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Note

Fast determination of some halocarbons in the atmosphere by gas chromatography-high-resolution mass spectrometry

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A complete analytical method for the sample collection and determination of halocarbons in the atmosphere has been developed by our group¹. This method, based on the use of highly selective gas chromatographic (GC) columns and high-resolution mass spectrometry (GC-HRMS), permits identification and quantitation of all the C₁ and C₂ halocarbons present in the atmosphere.

While both the accuracy and precision of the method are satisfactory, the overall analysis time, which is an important factor when a large number of samples has to be analysed, was still rather long.

In this paper the method has been modified in order to reduce the analysis time without affecting the specificity and selectivity, which are the actual advantages of our method with respect to those employing low resolution GC-MS^{2,3}. Although the main purpose was to optimize the simultaneous determination of CHFCl₂ (CFC21) and CFCl₃ (CFC11), the method here described can be actually used for a fast, precise and accurate determination of all the halocarbons with the exception of CHF₂Cl (CFC22) and it has been employed in field work carried out in the Sahara desert. As an example of its application, the results regarding the concentrations of CH₃CCl₃ and C₂F₃Cl₃ (CFC113) are also reported.

EXPERIMENTAL

Sampling apparatus

A portable automatic sampler (SEA, Rome, Italy), which employs a flow electronic transducer for flow-rate and sample-volume measurement, was tested and used.

The advantages of this sampling system, which is described in detail elsewhere⁴, are (a) absence of errors due to manual operation; (b) no practical effects of flow-rate variations during sampling, since these are automatically taken into account in the computation of the final volume; (c) automatic and instantaneous stop of sampling at values preselected by the operator and (d) digital display of the flow-rate and volume values under standard conditions. This sampler, when thoroughly tested over a period of two months in the flow-rate range 40-150 ml/min showed a high reliability and a precision of better than 1%. During actual sampling it is routinely used at an initial flow-rate of 100-110 ml/min. The sampling traps made of glass lined stainless

steel (30 cm × 0.3 cm I.D.) contain Carbpac C, 30–60 mesh (Supelco, Bellefonte, PA, U.S.A.), a graphitized carbon black with a surface area of 10 m²/g.

The following procedure was used to purge and prepare the traps. (a) The carbon black (15–20 g) was heated at 300–350°C for 12 h in a stream of ultrapure nitrogen further purified by means of molecular sieves kept at –90°C. (b) The traps were filled for about two thirds of their length with 0.8 g of Carbpac C by gentle vibration. Silanized glass wool, previously purged through step (a) was used to keep the packing in place. (c) Each trap was then checked by GC electron-capture detection and, finally, one out of five, randomly chosen, were checked by GC-MS following the same procedure employed for sample injection. During sampling the temperature of the traps was kept at –90°C via dry-ice refrigeration. Samples were injected by heating the traps at 100°C.

Instrumentation and column

A DANI 3900 gas chromatograph (DANI, Monza, Italy) was directly coupled by means of a jet separator to a VG Micromass 70-70H double-focusing mass spectrometer (VG Organic, Altrincham, U.K.) employed in the selected ion-monitoring (SIM) mode using an eight-channel microprocessed multiple ion detector. All the analyses were carried out at a resolving power of *ca.* 3000 (10% valley). Multiple ion detection programs and the injection and calibration system have been extensively described elsewhere^{1,5}. The system was also equipped with a standard syringe injector and ultrapure helium, further purified by a trap containing molecular sieves kept at –90°C, was used as carrier gas for the GC system and the permeation tubes.

The GC column was made of glass (2 m × 2 mm I.D.) and packed with Carbpac C, 80–100 mesh, coated with 0.1% of SP1000, a free-fatty-acid polar liquid modifier.

RESULTS

Two main advantages arise from the use of Carbpac C, 30–60 mesh, instead of Carbpac B, 60–80 mesh, as the sampling material⁶. The lower mesh range allows use of higher flow-rates so that sampling can be carried out in a shorter time (20 min for 4 l of air). On the other hand, because of the different surface area (10 m²/g against 100 m²/g for Carbpac B) a lower desorption temperature (100°C) can be used in the injection step. Samples are injected into the column by heating the trap for 35 sec in an oven kept at a constant temperature of 300°C. These conditions were chosen after studying the variation of the trap temperature with time for different oven temperatures (Fig. 1).

The trap temperature was measured by inserting a thermocouple into the centre of the trap. Further shortening of the heating time (curve a) was disregarded because problems arose due to the lower homogeneity of the temperature throughout the trap. The higher oven temperature may cause a much too high temperature of the trap periphery which might lead to possible decomposition. Longer heating times (curves c–e) may also cause decomposition, while for temperatures lower than 100°C not all the compounds are completely desorbed. On the basis of these considerations curve b was the one selected for use. Carbpac C traps do not allow simultaneous sampling of CFC22 because this compound shows a very low breakthrough volume (BTV) at –90°C on this adsorbent (Table I).

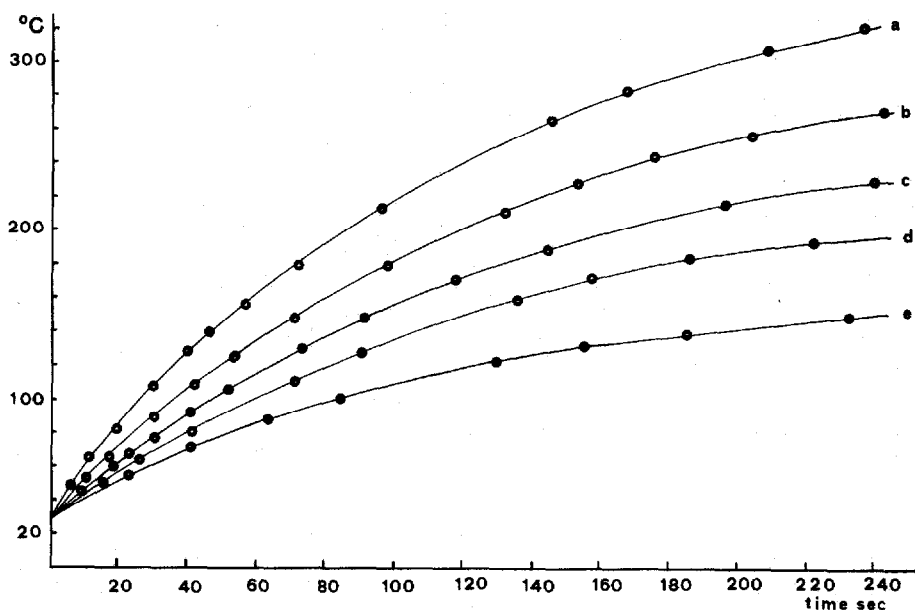


Fig. 1. Variation of the trap temperature with time at oven temperatures of (a) 350, (b) 300, (c) 250, (d) 205 and (e) 155°C.

CF_2Cl_2 (CFC12) can be retained if the volume of the samples does not exceed 0.3 l. However, this volume would be large enough to determine the concentration of CFC12 and other halocarbons such as CFC11 because of their relatively high atmospheric abundance. Furthermore, although differences exist in the detector response owing to the different ionization efficiency of the molecules and to the E/E_0 values of the accelerating voltage during the SIM program, the response of the mass spectrometer towards different halocarbons is quite uniform¹ especially when compared to the electron-capture detector. This is true unless very peculiar situations arise, as in the case of CFC21, which is often present in ultratrace amounts [< 2 parts

TABLE I

CRITICAL PARAMETERS OF THE PRESENT METHOD FOR ANALYSIS OF CFCs

Compound	Breakthrough volumes (ml at standard temperature and pressure on Carbopack C at -90°C)	Detection limit (ppt) with a 300 ml air sample	Average background concentration (ppt)
CFC22	30	—	42-52
CFC12	300	16	270-300
CFC21	4000	4.0	0-3*
CFC11	> 10000	4.0	170-190
CFC113	> 10000	2.6	12-22
CH_3CCl_3	> 10000	4.0	130-140
C_2HCl_3	> 10000	2.6	10-15
CCl_4	> 10000	21	130-135

* Most probable atmospheric concentration.

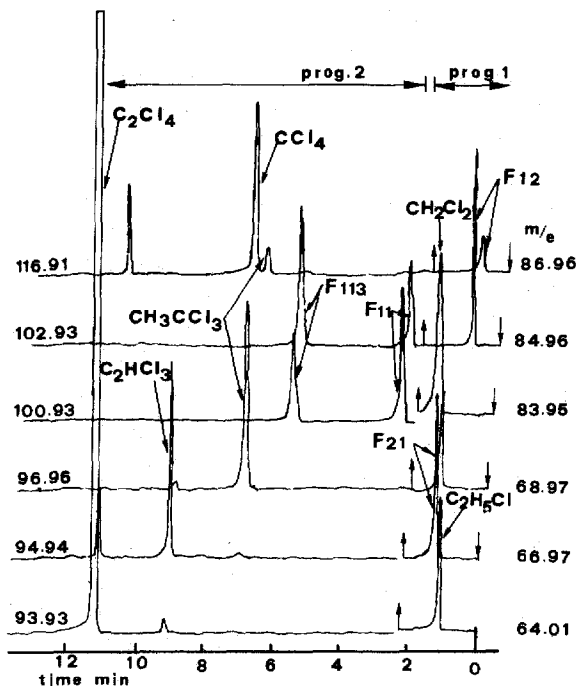


Fig. 2. Mass spectrum of a standard halocarbon mixture. Column: Carbopack C, 80-100 mesh, +0.1% SP1000. Conditions: *P*, 3 atm; initial flow-rate, 40 ml/min; temperature programme, 4 min at 40°C, rising at 20°C/min to 200°C.

per trillion (ppt)*] so that larger volumes of air are needed. The maximum amount of air that can be sampled is 4 l, this value being the CFC21 breakthrough volume on Carbopack C. Under these conditions, 0.3 ppt of CFC21 can be detected while the determination of other halocarbons is not affected because of the wide range of linearity of the mass spectrometer¹.

Fig. 2 shows the mass spectrum of a standard halocarbon mixture obtained with the Carbopack C column used in this work. It should be noted that it is possible to carry out the analysis in less than 12 min and that in particular the time required for determination of CFC21 and CFC11 is lower than 3 min (42 and 17 min, respectively, were required, for the same determinations with the Carbopack B column). This is quite a remarkable result if one takes into account that it was obtained without losing the selectivity and specificity of the previous method¹.

The precision of the method was tested by the following experiment carried out on CFC11, CFC21 and CH₃CCl₃. A constant artificial atmosphere was generated using permeation tubes as sources of these compounds, 4 l of which were sampled with the apparatus described and analysed. The results obtained gave relative standard deviations of ±3.4, 3.7, 4 and 3.8% for CFC11, CFC21, CH₃CCl₃ and CFC113, respectively.

* Throughout this article the American trillion (10¹²) is meant.

In actual atmospheric measurements, the relative standard deviation values did not differ from the values obtained in the first experiment for CFC11. For CH_3CCl_3 and CFC113 a standard deviation of about 10% was found in field measurements. The higher standard deviations found may be ascribed to the lower concentration of CFC113 in field measurements, but we have no ready explanation of the higher value for CH_3CCl_3 .

The method here described has been used to measure the concentration of some halocarbons in the atmosphere in the Northern Sahara desert at two locations: El Dabah, which is located on the Egyptian coast 200 km west of Alexandria, and Baharyia, which is an oasis about 300 km south of the first location. Parallel samples were taken at both locations at three different hours each day. The concentrations of two compounds, $\text{C}_2\text{Cl}_3\text{F}_3$ (CFC113) and CH_3CCl_3 , are reported in Tables II and III (for El Dabah and Baharyia, respectively). Each result is the average of two values obtained from the paired samples except for cases where problems arose during sampling and/or analysis. The mean hourly values (\bar{x}) and the mean value obtained from all the measurements are (\bar{X}) also reported, together with the standard deviations.

The single values are in good agreement, as are the hourly mean values, and this shows that the concentration is fairly constant both throughout the day and over all the period of sampling. Moreover, the concentration is, within experimental error, the same at the two locations.

In conclusion, by properly exploiting the advantages of HRMS, it is possible

TABLE II

 CH_3CCl_3 AND CFC113 CONCENTRATION VALUES (ppt) AT EL DABAH

GMT = Greenwich mean time. Year, 1982

Day	CH_3CCl_3			CFC113		
	Time (GMT)					
	0600	1200	1800	0600	1200	1800
6/5	126	115	137	28.0	28.5	41.3
7/5	128	136	131	31.2	31.5	28.0
8/5	—	152	141	29.8	36.7	34.5
9/5	114	129	—	31.6	37.5	42.8
10/5	129	123	123	27.2	32.9	34.1
11/5	125	—	—	33.0	31.4	33.9
12/5	—	—	113	—	—	29.9
13/5	112	133	128	29.6	—	—
16/5	138	126	148	29.2	27.6	34.7
17/5	149	125	98	35.4	33.6	28.3
18/5	134	—	136	35.5	32.9	34.6
19/5	124	133	124	34.1	33.8	33.0
20/5	132	122	120	33.8	32.0	32.7
21/5	123	132	119	32.8	34.1	37.8
22/5	128	—	—	35.6	—	—
$(\bar{x}) \pm \sigma$	127.8 ± 9.6	129.6 ± 9.6	126.5 ± 13.5	31.9 ± 2.8	32.7 ± 2.9	34.3 ± 4.4
$(\bar{X}) \pm \sigma$		128.0 ± 10.9			33.0 ± 2.9	

TABLE III

CH₃CCl₃ AND CFC113 CONCENTRATION VALUES (ppt) AT BAHARYIA

GMT = Greenwich mean time. Year, 1982.

Day	CH ₃ CCl ₃			CFC113		
	Time (GMT)					
	0600	1200	1800	0600	1200	1800
6/5	123	—	149	—	—	32.0
7/5	154	114	108	26.6	34.0	30.0
8/5	139	157	128	29.2	31.0	31.7
9/5	128	124	138	29.9	30.4	32.5
10/5	113	117	—	38.4	26.3	31.1
11/5	114	125	115	28.5	20.2	29.3
12/5	—	121	—	33.8	31.2	33.7
13/5	132	129	120	33.6	28.0	31.0
16/5	112	—	134	32.6	—	31.4
17/5	164	138	—	36.5	35.3	37.0
18/5	140	120	124	33.7	30.9	30.5
19/5	138	122	111	32.9	30.5	30.1
20/5	135	149	126	29.8	32.5	29.4
21/5	129	128	—	31.9	32.6	36.8
22/5	—	—	—	—	—	—
(\bar{x}) ± σ	132.4 ± 15.4	128.7 ± 12.2	125.3 ± 12.0	32.1 ± 3.4	30.2 ± 4.0	31.9 ± 2.4
(\bar{X}) ± σ		128.8 ± 13.2			31.4 ± 3.1	

to use shorter and less retentive GC columns which allow a much faster elution of the compounds of interest. This is true provided that for compounds with the same retention time it is possible to choose ions with different m/e values. This is clearly impossible if one uses electron-capture detection or low-resolution MS.

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