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Analysis of chlorofluorocarbon replacement compounds by capillary gas chromatography

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ABSTRACT

Several thick film wall-coated open tubular and porous-layer open tubular (PLOT) type capillary columns have been investigated for the separation of wide boiling range (−57.8 to 61.2°C) of hydrofluorocarbons (HFCs) and halocarbons. The aim is to select the best column in terms of resolution, analysis time and conditions suitable for use in conjunction with an automated air analysis method for these compounds which are intended as replacements for the ozone-depleting chlorofluorocarbons. The problems associated with each column are reported with emphasis on the catalytic activity of two types of alumina PLOT columns towards certain HFCs and halocarbons. Due to their inherent basicity, the alumina PLOT columns induce dehydrochlorination reactions in spite of the additional deactivation of the alumina with KCl and Na_2SO_4.

INTRODUCTION

The use of many fully halogenated compounds is restricted by international agreement because chlorine has been linked to the destruction of stratospheric ozone [1]. Concern over the global environmental consequences of chlorofluorocarbons (CFCs) has lead to the development of alternative compounds [2]. Candidate replacements are composed of either carbon, hydrogen and fluorine (hydrofluorocarbons or HFCs) or carbon, hydrogen, chlorine and fluorine (hydrochlorofluorocarbons or HCFCs). For simplicity, both classes of compounds are referred to here as HFCs. The HFCs, unlike CFCs, are destroyed by reaction with atmospheric hydroxyl radicals due to the presence of the more labile carbon to hydrogen bond. This occurs principally in the troposphere —thus reducing the amount of chlorine radicals entering the stratosphere and the loss of ozone [3]. However, a portion of the emitted HFCs will eventually reach the stratosphere and with large estimated global release they will add substantially to the chlorine content of the stratosphere. More importantly, HFCs are highly effective absorbers of infrared radiation and their unrestrained use would contribute eventually to global warming [4]. Thus, it is vital to be able to identify and quantify individual HFCs and other halocarbons to assess their rates of accumulation. Any monitoring technique will require the separation of all HFCs with high resolution to allow correct identification and accurate quantitation.

Most early gas chromatographic analyses of volatile compounds in air have been performed on packed columns due to the ease of sample introduction and the advantageous phase ratio of this type of column. However, very volatile compounds (boiling point <150°C) can also be

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analysed by capillary gas chromatography due to the development of both thick-film wall-coated open tubular (WCOT) and high-capacity porous-layer open tubular (PLOT) columns [5]. Specialized packed columns and combination packed columns, operated in series, have been described for the analysis of complex CFC and HFC mixtures [6,7]. In this paper, several types of capillary columns are evaluated in conjunction with a flame ionization detector for the analysis of volatile HFCs and halocarbons, both qualitative and quantitative observations are reported.

PLOT columns with aluminium oxide-coated fused-silica stationary phases have proved very suitable for GC separation of volatile organic compounds such as C_1–C_{10} hydrocarbons [8–10] and C_1–C_2 halocarbons [11]. However, without additional deactivation, the activity of the alumina surface causes peak tailing and the retention mechanism is very sensitive to the water content of the carrier gas. These adverse effects are reduced either by KCl or Na_2SO_4 deactivation of the alumina phase. Previous work has shown that the alumina/KCl PLOT column [12] and packed alumina columns [13] induce catalytic dehydrohalogenation of some halogenated compounds, due to the basicity of the alumina, which is enhanced by the presence of water or chlorine, thus forming a strong Brönsted acid. This catalytic activity, which is most efficient at the maximum operating temperature of the columns (200°C), may abstract HCl molecules from the HFCs —forming carbonium ions and subsequent reaction byproducts. The alumina/KCl column, already known for its destruction of HFC 22 [14], was also found in the experiment described below, to destroy CH_3Cl. Additional HFC's were also found to be destroyed on the alumina/Na_2SO_4 PLOT column, especially at elevated temperatures. The suspect HFCs were examined by comparison of their peak areas after separation on a WCOT CP Sil-5 CB (inert) column and on the alumina PLOT columns —to ascertain the suitability of these columns in the analysis of HFCs. Any decomposition of HFCs obviously restricts the use of these alumina PLOT columns despite the excellent baseline resolution of the HFC's from other ubiquitous halocarbons, CFCs and potentially interfering trace atmospheric gases.

To avoid any complications provided by the activity of the alumina towards volatile organic compounds [15], the utilization of porous polymers as packing materials [16] is now widespread in GC. Therefore, an assessment of the separation capabilities of three PoraPLOT columns (Q, S and U) was included in this study. PoraPLOT columns are conventional fused-silica PLOT capillary columns coated with styrene–divinylbenzene copolymers of different surface areas and polarities. The adsorbent is deposited onto the column as a thin layer of between 5–20 μm and achieves higher resolving power over the standard Porapak packed column [17]. These columns provide high selectivity for volatile compounds, short analysis times and good reproducibility. Their relative non-sensitivity to oxygen and water, and maximum operating temperature of 250°C are advantageous in temperature programming. Their principal disadvantages are their relatively long retention times for higher boiling compounds and bleed at elevated temperatures which complicates their use in GC–MS applications.

Three WCOT CP-Sil CB columns (CP-Sil 5 CB, 13 CB and 19 CB) were also studied to assess their separating ability for various HFC–halocarbon mixtures. These WCOT columns are again superior to packed columns due to greater inertness, longer life, shorter retention times, lower bleed, higher efficiencies and greater reproducibility. The stationary phase is a mixture of different chemically bonded siloxanes, allowing a variation in column polarity and selectivity. The simultaneous determination of polar and non-polar low-molecular-mass compounds has been demonstrated on these columns [18], but limited data is available on the behaviour of these columns relative to the resolution of HFCs. Earlier tests on the CP-Sil 5 CB column gave incomplete baseline resolution of the most volatile HFCs —even at a column temperature of 30°C. The two alternative CP-Sil 13 CB and 19 CB columns exhibit slightly greater polarity which it is hoped would enhance the resolution of the HFCs.

EXPERIMENTAL

Reagents and materials

Individual HFCs and CFCs investigated in the study are listed with their boiling points, structures and molecular mass in Table I. Individual HFC standards were prepared by dilution with nitrogen of pure standards supplied by ICI Chemicals (Runcorn, UK) in deactivated stainless steel canisters; 13B1 and CH_3Cl were purchased in lecture bottles (BDH, Poole, UK); 12B1 (BCF) from a fire extinguisher, CH_2Cl_2 and $CHCl_3$ as headspace from liquids (Aldrich, Gillingham, UK) and methane gas from the natural gas supply in the laboratory (% CH_4 in natural gas supply is 93% from independent experiment). Hydrogen, air and oxygen free nitrogen (BOC, Guildford, UK) were used for the flame ionization detector. The column carrier gas was purified helium (BOC).

Chromatographic conditions

The experiments were carried out on a CP 9000 gas chromatograph (Chrompack, Middelburg, Netherlands) with a flame ionization detector at 200°C and an injection temperature of 150°C. The columns, supplied by Chrompack, are shown in Table II. A helium carrier gas flow-rate of *ca.* 2 ml/min was used on the narrow-bore (0.32 mm I.D.) columns and *ca.* 5 ml/min on the wide-bore (0.53 mm I.D.) columns.

Individual HFCs and methane were injected at a series of different isothermal column temperatures. Syringe injections of 100 μl of halocarbons were made for narrow-bore columns using a 500-μl gas-tight Hamilton syringe. A sample loop of 50 μl and valve injection system was incorporated for the wide bore PoraPLOT S column. Columns were operated isothermally over a range of temperatures and with temperature programming. The isothermal retention data was used for the optimization of the various temperature-programmed gas chromatograph separations of the prepared HFC standard mixture, shown in Table III, on the PoraPLOT and Alumina PLOT columns. Temperature programming was not required on the WCOT columns.

Temperature programmes (TPs). TP 1: 40°C (3 min) 9°C/min; 85°C (3 min) 10°C/min; 140°C. A faster temperature gradient could be included at the end of the programme for the alumina PLOT columns to elute the less volatile CH_2Cl_2, HFC 123 and $CHCl_3$ in a more reasonable analysis time, so the following were used: TP 2: 30°C (3 min) to 180°C at 10°C/min, and TP 3: 40°C to 180°C at 10°C/min. However, the least volatile compounds are obscured by the greater column bleed on the alumina/Na_2SO_4 PLOT column at these higher temperatures.

Several olefins (ethene, propene, *n*-butene and pentene), CFCs (11, 12 and 113) and CH_3CCl_3 and CCl_4 (all ubiquitous in ambient air samples) were included in the temperature programmed analyses to see if they coeluted with any of the HFCs under study.

Analysis of a standard HFC mixture, containing HFCs as shown in Table III up to and including compound 12B1, on the WCOT columns at isothermal temperature was obtained for comparison of peak areas to assess the losses of the susceptible HFCs on the alumina PLOT columns. Examples of the separations of the HFCs obtained on all the columns are shown (Figs. 1–4).

TABLE I

COMPOUND DESCRIPTION

Trade name	Compound	Boiling point (°C)	Molecular mass
13B1	CF_3Br	−57.9	148.87
125	CF_2HCF_3	−48.8	120.02
143a	CF_3CH_3	−47.6	84.04
22	$CHClF_2$	−40.8	86.47
12	CF_2Cl_2	−29.8	120.00
134a	CH_2FCF_3	−25.9	102.03
40	CH_3Cl	−24.0	50.49
124	CF_3CFHCl	−11.8	136.48
142b	CH_3CF_2Cl	−9.8	100.50
12B1	$CBrClF_2$	−4.0	165.33
123	CF_3CHCl_2	20.0	152.93
11	$CFCl_3$	23.6	136.00
30	CH_2Cl_2	40.0	84.94
113	$CF_2ClCFCl_2$	47.7	186.00
20	$CHCl_3$	61.2	119.39

TABLE II

DESCRIPTION OF COLUMN TYPES

(A) Alumina PLOT columns			
Column type	PLOT-fused-silica		
Column length	50 m		
Stationary phase	Alumina (Al_2O_3)		
Deactivation by	(1) KCl;	(2) $NaSO_4$	
Film thickness (μm)	5.00	5.00	
I.D. (mm)	0.32	0.32	
O.D. (mm)	0.43	0.43	
(B) PoraPLOT columns			
Column type	PLOT fused-silica		
Column length	27.5 m × 2.5 m inclusive particle trap		
Stationary phase[a]	PoraPLOT Q	PoraPLOT S	PoraPLOT U
Surface area/m^2/g	582	460	366
Polarity	2.0	3.5	7.0
Film thickness (μm)	10	20	10
I.D. (mm)	0.32	0.53	0.32
O.D. (mm)	0.43	0.70	0.43
(C) WCOT columns			
Column type	WCOT fused-silica		
Column length	50 m		
Stationary phase	CP-Sil 5 CB	CP-Sil 13 CB	CP-Sil 19 CB
Chemical composition			
Dimethyl siloxane	100%	86%	85%
Phenyl siloxane		14%	7%
Cyanopropyl siloxane			7%
Vinyl siloxane			1%
Film thickness (μm)	5.00	2.50	2.50
I.D. (mm)	0.32	0.32	0.32
O.D. (mm)	0.43	0.43	0.43

[a] PoraPLOT Q = Styrene–divinylbenzene; PoraPLOT S = divinylbenzene–vinylpyridine; PoraPLOT U = divinylbenzene–ethyleneglycol–dimethylacrylate.

TABLE III

HFC STANDARD MIXTURE

Trade name	Volume (μl) in 100 ml	nmol/μl	μg/μl
13B1	400	0.179	26.583
125	100	0.045	5.358
143a	100	0.045	3.752
22	200	0.089	7.721
134a	100	0.045	4.555
40	100	0.045	2.254
124	100	0.045	6.093
142b	100	0.045	4.487
12B1	400	0.179	29.523
123	200	0.089	13.654
30	1000	0.446	37.920
20	1500	0.670	79.949

RESULTS AND DISCUSSION

The reproducibility of the retention times in both isothermal and temperature programmed analyses proved to be excellent for all the alumina/PLOT, PoraPLOT and WCOT columns studied. Data shown in Table IV.

Alumina/KCl PLOT and alumina/Na_2SO_4 PLOT capillary columns

Extensive hydrogen bonding was observed between the HFCs and the alumina PLOT columns which increases the retention of HFCs on these columns and alters their elution order from following the boiling point order exactly. The greatest increase in retention time is observed with HFC 125 and 124 and is probably due to the

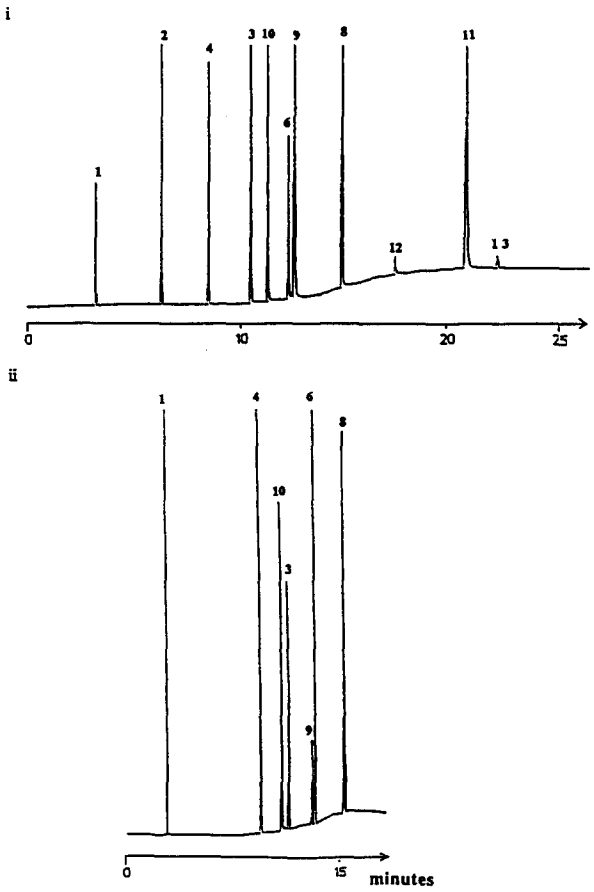

Fig. 1. Separation of HFC Standard mixture. Temperature programme: 40 to 180°C at 10°C/min. (i) Column: 50 m × 0.32 mm I.D. alumina/KCl PLOT; carrier gas: 100 kPa helium. (ii) Column: 50 m × 0.32 mm I.D. alumina/Na_2SO_4 PLOT; carrier gas: 120 kPa helium. Peak identification (also for all subsequent chromatograms): 1 = CH_4; 2 = 13B1; 3 = HFC 125; 4 = HFC 143a; 5 = HFC 22; 6 = HFC 134a; 7 = CH_3Cl; 8 = HFC 124; 9 = HFC 142b; 10 = 12B1; 11 = HFC 123; 12 = CH_2Cl_2; 13 = $CHCl_3$.

TABLE IV

REPRODUCIBILITY OF RETENTION TIMES FOR HFC 125 AND HFC 134

Compound	Column type	Conditions	Retention times (min) ($n = 6$)
125	Alumina/KCl	T.P. 2	14.35 ± 0.03%
	PoraPLOT Q	T.P. 1	6.35 ± 0.07%
	CP Sil 13 CB	40°C	4.74 ± 0.07%
134a	Alumina/KCl	T.P. 2	16.25 ± 0.04%
	PoraPLOT Q	T.P. 1	7.86 ± 0.09%
	CP Sil 13 CB	40°C	4.79 ± 0.08%

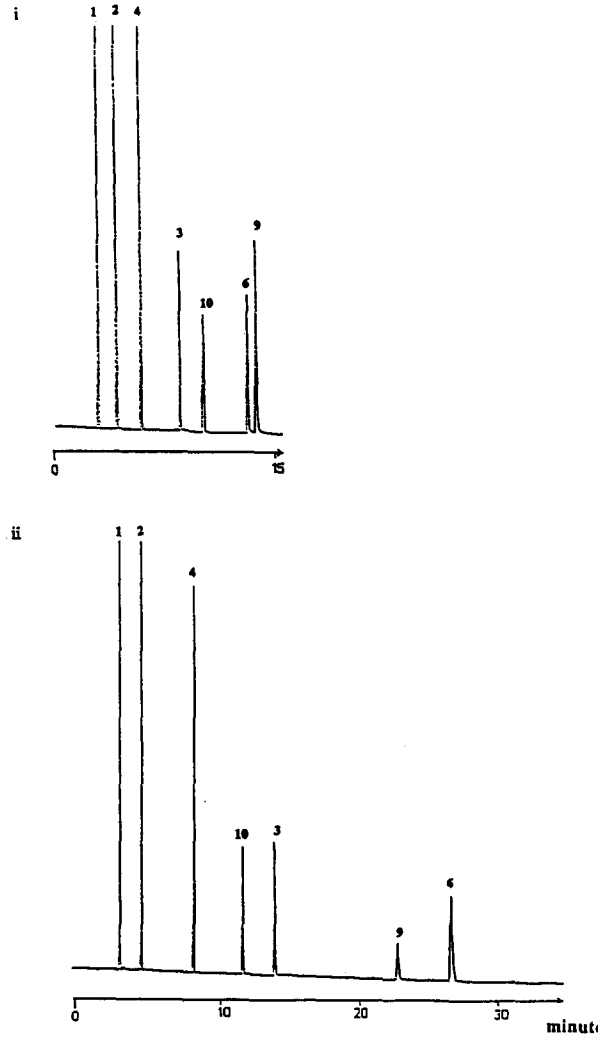

Fig. 2. Separation of HFC standard mixture up to and including compound 12B1 at 100°C, showing dehydrohalogenating effects on (i) alumina/KCl PLOT; carrier gas: 90 kPa helium; and (ii) alumina/Na_2SO_4 PLOT; carrier gas: 120 kPa helium.

presence of a lone polarisable hydrogen atom. Compounds 13B1 and 12B1, containing no hydrogen atoms, are the least retained compounds on both alumina columns with only HFC 143a eluting before 12B1 on the alumina/Na_2SO_4 PLOT at 100°C.

In addition to HFC 22 —already known to be dehydrohalogenated by the alumina/KCl PLOT column, CH_3Cl was progressively destroyed with increasing column temperatures. This resulted in the complete loss of response to CH_3Cl in all

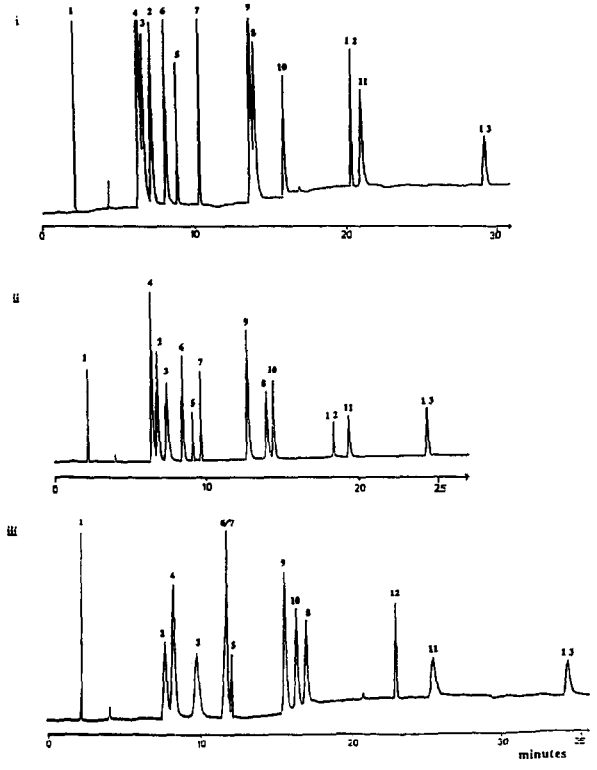

Fig. 3. Separation of HFC standard mixture on PoraPLOT columns. Temperature programme: 40°C (3 min) to 85°C at 9°C/min, 85°C (3 min) to 140°C at 10°C/min. (i) PoraPLOT Q; carrier gas: 65 kPa; (ii) PoraPLOT S; carrier gas: 25 kPa; and (iii) PoraPLOT U; carrier gas: 65 kPa.

temperature programmes. Similarly on the alumina/Na_2SO_4 PLOT column, both compounds HFC 22 and CH_3Cl are destroyed, and in addition HFC 142b is also partially dehydrohalogenated, especially at higher temperatures. The inherent basicity of the alumina stationary phase causes dehydrochlorination of certain HFCs probably leading to the formation of the corresponding unsaturated material. The extent of this breakdown varies according to the substituents on the carbon atoms, the more polar compounds having the highest tendency to undergo dehydrochlorination.

The stability factor K_s [15] is a measure for the inertness of a compound with respect to the reactivity of the alumina stationary phase and is expressed as:

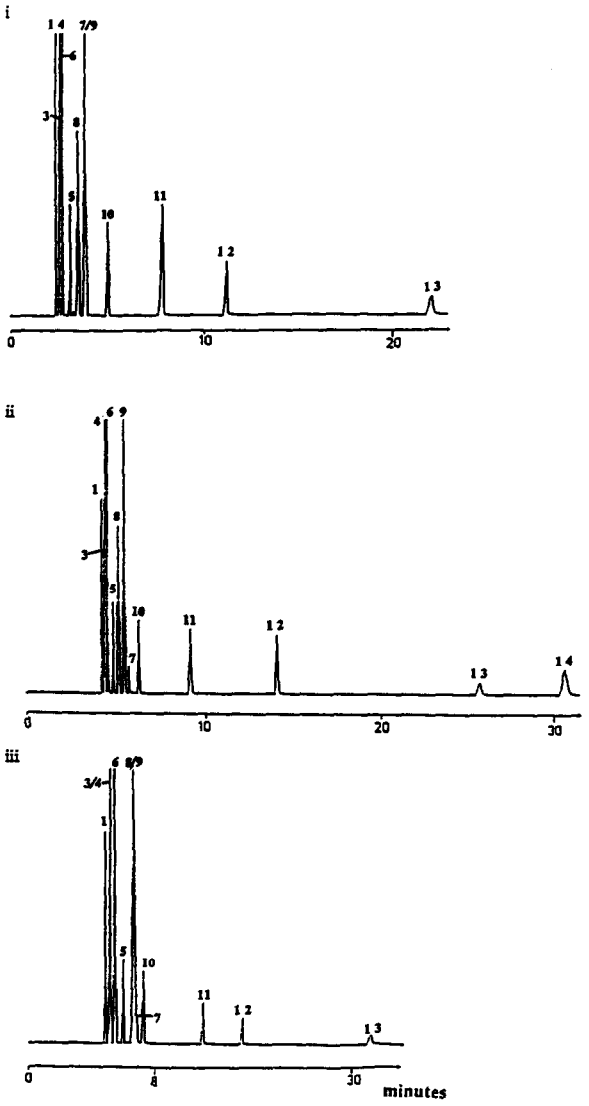

Fig. 4. Separation of HFC standard mixture on CP Sil CB columns at 40°C on (i) CP Sil 5 CB; carrier gas: 100 kPa; (ii) CP Sil 13 CB; carrier gas: 70 kPa; additional peak 14 = CH_3CCl_3; and (iii) CP Sil 19 CB; carrier gas: 70 kPa.

$$K_s = \frac{(A_j/A_s)_2}{(A_j/A_s)_1}$$

where A is the peak area of the respective HFC (j) and internal standard (s) for the CF Sil-5 CB column (1) and the alumina PLOT column (2). Irreversible adsorption or catalytic decomposition on the alumina PLOT column is indicated by $K_s = 0$ and no catalytic reactivity is indicated

by values close to unity. A comparison of the K_s values of several compounds are listed in Table V for the alumina/Na_2SO_4 PLOT column at various temperatures compared against the WCOT CP Sil-5 CB column, where no dehydrohalogenation occurs.

From Table V it is clear that the fluorine substituted HFCs (143a, 125 and 134a) all have K_s values close to unity and are therefore unaffected by the catalytic activity of the alumina phase. Similarly, the fully halogenated 12B1 is stable. Subsequent experiments have shown this is also true for all fully halogenated compounds. The compounds specifically affected are HFC 22, 142b, 123 [19] and CH_3Cl. Peaks corresponding to HFC 22 and CH_3Cl are absent on the alumina/Na_2SO_4 PLOT column and a significant decrease in the area of HFC 142b is also found as the temperature increases. Surprisingly HFC 124, which could potentially be dehydrochlorinated, appears to be stable [19].

Isothermal operation of the columns above 100°C is required for the elution of the higher boiling HFC 124 in a reasonable time and with good peak shape. The separation of all the compounds of interest is obtained on both alumina PLOT columns with high chromatographic resolution, and there is almost no coelution with other atmospheric CFCs. Isothermal operation below 100°C, although suitable for the most volatile compounds, causes severe peak broadening for compounds with boiling points greater than −10°C. However, despite the excellent peak resolution achieved, the dehydrohalogenating activity of these Alumina columns at elevated temperatures restricts their use to the fully halogenated and fluorine-substituted HFCs. It would, of course, still be possible to use multidimensional chromatography where the alumina PLOT column is used to resolve the stable HFCs, and a thick film WCOT column is used in the analysis of a wide boiling range of HFC and halocarbon mixtures, containing compounds specifically susceptible to dehydrochlorination.

TABLE V

STABILITY FACTORS (K_s) FOR CERTAIN HFCs ON THE ALUMINA/Na_2SO_4 PLOT COLUMN AT VARIOUS TEMPERATURES

HFC	Temperature (°C)					
	95	105	115	125	TP2	TP3
143a	0.95	1.01	0.93	0.94	0.98	1.03
12B1	1.07	1.22	1.08	1.14	1.14	0.93
125	0.93	1.02	0.93	0.94	0.99	1.07
142b	0.52	0.43	0.35	0.26	0.13	0.000025
134a	0.89	0.98	0.90	0.90	0.93	0.94
124	–	0.97	0.88	0.91	0.95	1.01
22	0.00	0.00	0.00	0.00	0.00	0.00
CH_3Cl	0.00	0.00	0.00	0.00	0.00	0.00

PoraPLOT columns

Both molecular mass and boiling point govern the separation of the HFCs and halocarbons on PoraPLOT columns, although the polarity of the sorbate and sorbent appear to be of some influence —this becoming more apparent on PoraPLOT S and U columns. The elution order and retention times can be explained by taking into account a compound boiling point along with its molecular size and possible surface interactions with the PoraPLOT stationary phase.

Surface area effect. The effect of interaction between the porous polymer surface and compound molecular size is especially prominent for compounds 13B1 and 12B1. These two compounds are essentially non polar and do not contain a polarisable hydrogen atom so any polarity effects can be ignored. Therefore, the retention of these compounds is governed by interaction of the large bromine group with the polymer surface. For PoraPLOT Q, which has the largest surface area, 13B1 is retained for longer than both the higher boiling, less volatile HFC 125 and 143a. For PoraPLOT S, 13B1 elutes between HFC 143a and 125; while on PoraPLOT U, 13B1 elutes first and the elution order follows increasing boiling points. Therefore, on PoraPLOT U, surface interaction with the large bromine atom does not appear to occur indicating a smaller surface area for this polymer type. This clearly demonstrates the reduction in polymer surface area of the PoraPLOT columns *i.e.* Q > S > U. 12B1 also contains a single

bromine atom and is less retained on the PoraPLOT U than on both the PoraPLOT Q and S columns, clearly shown by the reversal in elution order of HFC 124 and 12B1. Thus, the inclusion of a larger bromine atom in a compound will increase that compound's retention time relative to those of similar volatility due to a surface area interaction provided there is a similarity in compound size and stationary phase pore size.

Polarity effect. From all the results, it can be seen that the compounds containing a single polarisable hydrogen, HFCs 125, 22, 124 and 123, are retained longer on all the PoraPLOT columns than the compounds of similar volatility in the series studied. This indicates polarisation occurs between the lone hydrogen and porous polymer which increases the compound's retention. This explains the disruption of elution order in terms of compound boiling point.

It is possible to assign the polarity order of the three columns from the retention data, and calculation of column capacity factors k'. Taking compounds HFC 143a and 125:

PoraPLOT column	k'		Difference in k' values
	HFC 143a	HFC 125	
Q	1.88	2.00	0.12
S	1.83	2.23	0.40
U	2.62	3.28	0.66

The widest separation is achieved with the PoraPLOT U column —which is the highest polarity column available— so the greatest interaction is observed between the lone polarisable hydrogen present in HFC 125 and the stationary PoraPLOT U phase. The above data indicates the column polarity order of Q < S < U, as expected. However, stronger adsorption of the more polar HFCs, on the more polar PoraPLOT U column results in broader, less symmetrical peaks.

Overall, the PoraPLOT S column, a wide-bore column (25 m × 0.53 mm I.D.), gave the best chromatographic separation in the shortest time and with the least column bleed at the higher column temperatures. The capacity of a wide-bore column is higher than that of the narrow-bore columns, and they also have a higher net retention. This is especially important for PLOT columns, because the retention is directly related to the amount of adsorbent present in the column. The wide-bore PoraPLOT S column has a layer thickness of 20 μm which permits greater loadability [20]. However, CFC 12, a major contaminant of atmospheric air, was shown to co-elute with CH_3Cl at all temperatures, therefore CFC 12 could cause interference in any air samples analysed for this compound. The PoraPLOT Q column produced no co-elution for any of the relevant compounds, but the overall resolution for the compounds, especially the pairs HFCs 143a/125 and HFCs 142b/124, was poorer than on PoraPLOT S and greater column bleed was apparent at the higher column temperatures.

WCOT CP-Sil CB columns

The essentially non-polar CP-Sil 5 CB column elutes the compounds of interest in terms of their boiling point with the exception of HFC 22 which elutes after HFC 134a due to its methanogenic nature. However, even at the lowest possible column operating temperature (without the use of cryogenics), the earliest eluting HFCs, namely 125, 143a and 134a are not sufficiently separated to achieve baseline resolution. The more polar CP-Sil 13 CB column appears to give similar results, but with HFC 143a interacting more strongly with the stationary phase than HFC 125 giving separation of these two HFCs. Although the additional polarity of the CP-Sil 19 CB column enhances interaction of the phase with the single hydrogen of HFC 125, less interaction is observed between HFC 143a and the stationary phase resulting in co-elution. HFC 124 interacts more strongly with the stationary phase on the CP Sil 19 CB column than on the CP Sil 13 CB column, causing co-elution with HFC 142b. Thus, overall resolution is degraded on the CP Sil 19 CB column causing co-elution of HFCs 125/143a and HFCs 142b/124.

Unfortunately a direct comparison between the three columns is not possible due to the different film thickness of the stationary phases. Nevertheless, all the CP-Sil CB columns have

the advantage of low column operating temperatures, thus minimizing effects of column bleed, while still giving rapid analysis times and excellent peak shapes.

CONCLUSIONS

Complete chromatographic resolution of the HFCs and CFCs has proved difficult, due to their similar boiling points and physical properties. Consequently, no one chromatographic column was found to separate all of the compounds of interest. In general, the WCOT columns proved to be very successful for separation of all but the most volatile, earlier eluting HFCs. These columns had the advantage of low column operating temperatures. Conversely, the Pora-PLOT columns were effective for these more volatile HFCs, but not as suitable for the less volatile HFCs due to the higher operating temperatures required. The alumina PLOT columns were potentially the most attractive option since they exhibited excellent resolution of all compounds, although their use is complicated by catalytic activity towards certain HFCs and halocarbons. Passivation of the stationary phase is a possible solution, and work is continuing in our laboratory with an alumina PLOT column passivated with CH_3Cl, to determine whether dehydrohalogenating effects have been eliminated without the loss of the overall superior resolution of the HFCs.

REFERENCES

1 F. Sherwood Molina, *Environ. Sci. Technol.*, 25 (1991) 622–628.
2 G. Webb and J. Winfield, *Chem. Br.*, 28 (1992) 996–997.
3 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) 508–512.
4 D.A. Fisher, C.H. Hales, W. Wang, M.K.W. Ko and N. Dak Sze, *Nature*, 344 (1990) 513–516.
5 J. de Zeeuw, R.C.M. de Nijs and L.T. Heinrich, *J. Chromatogr. Sci.*, 25 (1987) 71–83.
6 J.L. Glajch and W. Schindel, *LC · GC*, 4 (1986) 574–577.
7 D.G. Gehring, D.J. Barsotti and H.E. Gibbon, *J. Chromatogr. Sci.*, 30 (1992) 280–285.
8 R.C.M. de Nijs, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 612–615.
9 L. Do and F. Raulin, *J. Chromatogr.*, 514 (1990) 65–69.
10 R.C.M. de Nijs and J. de Zeeuw, *J. Chromatogr.*, 279 (1983) 41–48.
11 F.R. Reinke and K. Bachmann, *J. Chromatogr.*, 323 (1985) 323–329.
12 L. Burgess and D.M. Kavanagh, *The Use of PLOT/Alumina columns in the Analysis of Hydrofluorocarbons*, Technical Note No. 12, IC 08596/12, ICI Chemicals & Polymers, September 1989.
13 W. Asche, *Chromatographia*, 11 (1978) 411–412.
14 Th. Noij, P. Fabian, R. Borchers, C. Cramers and J. Rijks, *Chromatographia*, 26 (1988) 149–156.
15 Th. Noij, J.A. Rijks and C.A. Cramers, *Chromatographia*, 26 (1988) 139–141.
16 J. de Zeeuw, R.C.M. de Nijs, J.C. Buyten and J.A. Peene, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 162–167.
17 L. Do and F. Raulin, *J. Chromatogr.*, 481 (1989) 45–54.
18 L. Do and F. Raulin, *J. Chromatogr.*, 591 (1992) 297–301.
19 S. O'Doherty, *LINK-TAPM Report*, personal communication, 1992.
20 J. de Zeeuw, R.C.M. de Nijs, D. Zwiep and J.A. Peene, *Am. Lab.*, 23 No. 9 (1991) 44–51.