Note

Preparation of efficient packed columns with a polyperfluoroalkyl ether stationary phase

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Fluorocarbon stationary phases (*e.g.*, perfluoroalkanes, Kel-F oils, fluoroalkyl esters) have been used for the gas chromatographic (GC) separation of compounds with high reactivity (*e.g.*, UF_6, ClO_2F, SF_5Cl, etc.)[1–6]. For the above applications the fluorocarbon stationary phases were selected because of their chemical inertness. Columns prepared with these fluorocarbon phases on PTFE or diatomaceous supports invariably exhibited poor column efficiencies and generally restricted temperature operating ranges compared to silicone and polyester phases introduced at about the same time. Typical column efficiencies were stated to be in the range of 30–225 theoretical plates per meter[1–6], a value which would be considered too low for general use. More recently, Chromatographic Specialties Ltd. have introduced column packings coated with Fluorad FC-431 which provides moderately efficient columns suitable for separating alcohols, phenols and amines at temperatures up to 200°C[7]. Fluorad FC-431 is a fluoroalkyl ester produced by the 3M Company (St. Paul, MN, U.S.A.). Its exact composition is proprietory information. The perceived and real difficulties anticipated in the preparation of efficient and thermally stable perfluorocarbon stationary phase packings have diverted attention away from their potential usefulness as general phases in gas chromatography.

Chemical inertness is only one useful property of fluorocarbon compounds. Intermolecular forces in fluorocarbon compounds are very weak resulting in lower-than-expected boiling points[8] and low retention on non-polar and polar organic stationary phases. For many years chromatographers have taken advantage of this property by preparing perfluorinated derivatives for the analysis of polar compounds of low volatility[9,10]. The perfluorinated derivatives invariably being more volatile than the parent compounds of similar hydrocarbon-containing derivatives. It should, therefore, be possible to chromatograph organic compounds on perfluorocarbon stationary phases at lower temperatures than is currently possible with conventional stationary phases. In such circumstances, it might be feasible to chromatograph higher-molecular-weight organic compounds than is presently possible or to chromatograph thermally labile compounds at a sufficiently low temperature that they are stable. To test the above hypothesis a thermally stable fluorocarbon stationary phase having reasonable selectivity for organic compounds and acceptable coating efficiency is required.

As a candidate stationary phase the polyperfluoroalkyl ether, Fomblin YR, the structure of which is

$$CF_3$$
$$|$$
$$(O-CF-CF_2)_n-(O-CF_2)_m$$
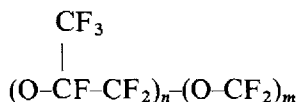
was selected. It has an average molecular weight of 6000–7000, is a liquid with a pour point of $\approx -20°C$ and is thermally stable to temperatures in excess of 300°C. The polyperfluoroalkyl ethers are commercially available, synthetic, inert, functional fluids used as engine lubricants and vacuum pump oils[11-13]. Fomblin-L, a lower-molecular-weight homologue of Fomblin YR, has been used as a reference standard for calibrating mass spectrometers in the high mass range[14].

EXPERIMENTAL

Test compounds were available in kit form (Thetakits, Anspec, Ann Arbor, MI, U.S.A.). Perfluorokerosene-L, b.p. $\approx 90°C$ was obtained from PCR Research Chemicals (Gainesville, FL, U.S.A.), and WD-40 oil from WD-40 Company (San Diego, CA, U.S.A.). Trichlorofluoromethane (Freon 11) was obtained from Matheson Gas Products (East Rutherford, NJ, U.S.A.) and 1,1,2-trichlorofluoroethane (Freon 113) from Aldrich (Milwaukee, WI, U.S.A.). Fomblin YR was obtained from Montedison (New York, NY, U.S.A.).

Column packings were prepared by the rotary evaporator coating technique using Freon 113 as solvent. The air-dried packings were sieved before use. Glass columns of various lengths were packed by vacuum suction and gentle vibration. On-column silylation was performed before use by injecting slowly 100 μl of silyl-8 or bis(trimethylsilyl)trifluoroacetamide (BSTFA) into the column at 150°C with a nitrogen carrier gas flow-rate of 30 ml min^{-1}.

For GC a Varian 3700 gas chromatograph with an on-column heated injector and flame ionization detector was used. Separation conditions are given in the figure legends.

RESULTS AND DISCUSSION

Fluorocarbon stationary phases have not been widely used in GC due to their poor coating characteristics and low maximum operating temperatures. Fomblin YR is a chemically and thermally stable functional fluid with a wide liquid range; properties desired in a stationary phase for GC. The presence of ether oxygens in Fomblin YR should also enhance partitioning and/or adsorption of organic compounds as well as providing an anchor site to enable efficient columns to be prepared on diatomaceous supports.

In contrast to the difficulties reported by other workers for the preparation of efficient packings with perfluorocarbon stationary phases[1-6], efficient columns are relatively simple to prepare with Fomblin YR. With a phase loading of 3–15% (w/w) of Fomblin YR on Chromosorb P (100–120 mesh), columns yielding 2000–2500 theoretical plates per meter have been prepared routinely using the rotary evaporator
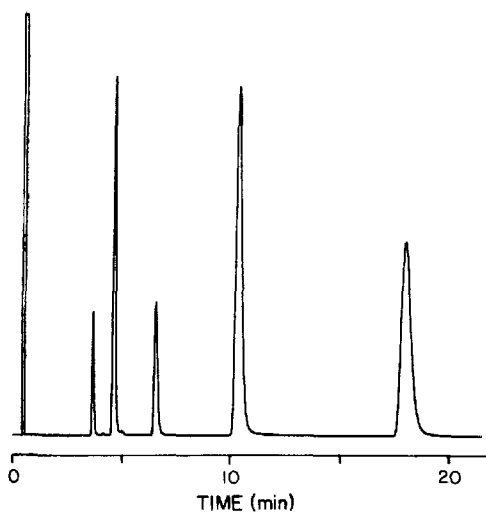
Fig. 1. Separation of C₅ through C₉ *n*-alkanes on a 3 m × 2 mm I.D. glass column packed with 10% (w/w) Fomblin YR on Chromosorb P (100–120 mesh), temperature 45°C, nitrogen carrier gas flow 20 ml min⁻¹.

coating technique. Fig. 1 shows a test chromatogram of one such column. Fomblin YR is almost insoluble in most common organic solvents excepts for Freon 113, which is the solvent recommended for column preparation. Packings prepared by stirring in an open dish using an infrared lamp for solvent evaporation invariably produced columns of lower efficiency. Typical values being 800–1500 theoretical plates per meter. Columns which were not silylated after preparation always showed lower efficiency, peak asymmetry and poor column stability at high temperatures. Silylation seems to be necessary to remove active sites and also to provide a stable liquid film at elevated temperatures. However, persilylation prior to coating may be an undesirable feature. All attempts to prepare packings with Gas-Chrom Q resulted in columns of low efficiency having 200–300 theoretical plates per meter. Columns tested at 45°C gave symmetrical peaks for the hydrocarbon test mixture (Fig. 1), but

TABLE I

COMPARISON OF THE ADJUSTED RETENTION TIME OF *n*-HYDROCARBONS ON FOMBLIN YR AND SQUALANE

All measurements were made with a 3 m × 2 mm I.D. column packed with 10% (w/w) stationary phase on Chromosorb P (100–120 mesh), temperature 45°C and carrier gas nitrogen flow of 30 ml min⁻¹.

Hydrocarbon	Adjusted retention time (min)		Ratio squalane to Fomblin YR
	Fomblin YR	Squalane	
Pentane	0.3	3.9	13
Hexane	0.7	10.9	16
Heptane	1.4	29.8	21
Octane	3.3	85.1	26
Nonane	6.2	223.0	36
Decane	11.2		

Fig. 2. Separation of C_{36}, C_{38} and C_{40} *n*-alkanes on a 1 m × 2 mm I.D. glass column packed with 10% (w/w) Fomblin YR on Chromosorb P (100–120 mesh), temperature 255°C, nitrogen carrier gas flow 20 ml min^{-1}.
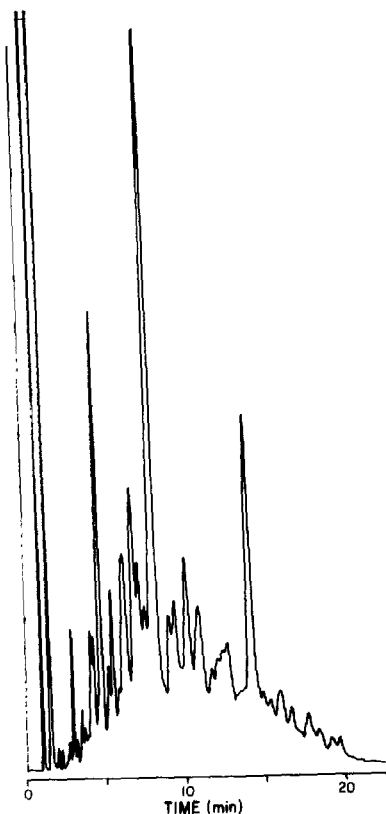
Fig. 3. Separation of WD-40 oil (a petroleum product used for lubrication, rust proofing and to displace moisture from electrical systems). The column is the same as in Fig. 1. Temperature programmed from 35°C to 100°C at 5°C min^{-1}, and nitrogen carrier gas flow 30 mol min^{-1}.

after heating briefly to above 100°C, and returning to 45°C for re-evaluation, asymmetric peaks with diminished retention were obtained. This suggests that the stationary phase film is not stable on Gas-Chrom Q and redistributes itself on the packing surface unevenly at higher temperatures. A similar phenomenon occurred with the packings prepared with Chromosorb P and on-column silylated prior to use, but only at much higher temperatures. Packings containing 3% (w/w) Fomblin YR can safely be used up to 200°C and columns with a 10% phase loading up to 255°C. Both temperatures are below the maximum allowable operating temperature of the phase which was established as 275°C. Thus, for Fomblin YR the upper operating temperature for the column is set by the stability of the liquid phase film on the support and not by column bleed.

The upper operating temperature of the Fomblin YR columns prepared with Chromosorb P is sufficient to allow a wide range of organic compounds to be separated, the more so, as the absolute retention of organic compounds on Fomblin YR

is a great deal less than is found for conventional liquid phases. For example, the adjusted retention time of a series of *n*-alkanes on Fomblin YR is more than an order of magnitude lower than observed on an identical squalane column, Table I. This facilitates the elution of high-molecular-weight hydrocarbons at low column operating temperatures. Fig. 2 illustrates the rapid separation of C_{36}, C_{38} and C_{40} hydrocarbons at a column temperature of 255°C. Some tailing can be observed in this chromatogram, perhaps because the upper temperature limit of the liquid phase film stability had been reached, or because of low solubility in the stationary phase (assuming a partition mechanism) of the hydrocarbons, or because the column temperature was too low to adequately vaporize the sample. A more representative application of the stationary phase is shown in Fig. 3 for the separation of a sample of petroleum oil distillate. Fig. 4 is a temperature programmed separation of a mixture of C_6–C_{15} *n*-alkanes and 1-alkenes. Not all members of the series are separated and the separation obtained cannot simply be accounted for by boiling point difference.
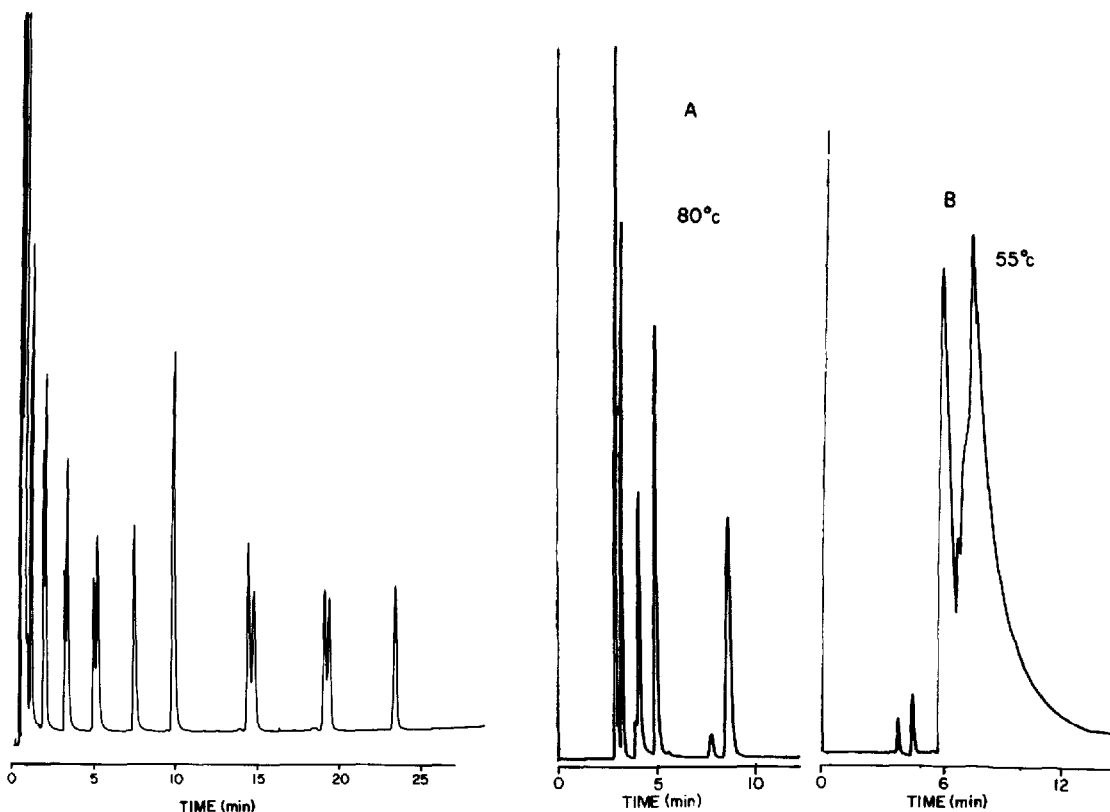

Fig. 4. Separation of a mixture of C_6 through C_{15} alkanes and 1-alkenes on the same column as used in Fig. 1. Temperature programmed from 45°C to 175°C at 5°C min⁻¹, and nitrogen carrier gas flow 30 ml min⁻¹.

Fig. 5. Separation of McReynolds test probes on the same column as used in Fig. 1, carrier gas flow 30 ml min⁻¹. A, Symmetrical test probes in order of elution: benzene, 1,4-dioxane, 1-iodobutane, 2-octyne and *cis*-hydrindane at 80°C. B, Asymmetric polar test probes at 55°C.
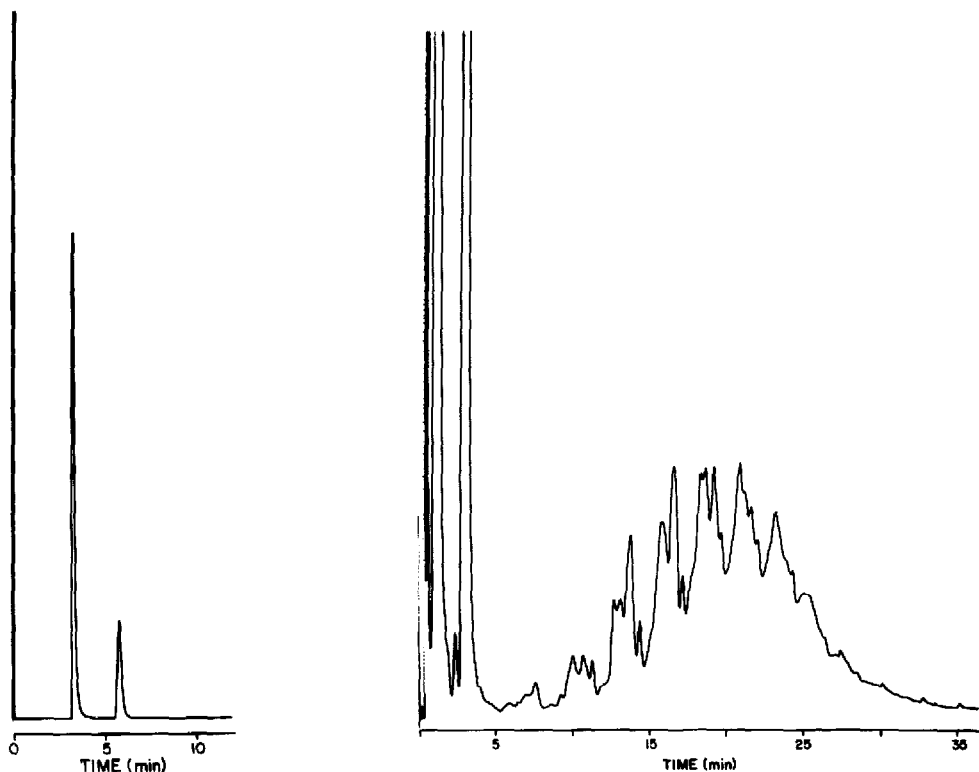
Fig. 6. Separation of Freon 11 and Freon 113 on the same column as used in Fig. 1, nitrogen carrier gas flow 30 ml min⁻¹ and column temperature 35°C.

Fig. 7. Separation of impurities in a sample of perfluorokerosene-L. Same column as used in Fig. 1, nitrogen carrier gas flow 30 ml min⁻¹ and column temperature isothermal (22°C) for 4 min, and then programmed at 5°C min⁻¹ to 180°C.

This would indicate that Fomblin YR shows some selectivity for the separation of saturated and unsaturated hydrocarbons.

The McReynolds test probes can be divided into two groups based on their chromatographic properties on Fomblin YR. Benzene, 1,4-dioxane, 1-iodobutane, 2-octyne and *cis*-hydrindane can be chromatographed with good peak shape (Fig. 5A). The more polar test probes butanol, nitropropane, pyridine, 2-methyl-2-pentanol and 2-pentanone produce asymmetric peaks with very low retention (Fig. 5B). Poor solubility of the polar probes in the stationary phase and/or the possibility that Fomblin YR provides poor shielding of active sites on the support is probably the reason for the results obtained. Fomblin YR is not a suitable stationary phase for the separation of polar organic compounds.

Perfluorocarbon compounds are often difficult to separate on conventional liquid phases due to a lack of selectivity. Perfluoroalkyl ether phases might prove useful for separating these compounds. Freons can be chromatographed with good peak shape on Fomblin YR, Fig. 6. The minor impurities in perfluorokerosene-L are also reasonably well separated on Fomblin YR, Fig. 7.

ACKNOWLEDGEMENTS

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