Wei and M. Kaufmann, *Anal. Chem.*, 48 (1976) 2029.
- 13 F. Bruner, G. Bertoni and G. Crescentini, *J. Chromatogr.*, 167 (1978) 399.
- 14 W. Averill and J. E. Purcell, *Chromatogr. Newsletter*, 6 (1978) 30.
- 15 T. V. Barmakova, *Cand. Sci. Thesis*, (in Russian), Moscow, 1975.
- 16 T. V. Barmakova, A. V. Kiselev, N. V. Kovaleva and L. G. Ryabukhina, *Kolloidn. Zh.*, 41 (1979) 528.
- 17 N. N. Avgul, A. V. Kiselev and Yu. P. Poshkus, *Adsorption of Vapours and Gases on Homogeneous Surfaces*, (in Russian), Khimiya, Moscow, 1975.
- 18 T. V. Barmakova, A. V. Kiselev and N. V. Kovaleva, *Kholloidn. Zh.*, 36 (1974) 934.