

ortho isomers should separate from the next higher homologs.

This order of two-stage development is to be preferred to the reverse order, because the cyclohexane-acetic acid solvent provides more discrete spots.

Alternatively, it would be possible to develop the monohydroxyphenols with cyclohexane-acetic acid on one paper strip and move them a considerable distance on a second strip with the same solvent. Then di- and trihydroxyphenols could be developed on the second strip with the water-acetic acid system.

Preliminary diagnosis of some unknown mixtures could also be derived by comparing the development provided by the two solvent systems upon

separate papers. Then the reversed order of development of the homologous alkyl phenols could be observed relative to one or two known compounds.

Finally, heavy papers impregnated with polyamides might provide a convenient alternative to the powdered polymer for the separation of larger quantities of phenols.

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Separation of Some Fluorocarbon and Sulfur-Fluoride Compounds by Gas-Liquid Chromatography

R. H. CAMPBELL and B. J. GUDZINOWICZ

Special Projects Department, Research and Engineering Division, Monsanto Chemical Co., Everett, Mass.

► Recent exploratory studies of reactions between fluorocarbons and sulfur-halide compounds required an efficient rapid method for the separation and characterization of the reaction products. A combination of gas-liquid chromatographic and infrared spectrophotometric techniques adequately fulfilled the analytical requirements of these investigations. Furthermore, the feasibility of resolving mixtures of low molecular weight fluorocarbons and such sulfur-fluoride compounds as SF_4 , SF_6 , SOF_2 , and S_2F_{10} was demonstrated.

RECENT EXPLORATORY STUDIES of reactions between fluorocarbons and sulfur-halide compounds required an efficient rapid method for the separation and characterization of the reaction products. A literature survey revealed few publications on gas-liquid chromatographic analyses of fluorocarbons and none for mixtures of low molecular weight fluorocarbons and sulfur-fluoride compounds such as SF_4 , SF_6 , SOF_2 , and S_2F_{10} .

However, the literature search did reveal some published works on related problems which indicated the chromatographic resolution of such mixtures to be possible.

Hall *et al.* (5) noted that stationary liquid phases such as benzyl ether and diisodecylphthalate were both equally effective for the separation of ethyl ether and fluothane (2-bromo-2-chloro-

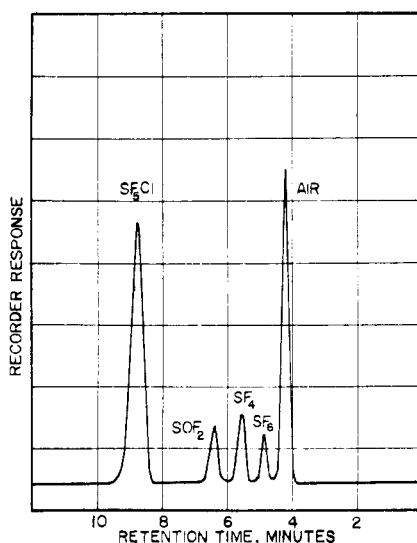


Figure 1. Gas chromatogram of typical components in SF_5Cl production

1, 1,1-trifluoroethane). Using a column packed with activated alumina and hydrogen as carrier gas, Foulletier and Elchardus (4) resolved chlorofluorinated hydrocarbon mixtures of CCl_4 , CCl_2F_2 , and CClF_3 . Percival (8) found both di-*n*-octylphthalate and alumina satisfactory for the separation of Freon gases.

Reed (9) evaluated the resolving power of a number of stationary liquid phases and reported $\text{Cl}(\text{CF}_2\text{CFCl})_2\text{CF}_2\text{COOC}_2\text{H}_5$ (the ethyl ester of Kel-F

acid 8114) to be the most effective for the gas-liquid partition chromatography of fluorocarbons. Dresdner *et al.* (2) also employed this Kel-F ester and hexadecane to analyze 6- and 12-carbon fluorocarbon derivatives of sulfur hexafluoride.

Ellis, Forrest, and Allen (3) used columns packed with 50% by weight of grade 10 Kel-F oil on 30- to 60-mesh Fluon powder to separate corrosive inorganic compounds such as ClF , HF , Cl_2 , ClF_3 , UF_6 , and Br_2 . Nitrogen trifluoride and CF_4 mixtures were investigated by Nachbaur and Engelbrecht (7) using moist silica gel with hydrogen as carrier gas at 0°C .

APPARATUS AND REAGENTS

The gas chromatographic instruments employed for these investigations were the Perkin-Elmer Model 154B and 154C Vapor Fractometers with helium (Airco) as the carrier gas. Furthermore, since these chromatographs can accommodate two columns in series, it was possible to test several combinations of column packings simultaneously.

In addition to the standard Perkin-Elmer 6 feet long by $1/4$ inch in diameter column A containing diisodecylphthalate as liquid stationary phase used in this work, the 6-, 9-, and 20-foot by $1/4$ -inch copper columns were packed with 33% by weight grade No. 3 Kel-F polymer oil (Minnesota Mining and Manufacturing Co.) loaded on 35- to 80-mesh Chromosorb W (Johns-Manville Co.). To prepare this column material, sufficient Kel-F oil was weighed, dis-

Table I. Relative Retention Volumes for Several Fluorocarbons and S₂F₁₀ at Various Operating Conditions(CF₃CF=CF₂ = 1.00)

Compound	A				B				C			
	<i>t_m</i> ^b	<i>V_R</i> ^c	<i>V_R</i> ^d	Rel. ret. vol.	<i>t_m</i>	<i>V_R</i>	<i>V_R</i> ^d	Rel. ret. vol.	<i>t_m</i>	<i>V_R</i>	<i>V_R</i> ^d	Rel. ret. vol.
CF ₂ =CF ₂	2.5	81.0	64.6	0.86	3.8	112.5	77.6	0.79	3.9	76.5	55.8	0.86
CF ₃ CF=CF ₂	2.9	94.2	75.1	1.00	4.8	142.5	98.3	1.00	4.5	88.5	64.6	1.00
Cyclic-C ₄ F ₈	7.0	229.5	182.9	2.44	5.4	160.5	110.7	1.13	5.0	98.5	71.9	1.11
S ₂ F ₁₀	11.4	340.5	234.9	2.39	9.0	178.5	130.3	2.02				

^a Operating conditions: A. 9-ft. column with 33% by weight Kel-F on Chromosorb W, 33° C. column temperature, 33 cc./min. helium flow rate at 1 atm. and 25° C.

B. 15-ft. column with 33% by weight Kel-F on Chromosorb W, 33° C. column temperature, 30 cc./min. helium flow rate at 1 atm. and 25° C.

C. 6-ft. column with 33% by weight Kel-F on Chromosorb W plus 6-ft. column A, 29° C. column temperature, 20 cc./min. helium flow rate at 1 atm. and 25° C.

^b *t_m* = Observed time for peak maximum, minutes.^c *V_R* = Total retention volume corrected for void volume at column temperature.^d *V_R*^d = Corrected retention volume = $V_R \times \frac{3}{2} \times \frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]}$ where: *P_i* = inlet pressure
P_o = outlet pressure

solved in ten volumes of carbon tetrachloride, and added to the required amount of Chromosorb W in a shallow dish. The desired 1:2 liquid-solid column packing composition was achieved after the complete evaporation of the solvent on a steam hot plate.

The various fluorocarbons, CF₄, C₂F₄, C₃F₈, cyclic-C₄F₈, and iso-C₄F₈, were obtained from low temperature distillation of the pyrolytic degradation products of commercial Teflon.

Sulfur tetrafluoride (SF₄) and disulfur decafluoride (S₂F₁₀) were obtained from E. I. du Pont de Nemours & Co., Inc., and the Defense Research Board of Canada, Chemical Laboratories, Ottawa, respectively. The pyrolysis of S₂F₁₀, at 250° C. yielded mixtures containing SF₄, SF₆, and S₂F₁₀.

EXPERIMENTAL

During these exploratory studies, it was observed that successful analyses of fluorocarbon and sulfur-fluoride mixtures depended primarily upon the selection of a suitable liquid-solid column packing material. On the other hand, variables such as carrier gas pressure and flow rate, column temperature, and column dimensions were physical parameters for which optimum values could be readily established. Among the liquid stationary phases evaluated for the separation of these mixtures were Apiezon L, a polymeric methyl phenyl ether (mol. wt. \approx 15,000), and diisodecylphthalate. These were ineffective since poor resolution was obtained.

In Table I, the relative retention volumes corrected for void volume and pressure drop for several fluorocarbons and S₂F₁₀ are compared at the various operating conditions shown.

Although the 15-foot Kel-F column gave satisfactory resolution of some compounds studied, better separations were desired. Therefore, a 20-foot

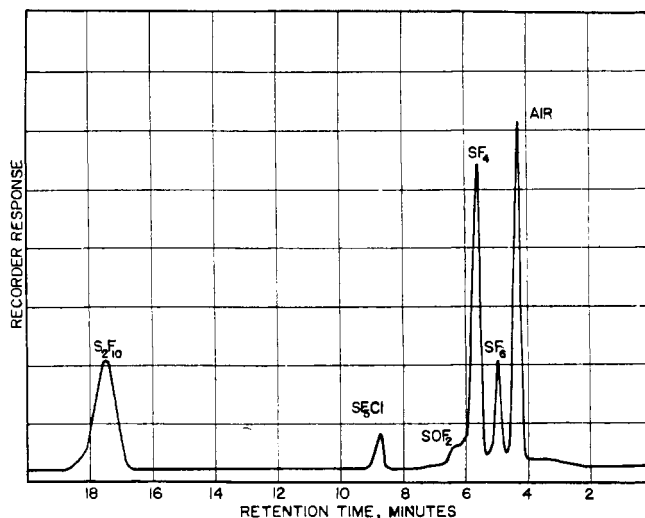
Table II. Relative Retention Volumes for Some S-F and C-F Compounds (SO₂ = 1.00)

Compound	<i>t_m</i>	<i>V_R</i>	<i>V_R</i> ^d	Rel. Ret. Vol.
SF ₄	5.40	198.3	126.5	0.80
SF ₆	4.95	181.7	115.9	0.74
SO ₂	6.70	246.4	157.2	1.00
SF ₅ Cl	8.50	313.0	199.7	1.27
S ₂ F ₁₀	17.00	627.5	400.3	2.55
CF ₄	4.50	165.0	105.3	0.67
CHF ₃	4.60	168.7	107.6	0.68
C ₂ F ₄	5.00	183.5	117.1	0.74
C ₂ H ₄ F ₂	6.20	227.9	145.4	0.92
C ₃ F ₈	6.20	227.9	145.4	0.92
cyclic-C ₄ F ₈	7.10	261.2	166.6	1.06
iso-C ₄ F ₈	9.60	353.7	225.7	1.44

column was prepared. A study of flow rate and temperature variables using this column showed that optimum conditions, based on satisfactory resolution of components and reasonable elution times, were obtained at 25° C. with a helium flow of 37 cc. per minute metered

at 1 atmosphere and 25° C. These conditions were henceforth applied to all separations except where otherwise stated. The relative retention volumes of some analyzed substances are cited in Table II using these conditions. The longest retention time of sulfur-

Figure 2. Gas chromatogram of sulfur-halide compounds identified by trapping and infrared techniques



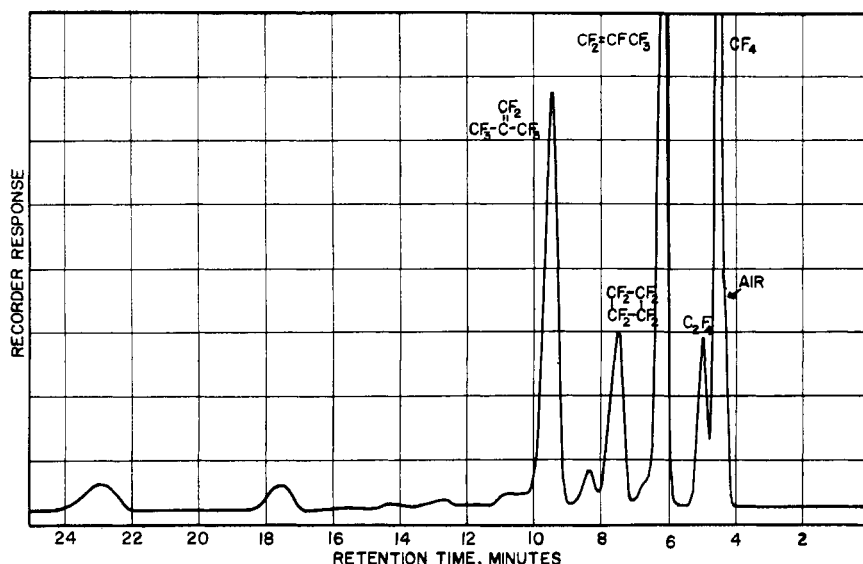


Figure 3. Gas chromatogram of Teflon thermal degradation products

fluoride compounds studied was 17.0 minutes for S_2F_{10} . This proved to be a reasonable elution time when many analyses were required.

These optimum conditions were employed in monitoring and evaluating the production of sulfur pentafluorochloride (SF_5Cl) by a new chemical synthesis process. Figure 1 is a chromatogram showing typical by-product components found in this reaction mixture. The presence of SF_5Cl in this mixture (Figure 1) was confirmed spectrophotometrically by trapping the eluted component directly into an evacuated infrared gas cell. The infrared spectrum obtained agreed with that reported by Cross *et al.* (1).

In gaseous mixtures where unknown compounds appeared in trace amounts, individual components of interest were collected in a liquid nitrogen trapping device by repeated injections of 25-ml. gas samples. After a sufficient quantity of the component had been isolated, its molecular structure was established by infrared studies. For example, the SF_5Cl and S_2F_{10} peaks in Figure 2 were identified using this technique.

The chromatographic operating conditions suitable for S-F mixtures were also applied to the pyrolytic degradation products of Teflon. The separation of a representative crude sample

of such C_1 to C_4 fluorocarbons is shown in Figure 3.

Other exploratory studies undertaken dealt with novel reactions of S-F and C-F compounds. The separation of several of the lower boiling components of the mixture, namely, SF_6 , SF_4 , C_3F_8 , cyclic- C_4F_8 , and S_2F_{10} , are noted in Figure 4.

Although Genetron gases were not our primary concern in this work, these conditions were applicable to the separation of CHF_3 (Genetron-23) and $\text{C}_2\text{H}_4\text{F}_2$ (Genetron-152A).

DISCUSSION

A decrease in the prescribed carrier gas flow rate provided better resolution of components, but this advantage was offset by correspondingly longer retention times. For better resolution, the gas flow was altered. For mixtures containing SF_6 and C_2F_4 , where C_2F_4 had only a 0.05-minute longer retention time than SF_6 , a reduction in helium flow from 37 cc. per minute to 24 cc. per minute resulted in a 0.10-minute separation, whereas a flow of 15 cc. per minute resolved the two compounds by 0.25 minute.

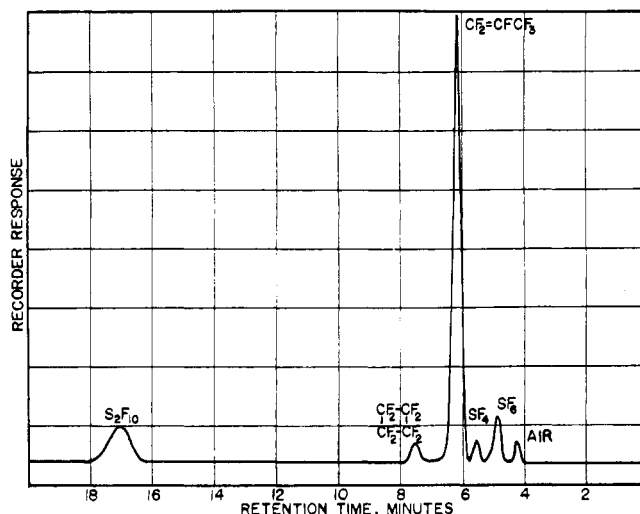


Figure 4. Gas chromatogram of mixture of fluorocarbons and sulfur-halide compounds

Table III. Effects of Flow and Temperature on Relative Retention Volumes
($\text{SOF}_2 = 1.00$)

Compound	A				B				C			
	t_m	V_R	V_R°	Rel. ret. vol.	t_m	V_R	V_R°	Rel. ret. vol.	t_m	V_R	V_R°	Rel. ret. vol.
SF_6	5.00	183.5	117.1	0.74	3.10	231.0	116.7	0.76	3.20	222.5	112.4	0.86
SF_4	5.60	205.7	131.2	0.83	3.65	272.3	137.5	0.89	3.40	236.5	119.4	0.92
SOF_2	7.70	246.4	157.2	1.00	4.10	306.0	154.4	1.00	3.70	257.5	130.0	1.00
SF_5Cl	8.80	324.1	206.8	1.32	5.35	399.8	201.9	1.31	4.10	285.5	144.2	1.11

* Operating Conditions: A. 25° C. column temperature, 37 cc./min. helium flow rate at 1 atm. and 25° C.
B. 25° C. column temperature, 74 cc./min. helium flow rate at 1 atm. and 25° C.
C. 82° C. column temperature, 70 cc./min. helium flow rate at 1 atm. and 25° C.

Using the 20-foot column, the combined effects of increased column temperatures and carrier gas flow on the relative retention volumes of sulfur-halogen compounds are noted in Table III. These results were obtained by introducing a 0.25-cc. aliquot of the same gas at the different operating conditions.

From this work, it seems very probable that this 20-foot packed column can also be utilized at higher temperatures and flow rates to separate high boiling fluorocarbons.

In the calculation of the effective theoretical plates for the 20-foot Kel-F column, the equation by Keulemans (6) gives a H.E.T.P. of 2.76 mm. and

a theoretical plate value of 2210 for SF_6 as shown in Figure 1. If more theoretical plates are desirable, they can be obtained by increasing the column length.

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Some Characteristics of a Strontium-90 Beta-Particle Detector for Gas-Liquid Chromatography

FRANK T. UPHAM, FRANK T. LINDGREN, and ALEX V. NICHOLS

Donner Laboratory of Medical Physics and the Lawrence Radiation Laboratory, University of California, Berkeley, Calif.

► Performance characteristics of a large beta-particle ionization detector employing a Sr^{90} source are described in some detail. The critical components of this apparatus are evaluated and discussed in relationship to gas chromatography involving methyl esters of the long-chain fatty acids. Useful information includes calibration data as well as details of the detector geometry and the injection assembly. Under favorable conditions of operation this detector has a large dynamic range and a high signal to noise ratio.

ONE of the most useful and flexible detection devices applied to gas-liquid chromatography has been the beta-particle detector (4) using argon as a carrier gas. Although utilized extensively for biochemical analysis (3), there has been a limited amount of technical data relating to the characteristics and properties of this type of detector. It is our purpose to describe in some detail the characteristics and performance data of an apparatus employing a beta-particle ionization detector which has been applied to gas liquid chromatography of the methyl esters of long-chain fatty acids.

EXPERIMENTAL

In over-all design our gas-liquid chromatographic unit is similar to the apparatus described by Farquhar *et al.* (1). Figure 1 illustrates schematically the components and general character

of our complete gas-liquid chromatographic apparatus. Prior to the entrance of the carrier gas into the injection chamber the gas must pass through a preheating system which ensures that the carrier gas entering the injection chamber and column is at or slightly above the column temperature. The usual column temperature is 195°C . as checked by a test column filled with uncoated 48- to 65-mesh Chromosorb in which are embedded six thermocouple probes spaced throughout the length of the column. Thus, adjustments of all heaters to achieve column temperature uniformity may be made under typical operating conditions, including gas flow. The main heater is adjusted so that with the auxiliary heater off, the column is maintained at approximately 6°C . below the desired operating temperature. Linearity to

within $\pm 0.5^\circ\text{C}$. in temperature throughout the column is achieved by compensation of heat losses at the two oven ends by appropriate adjustment of the top, bottom, and chamber heaters.

Our injection system, designed for solvent injection, connects the gas preheater to the top of the gas chromatographic column (Figure 2). Two pins in the injection block provide for alignment of the seven injection holes in the compression plate with the seven corresponding holes in the injection block. The injection seal consists of a $1/16$ -inch silicone rubber disk firmly compressed by the seven-hole compression plate. A hypodermic needle may be inserted and removed through any hole without gas leakage. This feature is extremely important because gas leaks in the inlet system result in harmful base line drifts and sporadic fluctuations. Also, be-

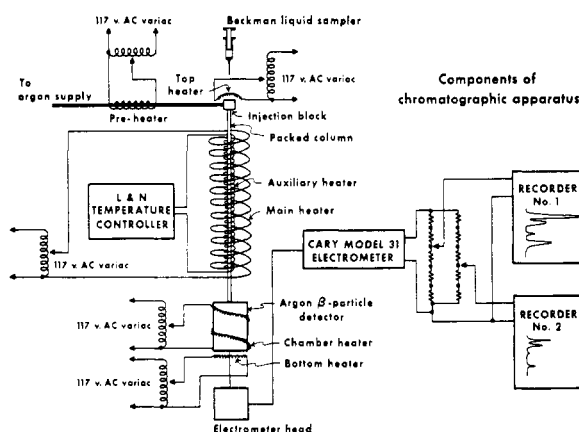


Figure 1. Schematic diagram of gas-liquid chromatographic apparatus