Gas chromatographic separation of sulfur tetrafluoride and thionyl fluoride

Sulfur tetrafluoride can be obtained in a purity of about 90 % by distillation, but further purification is difficult[1]. The main contaminant present after distillation is thionyl fluoride. Because SF_4 was needed in the purest form possible for physical studies, gas chromatography was explored as a means of purifying the compound. In purifying SF_4 by this technique, it is necessary to use a column that will separate SF_4 not only from SOF_2 but also from SiF_4 and HF which are either present in the crude product or formed by adventitious hydrolysis of SF_4. Furthermore, the choice of both solid support and liquid substrate is limited by the reactivity of SF_4, *e.g.*, its activity as a fluorinating agent for organic carbonyl compounds[2] and for inorganic oxides and sulfides[3]. These restrictions eliminate most of the known conventional columns, and others which meet these qualifications are not effective.

Since sodium fluoride is known to be an effective adsorbent for HF, a possible contaminant in the mixtures to be separated, it was tried as a candidate for the solid support. The use of sodium fluoride coated with either tetramethylene sulfone or tetraethylene glycol dimethyl ether ("tetraglyme") proved to be effective for the separation.

A U-shaped 6 ft. × 3/4 in. copper column with 2000 Ω "VECO" thermistors in the detection cell was used. The entire system was constructed of metal. Glass was avoided to eliminate SiF_4 formation when HF was present. The column was packed with 10 % by volume "tetraglyme" on sodium fluoride which had been pelleted, crushed, and screened to 35–60 mesh. Resolution differed widely with NaF from various sources but was best with that obtained from Harshaw Chemical Company.

The column was immersed in a refrigerated bath at 0° while the detection cell was maintained at room temperature. Helium flows of 500–1000 ml/min were required to obtain satisfactory separations with retention times of 30 min or less.

Crude SF_4 was introduced to the column in the gas phase with the aid of a reduction valve and manifold on the SF_4 cylinder leading to a 150-ml stainless steel cylinder valved at both ends. With the exit end of the 150-ml cylinder connected to the column, it was possible to introduce repeated samples to the gas chromatographic system without opening it to the atmosphere. (See schematic system for purification of SF_4, Fig. 1.) The product trap is also a stainless steel cylinder fitted with inlet and outlet valves on the upper end. Thus, with the aid of a line valve, the desired fraction can be directed into the product cylinder and condensed by a liquid nitrogen bath which surrounds this cylinder. It is very important to first remove residual water from the product trap by heating while evacuating to 1 μ or less.

A number of trial runs must be made to condition the system. The HF formed from any residual water is complexed with the sodium fluoride. Thus, once the apparatus is dry, no further hydrolysis will take place until a shutdown occurs, at which time it is necessary to repeat the conditioning procedure.

Scouting runs for this procedure were made on 6 ft. × 1/4 in. copper columns

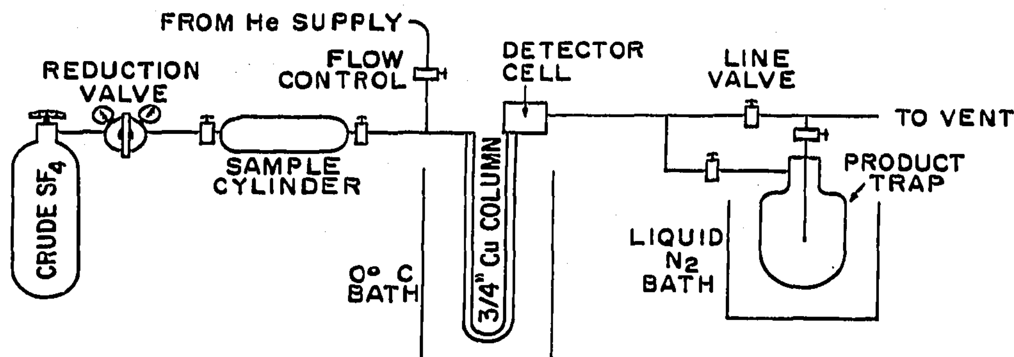

Fig. 1. Schematic system for purification of SF_4.

using either tetramethylene sulfone (TMS) or "tetraglyme" on 35–60 mesh sodium fluoride. The SOF_2 and the SF_4 elute and are separated by 1 to 10 min, depending on column conditions. The use of "tetraglyme" was preferred since it could be used without solidifying at 0° where the separation between SOF_2 and SF_4 is more effective. A run could be made in 15–20 min using one of these systems. Representative analytical results obtained on a "tetraglyme" column and by mass spectrometry are shown in Table I.

TABLE I

ANALYTICAL RESULTS ON SF_4–SOF_2 MIXTURES

Gas chromatography area %		*Mass spectrometry mole %*	
SOF_2	SF_4	SOF_2	SF_4
78	22	79	21
7	92	10	89
9	91	12	87
5	95	6	93

The importance of the correct particle size of sodium fluoride for the synthesis of SF_4 has been discussed[1].

Various types of sodium fluoride were examined for particle size, surface area, pore volume, and pore diameter, but no correlation was evident between the measurements and their effectiveness as supports. It is possible to partially separate the gas mixture by using 35-60 mesh NaF (Harshaw) alone without the use of a partitioning liquid, indicating that both adsorption and partition chromatography are involved in the separation.

A series of runs into a 1000-ml product cylinder gave the following results by mass spectrometry: SF_4–98.3 %; SOF_2–1.2 %; SiF_4–0.1 %; CS_2–0.1 %; and SO_2–0.1 %.

Although we are unable to explain the variation of results with the different sodium fluorides, it is possible to obtain 98 % SF_4 or better in a single pass ever a preparative gas chromatographic column. The extension of this separation to an analytical column requires very close control over all factors that might introduce

trace amounts of moisture into the system and several conditioning runs must be made each day before an analysis is attempted. Conditioning is completed when the SOF_2 peak, which eluted prior to the SF_4, stays the same on consecutive runs.

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Notes

Paper chromatographic and high-potential paper electrophoretic identification of β-hydroxyglutamic acid in the brain

Recently, β-hydroxy-γ-aminobutyric acid (β-OH-Gaba) was identified in the brain[1]. Regarding the precursor of β-OH-Gaba, it has been reported that Gaba may be converted to β-OH-Gaba by beta oxidation[2]. On the other hand, consideration should be given to the fact that β-hydroxyglutamic acid (β-OH-Glu) may be converted to β-OH-Gaba through decarboxylation[3] in the brain. However, until now, the presence of β-OH-Glu in the brain has not been detected.

In our experiments, fresh brain material was frozen, homogenized and deproteinized with 70% ethanol. The deproteinized liquid was subjected to petroleum ether extraction to remove lipids and was evaporated to dryness at 40° in a vacuum. The residue thus obtained was dissolved in a small amount of distilled water and applied to the bottom half of the starting line on Toyo-Roshi No. 50 filter paper for high-potential paper electrophoresis. A solution of a synthesized sample of *threo*-β-OH-Glu* was then applied to the upper half of the starting line of the filter paper[1]. After high-

* The synthetic racemic samples of *threo*-β-OH-Glu and *erythro*-β-OH-Glu were supplied by Ajinomoto Laboratory and by Dr. SELBY DAVIS, Head, Medical Chemistry, Department of Non-infectious Diseases, Lederle Laboratories, Pearl River, New York. The authors appreciate these generous gifts. *threo*-β-OH-Glu and *erythro*-β-OH-Glu are synonymous with *allo*-β-OH-Glu and β-OH-Glu respectively[4].