

Column materials and preparation. A 6 ft. composite column consisting of 2 ft. of 50/80 mesh Porapak (Waters Associate, Inc.) type T followed by 4 ft. of 50/80 mesh Porapak type N was used for the analysis. The column was packed in $\frac{1}{4}$ in. O.D. Type 316 stainless steel tubing. Before final installation in the chromatograph, the column was heated to 200° and purged with helium (60 ml/min) for 2 h. Prior to each series of runs the column was conditioned by passing three 250 torr samples of CF_2O through it.

Results and discussion

A typical chromatogram indicating the separation of CF_2O and CO_2 as obtained with the column described above is given in Fig. 1. The operating conditions corresponding to the results given in Fig. 1 are: column temperature 23° ; helium flow rate 60 ml/min. A plot of CF_2O peak area as a function of CF_2O pressure in the 2 ml sample volume is shown in Fig. 2. These results indicate that the detector response is linear over an eleven fold increase in CF_2O concentration. The curve given in Fig. 2 approaches the origin as the sample pressure is decreased. This behavior indicated that CF_2O absorption on this column is essentially nonexistent.

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Synthetic diamond—A solid adsorbent for corrosive gases

A satisfactory chromatographic system for the analysis of corrosive halogen gases has proven to be an illusive objective. Recent publications¹⁻⁵ in this area are indicative of continuing difficulties encountered in the separation of these reactive materials. Primarily chromatographic separations have been concerned with inorganic penta- and hexa-fluorides, chlorine trifluoride and anhydrous hydrofluoric acid. No substrate or support has been recommended for gaseous mixtures containing

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elemental fluorine. ROCHEFORT⁶ has proposed a chromatographic procedure for fluorine. However, this is achieved by a preliminary reaction with NaCl and chromatographic separation of the resulting chlorine.

Diamond is relatively inert to chemical attack and experiments were initiated to determine its suitability for the chromatographic separation of fluorine and other corrosive halogen gases. Diamond particles with sufficient surface area for chromatographic applications are now available from synthetic sources. Diamond crystallites, prepared by subjecting graphite to explosion developed shock waves, have a particle size of approximately 100 Å and a surface area of 200 to 260 m²/g. Although the surface functional groups on the shock-formed diamond have not been completely characterized, diamond's infrared spectra show carbonyl and hydroxyl absorptions. The nature and synthesis of shock-formed diamonds have been discussed previously⁷.

Experimental

Gas chromatography was carried out utilizing a custom built unit fitted with tubing and valves of nickel and monel. The detector used is a thermal conductivity cell, made by Gow Mac Instrument Company, Madison, N.J., fitted with nickel filaments mounted in a nickel block using polytetrafluoroethylene insulation.

Separations were made with an 18 ft. by 0.125 in. O.D. nickel column packed with a mixture of CaF₂-shock-formed diamond. The packing is prepared by shaking 9 parts CaF₂, 30-70 mesh, with 1 part synthetic diamond. Even though the diamond particles are considerably smaller no physical separation was observed. All separations were performed at ambient temperature. Samples of shock-formed diamond can be obtained from Industrial Chemicals Division, Allied Chemical Corporation, Morris-

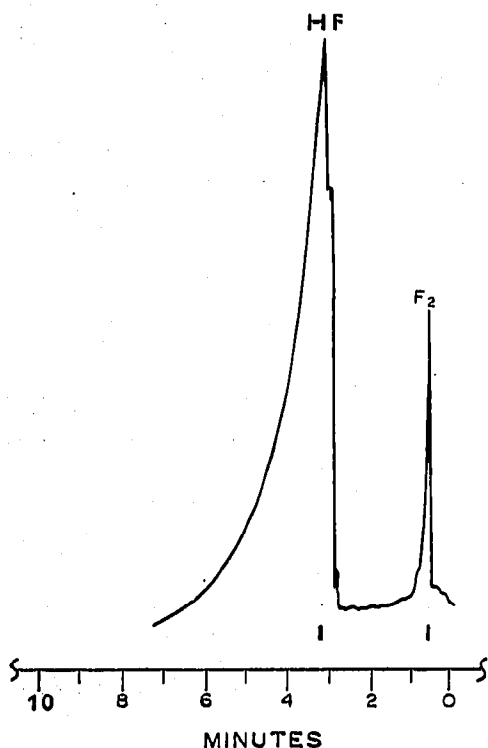


Fig. 1. Separation of HF and F₂. Conditions: Ambient temp., 80 cc/min He, 18 ft. × 1/4 in., 10% diamond-90% CaF₂.

town, N.J. High purity CaF_2 is available from Harshaw Chemical Company, Cleveland, Ohio.

Prior to use, the column and chromatograph were passivated by treatment with ClF_3 .

TABLE I

RELATIVE RETENTION ON DIAMOND- CaF_2 COLUMN AT AMBIENT TEMPERATURE

<i>Compound</i>	<i>Relative retention</i>
F_2	0.5
HCl	1.0
ClF_3	2.0
HF	2.5

Results and discussion

Columns packed with particles the size of shock-formed diamond inherently require a large applied pressure to maintain a nominal carrier gas flow. Attempts to alleviate this problem by using mixtures of shock-formed diamond with conventional chromatographic supports were unsuccessful. In each case the smaller diamond particles separated causing a severe restriction of the carrier gas flow. However, mixtures of CaF_2 and shock-formed diamond remain homogeneous. Adhesion of the diamond particles is apparently quite strong. We have encountered no difficulty in the operation of 18 ft. columns.

Binary mixtures of anhydrous HF- F_2 , HF-HCl and HF- ClF_3 were prepared. Vapor phase samples were injected into the chromatograph and separations effected at ambient temperatures with the helium flow at 80 cc/min. Retention data appear in Table I and a typical chromatogram in Fig. 1. Although the separation of fluorine and air was not achieved at room temperature, the proposed column appears to be adequate for the analysis of anhydrous HF. There was no indication of any reaction between fluorine and the adsorbent.

Supplementary data⁸ for the separation of various fluorocarbon derivatives indicate that the diamond columns are similar in behavior to silica gel.

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