Analysis of replacement chlorofluorocarbons using carboxen microtraps for isolation and preconcentration in gas chromatography–mass spectrometry

S.J. O'Doherty*, P.G. Simmonds and G. Nickless

Biogeochemistry Centre, University of Bristol, Cantocks Close, Bristol BS8 1TS (UK)

ABSTRACT

A microtrap containing a mixture of Carboxen 1000/1003 has successfully been developed for trapping and preconcentrating the very volatile replacement chlorofluorocarbons (CFCs) (fluorinated hydrofluorocarbons and hydrochlorofluorocarbons) from sample volumes of several litres. We have shown that a mixture of replacement CFCs can be quantitatively adsorbed and desorbed when a Carboxen-filled microtrap is held at −50°C, thus negating the need for cryotrapping, or cryofocussing using liquid nitrogen. The adsorbed compounds are rapidly desorbed by the direct ballistic heating of the microtrap to a temperature of 260°C in about 4 s. The application of these microtraps in the automated GC–MS analysis of the replacement CFCs and other environmentally important trace gases is presently under development in our laboratories for eventual deployment in remote atmospheric monitoring stations.

INTRODUCTION

The replacement chlorofluorocarbons (CFCs) fall into two groups, the hydrochlorofluorocarbons (HCFCs) and the fluorinated hydrofluorocarbons (HFCs), this latter term will be used to describe all of the replacement CFCs in this paper. Introduction of hydrogen atoms into the CFC molecule reduces the molecular energy, and hence the stability resulting in oxidative destruction of the HFCs in the troposphere, primarily by OH radical attack. The ozone depleting potentials of the HFCs is typically zero to ten percent that of CFCs and from 10 to 100 times less in terms of atmospheric warming potential [1–3]. Industrial sources indicate that, at the present time, the following HFCs are the most likely to be used as replacements; HFC 125, 143a, 134a, 22, 124, 142b and 123. The

chemical formulae, molecular masses, and boiling points are listed in Table I.

Methods for the analysis of atmospheric trace constituents include canister and cartridge sampling [4,5], and whole air cryotrapping with a post desorption cryofocussing step using liquid nitrogen [6–10]. There are logistic difficulties in supplying liquid nitrogen to remote locations on

TABLE I

PHYSICAL CHARACTERISTICS HFCs

Compound	Structure	Boiling point (°C)	M_r
HFC 125	CF_3CF_2H	−48.4	120
HFC 143a	CF_3CH_3	−47.6	84
HCFC 22	$CHClF_2$	−40.8	86
HFC 134a	CF_3CH_2F	−25.9	102
HCFC 124	CF_3CFHCl	−11.8	136
HCFC 142b	CH_3CF_2Cl	−9.8	101
HCFC 123	CF_3CHCl_2	28.0	152

---

* Corresponding author.

a routine basis, and the cost can be over US
$100/(day · system) [11]. An alternative approach
employs microtraps filled with a suitable ad-
sorbent which allows direct thermal desorption
into a capillary column thereby bypassing the
cryofocussing step [12–15]. We have followed
and improved this approach using very small
microtraps filled with carbon molecular sieve
type adsorbents ("Carboxens"). However, to
achieve adequate sensitivity for mass spectral
detection of the HFCs at ppt (v/v) concentra-
tions they must be quantitatively trapped from
several litres of air. Clearly for compounds such
as HFCs, which are not strongly retained by
most of the commonly used adsorbents, the need
to trap large sample volumes conflicts with the
design of a microtrap containing a minimal
amount of adsorbent. In an earlier paper [16] we
described how this problem could be solved,
using Carboxen-filled microtraps for the precon-
centration of very volatile HFCs at sub ambient
temperatures by maintaining the microtrap in a
small dewar cooled to a temperature of −50°C
using a Neslab Cryocool Immersion cooler
(Portsmouth, UK), thus avoiding the use of
liquid nitrogen. To achieve optimal chromato-
graphic resolution and efficiency it is important
to match the dimensions of the microtrap and
the gas flows to those of the capillary column. It
is also desirable to heat the trap as rapidly as
possible to prevent band spreading during the
desorption stage. We present here the means by
which the trapped HFCs can be quantitatively
desorbed from the Carboxen microtraps directly
onto a capillary column connected to a Finnigan
MAT ion trap mass spectrometer.

EXPERIMENTAL

Microtraps

The design of the microtraps used in the
experiments can be used in Fig. 1. The length of
the microtraps and the amount and type of
Carboxen material used could be varied to suit
the type of analysis being carried out. However,
the small dimensions of the trap coupled with the
small quantity of adsorbent used in these experi-
ments is consistent with the objective of main-
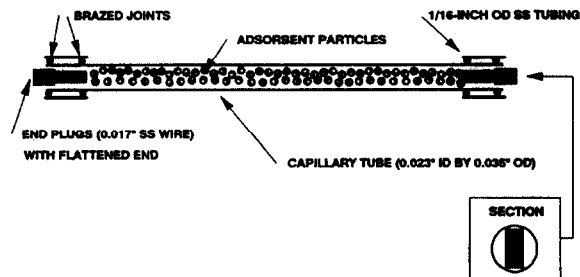taining rapid desorption and efficient chromato-

Fig. 1. Microtrap (overall length 18 cm). SS = Stainless steel;
" = inch (1 inch = 2.54 cm).

graphic resolution. The microtraps were main-
tained at −50°C by cooling the airspace in a
sealed dewer, using a Cryocool Immersion
cooler. The microtraps were heated in early
experiments by applying 60 V a.c. from a vari-
able transformer to an external heating wire
wrapped round the trap, this raised the tempera-
ture to approximately 260°C in 10 s. A more
rapid method of heating was subsequently
adopted by the use of direct resistive heating of
the microtrap itself.

Sample preconcentration

The major components of the sample pre-
concentration system are illustrated in Fig. 2. All
tubing used was SS 306 (stainless steel) (1/16 or
1/8 in. O.D.), connections were made either by
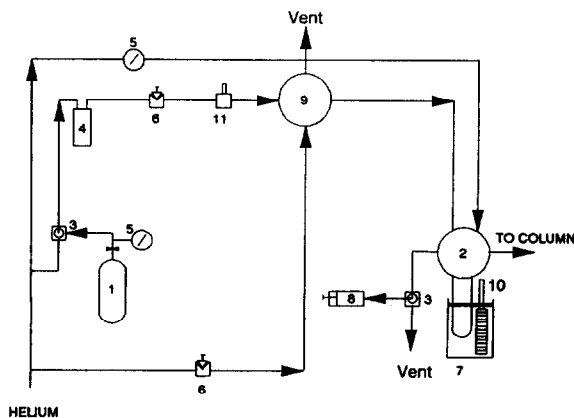stainless steel Swagelok or Valco fittings. A

Fig. 2. Cryogenic preconcentration apparatus. 1 = Sample
canister; 2 = 6-port valve; 3 = 3-way valve; 4 = Nafion drier;
5 = pressure regulator; 6 = needle valve; 7 = sample loop in a
dewer; 8 = volume measurement; 9 = 4-port valve; 10 =
cryoprobe; 11 = toggle valve.

standard HFC mixture was contained in a 30-l electropolished stainless steel canister. The canister was connected to a 3-way valve (Whitey ss-41xs2), which permitted either sample or helium to be passed through a drier, which consisted of nafion tubing in a container packed with molecular sieve 5A [17]. The flow-rate was controlled using a Nupro fine metering valve. Two Valco valves were used, the first 4-port valve enabled the system to this point be purged with helium or sample. The second valve, a 6-port switching valve, allowed sample or helium to be passed through the trap in one mode (sample or helium purge mode), in the other mode (desorption mode) helium column flow passed through the trap. The second 3-way valve (Hamilton, HVP 3-3) and syringe enabled determination of the volume of sample passed through the microtrap.

Gas chromatography–mass spectrometry (GC–MS) conditions

All experiments were carried out using a Finnigan ITS-40 GC–MS apparatus. Separation of the HFC mixture was carried out using two separate columns (a) CPSil-5 50 m, 0.32 mm I.D., 5-μm film thickness wall-coated open tubu-

lar (WCOT) capillary column, (b) Alumina Al_2O_3/KCl 50 m, 0.32 mm I.D., 5-μm film thickness porous-layer open tubular (PLOT) capillary column. The GC–MS conditions used in the experiments can be seen in Table II. Detailed chromatographic separations of a large number of HFCs and CFCs have been reported elsewhere [18].

RESULTS AND DISCUSSION

Carboxen 1003 using CP Sil-5 column

A microtrap containing Carboxen 1003 (30 cm × 0.058 cm I.D., 22 mg, 60/80 mesh), previously tested for its adsorptive properties, using methods described in an earlier paper [16], appeared to have a similar capacity to that of Carboxen 1000 (the strongest HFC absorber) for a number of HFC compounds. Desorption tests with this adsorbent were carried out at room temperature followed by tests at −50°C. Initial observations indicates that complete desorption of the HFCs, especially the higher boiling ones, was not possible at the heating rate employed (60 V a.c. for 10 s), the trap was heated 4 times before complete desorption was effected. Using a digital thermometer with a thermocouple connected directly to the trap the heating rate and maximum temperature achieved was monitored for different Variac output voltages. The optimum heating rate was determined by replicate desorptions from the Carboxen 1003 trap, while noting each HFCs peak area, peak width at half height and retention time. Fig. 3 illustrates the effect of altering the desorption heating rates on peak shape, as expected, the faster heating rate produces more efficient and better resolved peaks.

Using the optimised desorption heating rate (140 V a.c. for 2 s), increasing amounts of HFC mixture were adsorbed/desorbed from the trap and the regression lines for each HFC plotted. As can be seen from Figs. 4 and 5, each HFC standard can be quantitatively adsorbed/desorbed from Carboxen 1003 at room temperature for volumes ranging from 1–25 ml. However, in practice, where it is necessary to quantitatively trap trace amounts of HFCs from several litres of air then the microtrap must be cooled. A num-

TABLE II

GC–MS CONDITIONS

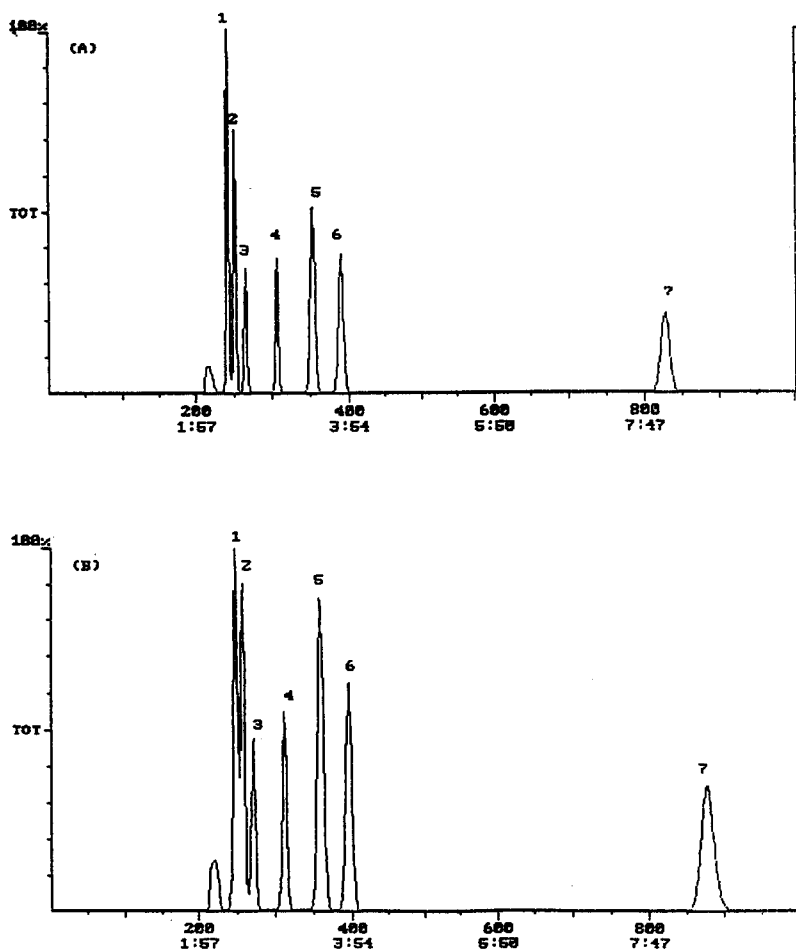| Conditions	CPSil-5 column	Al_2O_3/KCl column
GC conditions		
Carrier gas	Helium	Helium
Flow rate (ml/min)	1	1
Oven	30°C isothermal	30°C hold 3 min 15°C/min, 180°C hold 12 min
Transfer line (°C)	50	180
MS conditions		
Mass scan range	15–170	15–170
Acquire time (min)	10	30
Peak threshold	10	10
Mass defect	0	0
Ionization mode	Electron impact	Electron impact
Auto gain control	On	On

Fig. 3. Effect of different desorption heating rates on peak shape. (A) 140 V a.c. for 2 s; (B) 60 V a.c. for 10 s. Peaks; 1 = 125; 2 = 143a; 3 = 134a; 4 = 22; 5 = 124; 6 = 142b; 7 = 123. Scales on x-axis: (top) scan No.; (bottom) time in min:s.

ber of problems were encountered as soon as the trap was cooled using the Cryocool probe. Firstly the trap contained approximately twice the quantity of adsorbent necessary to quantitatively trap the least retained HFC at −50°C. This excess volume of adsorbent made it difficult to efficiently desorb the HFC standard at sub-ambient temperatures. Although, the trap heating rate was not affected significantly by the sub-ambient temperature, the post-desorption cooling rate was much more rapid resulting in possible readsorption of the HFCs before they have had a chance to leave the trap thereby compromising resolution and quantitation of the most volatile HFCs. Secondly, a problem of co-elution of residual contaminant compounds such

as carbon dioxide, nitrogen, water and oxygen can induce ion-molecule reactions which adversely affects quantitation of the early eluting HFCs. It has been reported [19] that when a trap is heated, any exogenous water collected on the trap will be transferred onto the GC column along with the compounds of interest, the water coats the column this creates a negative solvent effect and disrupts the proper interaction of the analytes with the column stationary phase. This could result in broadened peaks, reduced sensitivity and unstable quantitative % R.S.D.s, especially for those compounds that elute before or with the water; in addition reconstructed ion chromatography (RIC) baseline drop off at the end of water peak elution causes unstable area
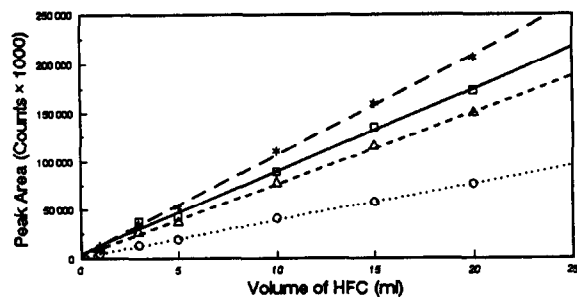
Fig. 4. Quantitation of Carboxen 1003 using total ion current (TIC) for HFC mixture at room temperature. Correlation coefficients: 125 (□) = 0.995; 143a (△) = 0.999; 134a (○) = 0.998; 142b (∗) = 0.998.
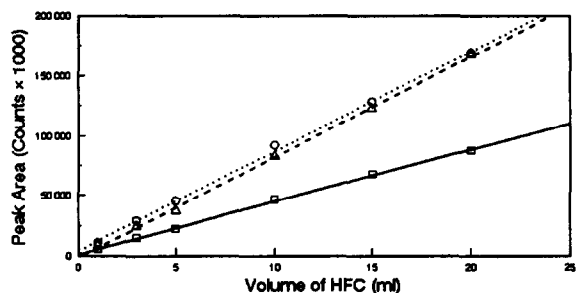

Fig. 5. Quantitation of Carboxen 1003 using TIC for HFC mixture at room temperature. Correlation coefficients: 22 (□) = 0.999; 124 (△) = 0.999; 123 (○) = 0.998.

peak counts for analytes that elute in the same region. Finally, background water can result in the loss of molecular ion intensity for some compounds due to a combination of charge exchange and proton transfer with water.

The preferred solution to these problems is to use the minimum amount of Carboxen adsorbent necessary for quantitative trapping of the least retained HFC, and to increase the retention time of the early eluting HFCs relative to the contaminant compounds.

Carboxen 1000 using alumina PLOT column

An alumina/KCl PLOT capillary column was used as an alternative to the CPSil-5 column since other studies carried out in our laboratory indicated that the HFCs and potential contaminants were better separated. However, it had also been previously reported from a number of separate sources [20–22] that owing to the basicity of alumina PLOT columns, they showed a
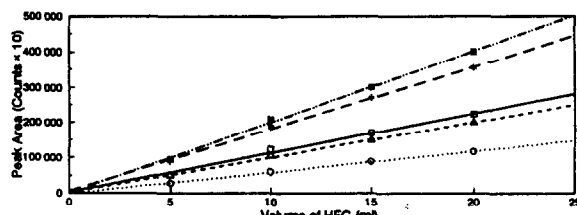

Fig. 6. Quantitation of Carboxen 1000 with HFC mixture using TIC results (alumina PLOT column). Trap at room temperature. Correlation coefficients: 143a (□) = 0.990; 125 (△) = 0.996; 134a (○) = 0.998; 142b (∗) = 0.998; 124 (■) = 0.998.

tendency to cause dehydrohalogenation of some HFCs. Also from earlier adsorbent studies using both direct and indirect methods to test adsorbent performance [17] Carboxen 1000 was found to be the strongest adsorbent for the lowest boiling HFCs. Therefore, a microtrap containing Carboxen 1000 was tested to determine if the HFCs could also be efficiently desorbed. A microtrap containing only 11 mg of Carboxen 1000 (18 cm × 0.058 cm I.D., 10 cm active length, 45–60 mesh) was subjected to the same tests described above for the Carboxen 1003 adsorbent. Figs. 6–8 illustrate that all of the HFCs except HFC 22 and the highest boiling HFC 123 can be quantitatively trapped and
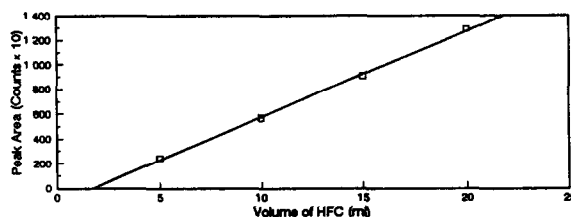

Fig. 7. Quantitation of Carboxen 1000 with HFC mixture using TIC results (alumina PLOT column): 22. Trap at room temperature. Correlation coefficient = 0.998.
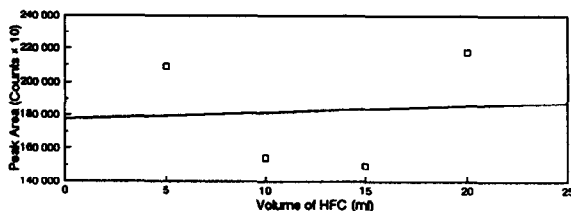

Fig. 8. Quantitation of Carboxen 1000 with HFC mixture using TIC results (alumina PLOT column): 123. Trap at room temperature. Correlation coefficient 0.005.

desorbed at room temperature, for standard sample volumes between 5 and 20 ml. Interestingly, Fig. 7 shows that HFC 22 is not only dehydrohalogenated but dehydrohalogenated quantitatively as indicated by a correlation coefficient close to the value of 1 and a negative intercept. Fig. 8 shows that no correlation exists between the amount of HFC 123 trapped and the amount desorbed, suggesting that Carboxen 1000 traps HFC 123 so strongly that it cannot be efficiently desorbed at the temperatures currently employed (*ca.* 260°C). Subsequent experiments revealed that CFC 123 is strongly retained and possibly dehydrohalogenated by the Alumina PLOT column which adversely affects its quantitation. It is clear from the above results that Carboxen 1000 is the adsorbent of choice for the low boiling HFCs, but perhaps too strong an adsorbent for the higher boiling HFCs. It was not necessary to continue further tests, at sub-ambient temperatures, since this would only accentuate the problem by increasing the adsorbents capacity. The logical progression from this point is to use a combination microtrap with a weaker adsorbent material in front of Carboxen 1000, so that the higher boiling HFCs would be trapped before reaching the Carboxen 1000. Any lower boiling HFCs, which break through the first adsorbent would be retained by the Carboxen 1000, thus enabling all HFCs to be quantitatively trapped and desorbed.

Carboxen 1003 and Carboxen 1000 dual adsorbent microtrap

A dual adsorbent microtrap containing Carboxen 1003 (6 mg) and Carboxen 1000 (5 mg) (24 cm × 0.058 cm I.D., 14 cm active length, 60–80 mesh) was tested using the same procedure as previously described. Since the CPSil-5 column was currently installed in the ITS-40, it was decided that quantitation of the less volatile HFCs (22, 142b, 124 and 123) would be carried out using this column, and quantitation of the most volatile HFCs (143a, 125 and 134a) would be carried out using the alumina PLOT column. This procedure for quantitation was also necessary since it has been previously demonstrated that the alumina PLOT column dehydrohalogenates HFC 22, and other CFCs and halocarbons.
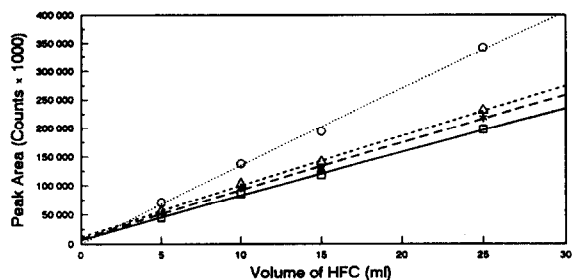

Fig. 9. Quantitation of a mixed Carboxen trap used to trap increasing volumes of HFC mixture (CPSil-5). Correlation coefficients; 22 (□) = 0.999; 124 (△) = 0.999; 142b (○) = 0.997; 123 (*) = 0.998. Trap at −50°C.

The results shown in Fig. 9 indicate that the less volatile HFCs can be quantitatively trapped and desorbed from a mixed Carboxen trap maintained at a sub ambient temperature of −50°C, in addition to this Fig. 10 shows that each of the HFCs (with the exception of HFC 124), can be trapped and will not be displaced even after passing 2 l of helium through the trap before the compounds are desorbed. Interestingly, if quantitation using peak heights is carried out it appears that HFC 124 is not displaced. It should be noted that HFC 123 behaves normally when desorbed onto the CPSil capillary, thereby confirming that earlier problems associated with this compound were related to losses on the alumina PLOT column and not the adsorbent.

These tests were then repeated using the alumina PLOT column. The results shown in Figs. 11 and 12 confirm the above results in addition to showing that the lower boiling HFCs can also be quantitatively trapped and desorbed at sub-ambient temperatures.
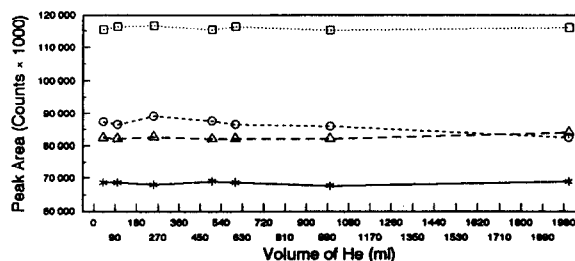

Fig. 10. Peak area *vs.* desorption of 10 ml of HFC sample after passing increasing volumes of helium through mixed Carboxen trap. CPSil-5 column; trap at −50°C. * = 22; ○ = 124; □ = 142b; △ = 123.
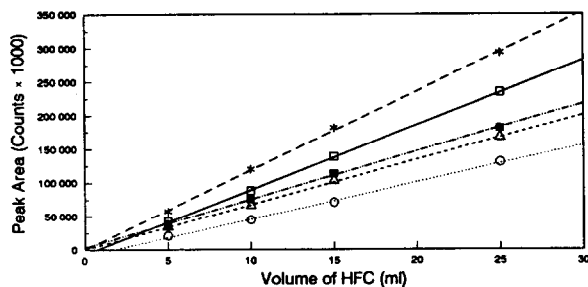
Fig. 11. Quantitation of a mixed Carboxen trap used to trap increasing volumes of HFC mixture (alumina PLOT column). Trap at −50°C. Correlation coefficients: 143a (□) = 0.999; 125 (△) = 0.999; 134a (○) = 0.997; 142b (*) = 0.999; 124 (■) = 0.999.

CONCLUSIONS

It has been shown that the very volatile HFCs can be quantitatively trapped and desorbed from a mixed Carboxen microtrap without the use of liquid cryogens. In order to determine the HFCs in ambient air we have assumed a basic detection threshold to be 1 ppt (v/v). For a compound such as HFC 142b with a molecular mass of 101 this is equivalent to $4.5 \cdot 10^{-15}$ g. Hence, with a mass spectrometer sensitivity of 10 picograms this would necessitate concentration of the compound from about 2.2 litres of ambient air. The results presented here indicate that it would be possible to trap and preconcentrate the HFCs from a 2–3 l air sample. In addition, a main concern was that by desorbing from a microtrap at a flow-rate of 1 ml/min (governed by the maximum flow-rate into the ion trap), the peak shape and resolution of the HFCs might not be preserved, this concern was proved to be unfounded. It is clear that the design of the microtrap with its near capillary dimensions, the
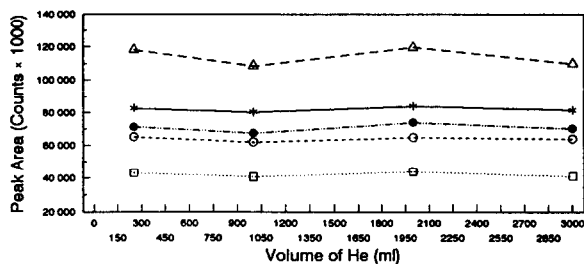

Fig. 12. Peak area vs. desorption of 10 ml of HFC sample after passing increasing volumes of helium through mixed Carboxen trap. Alumina PLOT column; trap at −50°C. * = 143a; ○ = 125; □ = 134a; △ = 142b; ● = 124.

small amount of Carboxen material needed to trap the HFCs at −50°C and the rapid and efficient heating system provide a simple, efficient and cost effective alternative to the usual method of cryogenic trapping and cryofocussing of very volatile compounds.

REFERENCES

1 Scientific Assessment of Stratospheric Ozone, Vol. II, Appendix: AFEAS Report, Sec. IX; Report No. 20, World Meteorological Organization Global Ozone Research and Monitoring Project, 1989, 380–401.
2 D.A. Fisher, C.H. Hales, D.L. Filkin, M.K.W. Ko, N. Dak Sze, P.S. Connell, D.J. Wuebbles, I.S.A. Isaken and F. Stordal, Nature, 344 (1990) 508–516.
3 Alternatives to Chlorofluorocarbons, Bulletin AG-1, Freon Production Laboratory, DuPont Chemicals, Wilmington, DE, 1991.
4 F.J. Reineke and K. Bachmann, J. Chromatogr., 323 (1985) 323–329.
5 S. Muller and M. Oehme, J. High Resolut. Chromatogr., 13 (1990) 34–39.
6 M. Teronia and G. Alaerts, J. Chromatogr., 328 (1985) 367.
7 N. Schmidbauer and M. Oehme, J. High Resolut. Chromatogr., 8 (1985) 404–406.
8 T. Kohno and K. Kuwata, J. Chromatogr., 587 (1991) 338–342.
9 P.V. Doskey, J. High Resolut. Chromatogr., 14 (1991) 724–728.
10 N. Kirshen and E. Almasi, J. High Resolut. Chromatogr., 14 (1991) 484–489.
11 E.A. Woolfenden and G.M. Broadway, LC-GC Int., 5(12) (1992) 28–35.
12 J.B. Phillips, J.R. Valentin and G.C. Carle, ASTM Spec. Tech. Publ., 13 (1982) 135–141.
13 W. Frank and H. Frank, Chromatographia, 29 (1990) 571–574.
14 K. Grob, A. Artho, C. Frauenfelder and I. Roth, J. High Resolut. Chromatogr., 13 (1990) 257–260.
15 H. Frank, W. Frank, H.J.C. Neves and R. Englert, Fresenius' J. Anal. Chem., 340 (1991) 678–683.
16 S.J. O'Doherty, P.J. Simmonds and G. Nickless, J. Chromatogr., 630 (1993) 265–274.
17 B.E. Foulger and P.G. Simmonds, Anal. Chem., 51 (1979) 1089–1090.
18 G.A. Sturrock, P.G. Simmonds and G. Nickless, J. Chromatogr., 648 (1993) 423–431.
19 E. Johnson and A. Madden, Technical Report No. 616, Finnigan MAT, Hemel Hempstead, UK.
20 T. Noij, J.A. Rijks and C.A. Cramers, Chromatographia, 26 (1988) 139–141.
21 T. Noij, P. Fabian, R. Borchers, C.A. Cramers and J.A. Rijks, Chromatographia, 26 (1988) 149–156.
22 L. Burgess and D.M. Kavanagh, New Fluorochemicals Team: Technical Note No. 12, ICI Chemicals & Polymers Ltd., September 1989.