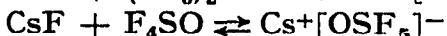
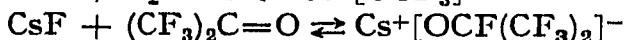
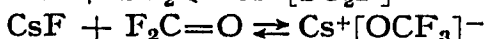
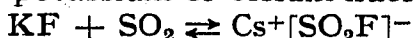


CHROM. 4754

## Alkali metal fluorides as column packing for gas-solid chromatography

Several publications have recently appeared on the use of simple inorganic alkali metal salts as solid adsorbents in gas-solid chromatography (GSC). One of these, a comprehensive report on the application of alkali metal chlorides and nitrates in GSC<sup>1</sup>, encompassed the chromatography of a rather wide range of aliphatic and aromatic compounds, including some with polar hydroxyl and amine substituents. The authors concluded that "physical adsorption", not chemisorption, predominated in the solute-adsorbent interaction. Little stress was placed on the analytical applications of these separations because of the relatively small elution times exhibited by most of the solutes.

In contrast, the use of alkali metal fluorides as a solid adsorbent has not heretofore received attention. This is somewhat surprising, as the formation of adducts between alkali metal fluorides and non-metallic oxides and oxyfluorides has been known for several years. Examples illustrative of such adduct formation are the reactions of SO<sub>2</sub> (ref. 2), F<sub>2</sub>C=O (ref. 3) (CF<sub>3</sub>)<sub>2</sub>C=O (ref. 3) and SOF<sub>4</sub> (ref. 4) with either potassium or cesium fluorides.



For a specific nonmetallic oxide or oxyfluoride the relative ratio of dissociation, *in vacuo*, at any specified temperature, is inversely proportional to the size of the alkali metal cation<sup>3,5</sup>.

REDWOOD AND WILLIS have taken this as direct corroboration of the formation of an oxyfluoride anion in the adduct as opposed to the coordination complex, [Cs ← OCF<sub>2</sub>]+F<sup>-</sup>. For a series of totally fluorinated alkali metal alkoxides (M<sup>+</sup>[OCF<sub>3</sub>]<sup>-</sup>, M<sup>+</sup>[OCF<sub>2</sub>CF<sub>3</sub>]<sup>-</sup> and M<sup>+</sup>[OCF(CF<sub>3</sub>)<sub>2</sub>]<sup>-</sup>), these authors have also shown that the extent of dissociation (*i.e.* M<sup>+</sup>[OCF]<sup>-</sup> → MF + O=C), at a specified temperature increases with increasing bulk of the nonmetallic oxyfluoride<sup>6</sup>. All the adducts studied by REDWOOD AND WILLIS are characterized by a rapid and reversible equilibrium with the dissociation products.

Considering these properties of alkali metal fluorides and their adducts, it seemed likely that the metal fluorides could have utility in GSC separation of gaseous mixtures containing certain metal oxides and oxyfluorides. In order to test this utility, the present investigation was conducted. The study was, however, limited to those salts (KF, RbF, CsF) which readily form adducts with F<sub>2</sub>CO and similar compounds.

### Experimental

The gas chromatographic experiments were performed using a Model 5000 Barber-Colman gas chromatograph fitted with a linear six-port manual gas sampling valve.

Pure CaF<sub>2</sub> (Harshaw Chemical Company) was ground to 60–80 mesh and ignited at 700° to remove all traces of organic impurities. High purity (99.9%) CsF (Ozark-

Mahoning Co.) was screened in a dry box and the 120–200 mesh fraction retained.

Sufficient CsF was added to the  $\text{CaF}_2$  to make a 10% by weight mixture of CsF in  $\text{CaF}_2$ \*. The mixture was then heated for 18 h at  $250^\circ$  and transferred under dry conditions to a 12-ft.  $\times$   $\frac{1}{4}$ -in. O.D. copper tube. After the column was attached to the chromatograph it was further conditioned by heating at  $250^\circ$  for 18 h while purging with helium (22 cc/min) was effected.

An equimolar mixture of  $\text{F}_2\text{C}=\text{O}$ ,  $\text{CF}_3\text{CFO}$ , and  $(\text{CF}_3)_2\text{C}=\text{O}$  was prepared and combined with  $\text{CF}_2=\text{CF}_2$  in the approximate volume ratio of 1:1:1:20. A representative chromatogram of this sample mixture obtained with a 1000  $\mu\text{l}$  vapor sample and a delayed temperature program ( $30^\circ$  for 5 min followed by  $25^\circ/\text{min}$  program up to  $250^\circ$ ) is shown in Fig. 1. All four components in the sample mixture are clearly separated.

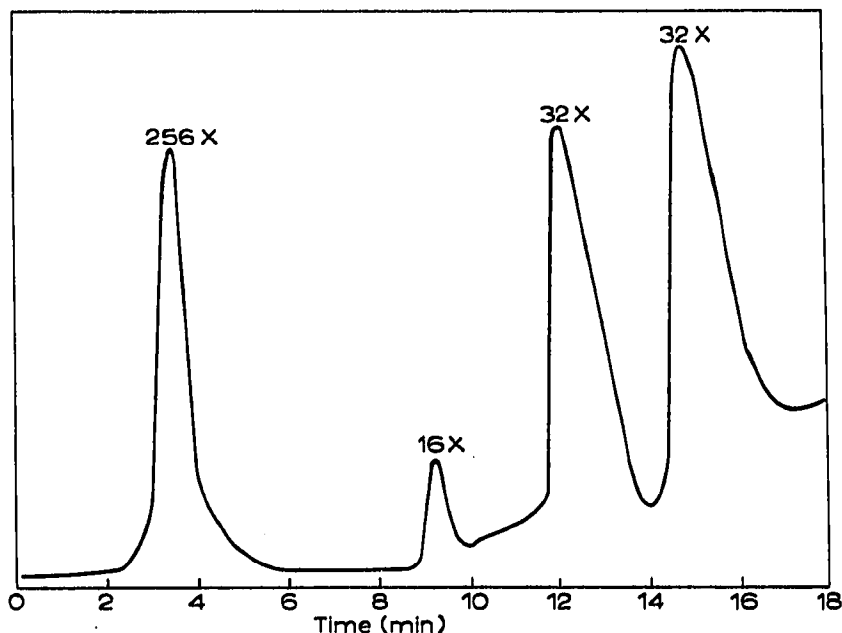


Fig. 1. Separation of  $\text{F}_2\text{C}=\text{O}$ ,  $\text{CF}_3\text{CFO}$  and  $(\text{CF}_3)_2\text{C}=\text{O}$ . Conditions: 12 ft.  $\times$   $\frac{1}{4}$  in. O.D. 10% CsF–90%  $\text{CaF}_2$  column; He 20 ml/min; isothermal  $30^\circ$  for 5 min, programmed  $25^\circ/\text{min}$  to  $250^\circ$ . Elution order:  $\text{CF}_2=\text{CF}_2$  3.4 min;  $(\text{CF}_3)_2\text{C}=\text{O}$  9.2 min;  $\text{CF}_3\text{CFO}$  12.0 min; and  $\text{F}_2\text{C}=\text{O}$  14.8 min.

### Results and discussion

Tetrafluoroethylene is not chemisorbed and elutes rapidly. The order of elution, Fig. 1, for the three oxyfluoro-compounds is the inverse of the order of their boiling points ( $\text{F}_2\text{C}=\text{O}$ ,  $-83^\circ$ ;  $\text{CF}_3\text{CFO}$ ,  $-59^\circ$ ;  $(\text{CF}_3)_2\text{C}=\text{O}$ ,  $-28^\circ$ ). However, their relative retention does parallel the decomposition rates determined by REDWOOD AND WILLIS<sup>6</sup>. For these selected compounds a reversible chemisorption process is therefore the predominant factor in achieving a chromatographic separation.

Separations other than those described can be visualized. Alkali metal fluorides discriminate, via adduct formation, between many nonmetallic oxyfluorides and their hydrolysis products. For example, CsF has been used in the laboratory scale separation

\* The  $\text{CaF}_2$  here serves only as a support for the alkali metal fluorides. Unlike the latter,  $\text{CaF}_2$  and other Group II fluorides show no tendency to form complexes with the oxides and oxyfluorides under consideration<sup>7</sup>.

rations<sup>7</sup> of SF<sub>4</sub> from SOF<sub>2</sub>, COF<sub>2</sub> from CO<sub>2</sub>, and SOF<sub>4</sub> from SO<sub>2</sub>F<sub>2</sub>. In all cases the alkali metal salt forms an adduct with the more highly fluorinated parent compound and not with its hydrolysis product, thus permitting a simple purification of the parent oxyfluoride.

Use of an alkali metal fluoride column in GSC is limited by two common impurities, H<sub>2</sub>O and HF. Because of the deliquescent nature of the metal fluorides care must be taken to minimize the adsorption of atmospheric water vapor during the preparation and packing of the column. Adsorption of moisture by the fluoride results in a marked decrease in the surface area and consequently in the number of active acceptor sites.

Hydrogen fluoride also readily interacts with the alkali metal fluorides to form the very stable bifluorides, MHF<sub>2</sub>.

Regeneration of an HF contaminated column has not been generally successful. As some HF cannot generally be avoided in the majority of samples containing non-metallic oxyfluorides, the only recourse is a periodic column replacement.

Although, as we have noted, there are some difficulties involved in the use of alkali metal fluoride columns in GSC, the novel separation which can be achieved warrants their consideration in any attempt to separate nonmetallic oxyfluoride derivatives.

Corporate Research Laboratories,  
Allied Chemical Corporation,  
Morristown, N.J. 07960 (U.S.A.)

R. P. HIRSCHMANN  
H. L. SIMON  
L. R. ANDERSON  
W. B. FOX

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Received February 13th, 1970

*J. Chromatog.*, 50 (1970) 118-120

CHROM. 4736

### Nickel complexes as adsorbents in gas-solid chromatography

The first attempt at modifying stationary phases of gas chromatographic columns with an inorganic electrolyte was by BRADFORD<sup>1</sup> and consisted of silver nitrate dispersed in glycol. Since this time, a number of papers concerned with using inorganic salts and salt-modified stationary phases has appeared<sup>2-5</sup>. PHILLIPS *et al.*<sup>6</sup> reported on the use of N-dodecyl salicylaldimines of Ni, Pd, Pt, and Cu and the methyl-n-octyl glyoximes of Ni, Pd, and Pt as stationary phases. They found that retardation

*J. Chromatog.*, 50 (1970) 120-126