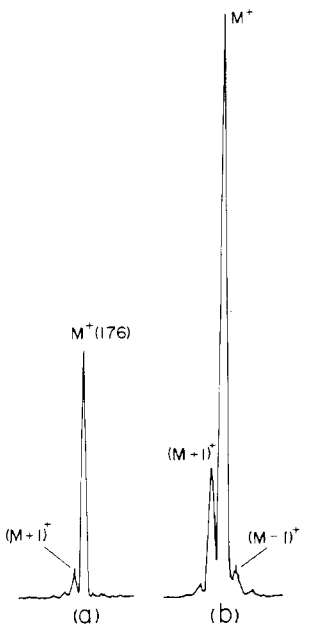


**Figure 5.** The parent ion group in FD mass spectra of ascorbic acid recorded with a 20-$\mu$m $Mo_2C$-emitter at different emitter temperatures. Sample amount, $\sim 2 \times 10^{-4}$ g; cathode potential, -4 kV; anode potential, +5 kV. Emitter heating current, 116 mA for (a), 134 mA for (b). Recorder sensitivity, 50 mV for (a), 1 V for (b)

The peaks at $m/e$ 18 and 19 in Figure 4 are due to residual water. Since a magnetic mass spectrometer cannot be outgassed entirely, water molecules are always present as an impurity inside its ion source. Residual water molecules are obstructive to FIMS surface studies, for they react with sample molecules on the emitter surface to produce a variety of reaction products, leading to the misinterpretation of surface signals of interest (*9–11*). The water effect is not negligible at background pressures of around $10^{-6}$ Torr (*10*). It is therfore desirable to keep the background pressure as low as possible in surface studies. In Figure 4, the $H_2O^+$ and $H_3O^+$ signals are very weak and, in addition, no peaks due to ethylene–water reactions are observed. The same was true of other FI samples and, consequently, the conclusion is reached that the effect of residual water can be reduced to a negligible level by maintaining the background below $10^{-7}$ Torr.

The so-called activated wire emitter developed by Beckey et al. (*12*) has been widely used in FD measurements. In the activated emitter, carbon needles densely grown on a 10-$\mu$m tungsten filament behave as the emission centers. In a recent year, one of us (F.O.) developed a technique to produce $Mo_2C$ needles on metal filaments, and the field emitters based on this technique have been called "$Mo_2C$-emitters" (*13*). In the present work, $Mo_2C$-emitters were employed to test the ion source in the FD mode. For wire emitters, the emitter positioning is not as critical as for foil emitters and, generally, they are operated at an emitter–cathode distance of $\sim$2 mm. Further decreasing the distance brings about no essential improvement in signal intensity. Figure 5 shows the parent ion group in the FD mass spectra of ascorbic acid recorded at different emitter temperatures using a 20-$\mu$m $Mo_2C$-emitter. (The emitter-operating conditions are given in the caption.) In both cases, the molecular ions constituted the base peak, whose intensity increased steeply with increasing the temperature. As suggested from the $(M-1)^+$ peak seen in Figure 5b, however, thermal degradation of sample molecules occurs at higher temperatures. This agrees completely with the observation by Schulten (*14*).

The experimental results presented above guarantee the practicality of our ion source. It is emphasized that the ion-source design proposed here may be adaptable for any horizontally arranged magnetic mass analyzer. We believe that the present investigation will be informative for researchers who are interested in FI- and FD-MS but cannot afford to purchase costly modern mass spectrometers.

## ACKNOWLEDGMENT

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# (Heptadecafluorodecyl)dimethylsilyl Bonded Phase for Reversed-Phase Liquid Chromatography

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In a previous paper we have reported on the influence of the hydrocarbon chain length of $n$-alkyldimethylsilyl bonded phases on the chromatographic separation process (*1*). From this study we concluded that the role of the chemically bonded

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hydrophobic phase is secondary to the influence of the mobile phase on the separation process, at least under reversed-phase conditions.

The preparation of these phases and of short chain *n*-propyl hydrocarbon bonded phases, containing terminal functional groups at the $\gamma$ position, has been published elsewhere (*2*). Although, in general, the influence of functional end groups is small under reversed-phase conditions (*3*), some exceptional selectivities have been observed. For example, amino phases are preferred for the separation of monosaccharides (*4*) and a propylcyclohexyl phase offers improved separation of dinitro aromatics (*3*).

In this paper we report on the synthesis and the properties of a polyfluorinated chemically bonded phase. Although fluorinated bonded materials have been used recently in gas chromatography (*5*), their possible potential for liquid chromatography has not been evaluated yet. As will be shown below, the proposed stationary phase shows specific interaction with solutes containing fluorine atoms. Consequently, the perfluorocarbon bonded phase can be applied for the analysis of certain fluorine-containing pharmaceuticals, herbicides, lubricants, flame retardants, etc.

## EXPERIMENTAL SECTION

**Chromatographic System.** The chromatographic apparatus used is a Waters liquid chromatograph equipped with a M 6000 pump, a U6K injector, and a detector (401 RI or variable 450 UV). Injector, column, and detector were thermostated (*6*).

Columns (300 × 4.6 mm) were packed according to the procedure described previously (*2*, *7*).

**Preparation of the Bonded Phase.** (Heptadecafluorodecyl)dimethylchlorosilane has been synthesized by using the catalytic hydrosilylation reaction of the fluorinated olefin (*2*) (eq 1) (Riedel-de Haën, Seelze-Hannover, GFR), according to the following procedure.

$$CF_3(CF_2)_7CH{=}CH_2 + HSi(CH_3)_2Cl \xrightarrow[H_2PtCl_6{\cdot}6H_2O]{} CF_3(CF_2)_7CH_2CH_2Si(CH_3)_2Cl \quad (1)$$

To 0.2 mol of the olefin add about 2 mg of catalyst. Heat the solution under continuous stirring to a temperature of 90 °C and slowly add an equivalent (or small excess) of dimethylchlorosilane. Boil the mixture under reflux for 20 h. After removal of a byproduct by fractional distillation (bp 45–47 °C at 12 mmHg), the product is obtained with 60% yield at 98–101 °C (12 mmHg). The proton nuclear magnetic resonance spectrum in $CCl_4$ shows a singlet (6 H) at $\delta = 0.51$ from the two methyl groups, a multiplet (2 H) between $\delta = 0.85$ and $\delta = 1.29$ from the silicon-bonded methylene group, and a multiplet (2 H) from $\delta = 1.60$ to $\delta = 2.69$ with a $J_{HF}$ coupling constant of 17.3 Hz from the methylene group adjacent to the fluorinated carbon chain.

The bonding reaction of the monochlorosilane with the activated silica support (batch EH12, charge no. 7518609) was similar to the procedure described previously (*2*).

## RESULTS AND DISCUSSION

Elemental analysis of the packing material gave 9.36% C and 21.11% F, respectively.

The percentages are converted to a true surface coverage using the expression derived previously (*8*), e.g., for fluorine

$$N(\mu\text{mol/m}^2) = \frac{10^6 P_F}{1900 n_F - P_F(M-1)} \frac{1}{S} \quad (2)$$

where $P_F$ is the measured weight percentage of fluorine, $S$ is the specific surface area (i.e., 281 $m^2/g$, measured in duplicate), $n_F$ the number of fluorine atoms, and $M$ the molecular weight of the bonded molecule.

The surface coverages obtained from the carbon and fluorine percentages of the perfluorocarbon bonded phase are in excellent mutual agreement: 3.44 and 3.45 $\mu mol/m^2$, respectively. They also agree very well with the results obtained for comparable *n*-alkyldimethylsilyl phases (*2*).

**Column Operation.** The extremely nonpolar character of the perfluorocarbon bonded phase has some practical consequences. Columns must be packed with a nonpolar liquid, such as $CCl_4$ (*7*). After the column is conditioned with pure methanol, the column is perfectly stable and usable with all mobile phases containing over 40% v/v methanol. If the solvent contains less methanol, the column performance gradually deteriorates; it is degraded more rapidly as the methanol content is reduced. Ultimately, highly aqueous solvents appear to be completely excluded from the modified silica particles. All solutes are then rapidly eluted from the column, and no separations are possible.

The phenomenon may be explained as follows. Although each mobile phase is subjected to ultrasonic agitation, it still contains dissolved air. Toward the low-pressure side of the column, gases may be liberated from the mobile phase and block the pores of the stationary phase. The effect may be related to the large interfacial tension between the extremely nonpolar fluorocarbon stationary phase and the highly polar aqueous mobile phase. The interfacial tension is smaller in methanol-rich mobile phases and with hydrocarbon stationary phases, so that the phenomenon is not (normally) observed under those circumstances. When the degraded column is flushed with a few milliliters of pure methanol and the detector outlet is dipped in methanol, the air is seen to be expelled from the pores and the column is restored to its original condition.

The phenomenon could be avoided by careful degassing of the mobile phase, but continuous percolation with helium is not possible with mixed solvents for fear of composition changes. However, liberation of air and deterioration of the column are easily prevented by narrowing the connection line between the column outlet and the detector cell, thus creating a pressure restrictor (500 psi) after the column.

**Chromatographic Characteristics.** The retention behavior of the fluorocarbon bonded phase has been studied in comparison to the corresponding *n*-alkyl bonded phase. In the following discussion the heptadecafluorodecyl phase is designated as RPF-10 and the corresponding *n*-decyl phase as RP-10.

Figure 1 presents chromatograms on *n*-propyl (RP-3), RP-10 and RPF-10 of a mixture of compounds, some of which contain several fluorine atoms, whereas the others do not. In general, the retention order of the compounds which do not contain fluorine is quite similar on all three phases. As reported previously (*1*), capacity factors are lower on RP-3 than on RP-10. Quite remarkably, however, the capacity factors for nonfluorinated compounds on RPF-10 are comparable to those on RP-3 rather than on RP-10.

The retention order of fluorine-containing compounds mutually is also similar on all three phases. Again, all solutes are eluted more rapidly on RP-3 than on RP-10. However, the retention of fluorine-containing compounds is much greater on the perfluorocarbon phase than on the alkyl phase. For example, trifluoroethanol elutes *before* phenol on RP-3 and RP-10 but *after* phenol on RPF-10. The selective retardation of trifluorotoluene on RPF-10 provides an excellent separation from toluene, whereas the two compounds coincide on the alkyl phases. Finally, a dramatic example is offered by the 1*H*,1*H*-perfluorooctanol, which cannot be eluted at all from the RPF-10 phase with 70/30 methanol/water. Indeed, even in pure methanol, where all other solutes have capacity factors around 0.1, this compound still shows a capacity factor of $k = 1.0$ on RPF-10.

Figure 1 demonstrates that the perfluoro-bonded phase offers no improvement for the mutual separation of *non*-fluorine-containing compounds. By contrast, some im-

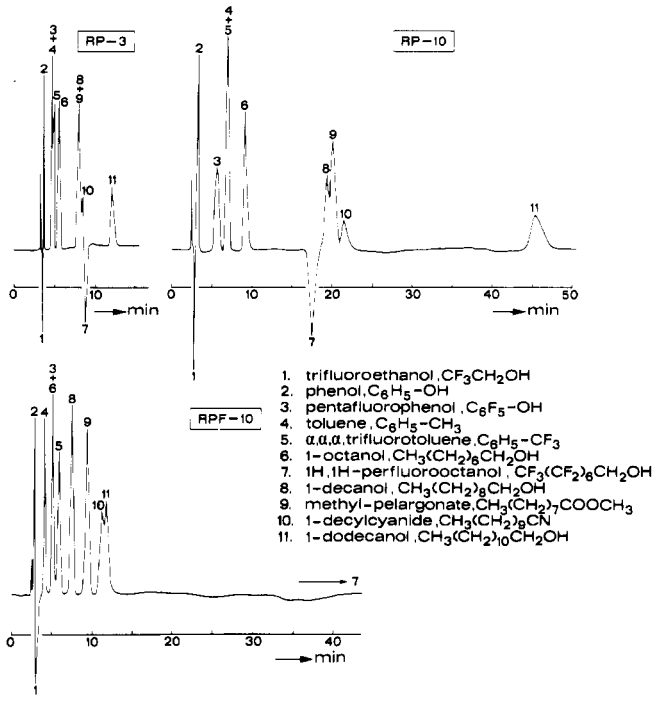


**Figure 1.** Chromatograms of a mixture of fluorinated and nonfluorinated solutes run in 70/30 v/v methanol/water on *n*-propyl (RP-3), *n*-decyl (RP-10), and heptadecafluorodecyl (RPF-10) bonded phases.

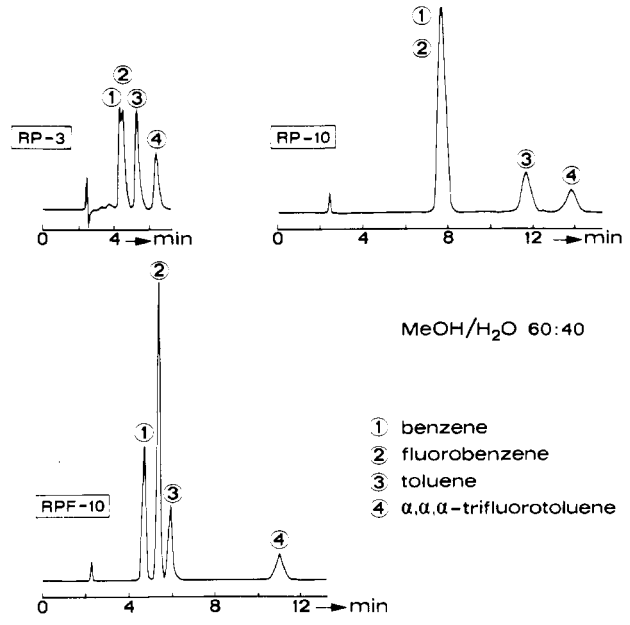


**Figure 2.** Improved selectivity for benzene/monofluorobenzene and toluene/trifluorotoluene on perfluorocarbon bonded phase (RPF-10) in comparison to alkyl phases (RP-3, RP-10).

provement in selectivity toward fluorinated compounds mutually is observed in Figures 1 and 2. Nevertheless, it is our experience that a mixture of fluorine-containing compounds only can usually be separated on *n*-alkyl bonded phases equally well as on RPF-10, provided that the mobile phase composition is optimized. An interesting exception will be discussed below.

However, the perfluorocarbon bonded phase displays its major strength in the separation of a fluorinated compound from the corresponding nonfluorinated analogue. The examples in Table I demonstrate the increased selectivity offered by RPF-10 over *n*-alkyl phases. This is also illustrated in Figure 2, where benzene and monofluorobenzene cannot be

Table I. Comparison of the Selectivity, α, on Three Chemically Bonded Phases at a Mobile Phase Composition of 70:30 (v/v) Methanol/Water

| | RP-3 | RP-10 | RPF-10 |
|---|---|---|---|
| $CF_3CH_2OH$ / $CH_3CH_2OH$ | 1.17 | 1.19 | 1.74 |
| $C_6F_5OH$ / $C_6H_5OH$ | 2.79 | 3.47 | 5.28 |
| $C_6H_5CF_3$ / $C_6H_5CH_3$ | 1.15 | 1.00 | 2.00 |
| $CF_3(CF_2)_6CH_2OH$ / $CH_3(CH_2)_6CH_2OH$ | 2.40 | 2.39 | >20 |

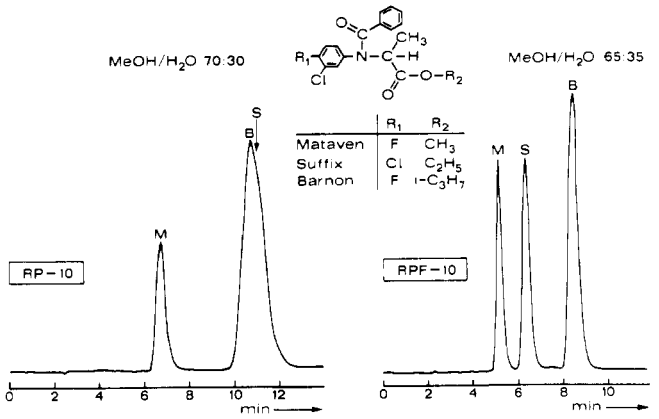


**Figure 3.** Improved separation of three herbicides on the perfluorocarbon phase (RPF-10), utilizing the selective retardation of monofluoro compounds.

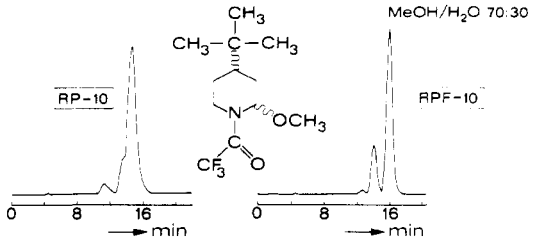


**Figure 4.** Separation of the diastereoisomers of 4-*tert*-butyl-2-methoxy(*N*-trifluoroacetyl)piperidine on the perfluorocarbon phase (RPF-10).

separated on RP-3 or RP-10 but are readily separated on RPF-10.

A more practical example is the separation of three herbicides in Figure 3. Whereas Mataven and Barnon contain a fluorine atom ortho to a chlorine atom, Suffix contains two chlorine atoms. On RP-10 the two fluorine compounds are readily separated on the basis of their different alkyl groups, $R_2$, in a 70:30 ratio (v/v) of methanol–water. By chance, however, Barnon and Suffix show nearly equal retention times. A changeover to the perfluoro phase, RPF 10, and 65:35 (v/v) methanol–water, not only decreased the analysis time but produced an excellent separation thanks to the selective retardation of Barnon relative to Suffix. Simultaneously, of course, the selectivity between Suffix and Mataven is *reduced* in going from RP-10 to RPF-10. However, this is perfectly acceptable in the present example. It is to be noted that the strong changes in selectivity arise from the presence of only a single fluorine atom in two of the three herbicides.

The final example in Figure 4 somewhat contradicts the general statement made earlier. Although, in general, fluorinated compounds are not mutually better separated on RPF-10 than on RP-10, Figure 4 presents an interesting exception. The diastereoisomers of 4-*tert*-butyl-2-methoxy-(*N*-trifluoroacetyl)piperidine cannot be separated on normal

n-alkyl bonded phases. By contrast, rapid base line separation is obtained in 70/30 methanol/water on the perfluorocarbon bonded phase.

## CONCLUSION

The (heptadecafluorodecyl)dimethylsilyl bonded phase shows specific fluorine–fluorine interaction and enhanced retention for fluorine-containing compounds. The retention increases with the number of fluorine atoms in the solute. This behavior can be used successfully for the separation of fluorine-containing compounds from their non-fluorine-containing analogues.

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# On-Column Cryogenic Trapping of Sorbed Organics for Determination by Capillary Gas Chromatography

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Various devices for low-temperature trapping and thermal focusing of samples for gas chromatographic analysis have been reported. These include both on-column (*1*, *2*) and extra-column (*3*, *4*) devices. In this report, we describe a simple on-column cryogenic trap suitable for capillary analysis that can be hand fabricated from common materials. This trap was developed for the purge-and-trap (*5*) analysis of wastewater and sludge samples by capillary column gas chromatography, where the resolution provided by capillary columns is considered essential in view of the complexity of the sample.

Three different cold trap designs were evaluated, as depicted by Figure 1. Design A consists of a notched tube of $^1/_4$ in. o.d. copper, prebent to a 5.5-cm radius to conform to the curvature of the capillary column. Liquid nitrogen is introduced under modest pressure. (In this and the other designs, the throttled headpressure from the liquid nitrogen reservoir was used to deliver up to 25 mL/min of coolant.) Design B consists of two machined aluminum plates sandwiched together around the column to form the trap and held in place with metal clips. Liquid nitrogen is delivered to one side of the trap, and warm air can be introduced from the other. Design C is a thin wall ($^1/_8$-in. o.d.) stainless steel tube bent to fit the capillary column. It is lightweight enough to be threaded onto the column prior to end straightening and can be installed with the column. (Newly introduced fused-silica capillary columns (*6*) do not require straightening and will conform to the shape of the cryotrap, simplifying its construction.) All three designs can be mounted from a central support or supported from the liquid nitrogen supply tube, which was bulkhead mounted (as depicted schematically in Figure 2). When installed, each of the three designs covers approximately 10 cm of the column. This provides a residence time of about 0.2 s for normal flow rates between 1 and 2 mL/min, which is sufficient at liquid nitrogen trapping temperatures to capture even the most volatile organic compounds, such as chloromethane.

Typical operation of the device as part of an analysis of aqueous samples for purgable organics is as follows: The sample (a standard containing all Environmental Protection Agency (EPA) priority purgables except acrolein and acrylonitrile at 4 ppb) is purged with organic-free helium for 15 min at 20 mL/min. The purged organics are trapped on conditioned Tenax-GC. During the last 5 min of Tenax trapping, the cryogenic trap is precooled. (When the trap is fully cooled by liquid nitrogen flow, air will condense on the outside, adding to whatever liquid nitrogen overflows from the trap.) The coolant flow is continued throughout the cryogenic trapping, which takes place for 10 min during which time the sorbed organics are thermally desorbed into the carrier gas stream (at 2 mL/min flow rate). During this period, the Tenax is heated to 200 °C. Upon warming of the cold trap by a vigorous flow (in excess of 500 mL/min) of gas supplied from a compressed air tank and heated to 40 °C by passage through a heated copper coil, the gas chromatographic separation begins. Normally, this heating method produces elution of nonretained components from the cryogenic trap (such as carbon dioxide) within 5 s of the column dead time as determined by methane injection. This indicates that heating up of the cryogenic trap is approximately that rapid.

When device C was used in the manner described, the result was as depicted in Figure 3. This particular analysis utilized mass spectrometry detection, which revealed no breakthrough of organics during cryogenic trapping. The analysis was performed on a Hewlett-Packard 5840-A gas chromatograph and a 30-m SE-54 (0.25-88 i.d., J&W Scientific) glass capillary column. The gas chromatograph was coupled by a direct glass-lined steel tube interface to a Finnegan 4023 mass spectrometer data system. Helium carrier gas at 40 cm/s linear velocity (at 30 °C) was used. The gas chromatograph oven temperature was increased from 30 to 50 °C at 4°/min and from 50 to 280 °C at 8°/min.

The results obtained by using design A showed poor peak shape and occasional split peaks for compounds more volatile than dichloromethane; this was apparently due to insufficiently rapid heat up of the cryogenic trap. This shortcoming was eliminated in design B, which permits the use of a warm air back-flush of the cryogenic trap as a means of initiating the chromatographic analysis. However, design B was cumbersome to install due to its weight and rigidity. Design C,

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