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Review

Gas chromatographic separation of perfluorocarbons

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ABSTRACT

This paper presents an overview of the gas chromatographic separation of perfluorocarbons. A summary is given of relevant information on the separation and identification of individual molecules, isomeric mixtures and multi-component mixtures of perfluorocarbons. Different types of columns (packed and capillary), fluorinated stationary phases, and detectors are described. Future work towards quantitative analysis with the possible use of fluorinated capillary columns is indicated.

CONTENTS

1. INTRODUCTION

The term "perfluoro" denotes fluorine substitution of all hydrogen atoms attached to carbon atoms except those whose substitution would affect the nature of the functional group. Perfluorocarbons vary in their physical state depending on their molecular formula, in general, C_1–C_4 are gases, C_5–C_{19} are liquids and C_{20}–C_{24} are solids [1]. They have structures analogous to the familiar hydrocarbons but possess very different chemical and physical properties. They are generally chemically inert but have varying degrees of toxicity, ranging from the "non-toxic" fluids such as n-perfluorohexane, perfluorodecalin and perfluoro(1-methyldecalin) [2] to the most toxic of all perfluorinated molecules, perfluoroisobutylene (iso-C_4F_8). The latter is ten times more toxic than phosgene and has a T.W.A. (time weighted average, v/v) of 10 ppb [3].

A preliminary investigation by our research group [4], into the gas-phase pyrolysis of perfluorocarbons, mainly perfluoroalkanes, -alkenes

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and -cycloalkanes suggested that gas chromatography (GC) would be the preferred analytical technique for the identification and quantitative analysis of their decomposition products. Since the advent of GC in 1952 [5], perfluorocarbons have been studied mainly in tandem with chloro and hydrofluorocarbons. Perfluorocarbons have also been studied as a specialist class of compounds for use both as atmospheric tracers [6–9] and in tagging applications [10,11]. The present article has been compiled to give an overview of the GC separation of perfluorocarbons. The perfluorocarbon compounds reviewed are those containing carbon and fluorine only, with no functional group. The GC of perfluorocarbons will be discussed under three main headings: separation (packed and capillary column), detector response and fluorinated stationary phases.

2. SEPARATION OF PERFLUOROCARBONS

Early GC studies involved a search for suitable columns to separate and identify individual or small specific groups of perfluorocarbons. Perfluorocarbons often have very low polarity, hence a non-polar column is expected to be more suitable. However, the separation and identification of multi-component perfluorocarbon mixtures has proved difficult due to their varying degrees of polarity and differences in their physical properties, especially their wide range of boiling points.

2.1. Packed columns

As early as 1955, Tatlow and co-workers separated perfluorohexabenzene [12] and numerous perfluorocyclohexadienes [13,14] on a 6-ft. (1 ft. = 30.48 cm) glass column containing a 1:2 ratio of dinonylphthalate liquid substrate with kieselguhr (Celite 545) as the solid support. These authors made the suggestion that "other high boiling liquids such as the chlorofluoro oils and silicones..." would be useful stationary phases for perfluorocarbon analyses. This led Reed [15] to investigate the chromatographic behaviour of n-perfluoropentane, n-perfluoroheptane and n-perfluorononane on several fluorocarbon and hydrocarbon stationary phases.

Results showed that these fluorocarbon phases —the ethyl ester of Kel F acid 8114 $[Cl(CF_2CFCl)_3CF_2CO_2C_2H_5]$, Kel F No. 90 grease $[Cl(CF_2CFCl)_3CF_3]$, perfluorokerosine and perfluorotributylamine— gave better separation of perfluorocarbon mixtures than the hydrocarbon stationary phases —di-(2-ethylhexyl) sebacate $[X–(CH_2)_8–X$, where $X = CO_2CH_2$-$CH(C_2H_5)(CH_2)_3CH_3]$ and n-hexadecane. However, these fluorinated phases were not suitable for the separation of perfluorocarbon isomers with similar boiling points. Fluorinated stationary phases will be discussed further in section 4.

Pyrolytic studies of chlorodifluoromethane [16] yielded several C_3–C_5 perfluorocarbons. However, these products eluted too rapidly when separated on a 9-ft. column containing firebrick impregnated with dibutylphthalate. Campbell and Gudzinowicz [17] studied the separation of CF_4, C_2F_4, C_3F_6, cyclo- and iso-C_4F_8, obtained from the pyrolytic degradation of PTFE; four different liquid substrates on a Chromosorb W (diatomite–amorphous silica [18]) solid support were used. They found that the three non-fluorinated stationary phases, Apiezon L (hydrocarbon grease), a polymeric phenyl ether with a molecular mass ≈ 15 000 and diisodecylphthalate gave poor performance and suggested that the Kel F No. 3 oil $[Cl(CF_2CFCl)_7CF_3]$ was superior for the separation of perfluorocarbons. Reed and co-workers then reported the separation of both the C_6F_{14} [19,20] and C_7F_{16} isomers [21] by use of n-hexadecane on Chromosorb P held at 30°C. A very long column (17 m) was used which is limited to the separation of perfluorocarbon isomers with less than 8 carbon atoms by the narrow operating temperature range 20–50°C of n-hexadecane. However, MacKenzie and Wilson [22], using n-hexadecane did identify perfluoro-1,1-dimethylcyclopentane (C_7F_{14}) from the pyrolysis of perfluorobicyclohexyl.

Greene and Wachi [23] concluded that the Kel F oils were not completely satisfactory for separating low-molecular-mass perfluorocarbons $(C_1–C_4)$ and they reported the separation of $C_1–C_4$ perfluorocarbons on a GSC column of silica gel and on a GLC column of 1H,7H-dodecafluoroheptyl acrylate (DFHA) $[CH_2=$

CHCO$_2$CH$_2$(CF$_2$CF$_2$)$_3$H] on Chromosorb W. The silica gel column was programmed from room temperature to 180°C, with a total elution time of 60 min for the eleven C$_1$–C$_4$ compounds. However, the *cis* and *trans* isomers of perfluoro-2-butene were not separated. With the GLC column, the eleven C$_1$–C$_4$ perfluorocarbons were separated in about 18 min at 0°C including the *cis* and *trans* isomers of perfluoro-2-butene. Cyclo-C$_3$F$_6$ and perfluoro-1-propene were not resolved. Davenport and Miller [24] and Rogers *et al.* [25] using the same type of columns as Greene and Wachi [23], silica gel and DFHA on Chromosorb W, studied the breakdown products of the photolysis of perfluorocyclobutane [24] and pyrolysis–GC of *n*-perfluoropentane [25]. Davenport and Miller reported up to 47 chromatographic peaks with an elution time of 15 h, most of which were unidentified. However, they did identify C$_2$F$_4$, C$_2$F$_6$, C$_3$F$_8$ and cyclo-C$_4$F$_8$. Rogers *et al.* identified five pyrolysis products in all, C$_2$F$_4$, C$_2$F$_6$, C$_3$F$_6$, C$_3$F$_8$ and *n*-C$_4$F$_{10}$ with a total elution time of 10 minutes. Meanwhile Tatlow and co-workers [26–30] again using a column containing dinonylphthalate on kieselguhr separated and identified several perfluoroaromatic compounds. These had been obtained from the defluorination of cyclic aliphatic fluorocarbons [26,27] and highly fluorinated cyclohexanes [27–30], and from pyrolytic reactions of perfluoroisopropylcyclohexane [30].

In 1968, Drennan and Matula [31], using a composite Porapak column (2 ft. 50–80 mesh Poropak T in series with 4 ft. of 50–80 mesh Poropak N), separated a carbonyl fluoride–carbon dioxide mixture. Bright and Matula [32] using various Porapak supports of differing polarity (N, Q, R, S and T) separated fourteen low-molecular-mass perfluorocarbons ranging from CF$_4$ to iso-C$_4$F$_8$. The advantage of this type of column was the elimination of liquid substrate bleed onto the detector, enabling operation up to 200°C with minimum retention times. The aim was to use Porapak columns for the analysis of combustion products of low-molecular-mass perfluorocarbons. One point to note is that Fig. 1 of reference 32 contains several errors, for example, two individual peaks in the chromatogram of their Fig. 1 are assigned retention times of 10.4 min for iso-C$_4$F$_8$ and 15.4 min for (CF$_3$)$_2$C=CF$_2$, respectively. Unfortunately, (CF$_3$)$_2$C=CF$_2$ and iso-C$_4$F$_8$ represent the same compound under different nomenclature. The peak at 10.4 min could be perfluoro-1-butene, with iso-C$_4$F$_8$ having the retention time of 15.4 min. Nevertheless the Porapak column proved to be the most suitable for separating low-molecular-mass perfluorocarbon mixtures. Wright and Askew [33] extended the use of the silica gel column [23–25] by separating the C$_1$–C$_8$ *n*-perfluoroalkanes into their respective molecular mass classes. A dual-column system was used to eliminate the base line drift observed in earlier studies [33]. The authors listed no overlapping peaks, no tailing and a satisfactory separation of air and CF$_4$, as advantages for the dual column method. However, the separation of isomers was not realized.

In 1978, Shields and Nieman [34] reported the separation of selected hydrocarbons and perfluorocarbons (isomers of C$_5$F$_{12}$, C$_6$F$_{14}$ and C$_7$F$_{16}$) on a graphitized carbon black column to which a moderately polar stationary phase 0.1% (w/w) SP-1000 (prepared from polyethylene glycol and tetraphthalic acid) had been added. Various investigators [35–39] had reported the use of graphitized carbon black as an efficient material for separating hydrocarbon isomers. Results showed that this new column allowed the separation of isomeric perfluorocarbons as effectively as the *n*-hexadecane column. In addition, it operates over a larger molecular mass range and with improved analysis times. Its only disadvantage is the rather low sample capacity, not a problem for analytical applications.

In the early 1980s GC of perfluorocarbons centred around the detection of the highly toxic perfluoroisobutylene (iso-C$_4$F$_8$) because of its formation in the work place in processes such as condensation reflow soldering [40]. Markevka *et al.* [41] generated a reference sample of iso-C$_4$F$_8$ and quantitatively determined it in air mixtures using a Carbowax 400 (polyethylene glycol) on a Porasil C (pure silica) column. However, no attempt was made to separate other perfluorocarbons. Meanwhile, Buravtsev *et al.* [42] using a Porapak column, identified iso-C$_4$F$_8$ in the dimerization of tetrafluoroethylene in an adiabatic compression device.

More recently, Ainagos [43] used a silica gel column to study the pyrolysis products of n-perfluorohexane. A similar study of the pyrolysis of n-perfluorooctyl-1-sulphonyl fluoride [44] identified products such as n-C_8F_{18}, n-$C_{12}F_{26}$ and n-$C_{16}F_{34}$. These were separated using a GLC column containing 5% SE-30 (dimethylsiloxane) on Chromosorb P. The GC separation and determination of impurities in sulphur hexafluoride [45] was performed using a silica gel column containing 25% diisooctyl sebacate. Impurities discovered included CF_4, C_2F_6, C_3F_8 and n-C_4F_{10}. Table 1 (GLC) and Table 2 (GSC) list the most useful packed columns reported.

2.2. Capillary columns

A recent advance in chromatography is to distribute the stationary phase as a film of liquid on the internal wall of columns with capillary dimensions (capillary or open tubular columns). However capillary columns have not been fully exploited for the analysis of perfluorocarbons. Only a few examples have been found and are given in Table 3. Ghaoui et al. [46] used an alumina open tubular column to separate C_5 and C_6 perfluoroalkanes. DeBortoli and Peechio [47] used a fused-silica capillary column for determining n-perfluoroheptane and n-perfluorooctane in air after trapping on a graphitized carbon black bed. The use of perfluorocarbons as tracers in the atmosphere [48] led Begley et al. [49] to study high-molecular-mass perfluorocarbons

($M_r > 250$) such as perfluorodecalin. They employed a fused-silica capillary column coated with SE-54 (5% diphenyl/94% dimethyl/1% vinyl polysiloxane). Femtogram level detection was achieved by using electron-capture negative ion chemical ionization mass spectrometry (ECNICI-MS).

TABLE 2

GSC PACKED COLUMNS

Column	Perfluorocarbons separated	Refs.
Silica gel	CF_4, C_2F_4, C_2F_6, C_3F_8, cyclo-C_4F_8, iso-C_4F_8	23–25, 43
	n-(C_2F_6, C_3F_8, C_4F_{10}, C_5F_{12}, C_6F_{14}, C_7F_{16}, C_8F_{18})	33
	C_2F_4, C_2F_6, C_3F_6, C_3F_8, n-C_4F_{10}	43
Porapak	CF_4, C_2F_4, C_2F_6, C_3F_6, C_3F_8, 1-C_4F_8, 2-C_4F_8, iso-C_4F_8	32
	Iso-C_4F_8	42

TABLE 3

CAPILLARY COLUMNS

Column	Perfluorocarbons separated	Ref.
Alumina plot	n-C_5F_{12}, n-C_6F_{14}	46
Fused silica	$C_6F_{13}CF_3$, $C_6F_{12}(CF_3)_2$	47
Fused silica/SE-54	$M_r > 250$	49

TABLE 1

GLC PACKED COLUMNS

Column	Perfluorocarbons separated	Refs.
Dinonylphthalate on kieselguhr	C_6F_6, cyclo-C_6F_{10}	12–14, 26–30
Kel F acid 8114 on Celite	Isomers of C_5F_{12}, C_7F_{16} and C_9F_{20}	15
Kel F No. 3 on Chromosorb W	CF_4, C_2F_4, C_3F_6, cyclo-C_4F_8, iso-C_4F_8	17
Hexadecane on Chromosorb P	C_6F_{14} isomers	19, 20
	C_7F_{16} isomers, C_7F_{14} isomers	21, 22
DFHA on Chromosorb W	CF_4, C_2F_4, C_2F_6, C_3F_6, C_3F_8, cyclo-C_4F_8, iso-C_4F_8	23–25
SP-1000 on graphitized carbon black	Isomers of C_5F_{12}, C_6F_{14} and C_7F_{16}	34
Carbowax 400 on Porasil C	Iso-C_4F_8	3, 40, 41
SE-30 on Chromosorb P	n-C_8F_{18}, n-$C_{12}F_{26}$, n-$C_{16}F_{34}$	44
Diisooctylsebacate on silica gel	CF_4, C_2F_6, C_3F_8 and n-C_4F_{10}	45

3. DETECTOR RESPONSE TO PERFLUOROCARBONS

Various detectors have been used for the detection of perfluorocarbons. The electron-capture detector, first introduced by Lovelock and Lipsky [50], can be the most sensitive for halogenated compounds and is also highly selective. In 1966 Clemons and Altshuller [51] measured the response of an electron-capture detector to numerous halogenated substances. They found that responses for perfluorocarbons varied from extremely low for CF_4 to high for C_6F_6. Christophorou et al. [52] reported on the general tendency of perfluorocarbons to undergo non-dissociative electron capture. As early as 1971 Lovelock [53] reported the presence of fluorinated hydrocarbons in the atmosphere which were detectable by electron-capture detection (ECD). Saltzman et al. [54] conducted successful tracer experiments with cyclo-C_4F_8. Other compounds detected with ECD such as perfluoromethylcyclohexane, perfluorodimethylcyclohexane and perfluorodecalin are tracers which can be separated from most atmosphere halocarbons on conventional silicone columns [55,56]. Dietz et al. [56] used perfluorinated taggants in blasting caps and explosives for later detection by electron-capture monitors. A useful general reference on the electron-capture detector is the book by Poole and Zlatkis [57]. Simmonds [58] successfully used the electron-capture detector as a monitor of halocarbons in the atmosphere. The large rate constant for electron attachment for C_7F_{14} has been reported by Chen and Wentworth [59].

The response of flame ionization detectors has been similarly investigated. In the 1970s the response of a flame ionization detector was investigated for CF_4–C_8F_{18} perfluoroalkanes using silica gel [60] and Porapak [61] columns. CF_4 showed essentially no response in comparison to a response approaching unity as the number of carbon atoms increases towards eight atoms. This is a result of the C–F bond being more difficult to break compared with the C–C bond in the perfluorocarbons and explains the high response of the flame ionization detector to larger molecular masses. A group of Japanese

TABLE 4

DETECTOR RESPONSE FOR CF_4

Detector	Response (Coulomb mol^{-1})	Column	Ref.
Electron-capture	$7.2 \cdot 10^{-7}$	Alumina	51
Flame ionization	$1.1 \cdot 10^{-6}$	Silica gel	60
Flame ionization	$7.6 \cdot 10^{-5}$	Porapak	61
Flame ionization, H$_2$ rich	$2.3 \cdot 10^{-5}$	Porapak	63
Flame ionization, H$_2$ rich	$2.7 \cdot 10^{-4}$	Silica gel	64
Helium ionization	$4.4 \cdot 10^{-3}$	Porasil	65

workers have determined the retention indexes of 221 halogenated organic compounds although only four perfluorocarbons were determined [62]. The use of a hydrogen-rich flame in connection with a flame ionization detector [63] showed that low carbon numbers, CF_4 and C_2F_6, increased their detector response compared with a normal flame ionization detector [60,61]. In addition, for high carbon number perfluorocarbons such as cyclo-C_6F_{12} and cyclo-C_7F_{14} [64], it was proved that they have a response similar to that of the corresponding hydrocarbon and independent of the conditions of the flame. The use of a helium ionization detector [65], (operating on the basis of ionization by metastable helium with sufficient energy (19 eV) to ionize CF_4 as well as the higher-M_r perfluorocarbons) showed a greater response for C_2–C_5 perfluorocarbons than that reported for both the flame ionization [60,61,63–65] and electron-capture detectors [51]. Table 4 shows the response to CF_4 for the various detectors.

4. FLUORINATED STATIONARY PHASES

A further development, in perfluorocarbon chromatography, has been the use of perfluorinated stationary phases. The intention was to extend the range of organic compounds that could be analysed by GC and also permit the analysis of thermally labile compounds. Intermolecular forces in fluorinated hydrocarbons are significantly weaker than in the equivalent hydrocarbon, thus making the separation of high-

molecular-mass or thermally labile samples possible at lower temperatures than on conventional non-fluorinated phases [61,66–68]. A more recent paper tested six phases one of which was perfluorodecalin [69].

Reed [15] initiated the use of perfluorocarbon stationary phases with his investigation into the chromatographic behavior of n-C_5F_{12}, n-C_7F_{16} and n-C_9F_{20} on perfluorokerosine and perfluorotributylamine. Results showed that these perfluorinated stationary phases gave better separation of perfluorocarbons than hydrocarbon phases. Campbell and Gudzinowicz [17] compared fluorinated and non-fluorinated stationary phases, during an investigation into the pyrolysis of commercial PTFE. They found that the non-fluorinated stationary phases gave poor performance and suggested that the Kel F oil-fluorinated phase was superior for the separation of high-boiling perfluorocarbons. Brown et al. [68] favoured the use of fluorinated stationary phases for the separation of perfluorocarbons and perfluoroalcohols. The pyrolytic reactions of perfluoroisopropylcyclohexane and various perfluorodicyclohexyl alkanes were investigated by Letchford et al. [30]. They used perfluoro-1,2-dicyclohexylethane as the stationary phase to separate and identify newly prepared perfluorocyclopentenes. However, column efficiencies were generally poor.

In 1975, Vernon and Edwards [70,71] studied four fluorinated stationary phases. Three of the phases, Kel F No. 90 grease, Fluorolube 2000 (chlorofluorocarbon) and silicone QF-1 [poly(methyl-3,3,3-trifluoropropyl siloxane)] had been available for some time, while the fourth phase Krytox 240 AC (perfluoroalkyl ether) was

a new stationary phase. A range of aromatic perfluorocarbons, perfluoroparaffins and perfluorolefins were studied chromatographically on these four stationary phases. The authors compared these phases using column efficiencies, retention indices (I) and McReynolds constants (ΔI) as defined in refs. 72–75.

Table 5 gives the McReynolds constants for the stationary phases investigated by Vernon and Edwards [70]. All are of low polarity, with Krytox the least polar and silicone QF-1 having the highest polarity. The authors found that the film stability and column efficiency of fluorinated phases could be dramatically enhanced by incorporating polar anchor groups into its structure. Krytox was the first of this stationary phase type and was found to give the highest retention indices.

In 1983, Dhanesar and Poole [76,77] described the properties of a new perfluorocarbon stationary phase, Fomblin YR [$(OCFCF_3CF_2)_n$–$(OCF_2)_m$] similar to Krytox. This new phase provided thermally stable column packings with acceptable column efficiency for general chromatographic use, especially for low-polarity organic compounds. Fomblin YR, with a molecular mass of 6000–7000, provides columns of high efficiency that can be used at temperatures up to 250°C. Above this temperature the stationary phase film is no longer homogenous and the column efficiency declines. Fomblin YR provides some of the weakest non-polar interactions exhibited by any thermally stable phase. The authors suggested that this perfluoroalkyl ether phase might prove useful for separating perfluorocarbons.

Fluorocarbon surfactants containing polar

TABLE 5

McREYNOLDS CONSTANTS FOR VARIOUS STATIONARY PHASES AND SOLUTES [70]

Phase	McReynolds constant				
	Benzene	n-Butanol	2-Pentanone	Nitropropane	Pyridine
Krytox	4	148	86	147	93
Kel F No. 90	41	135	134	153	111
Fluorolube 2000	75	192	148	200	158
Silicone QF-1	130	225	336	432	281

functional groups, for example Fluorad FC-430, an aliphatic perfluoroalkyl polymeric ester, were shown to function effectively as a stationary phase for GC [78,79]. Potential applications included separation of thermally sensitive brominated compounds, low level hydrocarbons and the separation of oxygenated hydrocarbons in aqueous systems. Likewise, the tetraalkylammonium perfluoroalkane sulphonate liquid organic salts proved to have acceptable chromatographic properties towards a wide range of polar solutes [66,67].

A chromatographic investigation [80,81] into several perfluorinated {PTFE, fluortensid [$CF_3(CF_2)_nCF=CF-CF_2(OCH_2CH_2)_mOCH_3$] where $n = 6–8$ and $m = 2–5$ and a Kel F oil $Cl(CF_2-CFCl)_nCl$} and non-fluorinated (squalane, polyethylene glycol) stationary liquid phases coated on a Chromosorb P support was carried out. Retention indices and McReynolds constants were reported for each individual stationary phase, using the following perfluorocarbon solutes: perfluoro(C_6–C_{10}) carboxylic methyl esters [80], normal C_6–C_{10} perfluoroalkanes and perfluorocyclobenzene [81]. These results showed that the fluorinated stationary phases were more selective for perfluorocarbons than the non-fluorinated phases. However, no results were given for low-molecular-mass (C_1–C_4) perfluorocarbons. Glajch and Schindel [82] used Krytox to separate numerous chlorofluorocarbons (Freons) and their isomers in the presence of reactive gases, such as HF and HCl. The columns employed were a 5% Krytox 143 AC on Carbopack (graphitized carbon black) and a 2.5% krytox/2.5% benzophenone on Carbopack. Both these columns were found to be inert to reactive gases and therefore could be used for on-line analysis of fluorocarbons in processes in which acid gases might be present. The columns gave excellent selectivity for the chlorofluorocarbons and fast analysis times at reasonable temperatures [82].

Pomaville and Poole [83] studied the chromatographic properties of eight fluorinated phases: perfluoroalkane ($C_{22}F_{46}$), Kel F oil [17,71], Fluortensid [81], Krytox [70,71,82], Fomblin YR [76,77]. Zonyl E-91 (fluoroalkyl ester of camphoric acid) [78], Fluorads FC 430 and FC 431 (fluorocarbon surfactants) [78,79] and PPF-20 (a polyperfluorophenylene ether). The McReynolds constants and column efficiencies were given for each phase; the retention mechanism of organic solutes and the strength of dispersion interactions with each phase was established. Reduced peak tailing and faster elution times were observed for compounds containing hydrogen-bonding functional groups. Preparation of efficient column packings with these phases was also reported. However, the authors were mainly concerned with the chromatographic properties of their phases and not

TABLE 6

FLUORINATED STATIONARY PHASES

Name	Structure	Refs.
Fluorad FC 430, 431	Fluorocarbon surfactant	78, 79
Fluorolube	$Cl(CF_2CFCl)CF_2COOR$	71, 83
Fluortensid	$CF_3(CF_2)_nCFCFCF_2(OCH_2CH_2)_3OCH_3$	80, 81, 83
Fomblin	$-(OCFCF_3CF_2)_n-(OCF_2)_m$	76, 77, 83
Kel F	$Cl(CF_2CFCl)_nCF_3$	17, 70, 71, 83
Krytox	$F-(CFCF_3-CF_2O)_n-CF_2CF_3$	70, 71, 82, 83
PTFE	$-(CF_2)_n-$	80, 81
PPF-20	Poly(perfluorophenylene) ether	83
Perfluorodicyclohexylethane	$(C_6F_{11})_2CFCF_3$	30
Perfluorokerosine	$C_{14}F_{30}$	15
Perfluorotributylamine	$[CF_3(CF_2)_3]_3N$	15
Silicone QF	Poly(methyl-3,3,3,trifluoropropylsiloxane)	70, 71
Zonyl E-91	Fluoroalkyl ester of camphoric acid	83

the separating of any particular solutes except those for the calculation of the McReynolds constant. They suggested that new perfluorinated phases should be synthesized and investigated exclusively for chromatographic purposes. Table 6 gives a list of the highly fluorinated stationary phases used in GC.

5. DISCUSSION

As outlined above numerous researchers have investigated the GC of perfluorocarbons, each one employing columns and detectors for their own area of interest. A variety of columns have been employed to separate and identify various perfluorocarbons (Tables 1, 2, 3 and 6). Some columns have been used to analyze for one individual perfluorocarbon, others have been designed to separate isomeric and multicomponent mixtures. The different physical properties associated with perfluorocarbons —gases (C_1–C_4), liquids (C_5–C_{19}) and solids (C_{20}–C_{24})— present a difficulty in making the simultaneous separation of low- to high-molecular-mass perfluorocarbons on a single column. The majority of the chromatographic analyses have been performed on the separation and identification of the gases and C_5–C_9 liquids. The present survey has revealed little information regarding the analysis of the C_{10}–C_{19} liquids and C_{20}–C_{24} solids. A difficulty is that thick film GC columns are required to separate the low-boiling-point compounds as well as starting from a subambient temperature. When temperature programming this type of column the upper temperature limit of the phase is reached quite quickly and the detector is affected by column bleed. It is therefore usual to use columns that cover the boiling point range for each compound. Sometimes the capillary columns are coupled together to extend the range of compounds that can be separated.

The silica gel column [23–25,33,43,45,60] proved to be the most successful column for the separation of gas and liquid mixtures of perfluorocarbons. However, elution times are often impractical. The Porapak column [32] proved to be more efficient with reasonable elution times for C_1–C_4 gas analysis. Note, that this column

renders an electron-capture detector inoperative, due to a high level of polymeric bleeding [4]. Isomeric mixtures were first separated by Reed [15,20] and Askew and Reed [21] using a n-hexadecane on Chromosorb P column. Shields and Nieman [34] continued with this work, using the column, SP1000 on graphitized carbon black, which allowed the separation of (C_5–C_7) isomers. They found their column to be more efficient than the n-hexadecane column, with shorter analysis times and the ability to separate over a larger molecular mass range.

Research into new perfluorinated stationary phases, as suggested by Pomaville and Poole [83], has not been reported. Table 6 lists the fluorinated stationary phases which are used in GC. These phases have been used mainly for the separation of chemically reactive compounds such as metal halides, interhalogen compounds, and the halides of hydrogen, sulphur, phosphorus, freons and other high fluorinated organic molecules [66–68,70,71,76,77,79–84]. Little work has been done with these columns for the analysis of perfluorocarbons. Nevertheless, they have extended the molecular mass range of samples that can be analyzed by GC and permit the analysis of thermally labile substances. However, with the introduction of Krytox [70,71,82,83] and Fomblin [76,77,83] and the investigation into other fluorinated stationary phases, it has been observed that the new fluorinated stationary phases may be selective for perfluorocarbons. Although film stability deteriorates markedly at about 100°C for the early fluorinated phases, due to their weak interactions with the support. The temperature tolerance of the new fluorinated phases is in the range 200–250°C [83]. The relative simplicity in the preparation of these chemically inert, low polarity functionalized fluorinated phases makes them favourable for the separation of low polarity perfluorocarbons. Conventional packed columns have been used extensively to separate perfluorocarbons. Capillary columns with their greater resolution and efficiency, have yet to be fully exploited for perfluorocarbons although they are now widely used for other halocarbons. For the gases usually subambient temperatures are required as well as 5-μm thick films or

porous-layer open tubular columns to obtain longer retention times for these more volatile compounds.

The flame ionization and electron-capture detectors are the two most popular detectors for perfluorocarbons. The bulk of the work has been done with conventional flame ionization detection. However, for low-molecular-mass perfluorocarbons a hydrogen-rich flame or metastable helium ionization is necessary to provide reasonable response factors. The electron-capture detector is generally more sensitive but can become unworkable due to polymeric bleeding from some columns. Mass spectrometer detectors, again very sensitive, will become increasingly important when capillary columns become more widely used for perfluorocarbon analysis.

6. CONCLUSIONS

GC has been effective in separating C_1–C_9 perfluorocarbons. The majority of the analyses have been performed on packed columns. This is due to their simplicity in preparation compared to the difficulty in preparation and cost of a capillary column. Future work needs to be directed towards capillary GC especially for the separation of low-molecular-mass perfluorocarbons. In addition, the separation of high-molecular-mass C_{18}–C_{24} perfluorocarbon molecules needs to be studied more extensively. No chromatography column, as yet mentioned in the literature will separate all perfluorocarbons. The possible use of perfluorinated stationary phases for capillary GC may be one way forward.

In the past most authors carried out qualitative GC analysis of perfluorocarbons with only a few reporting quantitative results. In China some workers have carried out a quantitative analysis on fluorocarbons in artificial blood preparations using perfluorobenzene as an internal standard. One of the blood substituents was relatively "non-toxic" perfluorodecalin [85]. There is also a demand now for quantitative results particularly when handling toxic compounds such as perfluoroisobutylene. Therefore limits of detection and sensitivity of the detector will need to be determined, in order to measure the very low levels of perfluorocarbons and their breakdown products in complex mixtures, for example air samples.

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