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Short communication

Separation of hydrohalocarbons and chlorofluorocarbons using a cyclodextrin gas solid chromatography capillary column

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Abstract

Chromatographic analysis of very volatile hydrohalocarbons and chlorofluorocarbons has proved to be a difficult task due to the generally poor retention of these compounds on commercially available wall coated open tubular capillary columns. Although porous layer open tubular (PLOT) capillary columns coated with alumina/KCl, or alumina/Na_2SO_4 provide adequate resolution for this class of compound they induce dehydrochlorination of certain hydrohalocarbons. More recently PLOT columns coated with Porapak porous polymer materials Q, S and U have been shown to provide inadequate resolution and high column bleed at the high column temperatures required for separation. We present results from the analysis of mixtures of hydrohalocarbons, chlorofluorocarbons, halocarbons, and halons, using a commercially available cyclodextrin PLOT column. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Capillary columns; Hydrohalocarbons; Chlorofluorocarbons

1. Introduction

The deleterious effect of chlorofluorocarbons (CFCs), halons and certain halocarbons on stratospheric ozone has led to the signing of international treaties to end their production and use [1]. The intermediate replacement compounds, the hydrochlorofluorocarbons (HCFCs), still contain ozone damaging chlorine and production in developed countries is due to be phased out by the year 2030 in accordance with the Copenhagen amendment to the Montreal Protocol. The hydrofluorocarbons (HFCs) although containing no chlorine, are strong infra-red absorbers and so important Greenhouse gases and as such have high global warming potentials (GWP) [2,3]. At present all of these types of compounds are being emitted or are present in the atmosphere and it is important to be able to identify and quantitate individual compounds to assess their rate of accumulation or decline [4–6].

The majority of compounds analysed in this study are gases which have high vapour pressures. The high volatility and wide boiling point range of these compounds has resulted in poor separation, even using wall coated open tubular capillary columns with sub-ambient cooling [7–9]. Gas–solid chromatography (GSC) columns utilise interactions between the solute and a solid stationary phase surface, as opposed to partition of a solute between vapour and liquid phases, as is the case in gas–liquid chromatography (GLC). It has been reported that the separation of low-molecular-mass volatile gases is easier using GSC due to the preference of transfer from a gas to a solid over a gas to a liquid [10].

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There are a number of different types of GSC column which include alumina porous layer open tubular (PLOT), molecular sieve PLOT and porous polymer PLOT, however, each of these types of column have been shown to exhibit deleterious effects with regard to the analysis of the range of volatile halocarbons we are interested in.

Alumina PLOT columns have been shown to dehydrochlorinate certain atmospherically important halocarbons such as CH_3Cl, CH_3CCl_3, $CHClF_2$ (HCFC-22), CH_3CClF_2 (HCFC-142b) and $CHCl_2CF_3$ (HCFC-123) [8,11–14]. This class of column also strongly retains water which can effect the efficiency of sample retention. Molecular sieve PLOT columns also strongly retain water and carbon dioxide. Porous polymer PLOT columns retain the less volatile halocarbons very strongly requiring high column temperatures to be used, this tends to cause an unacceptable level of column bleed from the stationary phase especially if mass spectrometry is the chosen form of detection.

The use of a cyclodextrin PLOT column offers a different approach to the separation of this type of compound. Cyclodextrins are cyclic oligosaccharides, the cyclic units form a conical structure with hydroxyl groups surrounding the two rims, which render the top and bottom of the cyclodextrin structure polar. Cyclodextrin PLOT columns are thought to retain analytes using two distinct retention mechanisms as a consequence of the different nature of the polar cavity edge and the non-polar cavity interior. Polar compounds have the capability to form hydrogen bonds to hydroxyl groups on the outer rim of the cavity whereas non-polar analytes are retained by inclusion within the hydrophobic cavity [15,16].

2. Experimental

2.1. Reagents

The compounds investigated in this study are listed with their boiling points, structures and molecular weights in Table 1, the compounds are listed with increasing boiling point. Individual halocarbons were injected onto the cyclodextrin column to determine elution order, as was a gas mixture. The mixture was gravimetrically prepared at the part per million level (ppt or μmol/mol) by Linde Gas UK (Stoke-on-Trent, UK) to achieve the highest possible accuracy, traceable to National Physical Laboratory (NPL) Weights (Accuracy ±1%).

2.2. Chromatographic conditions

Chromatographic analysis was performed using a Chrompack CP 9000 series gas chromatograph (Chrompack, Middelburg, The Netherlands) with a flame ionization detection (FID) system. Detector and injector temperatures were set at a temperature of 200°C and 150°C respectively. For sample introduction the instrument was equipped with a Valco air actuated sampling valve (VICI, Houston, TX, USA), and 15 μl gas-sampling loop. A commercial integrator (Phillips PU4810) was used to record the chromatograms. The elution order of electrophilic compounds, not easily detected using FID, was carried out using an HP6890 (Hewlett–Packard, Bracknell, UK) equipped with an electron-capture detection (ECD) system. The ECD temperature was set at 300°C and the nitrogen make up flow set at 25 ml min^{-1}. Separation was carried out using a cyclodextrin GSC capillary column (30 m×0.32 mm I.D., Astec, Whippany, USA) with a helium carrier flow-rate of 2 ml min^{-1}. The column flow was measured from the column outlet, at ambient temperature and pressure, on the Chrompack instrument. The flow was set at constant flow on the HP6890 using the on-board electronic pressure control (EPC). The oven temperature program was used for all analyses, unless otherwise stated was 35°C hold for 15 min, followed by a temperature ramp to 120°C at 5°C min^{-1}. A further 4-min hold was followed by a final ramp to 180°C at 5°C min^{-1}.

Individual compounds were injected (50 μl) using a set temperature program in order to elucidate the elution order of each compound, and provide information valuable for optimising the final temperature program. It should be noted that not all single compounds analysed were present in the gas mixtures and therefore, the location of certain species in the presented chromatograms can be inferred from the relative retention times listed in Table 1, assuming all chromatographic conditions were held constant.

Table 1
Compound description in boiling point order

Name	Formula	Boiling point (°C)	Concentration of prepared gas (ppmv[δ])	Relative retention time t'_R (min)[ϕ]
HFC 23[a]	CHF_3	−84.0	227	1.14
CFC 13	$CClF_3$	−81.0	1000	0.73
PFC 116	CF_3CF_3	−78.2	1000	0.41
Halon 1301[a]	$CBrF_3$	−57.8	212	3.51
HFC 32[a]	CH_2F_2	−51.6	130	5.22
HFC 125[a]	CHF_2CF_3	−48.4	167	10.60
HFC 143a[a]	CH_3CF_3	−47.6	171	11.49
HCFC 22[a]	$CHClF_2$	−40.8	332	12.39
PFC 218	$CF_3CF_2CF_3$	−39.0	1000	5.09
CFC 115[a]	CF_3CClF_2	−38.0	213	7.19
CFC 12[a]	CCl_2F_2	−30.0	1910	10.32
CFC 1113	$CClFCF_2$	−27.0	1000	10.81
HFC 134a[a]	CH_2FCF_3	−25.9	164	20.01
HFC 152a[a]	CH_3CHF_2	−24.7	179	23.93
CH_3Cl[a]	CH_3Cl	−24.2	1960	19.78
HFC 134	CHF_2CHF_2	−23.0	1000	22.60
HCFC 124[a]	$CHClFCF_3$	−11.8	167	25.40
HCFC 142b[a]	CH_3CClF_2	−9.8	170	25.40
Halon 1211[a]	$CBrClF_2$	−4.0	187	21.29
CH_3Br[a]	CH_3Br	3.6	153	25.11
CFC 114[a]	$CClF_2CClF_2$	3.7	179	24.39
HCFC 21	$CHCl_2F$	8.9	1000	27.09
CFC 11[a]	CCl_3F	23.8	990	26.75
HCFC 123[a]	$CHCl_2CF_3$	28.0	167	34.40
HCFC 141b[a]	CH_3CCl_2F	32.3	164	33.94
CH_2Cl_2[a]	CH_2Cl_2	40.0	165	31.60
CFC 113	$CClF_2CCl_2F$	47.7	1000	34.59
HCFC 225ca	$CHClCF_3CClF_2$	51.0	1000	41.55
HFC 143	CHF_2CH_2F	52.0	1000	27.78
HCFC 225cb	$CHClFCF_2CClF_2$	56.0	1000	42.37
$CHCl_3$[a]	$CHCl_3$	61.0	166	37.27
CH_3CCl_3	CH_3CCl_3	74.0	1000	42.66
CCl_4	CCl_4	76.3	1000	37.94
$CHClCCl_2$	$CHClCCl_2$	87.0	1000	40.43

[δ]Parts per million (v/v).

[a]Compounds present in Linde Gas Mixture.

[ϕ]$t'_R = t_R - t_M$ where t_R = retention time, t_M = retention time of unretained peak (N_2O). Temperature program used: 35°C hold 15 min, ramp at 5°C min^{-1} to 120°C, hold 4 min, ramp 5°C min^{-1} to 180°C hold 5 min.

3. Results and discussion

The separation of a mixture of halogenated compounds achieved using the cyclodextrin GSC column is shown in Fig. 1. As can be seen the more volatile compounds such as CHF_3 (HFC 23) and CH_2F_2 (HFC 32) are strongly retained by formation of host–guest inclusion complexes within cyclodextrin cavity interior, and hence have retention times which enable the compounds to elute as single baseline resolved peaks. All volatile compounds show excellent resolution and efficiency with the exception of three pairs of compounds. CCl_2F_2 (CFC 12) and CHF_2CF_3 (HFC 125), CH_3CClF_2 (HCFC 142b) and $CHClFCF_3$ (HCFC 124), co-elute and CH_3Cl and CH_2FCF_3 (HFC 134a) exhibit partial resolution. A number of temperature programs were attempted unsuccessfully to attain separation. It should be

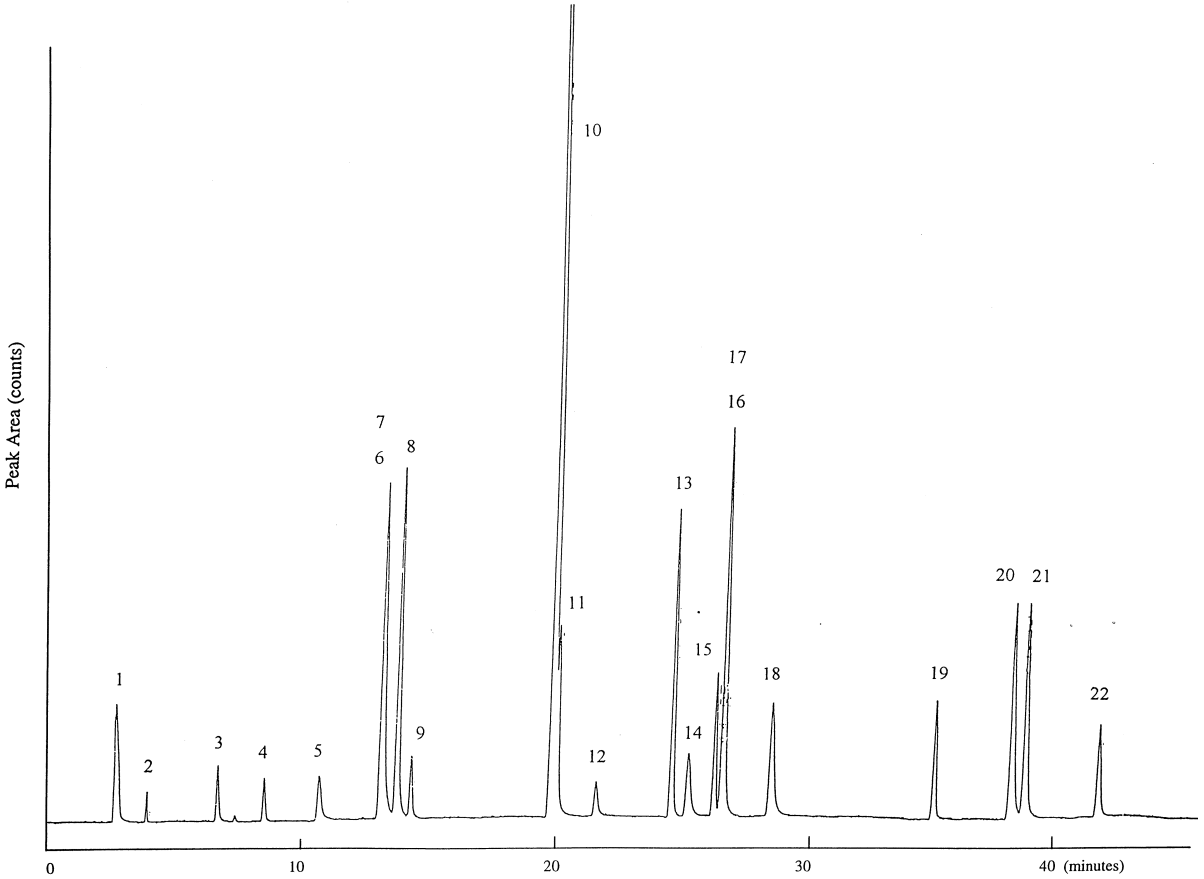

Fig. 1. Separation of halogenated compounds on 30 m cyclodextrin GSC column, GC–FID analysis. 1=N_2O, 2=CHF_3 (HFC-23), 3=$CBrF_3$ (Halon 1301), 4=CH_2F_2 (HFC-32), 5=CF_3CClF_2 (CFC-115), 6=CCl_2F_2 (CFC-12), 7=CHF_2CF_3 (HFC-125), 8=CH_3CF_3 (HFC-143a), 9=$CHClF_2$ (HCFC-22), 10=CH_3Cl, 11=CH_2FCF_3 (HFC-134a), 12=$CBrClF_2$ (Halon 1211), 13=CHF_2CH_3 (HFC-152a), 14=$CClF_2CClF_2$ (CFC-114), 15=CH_3Br, 16=CH_3CClF_2 (HCFC-142b), 17=$CHClFCF_3$ (HCFC-124), 18=CCl_3F (CFC-11), 19=CH_2Cl_2, 20=CH_3CCl_2F (HCFC-141b), 21=$CHCl_2CF_3$ (HCFC-123), 22=$CHCl_3$.

noted however, that these compounds can be deconvoluted using gas chromatography–mass spectrometry (GC–MS) by selecting ions characteristic to each compound. For example, CCl_2F_2 (CFC 12, m/z 85), CHF_2CF_3 (HFC 125, m/z 101), CH_3CClF_2 (HCFC 142b, m/z 85), $CHClFCF_3$ (HCFC 124, m/z 69), CH_3Cl (m/z 50) and CH_2FCF_3 (HFC 134a, m/z 69). The less volatile compounds in the mixture $CHCl_3$, $CHCl_2CF_3$ (HCFC 123), CH_3CCl_2F (HCFC 141b) and CH_2Cl_2 exhibit good peak shape and are well resolved. The retention time of these compounds is also not prohibitively long. A combination of boiling point, hydrogen bonding and number of chlorine atoms present in the molecule govern the elution order of these compounds. Molecules that can form hydrogen bonds are particularly strongly retained. Hydrogen bonding occurs between analyte hydrogen atoms, which are electron-deficient and the relatively electron-rich oxygen atoms of the cyclodextrin cavity rim hydroxyl groups. Compounds with adjacent hydrogen and fluorine atoms undergo this sort of interaction and have longer retention times than would be predicted on boiling point alone. A specific example is the elution of HFC 152a (CH_3CHF_2, b.p.=−24°C) after halon 1211 ($CBrClF_2$, b.p.=−4.0°C). Consequently compounds with higher boiling points, more hydrogen atoms and more chlorine atoms are retained longer.

The cyclodextrin column was evaluated for reproducibility of compound retention and response. This

was achieved by repeat injections ($n=5$) of the Linde gas mixture using the same sample introduction and gas chromatographic conditions. The R.S.D.s achieved for corrected retention time ranged from 0.07–1.24%, and peak area precision for resolved peaks ranged from 0.17–4.78%.

The proposed use of this column in this study is for the separation of volatile compounds, which are considered to be atmospherically important. Unlike the analysis of prepared standard mixtures, the compounds of interest are present in the atmosphere at vastly varying concentrations, they also need to be resolved from the myriad of other compounds present in the atmosphere. Fig. 2 shows an air sample (200 ml) which has been pre-concentrated using a method described elsewhere [3], and thermally desorbed onto the 30 m cyclodextrin column. Selective detection of the halogenated compounds is achieved using ECD. The chromatogram illustrates that the halogenated compounds are still well resolved from each other and from other possible interfering atmospheric compounds. Unfortunately, the same type of atmospheric analysis could not be carried out using FID because there was no FID system coupled to the pre-concentration device. It is envisaged however, that hydrocarbons present in atmospheric samples would cause a degree of interference. As previously mentioned this problem could be overcome using GC–MS and selecting ions characteristic of each halocarbon compound.

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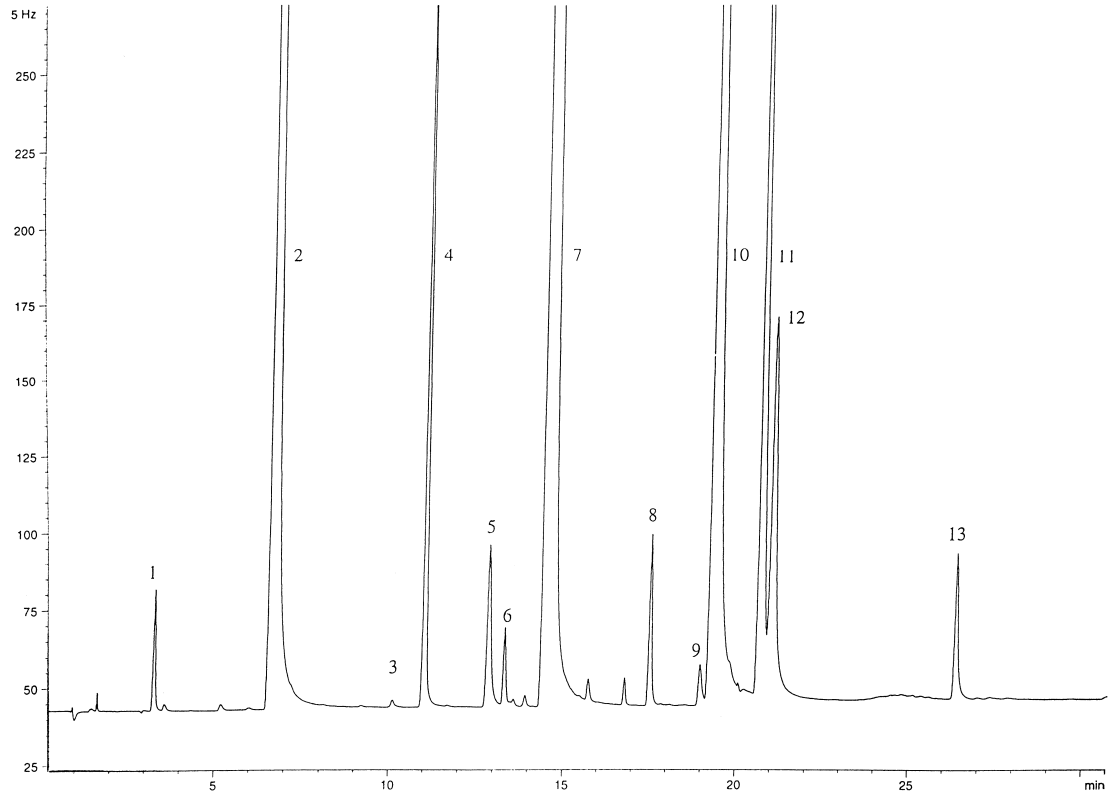

Fig. 2. Separation of ambient air sample (200 ml) on 30 m cyclodextrin GSC column, GC–ECD analysis. 1=$CBrF_3$ (Halon 1301), 2=CCl_2F_2 (CFC-12), 3=CH_3Cl, 4=$CBrClF_2$ (Halon 1211), 5=$CClF_2CClF_2$ (CFC-114), 6=CH_3Br, 7=CCl_3F (CFC-11), 8=CH_2Cl_2, 9=CH_3CCl_2F (HCFC-141b), 10=CCl_2FCClF_2 (CFC-113), 11=$CHCl_3$, 12=CCl_4, 13=CH_3CCl_3. Temperature program: 40°C hold 8 min, ramp 5°C min^{-1} to 150°C, hold 6 min. flow-rate 2 ml min^{-1}.

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