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Separation of selected polyfluorobenzenes by gas–liquid chromatography

A means of rapid and accurate analysis of a mixture of the polyfluorobenzenes was needed in order to follow the progress of the direct liquid phase fluorination of *p*-difluorobenzene. While these specific compounds are not treated in the literature, the general recommendations for the separation of substituted aromatic compounds by gas–liquid chromatography (GLC) are columns with stationary phases such as UCON-50[1], XF-1150[2], or Bentone-34-Apiezon L[3]. The recommended columns have been tried with little success. Examination of the boiling point data presented in Table I will indicate a portion of the difficulty in separating these compounds. A survey of a wider range of stationary phases has found Carbowax 20M most promising. The retention behavior of selected polyfluorobenzenes and additional factors which affect column–sample specificity are presented in this paper.

Experimental

Apparatus. All work was performed using a Varian Aerograph Model 90-P3 gas chromatograph equipped with a thermal conductivity filament detector and a 1-mV recorder. Columns used in the separation were purchased commercially or prepared in this laboratory using the "pan coating" method described by McNair and Bonelli[4]. All columns were conditioned in the chromatograph for 2 h at 175°. Helium carrier gas was used at a flow rate of 20 cc/min during column conditioning. Both the detector and injector port temperatures were maintained at 200°, and the detector bridge current was 150 mA. The helium used throughout was measured by means of a Hastings Model LF-100 mass flow meter.

Reagents. Authentic samples were purchased from the Pierce Chemical Company, Rockford, Ill., and PCR, Inc., Gainesville, Fla. Equal weights of the authentic compounds were blended together to make the injection mixture. A 1.0-μl injection was used throughout the study. Other columns tested included: 3% OV-101 on 80–100 mesh Chromosorb W, 15% XF-1150 on 60–80 mesh Chromosorb W, 10% QF-1 on 60–80 mesh Chromosorb W, 15% UCON 50-HB-2000 on 60–80 mesh Chromosorb W, 20% DEGS on 60–80 mesh Chromosorb W, 10% SE-30 on 60–80 mesh Chromosorb W, 10% Benton-34 on 60–80 mesh Chromosorb W, 20% Hallcomid M-180L on 60–80 mesh Chromosorb W, 15% Carbowax 20M on 60–80 mesh Chromosorb W, and 3% OV-25 on 80–100 mesh Chromosorb W.

Results and discussion

A mixture of seven fluorobenzenes was injected into the ten columns listed above and after optimization of each with respect to temperature and flow rate, a column consisting of 15% Carbowax 20M on 60–80 mesh Chromosorb W gave the best resolution and did so within the time limitation imposed by our kinetic studies. Fig. 1 illustrates the interesting elution obtained in our studies. From boiling point data presented in Table I, it can be seen that the first three compounds to elute from the column have lower boiling points than the last three. In Table I, one will also note that the lower boiling group elutes in order of increasing electric dipole moments.

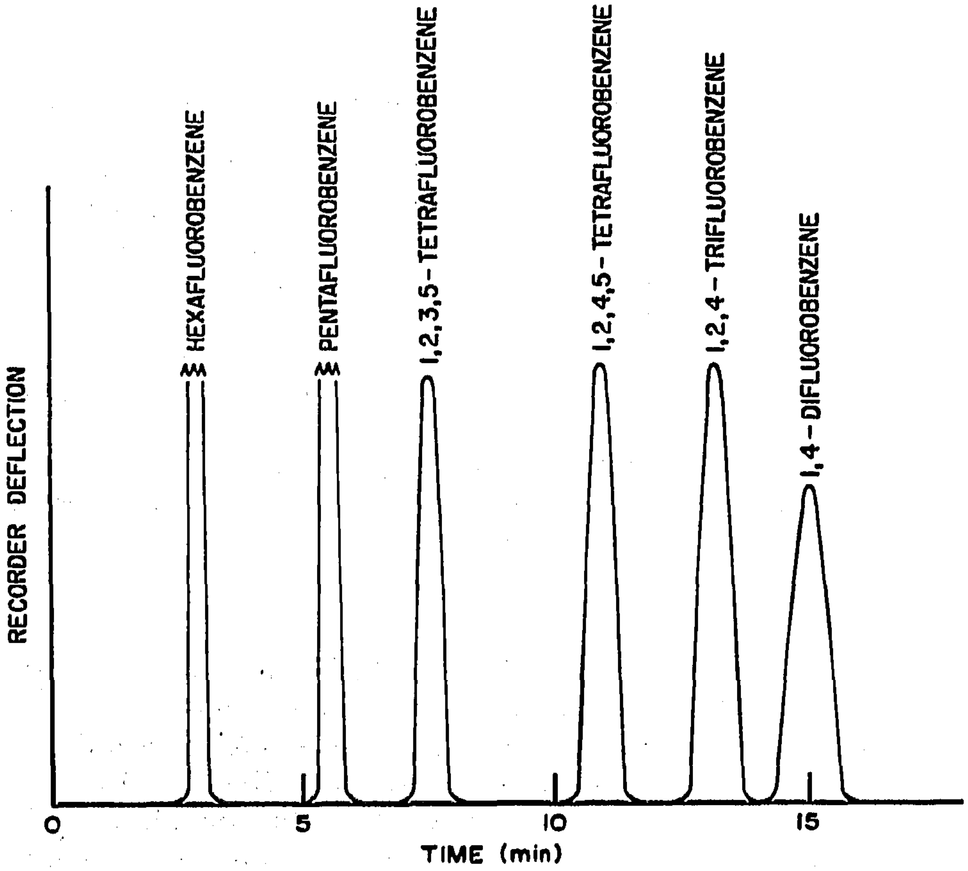

Fig. 1. Chromatogram of an authentic mixture of fluorobenzenes on a 10-ft. 15% Carbowax 20M on 60–80 mesh Chromosorb W column at 70°. Helium flow rate, 33 cm^3/min.

The higher boiling point group elutes in order of increasing electric dipole moments except for 1,4-difluorobenzene, which behaves in an unexpected fashion.

Table I lists five molecules which have essentially zero dipole moments, and somewhat similar boiling points. In an effort to better understand the above phenomenon a mixture of these five compounds was injected into the chromatograph to give the results presented in Fig. 2. It is with particular interest that the authors have noted the 6.7 min which separate the elution time of benzene (b.p. 80.6°;

TABLE I

PHYSICAL PROPERTIES OF SELECTED POLYFLUOROBENZENES

Material	*Boiling point*[5] *(°C/760 Torr)*	*Electric dipole moments*[a] *(Debye)*
Benzene	80.6	0
1,4-Difluorobenzene	88.5	0
1,2,4-Trifluorobenzene	88.5	1.5
1,3,5-Trifluorobenzene	75.5	0
1,2,4,5-Tetrafluorobenzene	88	0
1,2,3,5-Tetrafluorobenzene	83	2.55
Pentafluorobenzene	80.5	1.5
Hexafluorobenzene	80.5	0

[a] Dipole moments calculated by Law of Cosines according to FERGUSON[6].

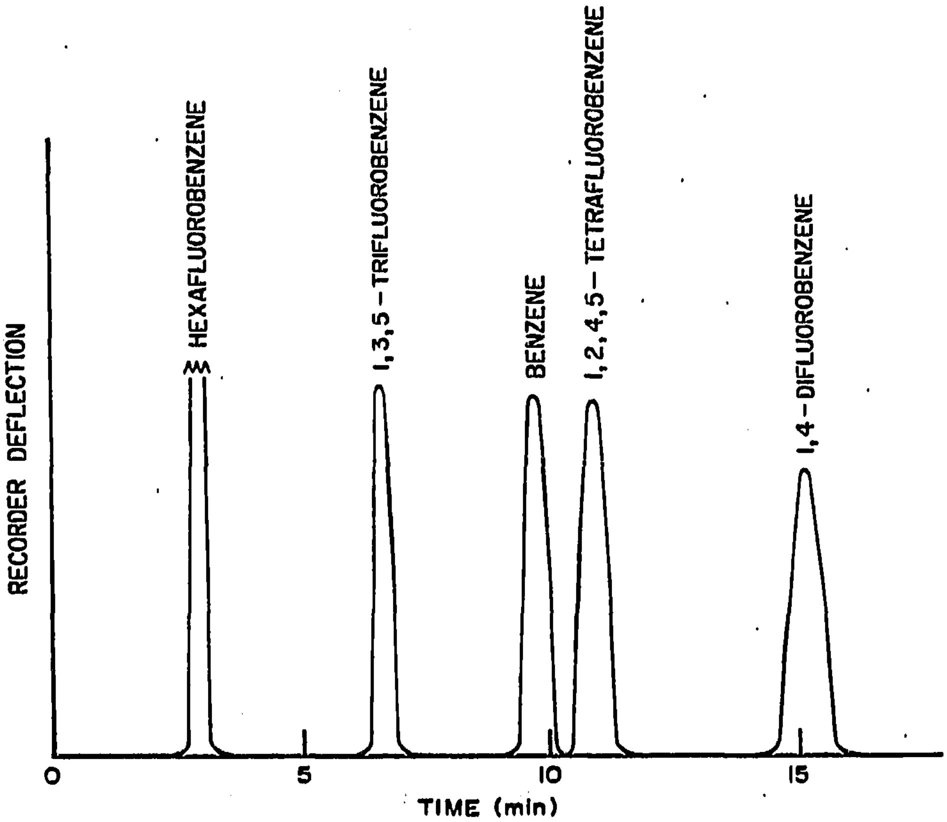

Fig. 2. Chromatogram of an authentic mixture of benzene derivatives on a 10-ft. 15% Carbowax 20 M on 60-80 mesh Chromosorb W column at 70°. Helium flow rate, 33 cm^3/min.

$\mu = 0$ D) and that of hexafluorobenzene (b.p. 80.5°, $\mu = 0$ D). Since there is little difference between the boiling points and dipole moments of these two molecules, one can only speculate as to why the rather polar Carbowax 20M column has significantly more attraction for benzene than hexafluorobenzene. One would expect the pi-clouds of benzene to be more prominant than those of hexafluorobenzene. Perhaps there is a significant attraction between the pi-clouds of benzene and the Carbowax 20M liquid phase. A similar case may be made of 1,2,4,5-tetrafluorobenzene (b.p. 88°, $\mu = 0$ D) and 1,4-difluorobenzene (b.p. 88.5°, $\mu = 0$ D).

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