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Separation of mixed halocarbons of environmental interest on a new type of silica-based porous-layer open tubular capillary gas chromatographic column

Brian R. Greally^{a,*}, Graham Nickless^a, Peter G. Simmonds^a, Michael Woodward^b,
Jaap de Zeeuw^b

^a*School of Chemistry, University of Bristol, Cantocks Close, Bristol, BS8 1TS, UK*

^b*Chrompack UK, Unit 4, Idescon Court, Millharbour, London, E14 9TN, UK*

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Abstract

A new type of capillary porous-layer open tubular (PLOT) column consisting of a hydrophobic silica layer on a fused-silica capillary has been tested for the separation of a mixture of environmentally sensitive halocarbons present in tropospheric air. The column shows high retention for a wide range of halocarbons, with elution orders following both boiling point order and hydrogen bonding capability. The resolution of the halocarbons is good and only one pair of halocarbons [CHFClCF_3 (HCFC 124) and $\text{CH}_3\text{CF}_2\text{Cl}$ (HCFC 142b)] cannot be resolved on this column type at all column temperature profiles. Unlike alumina PLOT columns, the silica PLOT column does not dehydrohalogenate labile halocarbons. Excellent reproducibility of retention times and peak areas for halocarbons on the column are reported. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorofluorocarbons (CFCs), which have been shown to destroy stratospheric ozone [1], are currently being phased out of use in their major applications including refrigerant fluids, foam blowing agents and as industrial solvents [2]. The compounds currently being used as replacements for CFCs include the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs) [3]. The HCFCs are degraded primarily in the troposphere due to their hydrogen content which makes them labile towards reaction

with tropospheric hydroxyl radicals (OH^\cdot) [4]. Some portion of the released chlorine will eventually reach the stratosphere and can participate in ozone depleting reactions [4]. The HCFCs possess a lower ozone depleting potential (ODP) than all previously used CFCs [5]. Thus the HCFCs are viewed as interim CFC replacement compounds, with a ceiling on their manufacture having been enforced in 1996 and their use being phased out by 2030 [6]. The long-term replacements, the HFCs, do not deplete stratospheric ozone [7]. The HFCs, which contain only carbon, hydrogen and fluorine, are predominantly removed in the troposphere by hydroxyl radical attack with no release of ozone depleting reaction products [4].

*Corresponding author.

However, they are effective greenhouse gases and have high global warming potentials (GWP) [5]. The perfluorocarbons (PFCs), which contain only carbon and fluorine, have zero ozone depleting potentials [8], extremely long atmospheric lifetimes (3000–10 000 years) and high global warming potentials [9]. The need exists to quantify the atmospheric concentrations of these CFCs, HCFCs, HFCs, PFCs and other important halocarbons such that their atmospheric lifetimes and growth rates are known. This information is useful to environmental chemists, atmospheric modelers, industrial manufacturers of halocarbons and to governments and international legislators. Substantial work towards this aim using gas chromatography has been achieved [10–14].

A vital part of the accurate quantitation of halocarbons in air samples is to optimise the resolution of individual halocarbons prior to quantitation. This can be accomplished using high-efficiency capillary columns, involving both gas–liquid chromatography (GLC) and gas–solid chromatography (GSC) techniques. Simmonds et al. [12] have found that a 5 μm thick film methyl silicone GLC column (CPSil 5 CB, 100 m \times 0.32 mm I.D.) is useful for resolving a number of C₂ halocarbons. However, this column does not resolve the more volatile of the C₁ halocarbons efficiently at ambient chromatographic oven temperatures. The separation of the volatile C₁ halocarbons is much more efficient using GSC due to their preference to transfer between a gas and solid phase over gas to liquid transfer [15]. The most common types of GSC columns include alumina porous-layer open tubular (PLOT), molecular sieve PLOT and porous polymer PLOT.

Alumina-based PLOT columns, the most popular and widely used PLOT column type, are composed of an Al₂O₃ layer deposited onto a fused-silica capillary. Native alumina PLOT columns give tailing chromatographic peaks so commercial alumina PLOT columns are partially deactivated by incorporating inorganic salts (KCl or Na₂SO₄) into the alumina matrix to reduce the column activity and improve peak shapes. Retention on alumina PLOT columns is governed by extensive hydrogen bonding between the alumina surface and polarizable molecules. Consequently, polar molecules like alcohols, hydroxy acids, water and CO₂ are extremely well retained on the solid phase. For hydrocarbons, unsaturated olefins are more retained than the corre-

sponding alkanes [16]. Alumina PLOT columns have been shown to give excellent resolution of C₁–C₁₀ hydrocarbons [17] and some C₁ and C₂ halocarbons [18]. However, alumina PLOT columns have been reported to dehydrohalogenate some of the atmospherically important halocarbons, principally 1,1,1-trichloroethane [19], CHF₂Cl (HCFC 22) [20], CH₃Cl [21], CH₃CF₂Cl (HCFC 142b) [21] and CHCl₂CF₃ (HCFC 123) [11]. This limits their use for the separation of halocarbons in air samples. Also, alumina PLOT columns strongly retain water [15] which reduces their capacity and retention, necessitating careful drying of air samples prior to analysis.

Porous polymer-based PLOT columns are composed of a co-polymer backbone (e.g. styrene–divinylbenzene, divinylbenzene–vinylpyridine) onto which analytes are retained. The porous polymer PLOT columns show good retention and resolution of highly volatile halocarbons [21]. The less volatile halocarbons are too well retained and require high column temperatures to elute from the column. This causes excessive bleeding of the column stationary phase, reducing the practical use of porous polymer PLOT columns in gas chromatography–mass spectrometry (GC–MS) applications.

Newer types of PLOT columns becoming available include those based on cyclodextrins. Cyclodextrins are cyclic oligosaccharides which are more commonly used in HPLC for the separation of enantiomers [22,23]. Cyclodextrin-based PLOT columns retain both polar and non-polar analytes using two distinct retention mechanisms [24]. Non-polar analytes are retained in the hydrophobic cyclodextrin cavity whilst polar compounds form hydrogen bonds with the hydroxyl groups on the outer rim of the cyclodextrin cavity. GSC PLOT columns based on cyclodextrins have recently been used for the separation of light hydrocarbons [25], inorganic gases [25] and halocarbons [26].

Silica is widely used as a HPLC stationary phase, although the development of silica as a GSC adsorbent has been slow for a number of reasons including:

(i) Silica surfaces are less active towards adsorption when compared to alumina and the number of active adsorption sites on silica can be up to 100 times less than those on alumina [15].

(ii) The selectivity of alumina PLOT columns,

especially towards light hydrocarbons, is superior to most other adsorbents.

(iii) Peaks eluting from silica PLOT columns have shown a greater degree of tailing compared to alumina based PLOT columns, especially for unsaturated or polar compounds and is due to the surface activity of the silica [15,27].

In this paper, we describe the separation and retention of CFCs, HCFCs, HFCs and other halocarbons on a new type of silica-based PLOT column. Specifically we will focus on obtaining baseline separation, acceptable peak shapes and reproducible retention on the column. Possible activity of the silica surface towards dehydrohalogenation reactions with respect to labile halocarbons is assessed. The silica PLOT columns tested here were prepared by static coating of a hydrophobic silica suspension in low boiling point organic solvents onto a fused-silica capillary. This was followed by a 2 h nitrogen flush

and activation for 12 h up to 260°C (Chrompack, Middelburg, The Netherlands). Results from the manufacturers [28] indicate that the capacity and retention of the GSC phase is not influenced by water and that the silica layer is stable up to 250°C.

2. Experimental

2.1. Reagents and materials

Standard mixtures of selected halocarbons were supplied in two high-pressure cylinders by Linde Gases (Stoke-on-Trent, UK) and are used routinely in our laboratory for the calibration of field-based instruments. The standards were certified by the supplier to be accurate to $\pm 1\%$ and the concentrations of halocarbons present in these gas standards are listed in Table 1. Individual halocarbons, sup-

Table 1
Compound description

Trade name	Formula	Boiling point (°C)	Cylinder concentration (ppmv ^a)	
			515164	510995
N ₂ O	N ₂ O	-91.0	Balance	Balance
HFC 23	CHF ₃	-84.0	227	-
Halon 1301	CF ₃ Br	-58.0	212	220
HFC 32	CH ₂ F ₂	-51.0	130	-
HFC 125	CHF ₂ CF ₃	-49.0	167	-
HFC 143a	CH ₃ CF ₃	-47.0	171	-
HCFC 22	CHF ₂ Cl	-41.0	332	445
CFC 115	CF ₃ CF ₂ Cl	-38.0	213	-
CFC 12	CF ₂ Cl ₂	-30.0	1910	1800
HFC 134a	CH ₂ FCF ₃	-27.0	164	-
HFC 152a	CH ₃ CHF ₂	-25.0	179	-
CH ₃ Cl	CH ₃ Cl	-24.2	1960	2020
HCFC 124	CHFClCF ₃	-12.0	167	-
HCFC 142b	CH ₃ CF ₂ Cl	-9.0	170	-
Halon 1211	CF ₂ ClBr	-2.5	187	215
CFC 114	CF ₂ ClCF ₂ Cl	3.8	179	-
CH ₃ Br	CH ₃ Br	4.0	153	205
CFC 11	CFCl ₃	23.5	990	905
HCFC 123	CHCl ₂ CF ₃	27.0	167	-
HCFC 141b	CH ₃ CFCl ₂	32.0	164	-
CH ₂ Cl ₂	CH ₂ Cl ₂	40.0	165	200
CHCl ₃	CHCl ₃	61.0	166	200
HFC 41 ^b	CH ₃ F	-79.0		
PFC 116 ^b	CF ₃ CF ₃	-78.0		
PFC 218 ^b	CF ₃ CF ₂ CF ₃	-39.0		
HFC 161 ^b	CH ₃ CH ₂ F	-37.0		

^a Parts per million (v/v).

^b These compounds are not present in either standard mixture and were injected as individual standards.

plied as pure gases or liquids were from the following sources: CF_2Cl_2 (CFC 12), $\text{CF}_3\text{CF}_2\text{Cl}$ (CFC 115), $\text{CF}_2\text{ClCF}_2\text{Cl}$ (CFC 114), CHF_2Cl (HCFC 22), CHFClCF_3 (HCFC 124), CHF_3 (HFC 23), CH_2F_2 (HFC 32), CH_3F (HFC 41), CHF_2CF_3 (HFC 125), CH_3CF_3 (HFC 143a), $\text{CH}_3\text{CH}_2\text{F}$ (HFC 161), CF_3Br (Halon 1301), CF_3CF_3 (PFC 116), $\text{CF}_3\text{CF}_2\text{CF}_3$ (PFC 218) from Fluorochem (Derbyshire, UK); $\text{CH}_3\text{CF}_2\text{Cl}$ (HCFC 142b), CH_3CFCl_2 (HCFC 141b), CHCl_2CF_3 (HCFC 123), CH_2FCF_3 (HFC 134a) from ICI Chemicals and Polymers (Runcorn, UK); CH_3Cl , CH_2Cl_2 , CHCl_3 from BDH (Poole, UK); CF_2ClBr (Halon 1211) from a fire extinguisher (John Morris and Sons, Cheshire, UK); CFCl_3 (CFC 11), CH_3Br from Aldrich (Gillingham, UK); CH_3CHF_2 (HFC 152a) from DuPont (Deepwater, NJ, USA).

Hydrogen, air and oxygen-free nitrogen (BOC, Guilford, UK) were used for flame ionization detection (FID). The column carrier gas was helium (purity 99.996%, BOC). The helium and the oxygen free nitrogen were passed through a combined molecular sieve 5A and charcoal trap prior to use in the gas chromatograph.

2.2. Chromatography

A Chrompack CP 9000 gas chromatograph fitted with a flame ionization detector was used for this work. The detector was held at 250°C throughout the analysis. Injection onto the column was achieved using two methods. The supplied injector port (held at 150°C) on the chromatograph was used to introduce individual standards (prepared by dilution of the pure gas or liquid headspace with nitrogen in a sealed 100 ml flask) into the chromatograph using a Hamilton gas-tight syringe ($50\ \mu\text{l}$) to identify peak retention values and determine compound elution order. An air actuated Valco gas sampling valve (Model A60, VICI, Houston, TX, USA) fitted with a $50\ \mu\text{l}$ gas sample loop was used to inject samples from the mixed halocarbon standard cylinders and was maintained at room temperature throughout this study. The chromatographic columns used (supplied by Chrompack) were (a) a $30\ \text{m}\times 0.32\ \text{mm}$ I.D. CP-SilicaPLOT and (b) a $60\ \text{m}\times 0.32\ \text{mm}$ I.D. CP-SilicaPLOT. Helium flow-rates of 2.0 ml/min, 2.5 ml/min and 3.3 ml/min were used as indicated in the tables and figures. The columns were conditioned

at 240°C overnight prior to use. Chromatograms, peak retention times and peak areas were recorded using a commercial integrator and JCL 6000 data acquisition software (Jones Chromatography, Mid Glamorgan, UK) on a Viglin 486 personal computer. Data acquisition was terminated after the last eluting peak.

Six consecutive $50\ \mu\text{l}$ aliquots of standard COC 510995 (10-component mixture) were injected onto the CP-SilicaPLOT for reproducibility studies. This standard mixture covers the wide range of volatility of environmentally important halocarbons coupled with baseline resolution of all components. For all chromatographic calculations, the retention time for N_2O was taken to represent the dead volume hold up time. N_2O is detected by FID because it represents the matrix gas for the standard cylinders and thus is the major component in the samples injected.

The CP-SilicaPLOT column was tested for possible dehydrohalogenation reactions occurring for the labile halocarbons HCFC 22 and CH_3Cl . A standard mixture containing 100 ppm (v/v) of CH_3Cl , 250 ppm (v/v) of HCFC 22 and 100 ppm (v/v) of HFC 152a was prepared by injection of aliquots of the pure gases into a sealed 1 l flask which had been filled with helium. HFC 152a was used as an internal reference standard which, containing only hydrogen, fluorine and carbon, does not undergo dehydrohalogenation [21] and does not coelute with HCFC 22 or CH_3Cl on the CP-SilicaPLOT in the temperature range studied. $50\ \mu\text{l}$ aliquots of this mixture were injected onto the column which was held isothermally at set test temperatures in the range $50\text{--}150^\circ\text{C}$ and the responses obtained used to calculate the stability of HCFC 22 and CH_3Cl towards the silica surface.

3. Results and discussion

3.1. Resolution and separation on the CP-SilicaPLOT

Initially, a $50\ \mu\text{l}$ aliquot of standard COC 515164 (22-compound mixture) was injected onto the 30 m column using the following temperature profile: 40°C for 10 min, rise at $2^\circ\text{C}/\text{min}$ to 200°C . The separation of the halocarbons was optimized by varying the

temperature profile such that the critical pairs of CFC 12+HFC 125 and HFC 134a+CH₃Cl were at least partially resolved and the early eluting compounds were not coeluting with each other. The two most abundant chlorine species in the free troposphere are CH₃Cl and CFC 12 [29] whilst HFC 134a is predicted to become the major replacement compound for CFCs in refrigeration and air conditioning [3], hence the need to separate these two sets of compounds. The optimum temperature profile was 35°C for 12 min, rise at 4°C/min to 150°C, hold to end. A typical chromatogram of the mixed halocarbon standard COC 515164 on the 30 m column using this temperature profile is shown in Fig. 1. Injection of individual halocarbon standards was performed to confirm elution order and identification of coeluting compounds. Coeluting compounds were present at all oven temperature profiles for the mixed halocarbon standard COC 515164.

It should be noted that the peaks for CFC 12 and CFC 11 are quite broad on both the 30 m and 60 m columns. The concentrations of both CFCs in the gas standard mixtures are designed to mimic their atmospheric concentrations in tropospheric air following dilution to parts per trillion (v/v) with zero air (80% N₂ and 20% O₂). The mass injected on-column in this study equate to 300–500 ng which appears to be

nearing the loading capacity of the 0.32 mm I.D. columns. The poor peak shape is also due to the use of a non-ideal detector. Both CFCs give a low FID signal. By contrast, the peak for CH₃Cl (present in similar concentration as CFC 12 and CFC 11 in the gas standards) is much larger than that of CFC 12 and CFC 11 due to CH₃Cl being much more responsive in FID.

All compounds are quite well retained including the very volatile HFC 23 and HFC 32 and most compounds are well separated, eluting as single baseline-resolved peaks (Fig. 1). Coelution on this column using this temperature program occurs for the peak pairs CH₃Cl and HFC 134a, for HCFC 124, HCFC 142b and CH₃Br, and for CFC 114 and HFC 152a. Limited resolution is achieved for CFC 12 and HFC 125. Values of retention and resolution of halocarbons on this column for the conditions stated are shown in Table 2.

3.1.1. CFC 12 and HFC 125

Lowering the initial oven temperature down to 30°C did not improve resolution for CFC 12 and HFC 125. Instead it caused peak broadening for all early eluting compounds, especially increasing the CFC 12 peak width significantly and causing an overall degraded chromatographic resolution even at

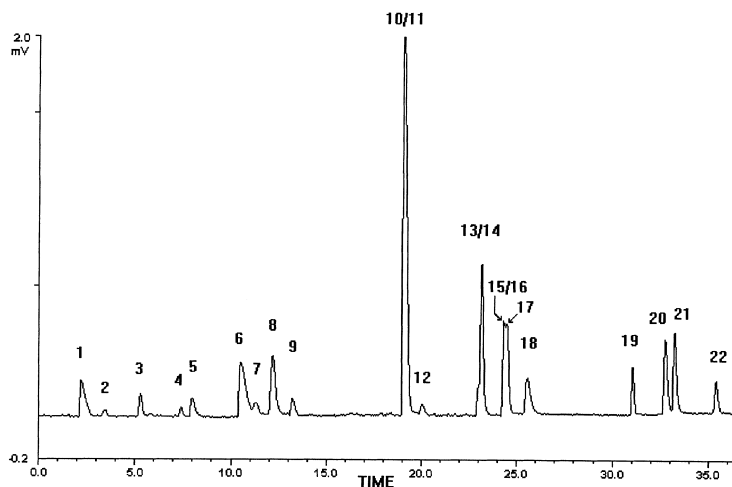


Fig. 1. 50 μ l of standard COC 515164 on 30 m \times 0.32 mm I.D. CP-SilicaPLOT. Conditions: helium flow at 2.0 ml/min, 35°C for 12 min, 4°C/min to 150°C. Peaks: 1=N₂O, 2=HFC 23, 3=Halon 1301, 4=HFC 32, 5=CFC 115, 6=CFC 12, 7=HFC 125, 8=HFC 143a, 9=HCFC 22, 10=HFC 134a, 11=CH₃Cl, 12=Halon 1211, 13=CFC 114, 14=HFC 152a, 15=HCFC 124, 16=HCFC 142b, 17=CH₃Br, 18=CFC 11, 19=CH₂Cl₂, 20=HCFC 141b, 21=HCFC 123, 22=CHCl₃. Time in min.

Table 2
CP-SilicaPLOT column retention, resolution and efficiency towards halocarbons

Compound	Relative retention time ^a (min) 30 m column	Resolution ^b 30 m column	Baseline peak width (min) ^c
HFC 23	1.23	2.90	–
Halon 1301	3.09	7.49	0.22
HFC 32	5.18	9.62	–
CFC 115	5.82	2.21	–
CFC 12	8.33	4.26	0.70
HFC 125	9.12	1.17	–
HFC 143a	10.00	1.77	–
HCFC 22	11.02	2.53	0.37
HFC 134a	16.81	15.13	–
CH ₃ Cl	16.81	0.00 ^d	0.48
Halon 1211	17.78	2.47	0.43
CFC 114	20.76	16.00	–
HFC 152a	20.89	0.60	–
HCFC 124	22.20	2.75	–
HCFC 142b	22.20	0.00 ^d	–
CH ₃ Br	22.29	0.35	0.26
CFC 11	23.33	3.72	0.65
CH ₂ Cl ₂	28.83	14.37	0.22
HCFC 141b	30.51	5.80	–
HCFC 123	31.00	1.32	–
CHCl ₃	33.15	6.11	0.35

^a Corrected for dead volume; conditions: 30 m×0.32 mm I.D. CP-SilicaPLOT, helium at 2.0 ml/min, 35°C for 12 min, rise at 4°C/min to 150°C, hold to end.

^b Resolution from previous eluting peak, values calculated using $2(t_2 - t_1)/W_2 + W_1$.

^c Calculated from the results obtained for standard COC 510995.

^d These compounds were not resolved from the previous eluting peak.

an elevated oven temperature ramp rate. The peak shape of CFC 12 can be improved by starting the analysis at a higher initial oven temperature (e.g. 50°C) but only up to a point where the resolution between the CFC 12 and HFC 125 peaks worsens.

3.1.2. HFC 134a and CH₃Cl

It is possible to partially resolve these coeluting peaks on the 30 m CP-SilicaPLOT by raising the initial temperature of the column. The effect of this can be seen in Fig. 2. In this case, at higher temperatures the HFC 134a peak elutes prior to the CH₃Cl peak until near baseline resolution occurs at an initial oven temperature of 70°C. As also seen from Fig. 2, coelution starts to occur for the less well retained halocarbons including merging of the CFC 12 and HFC 125 peaks.

3.1.3. CFC 114 and HFC 152a

Partial separation is achieved for the peak pair

CFC 114 and HFC 152a using the 30 m column. As in the previous case, the resolution of this pair may be improved by modifying the temperature profile but only at the expense of decreasing resolution for later eluting peaks. The retention of HFC 152a on the silica stationary phase is remarkable given that it has such a low boiling point (–25.0°C) relative to CFC 114 (3.8°C) and yet is retained to the same extent. The retention is caused by the compounds high hydrogen content which promotes hydrogen bonding interactions with the stationary phase. The unsymmetric distribution of fluorine will also cause a small dipole within the molecule. This will enhance its capacity to hydrogen bond with the silica surface.

3.1.4. HCFC 124/HCFC 142b and CH₃Br

The grouping HCFC 124/HCFC 142b/CH₃Br can only be partially resolved by changing the temperature profile. By sacrificing resolution elsewhere on the chromatogram, near baseline resolution of

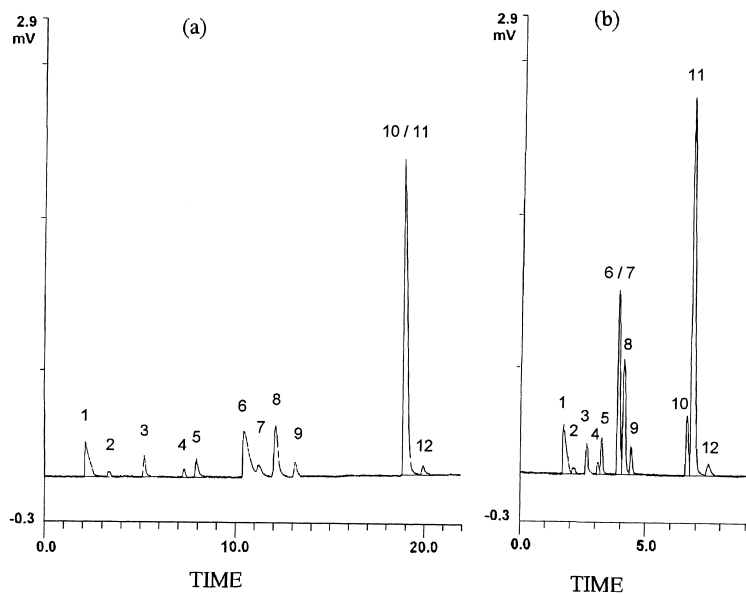


Fig. 2. Resolution of HFC 134a from CH_3Cl by raising the initial oven temperature. Partial chromatograms of 50 μl injections of standard COC 515164 on the 30 $\text{m} \times 0.32$ mm I.D. CP-SilicaPLOT are shown under the following temperature profiles: (a) 35°C for 12 min, 4°C/min to 150°C, (b) 70°C for 12 min, 4°C/min to 150°C. Peaks: 1= N_2O , 2=HFC 23, 3=Halon 1301, 4=HFC 32, 5=CFC 115, 6=CFC 12, 7=HFC 125, 8=HFC 143a, 9=HCFC 22, 10=HFC 134a, 11= CH_3Cl , 12=Halon 1211. Time in min.

CH_3Br from the two HCFCs can be achieved on the 30 m PLOT column. HCFC 124 and HCFC 142b could not be resolved on this column at any temperature profile and this is most probably due to their similar boiling points (Table 1). CH_3Br contains a higher dipole moment caused by polarization from the bromine group. The difference in polarization can be exploited to effect separation of CH_3Br from the two HCFCs.

The CP-SilicaPLOT is especially selective for very-low-boiling-point gases. Single standards of PFC 116 (b.p. -79.0°C), PFC 218 (b.p. -39.0°C), and HFC 41 (b.p. -79.0°C) were injected onto the 30 m column using the same temperature profile as for the halocarbon mixtures. Each compound had a symmetrical peak shape and were resolved from the other halocarbons present in COC 515164. HFC 161 (b.p. -37.0°C) showed very strong retention on the silica surface and tended to co-elute with CH_3Br . This is most likely due to extensive hydrogen bonding between the HFC 161 hydrogens and the silica surface.

Retention and separation trials were also carried out on a 60 $\text{m} \times 0.32$ mm I.D. CP-SilicaPLOT using

standard COC 515164. The peak tailing of all compounds was noticeably worse on the longer length column. Using similar conditions to the trials on the 30 m column (helium flow of 2.5 ml/min, 35°C for 12 min, rise to 150°C at 4°C/min) HFC 134a can be resolved from CH_3Cl without difficulty on the 60 m column while CH_3Br elutes clear of the combined HCFC 124 and HCFC 142b peak. However, coelution occurs for HFC 32 and CFC 115. The resolution between CFC 12 and HFC 125 is lost and generally poorer for the peak pairs CH_3Cl and Halon 1211 as well as HCFC 141b and HCFC 123. No major increase in the separation of other compounds was observed. A chromatogram obtained from the 60 m column is shown in Fig. 3.

3.2. Elution order on the CP-SilicaPLOT column

The elution order of halocarbons on the CP-SilicaPLOT are influenced by a number of factors. The results show the following trends.

(i) Retention is not solely governed by the compound boiling point. The boiling point order influences retention for the chlorofluorocarbons [CFC

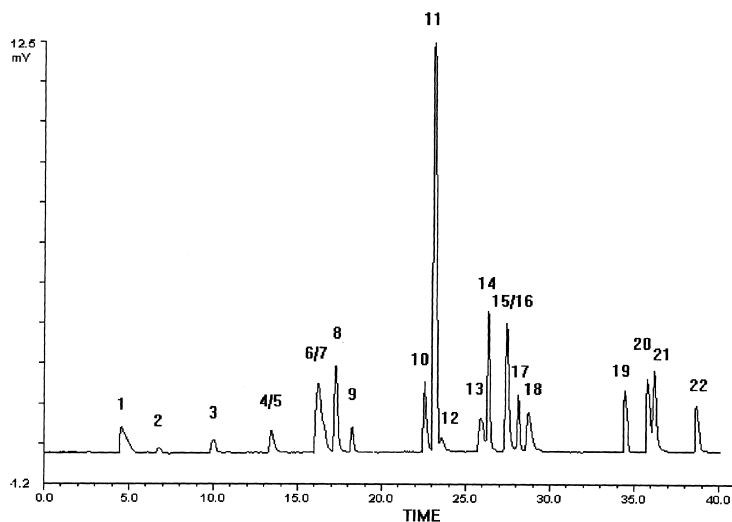


Fig. 3. 50 μ l of standard COC 515164 on 60 m \times 0.32 mm I.D. CP-SilicaPLOT. Conditions: helium flow at 2.5 ml/min, 35°C for 12 min, 4°C/min to 150°C. Peaks: 1=N₂O, 2=HFC 23, 3=Halon 1301, 4=HFC 32, 5=CFC 115, 6=CFC 12, 7=HFC 125, 8=HFC 143a, 9=HCFC 22, 10=HFC 134a, 11=CH₃Cl, 12=Halon 1211, 13=CFC 114, 14=HFC 152a, 15=HCFC 124, 16=HCFC 142b, 17=CH₃Br, 18=CFC 11, 19=CH₂Cl₂, 20=HCFC 141b, 21=HCFC 123, 22=CHCl₃. Time in min.

115 (b.p. -38.0°C)<CFC 12 (b.p. -30.0°C)<CFC 114 (b.p. 3.8°C)<CFC 11 (b.p. 23.5°C). This is also the case for the perfluorocarbons [PFC 116 (b.p. -78.0°C)<PFC 218 (b.p. -39.0°C)] and chloromethanes [CH₃Cl (b.p. -24.2°C)<CH₂Cl₂ (b.p. 40.0°C)<CHCl₃ (b.p. 61.0°C)]. For HFCs, the boiling points have some influence on the elution order [e.g. HFC 125 (b.p. -49.0°C)<HFC 143a (b.p. -47.0°C)<HFC 134a (b.p. -27.0°C)] but not to the same extent as for the CFCs, PFCs and chloromethanes.

(ii) Retention is also influenced by the number of hydrogens in the compound, due to the hydrogen bonding interactions between analytes and the stationary phase. For those HFCs with the same number of carbons, increasing hydrogen content leads to greater hydrogen bonding potential and hence greater retention. This retention mechanism is seen in the elution order for the methane-based hydrofluorocarbons [HFC 23 (CHF₃)<HFC 32 (CH₂F₂)<HFC 41 (CH₃F)] and the ethane-based hydrofluorocarbons [HFC 143a (CH₃CF₃)<HFC 152a (CH₃CHF₂)<HFC 161 (CH₃CH₂F)].

(iii) Those compounds with more chlorines are retained longer than those containing less chlorine. The hydrochlorofluorocarbons elute as per chlorine

content [HCFC 124 and HCFC 142b (both 1 chlorine) elute before HCFC 141b and HCFC 123 (2 chlorines each)].

3.3. Comparison of elution order of halocarbons on different types of PLOT columns

The elution order of some environmentally important halocarbons on various types of PLOT columns are shown in Table 3. The difference in selectivity of the CP-SilicaPLOT compared to a PoraPLOT Q (styrene–divinylbenzene co-polymer) and an alumina–KCl PLOT column can be clearly seen. The relative selectivity for each compound class on the three types of column highlight the different retention mechanisms for each stationary phase.

3.3.1. Relative selectivity for the chloromethanes

All three columns show the same elution pattern for the chloromethanes, i.e. more retention with increasing chlorine content. The alumina PLOT dehydrochlorinates CH₃Cl, but work by Sturrock [30] on passivating the alumina column by saturation with CH₃Cl has shown that CH₃Cl elutes before CH₂Cl₂.

Table 3
Comparison of elution order for halocarbons on different types of plot column

CP-SilicaPLOT (this work)	Alumina/KCl PLOT [21]	PoraPLOT Q [21]
PFC 116		
HFC 23		
Halon 1301	Halon 1301	
PFC 218		
HFC 32		
CFC 115		
HFC 41		
CFC 12		
HFC 125		
HFC 143a	HFC 143a	HFC 143a
HCFC 22	HFC 125	HFC 125
HFC 134a	Halon 1211	Halon 1301
CH ₃ Cl	HFC 134a	HFC 134a
Halon 1211		HCFC 22
CFC 114		CH ₃ Cl
HFC 152a		
HCFC 124 ^a	HCFC 142b	HCFC 142b
HCFC 142b ^a	HCFC 124	HCFC 124
HFC 161		Halon 1211
CH ₃ Br		
CFC 11		
CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂
HCFC 141b		
HCFC 123	HCFC 123	HCFC 123
CHCl ₃	CHCl ₃	CHCl ₃

^a These compounds co-elute on the CP-SilicaPLOT columns.

3.3.2. Relative selectivity for the hydrochlorofluorocarbons

Both the alumina and porous polymer columns will resolve HCFC 124 from HCFC 142b whilst the silica PLOT will not. The PoraPLOT Q column is more selective for HCFC 22 than the silica PLOT. This compound is dehydrochlorinated on the alumina PLOT. All three columns have very good retention for HCFC 123, but the peak is very broad on the PoraPLOT Q.

3.3.3. Relative selectivity for the hydrofluorocarbons

The silica PLOT displays a different elution order for the HFCs. On both the alumina and porous polymer PLOT columns, the eluting order is in line with increasing polarity of the CFH group on one side of the molecule. They follow the order of zero polarized hydrogens on HFC 143a (CH₃CF₃) <

polarized hydrogen on HFC 125 (CHF₂CF₃) < 2 polarized hydrogens on HFC 134a (CFH₂CF₃). On the silica PLOT, they elute in the order HFC 125 < HFC 143a < HFC 134a. This trend follows the hydrogen bonding capacity of these HFCs and their boiling point order with the latter outweighing the hydrogen bonding for HFC 125 and HFC 143a.

3.3.4. Relative selectivity for the halons

Both Halon 1301 and Halon 1211 are strongly retained on the porous polymer PLOT column, due to the interaction of the large bromine atoms with the surface area of the co-polymer [21]. Halon 1301 is poorly retained on both the alumina and silica PLOT columns due to its high volatility (boiling point of -58.0°C). The silica PLOT is more selective for Halon 1211 compared to the alumina PLOT.

3.4. Reproducibility of retention and activity towards labile halocarbons

The 30 m × 0.32 mm I.D. CP-SilicaPLOT was tested for column reproducibility of retention and peak area. Average retention times and peak areas, standard deviations (S.D.) and relative standard deviations (R.S.D.s) for each compound in the 10-component (COC 510995) mixed halocarbon standard is presented in Table 4. A sample chromatogram of this test mixture is shown in Fig. 4. Each peak is well defined and halocarbons encompassing a wide range of volatility (-58.0°C to 61.0°C) have been resolved. The reproducibility of retention is excellent for this column, with all values below an R.S.D. of 0.2%. Peak area is also reproducible with the most tailing peaks (i.e. CFC 12, Halon 1211 and CFC 11) showing the most variability. Reproducibility on the 60 m column was also excellent. The stability of the CP-SilicaPLOT at high oven temperatures is also shown in Fig. 4. This chromatographic run of COC 510995 was continued up to the column maximum allowable operating temperature. The baseline rise is small and constant, with little stationary phase bleed being observed.

The stability of the labile halocarbons HCFC 22 and CH₃Cl in relation to possible dehydrohalogenation on the silica surface was tested and the results are shown in Table 5. The relative responses of HCFC 22 and CH₃Cl to that of HFC 152a were

Table 4
Reproducibility of retention times and peak areas for halocarbons present in standard cylinder COC 510995

Compound name	Average retention time (min)	S.D. (min) (n=6)	R.S.D. retention time (%) (n=6)	Average peak area (area counts)	S.D. (area counts) (n=6)	R.S.D. peak area (%) (n=6)
N ₂ O	1.83	0.00	0.00	50 016	515	1.03
Halon 1301	4.08	0.00	0.11	17 733	516	2.91
CFC 12	7.78	0.01	0.17	98 978	1510	1.53
HCFC 22	9.68	0.01	0.13	18 684	496	2.65
CH ₃ Cl	15.86	0.01	0.06	337 241	3953	1.17
Halon 1211	16.82	0.01	0.05	16 590	700	4.22
CH ₃ Br	21.01	0.00	0.02	35 697	491	1.38
CFC 11	21.94	0.01	0.03	47 311	2060	4.36
CH ₂ Cl ₂	26.64	0.00	0.00	29 509	357	1.21
CHCl ₃	30.22	0.01	0.03	26 300	829	3.16

Time between each run was approximately 1 h. Conditions: 30 m×0.32 mm I.D. CP-SilicaPLOT, helium carrier gas at 2.5 ml/min, 40°C for 12 min, rise at 5°C/min to 150°C, hold to end. Injection volume 50 µl.

calculated as a function of column temperature to ascertain whether or not destruction of the halocarbons was occurring. The relative response was normalised to the relative response at 50°C, at which temperature dehydrohalogenation reactions are minimised. If dehydrohalogenation occurs on the silica surface of the CP-SilicaPLOT it would be accentuated on increasing the column temperature and a drop in relative response of the degrading halocarbon to HFC 152a would be seen [19,21]. The results in

Table 5 show that the relative response of both HCFC 22 and CH₃Cl to HFC 152a are essentially unity proving that no dehydrohalogenation occurs for these compounds on the CP-SilicaPLOT over the temperature range 50°C–150°C.

4. Conclusions

The CP-SilicaPLOT columns possess a number of

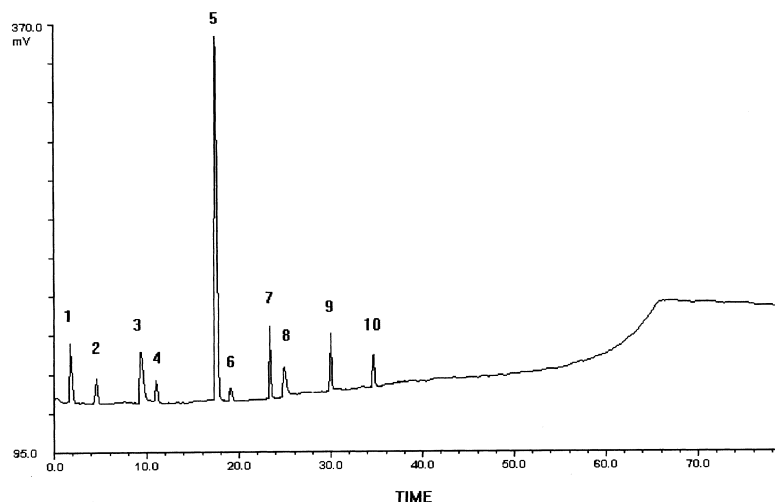


Fig. 4. 50 µl of standard COC 510995 on 30 m×0.32 mm I.D. CP-SilicaPLOT. Conditions: helium flow at 2.5 ml/min, 35°C for 12 min, 4°C/min to 250°C, hold 15 min. Peaks: 1=N₂O, 2=Halon 1301, 3=CFC 12, 4=HCFC 22, 5=CH₃Cl, 6=Halon 1211, 7=CH₃Br, 8=CFC 11, 9=CH₂Cl₂, 10=CHCl₃. Time in min.

Table 5
Influence of increasing column temperature on the stability of labile halocarbons

Temperature of column (°C)	Relative response of HCFC 22 to HFC 152a ^a	Relative response of CH ₃ Cl to HFC 152a ^a
50	1.00	1.00
75	0.98	0.98
100	1.00	0.99
115	1.00	0.99
130	0.99	0.99
150	1.00	0.98

Conditions: 30 m×0.32 mm I.D. CP-SilicaPLOT operated isothermally at temperature listed, helium carrier gas flow at 3.3 ml/min, 50 µl sample injection volume.

^a Relative response calculated using (area of HCFC 22 or CH₃Cl)/(Area of HFC 152a) normalised to relative response at 50°C.

important advantages over alumina and porous polymer PLOT columns. Crucially, the silica PLOT does not dehydrohalogenate labile hydrocarbons, as does alumina PLOT columns, so allowing the column to be used in the separation and quantitation of HCFC 22 and CH₃Cl. The retention and capacity of the silica PLOT is not influenced by water. Unlike the porous polymer-based PLOT columns, the silica PLOT elutes the less volatile compounds efficiently without the need for high (>200°C) oven temperatures. No bleed has been noted for the silica PLOT columns during these tests. The reproducibility of retention and of peak area are excellent. Overall the CP-SilicaPLOT column is amongst the most useful columns available for use in resolving halocarbons in tropospheric air. Halocarbons possessing a wide range of volatility can be baseline resolved with acceptable peak shapes. However, in common with all gas–solid columns, some peak tailing is found for the most strongly retained compounds.

The silica PLOT elutes the main halocarbon groups according to varying retention mechanisms. The mechanisms include (a) boiling point order for the chlorofluorocarbons, perfluorocarbons and chloromethanes, (b) hydrogen content and distribution within the molecule for the hydrofluorocarbons, and (c) chlorine content for the hydrochlorofluorocarbons. Only one pair of compounds (HCFC 124 and HCFC 142b) cannot be resolved using this column type. Because the silica PLOT is compatible with GC–MS, accurate determination of all tropospheric halocarbons should be possible using selective ions for quantitation. Work towards this aim is currently ongoing in our laboratory.

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