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TRACE ANALYSIS OF HALOGENATED HYDROCARBONS IN GASEOUS SAMPLES BY ON-LINE ENRICHMENT IN AN ADSORPTION TRAP, ON-COLUMN COLD-TRAPPING AND CAPILLARY GAS CHROMATOGRAPHY

I. METHOD AND INSTRUMENTATION

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SUMMARY

A method is described for the determination of halocarbons in gaseous samples down to the ppt level ($1:10^{12}$, v/v), consisting of successive on-line sub-ambient enrichment on an adsorbent, on-column cryofocusing, capillary gas chromatography and electron-capture detection. The quantitative aspects of sample transfer throughout the system, trapping/desorption efficiencies and maximum sample volumes of different adsorbents were studied, as well as the efficiency and focusing effect of on-column cold-trapping on capillary OV-101 and alumina porous layer open-tubular columns. The analytical power of the method is demonstrated in the analysis of stratospheric air and an highly complicated industrial problem, *viz.*, the determination of ppb amounts of sulphur–fluorine compounds in a matrix of polluted sulphur hexafluoride.

INTRODUCTION

A large variety of halocarbons is released into the atmosphere by both natural and anthropogenic processes. These compounds play an important role in the photochemical processes of the atmosphere, since they constitute the source of halogen radicals which catalytically destroy ozone. Some of these species also absorb radiation and thus have an effect on climate. Fully halogenated hydrocarbons such as

trichlorofluoromethane (CFC-11) or dichlorodifluoromethane (CFC-12) are almost inert gases in the troposphere. Consequently, they accumulate and gradually diffuse into higher layers of the atmosphere, where they are photolysed. The halogen atoms thereby released convert through catalytic reaction cycles the "odd oxygen species" O_3 and O into molecular oxygen[1]. Molina and Rowland[2] first pointed out that the rapid growth of anthropogenically released CFC-11 and CFC-12 might cause a depletion of the Earth's ozone layer, through chlorine-atom catalyzed destruction in the stratosphere.

The fully halogenated hydrocarbons found in the atmosphere are known to originate almost entirely from anthropogenic sources. Since stratospheric decomposition is the only route to removal of these substances, their atmospheric lifetimes are extremely long, ranging between 55 and 93 years for CFC-11[3] and 10 000 years tetrafluoromethane for (CFC-14)[4], which is the most stable one. Thus, even for modest injection scenarios it can be foreseen that the contribution of these compounds to the halogen budget of the stratosphere will increase with time. Partly halogenated hydrocarbons, e.g., methyl chloride, 1,1,1-trichloroethane or chlorodifluoromethane (CFC-22) or halocarbons with a double bond, e.g., perchloroethylene or trichloroethylene are less stable. They all react with hydroxyl radicals and are thus largely removed by tropospheric reactions. The global release rates of the first category, however, are so large that they nevertheless contribute considerably to the chlorine budget of the stratosphere.

At present, about 3 ppb ($1:10^9$ v/v) organically bound chlorine are present in the atmosphere. Most (78%) is of anthropogenic origin being contained in CFC-12, CFC-11, tetrachloromethane, 1,1,1-trichloroethane, CFC-22 and minor halocarbons such as CFC-113, CFC-114, CFC-115 and CFC-13. Methyl chloride is the only natural source of organically bound chlorine, being released from the oceans. At the present emission rates of halocarbons from anthropogenic sources, the amount of organically bound chlorine will almost double by the end of this century[5].

Compared to tropospheric halocarbon concentrations (Table I), the concentrations in the stratosphere are up to a factor 1000 lower, depending on the substance as well as the altitude. The measurement of halocarbons in the troposphere and stratosphere is important for assessing the sources of halogen radicals. Moreover, the vertical profiles of these compounds provide a powerful tool for testing photochemical models and thus improving our understanding of atmospheric photochemistry and dynamics. Considering their concentrations and the difficulties of taking samples at altitudes up to about 40 km with balloons provided with cryogenic samplers, highly reliable and sensitive analytical systems are required for the quantitation of halocarbons in tropospheric and stratospheric air samples.

In this paper a method is discussed that allows the determination of ppt's of halocarbons in stratospheric air samples by means of capillary gas chromatography (GC) and electron-capture detection (ECD). Necessary preconcentration of the samples prior to GC analysis is performed in an adsorption trap. The efficiencies and recoveries of different adsorption traps are studied and optimized. The required narrow input band width of the sample in the capillary column is obtained by a homemade, highly efficient, cryogenic trap. The reliable calibration methods which are required for the quantitative analysis of stratospheric air samples will be presented in part II of this work. The applicability of the system is demonstrated on a strato-

TABLE I

GLOBAL TROPOSPHERIC ABUNDANCE OF HALOCARBONS ACCORDING TO FABIAN[5]

All figures refer to the 1980 level.

Compound	Trade No.	B.p. (°C)	Average abun-dance (ppt)	Atmospheric lifetime (years)	Main sources
CH_3Cl	40	−24	617	2–3	Natural (oceanic emission)
CCl_2F_2	12	−29	300	105–169 ⎫	Refrigerant, aerosol propellant,
CCl_3F	11	24	175	55–93 ⎬	foam blowing agent
CCl_4	10	77	145	60–100	Solvent
CH_3CCl_3	140a	74	130	5.7–10	Industrial and dry cleaning solvent
$CHClF_2$	22	40	60	12–20	Refrigerant, foam blowing agent
CF_4	14	−129	67	10 000	Natural(?), aluminium production
CH_2Cl_2	30	40	32	0.5	Solvent
$CHCl_3$	20	61	30	0.3–0.6	?
$CCl_2=CCl_2$	1100	121	26	0.4	Solvent
$C_2Cl_3F_3$	113	48	18	63–122	Solvent
CH_3Br	40B1	3.6	115	1.7	Natural (oceanic emission)
$C_2Cl_2F_4$	114	4	11	126–310	Solvent
$CHCl=CCl_2$	1120	87	8	0.02	Solvent
C_2ClF_5	115	−38	4.1	230–550	Propellant and refrigerant
C_2F_6	116	−79	4	500–1000	Aluminium production
$CClF_3$	13	−81	4	180–450	Refrigerant
CH_3I	40I1	43	2	0.01	Natural (oceanic emission)
$CHCl_2F$	21	9	2	2–3	?
CF_3Br	13B1	−59	1	62–112	Fire extinguisher

spheric air sample and a very complicated industrial analytical problem involving the quantitative analysis of trace amounts (down to the ppb level) of disulphur decafluoride (S_2F_{10}) and disulphur oxydecafluoride ($S_2F_{10}O$) in arced sulphur hexafluoride (SF_6). The increasing use of SF_6 as a dielectric medium in electric power equipment has led to concern about its decomposition products, e.g., SOF_2, CF_4, F_2, SO_2F_2, SOF_4, SF_4, H_2S, HF, SO_2, S_2F_{10} and $S_2F_{10}O$[6].

EXPERIMENTAL

Sample introduction

Stratospheric air samples were collected by means of the cryogenic sampling method developed by the Max Planck Institut für Aeronomie[7]. When the proper precautions are taken, no adsorption nor contamination of the sample in the stainless-steel sample bottle is observed[8].

The air samples were enriched by means of the equipment shown in Fig. 1. A known quantity of air, corresponding to a pressure increment in the evacuated reference cylinder (RC) (Whitey 304-HDF4-500), was passed over the home-made adsorption trap (AT) at 100–200 ml/min. After actuation of the valves, the trap was backflushed and the compounds successively thermally desorbed. The released material was trapped and focused in the first part of a capillary column. After comple-
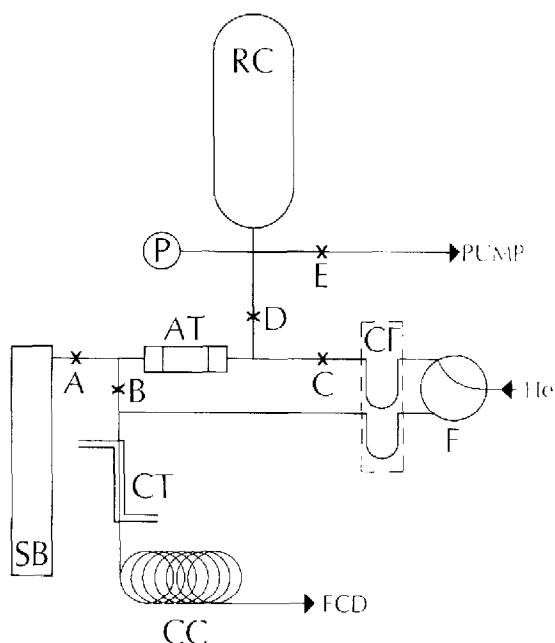
Fig. 1. Sample-introduction system. A–E = Metal bellows valves; F = three-way ball valve; SB = sample bottle; AT = adsorption trap; CT = cold-trap; RC = reference cylinder; P = pressure transducer; CC = capillary column; CF = charcoal filters.

tion of the desorption the trapped sample was re-injected by flash-heating of the cold-trap to start the chromatographic separation. The design allows minimum contact between the sample and stainless-steel surfaces present in the system. Any contact with other materials is excluded. Except for the three-way ball valve (Whitey B-41 XS 2), all valves were Nupro SS-4H metal bellows valves. Stainless-steel tubing was used together with Swagelock couplings. The pressure transducer was a Data Instruments Model AB (0–50 PSIA).

The helium carrier gas was purified by a molecular sieve 5A trap and then passed over two charcoal filters (0.8 m × 5 mm I.D.; charcoal, 10–18 mesh) placed as close as possible to the sample introduction system. These filters were immersed in a solid carbon dioxide–acetone slush (−78°C).

Gas chromatography

A Packard 427 gas chromatograph (Packard Becker, Delft, The Netherlands) was modified for installation of the sample introduction system on top of it. In the first instance a thick film wall-coated open-tubular (WCOT) OV-101 column was used (50 m × 0.22 mm I.D., d_f = 0.6 μm), operated at sub-ambient oven temperatures (increased from −40 to 80°C at 8°/min). The cryogenic unit consisted of a Packard 799 proportional current control, a Cryoson DR4 pressure control unit and a Cryoson NDA32 Dewar vessel (Cryoson Technical Laboratory, Midden Beemster, The Netherlands).

In a later stage of the investigation a new type of capillary column was selected:

a fused-silica porous layer open-tubular (PLOT) column (50 m × 0.32 mm I.D.) with alumina–potassium chloride as the stationary phase (Chrompack, Middelburg, The Netherlands). The GC oven temperature was initially 80°C and then increased to 200°C at 10°C/min. Helium was used as the carrier gas at an average linear velocity of 40 cm/s.

A Carlo Erba Type 40 electron-capture detector in combination with a control module 400 (Carlo Erba, Milan, Italy) was used in the constant-current mode (standing current 1.2 nA, pulse 20 V, pulsewidth 0.1 μs, 250°C). The make-up gas was argon–5% methane at 45 ml/min. Data were processed by a SP 4000 data system (Spectra Physics, Santa Clara, CA, U.S.A.).

Adsorption trap

The double-walled all-glass adsorption trap (Fig. 2) provides the possibility of trapping at sub-ambient temperatures. Cooled nitrogen gas was blown through the jacket via the two hose connections. Desorption takes place upon application of a voltage over the canthal heating wire (diameter 0.25 mm, electrical resistance 20 Ω/m) which is wound around the constricted inner part of the trap at about 15 coils/cm. This construction provides a minimum resistance to heat transport during desorption. The thick walled ends are connected to the inlet system by 0.25-in. Swagelock fittings, using Vespel ferrules. The temperature was recorded by a thermocouple, placed at the centre of the adsorption trap.

Cold-trap

In order to obtain sufficiently narrow injection bands, the desorbed material was cryo-focused on the first part of the chromatographic column. The cold-trap is made of polyimide rod (6 cm × 12 mm) with an axial hole of diameter 2 mm (Fig. 3). The column is passed through a helix of canthal heating wire (see above, ±35 coils/cm), placed inside the trap. Two hose connections enable entry and exit of the coolant. The trap temperature was recorded by means of a thermocouple, introduced via a nut, half-way along the trap. The top of the cold-trap is closed by means of a polyimide screwcap and a thin silicon-rubber septum. The bottom is screwed onto a metal rod passing through the GC injection block.

In the trapping mode, temperatures as low as −196°C can be reached when nitrogen gas is passed through liquid nitrogen. For flash desorption, initially a voltage, V_p, of 20–25 V was applied for several seconds. Then the applied voltage was reduced to a lower preset value, V_s.
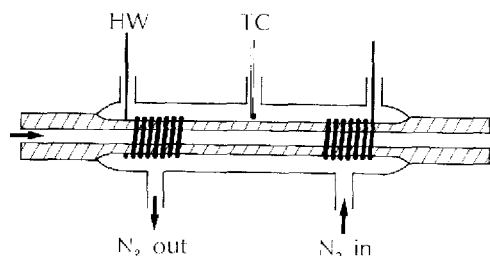

Fig. 2. All-glass adsorption trap. TC = Thermocouple; HW = heating wire. The arrows indicate the flow directions of cold nitrogen and the sample.
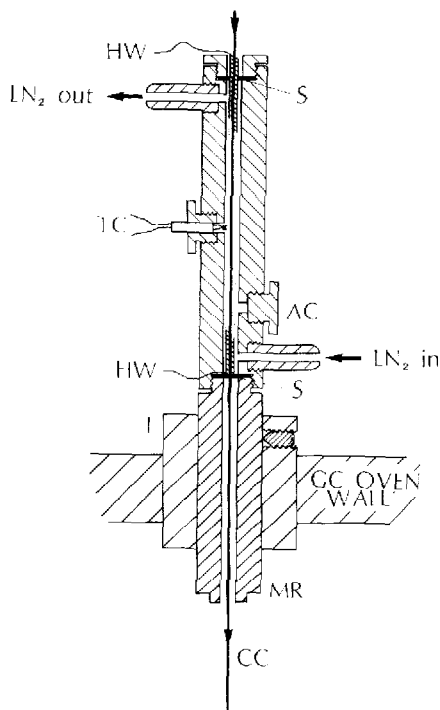
Fig. 3. Cold-trap for on-column cryofocusing. \\\\ = Polyimide parts; //// = metal parts; TC = thermocouple; HW = heating wire; S = rubber septum; MR = metal rod; I = injection block; AC = auxiliary connection; CC = capillary column. The arrows indicate the flow directions of liquid nitrogen and the carrier gas.

RESULTS AND DISCUSSION

Gas chromatography

  The alumina PLOT column is reported to be very suitable for the separation of permanent gases and low boiling compounds[9,10]. This particular type of capillary column does not require sub-ambient oven temperatures for an efficient resolution of halocarbons. As shown by Fig. 4, even both isomers of CFC-114 (dichlorotetra-fluoroethane) are separated, which was not possible on the thick film OV-101 column. Compared to non-polar liquid phases, the selectivity of the alumina stationary phase results in a shift of not completely halogenated hydrocarbons, *e.g.*, CFC-21 and CFC-22, towards longer retention times. Note that the negative baseline drift in Fig. 4 is probably due to a decreasing carrier gas flow caused by the combination of a pressure-controlled system and a high programming rate of the column oven.

  Since S_2F_{10} and $S_2F_{10}O$ could not be separated on the alumina PLOT column[6], the thick film OV-101 column was used for the determination of these compounds in sulphur hexafluoride samples. Temperature programming started with sub-ambient oven temperatures resulted in baseline separation of S_2F_{10} and $S_2F_{10}O$ (Fig. 5.).
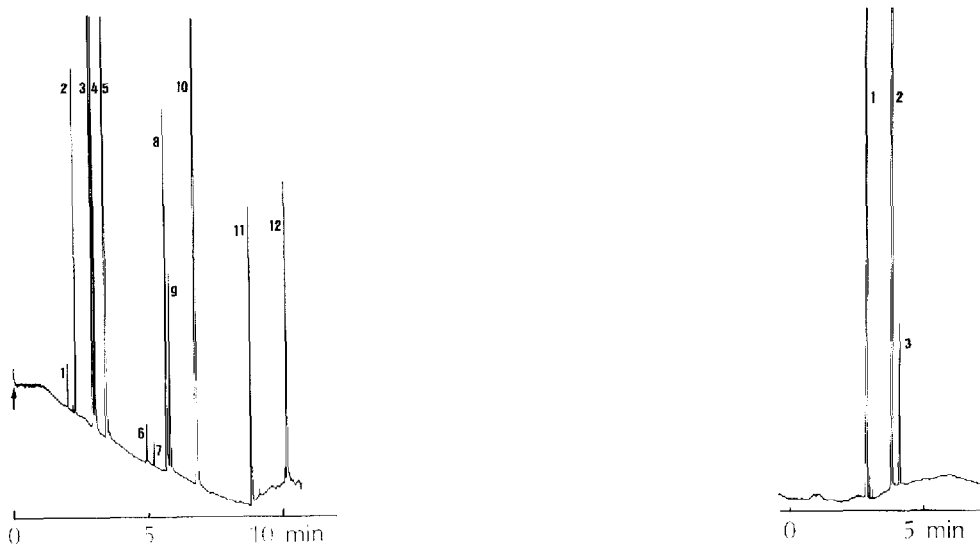
Fig. 4. Analysis of a test mixture of selected halocarbons on the alumina PLOT column (25-μl split injection, splitting ratio 1:120, concentrations between 20 ppm and 1%). Peaks: 1 = air; 2 = CFC-13; 3 = CFC-13B1; 4 = CFC-115; 5 = CFC-12; 6 = methyl chloride (CFC-40); 7 = CFC-22; 8,9 = CFC-114 + isomer; 10 = CFC-11; 11 = CFC-21; 12 = CFC-113.

Fig. 5. Analysis of SF_6, S_2F_{10} and $S_2F_{10}O$ in helium on the thick film OV-101 column (splitting ratio 1:100, sample volume 20 μl; concentrations 100 ppb for S_2F_{10} and $S_2F_{10}O$). Peaks: 1 = SF_6; 2 = S_2F_{10}; 3 = $S_2F_{10}O$.

Adsorption trap

As pointed out by Raymond and Guiochon[11], the enrichment of a gas stream by trapping on an adsorbent can be regarded as a frontal analysis technique. Quantitative trapping will occur until the gas volume that has passed the trap is equal to the retention volume of the compound minus half the base width of the peak ($V_R - \frac{1}{2} w$), in elution chromatography. This is shown in Fig. 6. The maximum sample volume (MSV) at a given temperature can be calculated from the retention volume, V_R, and the plate number, N, of the trap, according to:

$$\mathrm{MSV} = V_R \left(1 - \frac{2}{\sqrt{N}} \right) \tag{1}$$

This approach has been followed by several workers, *e.g.*, refs. 11–13. For reasons of reliability, the direct measurement of maximum sample volumes was preferred for traps with low plate numbers, *e.g.*, refs. 14–17. A helium gas stream of 100 ml/min containing 1 ppm of CFC-12 was fed continuously onto the adsorption trap. The trap was connected to the electron-capture detector via a splitter and a short fused-silica capillary. A typical recording of such an experiment is shown in Fig. 7. The maximum sample volume (MSV), taken as the amount of helium that has passed the trap when the signal has reached 5% of its maximum value, was determined at different temperatures for traps filled with Tenax (3.1 mg), Porapak Q (12 mg), Car-
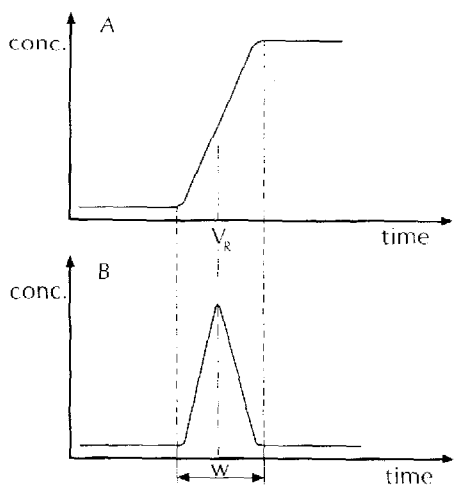
Fig. 6. Concentration profile at the column outlet for frontal analysis (A) and elution chromatography (B).

bopack A (22 mg), charcoal (16 mg) and alumina (43 mg). The experimental results are given in Table II. In those cases where no breakthrough was observed after 2 h of loading, the experiment was terminated. This corresponds to a sample volume of 12 l.

The adsorption capacities of both Tenax and Carbopack A are too small. For charcoal too high desorption temperatures are required. Porapak Q and alumina are suitable with respect to capacity and desorption temperature. In view of the fact that alumina is suspected to react with incompletely halogenated compounds at elevated temperatures[18], Porapak Q was selected as the most favourable adsorbent for the enrichment of air samples in this work.

The trapping efficiency of Porapak Q at different temperatures is demonstrated
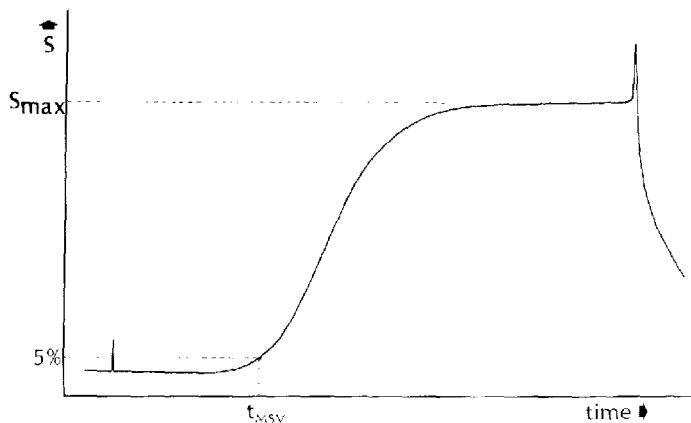

Fig. 7. Detector signal during a breakthrough experiment. S_{max} = Maximum signal; t_{MSV} = time at 5% breakthrough.
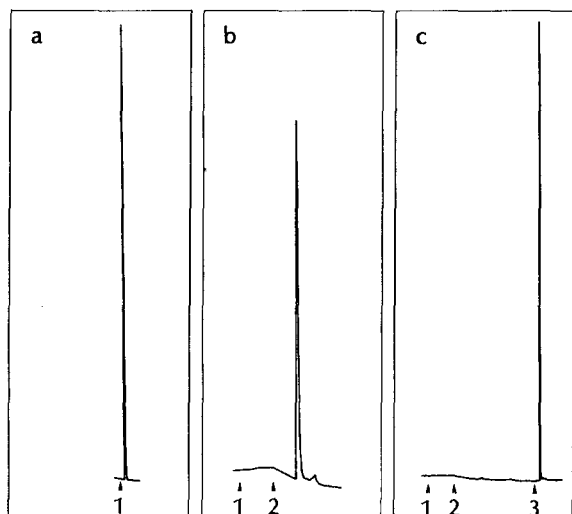
TABLE II

MAXIMUM SAMPLE VOLUMES FOR CFC-12 (1 ppm IN HELIUM FLOW-RATE OF 100 ml/min) ON DIFFERENT ADSORPTION TRAPS AT DIFFERENT TEMPERATURES

Traps: Tenax (3.1 mg); Porapak Q (12 mg); Carbopack A (22 mg), Charcoal (16 mg) and Alumina (43 mg).

Temp. (°C)	MSV (l)				
	Tenax	Porapak Q	Carbopack A	Charcoal	Alumina
150	0	0	0	>12	0
25	0	0	0	>12	0.04
0	0	0.3	0	>12	0.14
−25	0.03	1.2	0.1	>12	3.14
−50	0.1	12	0.1	>12	>12
−75	0.6	>12	0.5	>12	>12
−100	3.3	>12	12	>12	>12
−125	>12	>12	>12	>12	>12

for a number of halocarbons in Table III. The compounds have increasing boiling points ranging from −81°C for CFC-13 up to 48°C for CFC-113. For CFC-12 a temperature of −50°C is sufficiently low for a quantitative trapping, while CFC-13 is not trapped at all. No further improvement in the trapping efficiencies was observed for any of these components by decreasing the trap temperature from −100 to −150°C. Considering the effect of cooling and heating of the trap on the overall analysis time, a temperature of −100°C was selected as the optimum trapping temperature.

On-column cold-trapping

The effect of on-column cold-trapping on the peak shape and band broadening after adsorption/desorption on a Porapak Q adsorption trap is clearly demonstrated by Fig. 8. The injector and detector were successively connected to the adsorption trap, a splitter (splitting ratio 1:100), the cold-trap and a short capillary column. Injection of 25 μl of a helium sample with 100 ppm CFC-12 results in the peak of Fig. 8a when both traps are heated. An identical injection and intermediate trapping at −100°C on the Porapak Q trap followed by thermal desorption without on-column cold-trapping results in a serious peak tailing and band broadening as shown in Fig. 8b. Successive trapping and desorption from the adsorption trap in combi-

TABLE III

RELATIVE TRAPPING RECOVERIES AS A FUNCTION OF TEMPERATURE FOR SELECTED HALOCARBONS ON PORAPAK Q (REFERENCE −150°C)

Temp. (°C)	CFC-13	CFC-13B1	CFC-115	CFC-12	CFC-40	CFC-114	CFC-11	CFC-113
−50	0	26	83	102	100	100	103	106
−100	100	102	100	103	113	108	113	94
−150	100	100	100	100	100	100	100	100

Fig. 8. Effect of cryofocusing on the peak shape: (a) split injection of CFC-12 (20 μl, 100 ppm, splitting ratio 1:100). (b) as (a) with adsorption and thermal desorption on Porapak Q; (c) as (b) with on-column cryofocusing. 1, Injection; 2, desorption of adsorption trap; 3, re-injection by flash heating of cold-trap.

nation with on-column cryofocusing at $-196°C$ and flash-heating gives the result in Fig. 8c. Narrow injection bands, even better than those obtained with split injections at high splitting ratios, are obtained.

The temperature profile inside the cold-trap during flash-heating of the on-column cold-trap was measured off-line with a thin thermocouple placed inside a non-coated capillary (Fig. 9). The maximum temperature, T_{max}, depends on the initially applied so-called primary voltage, V_p, and the flash-heating time. The mini-
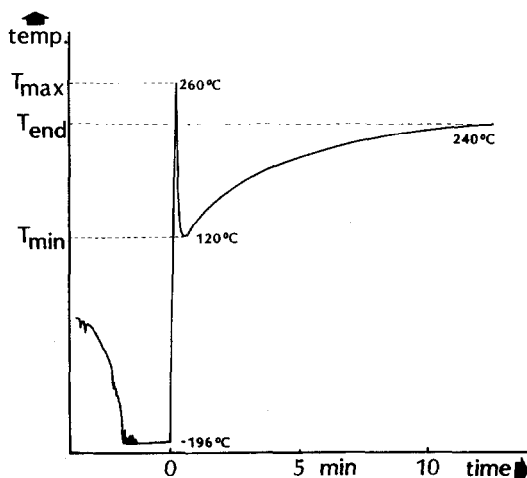
Fig. 9. Temperature profile measured inside the capillary of the on-column cold-trap. The temperatures shown refer to a primary voltage of 25 V, a secondary voltage of 8 V and a flash-heating time of 5 s.

TABLE IV

RELATIVE TRAPPING RECOVERIES AS A FUNCTION OF TRAPPING TIME FOR AN ALUMINA PLOT COLUMN

Trapping temperature: $-196°C$. Reference: split injection.

	CFC-13	CFC-13B1	CFC-115	CFC-12	CFC-114	CFC-11	CFC-113
5 min	92	106	93	104	100	112	133
10 min	92	104	93	96	100	93	133
15 min	89	94	86	91	93	97	142
R.S.D. (split, $n = 4$) (%)	3.5	2.5	1.6	2.9	2.2	13	8.6

mum temperature, T_{min}, depends on the primary voltage as well as on the reduced so-called secondary voltage, V_s, whereas the final temperature, T_{end}, depends only on V_s.

It was found by trial and error that optimum results are obtained when the secondary voltage is applied automatically 5 s after starting of the flash-heating. Apparently the trapping efficiency as well as the adsorption capacity of on-column cryofocusing are improved when alumina PLOT columns are used instead of WCOT OV-101 columns. Due to the adsorption mechanism of the alumina stationary phase, in addition to condensation of the components in the column, volatile compounds are trapped more efficiently. The quantitative performance of the cold-trap was tested by repeated split injections with and without cold-trapping. On the OV-101 column, approximately 100 pg of CFC-12, which was selected for this experiment because of its low boiling point ($-30°C$) and its relatively high ECD response, were trapped at $-196°C$. No losses were observed even after 30 min of trapping. On the alumina PLOT column, however, a representative mixture of halocarbons (quantities ranging
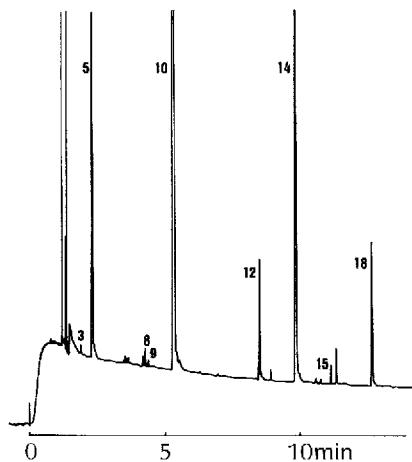

Fig. 10. Analysis of 90 ml of stratospheric air on the alumina PLOT column. Peaks: 3 = CFC-13B1; 4 = CFC-115; 5 = CFC-12; 8,9 = CFC-114 + isomer; 10 = CFC-11; 12 = CFC-113; 14 = CCl_4; 15 = C_2HCl_3; 18 = C_2Cl_4.

from *ca.* 30 pg for CFC-11 up to 10 ng for CFC-13) was trapped at −196°C. The recoveries as a function of trapping time are listed in Table IV. No losses could be observed, not even after a trapping time of 15 min.

Air samples

Stratospheric air samples, collected at an altitude of approximately 17 km[7], were processed using the sample-introduction system of Fig. 1. A representative chromatogram of a 90-ml air sample is shown in Fig. 10. Peak identification was done by addition of diluted standards. Referring to literature data[5], some typical approximate concentrations at this altitude are: CFC-13B1, 0.7 ppt; CFC-12, 200 ppt; CFC-114, 10 ppt; CFC-11, 100 ppt and CFC-113, 10 ppt.

Analysis of sulphur hexafluoride samples

In order to determine ppt concentrations of S_2F_{10} and $S_2F_{10}O$ by capillary GC and ECD, preconcentration of the trace components is required. Simultaneously owing to saturation of the detector with sulphur hexafluoride, most of this component has to be removed. Another complication is the difference in the response factors of S_2F_{10} and $S_2F_{10}O$ which is in the order of two decades, as illustrated in Fig. 5.

Therefore the equipment described in Experimental was slightly modified. The sulphur hexafluoride samples were introduced with a preheated Valco six-port valve (*ca.* 80°C) with a sample volume of 50 μl (Chrompack) and trapped in the first instance on the adsorption trap at −50°C. It was found that, at this particular temperature, SF_6 largely broke through while S_2F_{10} and $S_2F_{10}O$ remained trapped without losses. After passage of the bulk of SF_6 (of which 99.5% is vented via a splitter and only 0.5% is transferred to the capillary column and monitored by ECD, the material trapped on the adsorption trap was thermally desorbed, retrapped and focused on the on-column cold-trap at −196°C. Meanwhile the column oven was cooled to −40°C. On completion of the desorption of the adsorbed compounds and stabilization of the column inlet pressure, the chromatographic process was started by flash-heating of the cold-trap simultaneous with commencement of the GC oven
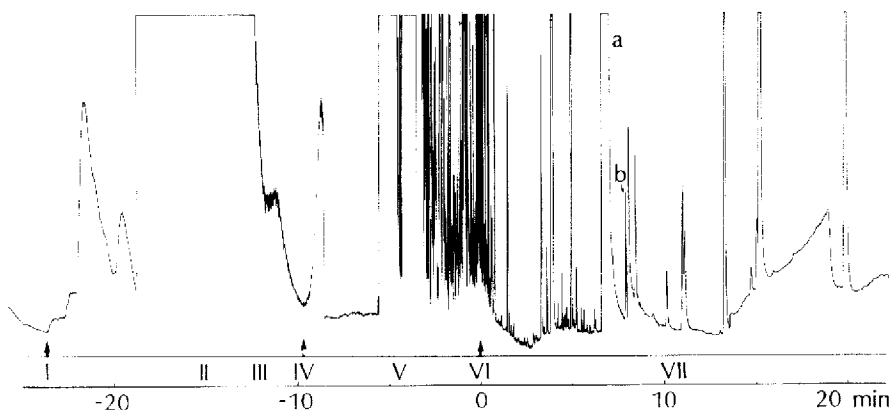

Fig. 11. Analysis of 50 μl of polluted SF_6 on the OV-101 column. For explanation of events I–VII see text. Peaks: a = SF_6; b = S_2F_{10}.

program and the integration. A typical chromatogram including all these steps is presented in Fig. 11. Switching of the six-port sample valve (I) results in the introduction of the sample. The signal of the large peak (II) represents about 0.5% of the SF_6 that has passed the adsorption trap and which is transferred to the column and the detector. At point III the signal suddenly decreases due to the start of cooling of the cold-trap a few minutes before. Thermal desorption of the adsorption trap is started at IV. This results in a breakthrough of SF_6 on the cold-trap (V). Flash-heating of the cold-trap is initiated at VI and the recording of the chromatogram (VII) is started. Peak a represents the residual SF_6, while peak b is S_2F_{10} at a concentration of about 1 ppb.

CONCLUSIONS

The sample-introduction system described provides the possibility of capillary GC analysis of traces of halocarbons present in gaseous samples in concentrations down to the ppt level (v/v). In combination with on-line trace enrichment in an adsorption trap and on-column cryofocusing, it has proved to be an efficient, reliable and powerful tool with the full benefit of the sensitivity and separation capacity of capillary GC.

Porapak Q was found to be the most favourable adsorbent for sub-ambient trapping of volatile halocarbons. A trapping temperature of $-100°C$ appears optimal for the enrichment of even the most volatile compounds. Baseline separations of the halocarbons are easily obtained with capillary alumina PLOT columns without the need for sub-ambient oven temperatures. Such columns also appear to be efficient cryofocusing traps even for traces of highly volatile halocarbons.

The design of the cold-trap allows temperatures as low as $-196°C$ and flash-heating up to $260°C$ within 5 s. The on-line sample enrichment on an adsorption trap and on-column cryofocusing is demonstrated to be an elegant, powerful and reliable method for the selective introduction of trace compounds present in a matrix of interfering bulk components with high ECD responses.

ACKNOWLEDGEMENTS

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