Practical Sulfur Isotope Separation by Distillation

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ABSTRACT

Sulfur isotopes were separated in 1.07 and 1.50–m experimental packed distillation columns at cryogenic temperatures under total reflux. The $^{32}S/^{34}S$ ratio at column top was as much as 19% different from the bottom ratio. The $^{32}S/^{33}S$ separations were the square root of $^{32}S/^{34}S$ separations. Typical relative volatilities of $^{32}S/^{34}S$ are 1.0023 for H_2S, 0.9978 for SF_4, 0.9985 for SF_6, 1.0006 for COS, and 1.0011 for CH_3SH. A $^{12}C/^{13}C$ volatility of 0.9982 was also seen in COS. Sulfur separations in SF_4 and SF_6 and the carbon separation in COS are reverse isotope effects.

Distillation is a feasible method for sulfur isotope separation. Hydrogen sulfide is the best candidate compound for a practical sulfur isotope separation. Existing distillation columns could economically produce as much as 50 kg/yr of contained ^{34}S at 15% enrichment. Smaller amounts of more highly enriched isotopes could also be produced.

INTRODUCTION

Small amounts of sulfur isotopes are used presently, but important and expanded uses have been proposed. Bioanalytic chemists are anxious for the availability of enriched ^{33}S for nuclear magnetic resonance studies. Acid rain tracing with ton quantities of labelled sulfur dioxide has been considered by the DOE. Most recently, human genome researchers want sizeable quantities of each sulfur isotope at high enrichments.

Sulfur isotopes are separated in small quantities by liquid thermal diffusion by Mound Laboratory and, to a lesser extent, by electromagnetic separation (calutrons) at ORNL. Recent costs of Mound materials are $402.40/g of contained isotope for 90% ^{34}S and $70,000/g contained isotope for 3% ^{36}S (1). Gas centrifuges have been used to enrich about 9 kg (contained) of ^{34}S to 10% enrichment, but a combination of the low enrichment and undesirable chemical form has resulted in almost no usage. ORNL has been the sole producer of enriched ^{33}S, but their recent catalog does not list any available now or in the immediate future (2).

Distillation can be operated over a wide range of production rates, and it can often operate at lower costs than alternative processes. Distillation processes have been developed for the enrichment of the heavy isotopes of carbon, nitrogen, oxygen, and neon at 3–10 kg annual rates (3). The unit costs of ^{13}C, ^{15}N, and ^{18}O dropped by factors of 10 to 20 as a result, and distillation is now the predominant means of separating these isotopes. Recently, several sulfur compounds have been studied in experimental distillation columns (4,5,6). Separations observed for some compounds are sufficiently large that practical enrichment of sulfur isotopes is possible.

APPARATUS

Three different packed distillation columns were used for experiments. Each column was a stainless steel tube packed with stainless steel wire helices (Heli-Pak) of different sizes.

Table 1. Distillation Column Details

Column	Condenser	Length (m)	I. D. (mm)	Packing Size (mm)
1	Heat Pipe	1.07	8	0.8x1.8x1.7
2	Heat Pipe	1.07	14	1.3x2.5x2.3
3	Helium Refrig.	1.50	14	1.3x2.5x2.3

In addition to the packed length of 1.07 to 1.50 m, each column had an unpacked length at the column top and bottom for condenser and boiler regions. Stainless steel screens supported the packing above the boiler and held down the packing at the condenser. Electrical band heaters at the boiler vaporized liquid to provide column boilup. The gaseous boilup was recondensed at the top of the column using either a heat pipe condenser (7) or a small helium refrigerator. Heat pipe-cooled columns had the condenser region extending into a closed secondary refrigerant bath, cooled in turn by liquid nitrogen (LN$_2$). The Column 3 condenser was mechanically attached to the cold head of the refrigerator. Column temperatures were measured by silicon diodes and copper-constantan

thermocouples bolted or soldered onto the column. Power to the boiler heaters was regulated by variable transformers, and temperature was thermostatically controlled by control units using the diodes and thermocouples. Each column was housed in a vacuum jacket and was wrapped with approximately 50 layers of aluminized Mylar for thermal insulation.

Manifolds to the columns were quite simple, as the columns were operated without flows. Two small-diameter lines from the manifold to the column top and bottom were used for gas introduction to the column and sampling. A relief valve which vented to a 4-L cylinder was fitted to the column top line. A 0.3-L stainless steel trap was used for gas purification. Pressure in the manifold or at the column top and bottom was measured by a pressure transducer on the manifold. A well-vented vacuum system was used to evacuate the manifold for sample collection.

The columns using heat pipe condensers had a separate manifold for the heat pipe system. This consisted of helium, propane, propylene, and vacuum lines tied to a common manifold with a pressure transducer. Rotameter-type flowmeters measured the amount of propane and propylene added to the heat pipe.

EXPERIMENTAL

For each column, the condenser was cooled first. Liquid nitrogen was used to condense a liquid propane-propylene mixture (LC_3) in the secondary refrigerant condenser for columns 1 and 2. Helium pressure above the LC_3 was adjusted to maintain the desired condenser temperature. Column 3 condenser temperature was maintained by a heat balance between a trimmer heater on the condenser and the cooling capacity of the helium refrigerator. Once the condenser was cold, gas was introduced and liquified to cool the entire column to operating temperature. Boiler power was then turned on, and additional gas was condensed until temperatures remained stable.

Chemicals distilled were commercial compressed gases of the highest available purity (typically C. P. Grade). The five sulfur compounds distilled included sulfur tetrafluoride, sulfur hexafluoride, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan. The gas was first condensed into a stainless steel trap with LN_2, and any volatile impurities were removed by pumping while the trap remained cold. The trap was then allowed to warm slowly, and the gas evolved was recondensed in the column. When evolution of gas from the warming trap slowed, the trap was isolated to retain any nonvolatile impurities. During subsequent operation of the column, any remaining impurities rapidly migrated to either the column top or bottom. Gas was vented from the ends of the column until mass spectrometer analyses indicated that pure compound remained.

To obtain the maximum number of separating stages with Heli-Pak, it was necessary to flood the packing with liquid. With each compound, sufficient liquid was condensed to completely fill the column with liquid. The column was then deflooded by withdrawing gas from the top until minimal bulk liquid remained in the packing. The amount of liquid remaining in the column was monitored by pressure drop through the packing.

The column was refluxed without drawoff, and daily samples were collected until steady-state concentrations were observed at the column top and bottom. All gas samples were analyzed without conversion to other chemical forms. Isotopic analyses were done on a CEC 21-621 cycloidal mass spectrometer and on Nuclide 6-60-RMS and 12-90-GQ magnetic sector mass spectrometers. Column top and bottom samples were analyzed in pairs to obtain the overall column isotopic separation. The overall separation, A, is the quotient of top and bottom isotopic ratios.

$$A_{32/34} \quad = \quad \frac{(^{32}S/^{34}S)_{top}}{(^{32}S/^{34}S)_{bot}} \tag{1}$$

After a repeatable separation was attained, the column temperature was changed and samples were taken under the different column conditions.

Isotopic separations were computed from mass spectrometer data in different ways for the various compounds. Isotopic ratios in SF_4 and SF_6 were calculated directly from the SF_3^+ and SF_5^+ peaks, as fluorine is monoisotopic. Fragmentation peaks of S^+ and HS^+ were observed when analyzing H_2S, but the fragmentation pattern relative to H_2S^+ was invariant with isotopic substitution. Accordingly, the ratio of $^{32}S^+/H_2^{34}S^+$ for column top and bottom samples was used to obtain the separation. For COS, the S^+ fragments were used to obtain the sulfur isotope separation, and the C^+ fragments were used for carbon isotopes. Both carbon isotopic peaks and a typical hydrocarbon fragmentation pattern complicate the isotopic analysis of CH_3SH. The peaks CH_xS^+ ($x = 0$ to 4) were used. First allowances were made for the natural abundance of 1.1% ^{13}C; then the data were fitted by least squares assuming fragmentation patterns to be isotope invariant.

Table 2 gives representative total column separations of $^{32}S/^{34}S$. A value of A>1 means the higher mass isotope was less volatile. In H_2S, COS, and CH_3SH, the higher mass sulfur isotopes were less volatile. This effect is normally observed for many simple molecules. A sizeable inverse isotope effect was found for SF_4 and SF_6. Separations of ^{32}S from ^{33}S were also measured for SF_4, SF_6, and COS. In each case, the $^{32}S/^{33}S$ separations were approximately the square root of the $^{32}S/^{34}S$ separations, which is in accordance with isotopic separation theory. Carbonyl sulfide exhibited the interesting behavior of a relatively large reverse isotope effect for carbon isotopes, while the sulfur isotope separation was normal and smaller. (An oxygen isotope separation was

not observed in COS). Isotopic separations of both $^{32}S/^{33}S$ and $^{32}S/^{34}S$ in SF_4 showed a definite temperature dependence. Strong temperature dependence of separations for other compounds was not observed.

Table 2. Total Column $^{32}S/^{34}S$ Separations

Compound	Pressure (torr)	Temperature (K)	Separation A	Col. Length (m)
SF_4	400	234	0.865	1.07
	660	237	0.838	1.50
	820	238	0.922	1.07
SF_6	1830	228	0.884	1.50
	2690	238	0.898	1.50
H_2S	300	196	1.127	1.07
COS	550	219	1.037	1.50
	700	223	1.031	1.07
	1050	237	1.048	1.50
CH_3SH	240	254	1.058	1.07

Table 3. Isotopic Relative Volatilities

Compound	Isotopes	Temperature (K)	Relative Volatility α
SF_4	$^{32}S/^{33}S$	234–238	0.9987–0.9991
	$^{32}S/^{34}S$		0.9976–0.9980
SF_6	$^{32}S/^{33}S$	228–238	0.9992–0.9995
	$^{32}S/^{34}S$		0.9984–0.9986
H_2S	$^{32}S/^{34}S$	196	1.0023
COS	$^{32}S/^{33}S$	219–237	1.0002–1.0003
	$^{32}S/^{34}S$		1.0004–1.0007
	$^{12}C/^{13}C$		0.9980–0.9984
CH_3SH	$^{32}S/^{34}S$	254	1.0011

The overall column isotope separation is related to the isotopic relative volatility, α, and the number of theoretical plates, N, by Eqn 2.

$$A \quad = \quad \alpha^N \tag{2}$$

To obtain an estimate of the number of theoretical plates, CO was distilled in the 1.50–m column, and isotopic separations were measured. This column was calculated to have 80 theoretical plates from the measured $^{12}C/^{13}C$ separation and data of Johns (8). The expected HETP for medium sized Heli-Pak with CO is 2.0 cm, which predicts 75 theoretical plates for the 1.50–m column. The slightly conservative value of 2.0 cm was used for the plate height in each column to calculate the inferred α's for each compound in Table 3. Plate height is not necessarily the same for different compounds on a particular packing, thus these numbers must bear that qualification.

DISCUSSION

Isotopic measurements for distillation of SF_4, SF_6, COS, and CH_3SH have not been reported by other investigators. Several Russian investigators have distilled H_2S with somewhat inconsistent results (9). The present H_2S data agree with the lower range of reported values.

While the assumption of constant plate height for different compounds is not necessarily accurate, it must be emphasized that the total column separations are actual separations in an actual column. If longer columns with the same packing are used, the sulfur isotope separations may be accurately projected from this data. The total $^{32}S/^{34}S$ separation for H_2S and SF_4 in the experimental columns was approximately one-third the $^{12}C/^{13}C$ separation in distillation of carbon monoxide, which is the standard ^{13}C separation process (8).

The sulfur isotope separations in SF_4 and SF_6 are exciting for both magnitude and reverse nature. Other multiply-halogenated compounds, notably BF_3 (10), exhibit rather large reverse isotope effects. Normally a sizeable vapor pressure isotope effect may be expected in a molecule where there is a large degree of intermolecular association (e.g., NO or H_2O). The relatively large effect in SF_6 is surprising, in view of its molecular symmetry and nonreactive nature; however, we have recently found sizeable reverse isotope effects by distilling SiF_4, another symmetrical molecule (11).

The carbon isotope separation in COS may shed some light on the pattern of reverse isotope effects in polyatomic compounds. Carbonyl sulfide has the structure O=C=S. In each case mentioned (*COS, *BF_3, *SF_4, *SF_6, *SiF_4), a reverse effect occurs for a central atom connected to other atoms which represent the bulk of the molecular mass . The normal isotope effect occurs when the atom in question is relatively heavy or is not

in a central location in the molecule ($H_2{}^*S$, $CH_3{}^*SH$, CO^*S). This rule also predicts the reverse isotope effects found in $^*CHF_3$ and $^*TiCl_4$ (12,13)

PRACTICAL SULFUR SEPARATION COLUMNS

Based upon the separations observed in SF_4, SF_6, and H_2S, distillation is a practical means of separating sulfur isotopes. The isotopic separations are roughly the same for the various compounds, but several practical considerations make H_2S the preferable choice for a working material. Sulfur tetrafluoride is not produced in bulk quantities and is relatively expensive. Both SF_4 and SF_6 have the reverse effect which concentrates heavy isotopes at column tops. With the reverse effect, some advantages of using physically tapered columns (e.g., Column D, Fig.1) to minimize holdup of heavy isotope are lost. Sulfur hexafluoride is non-reactive, and the inability to easily label sulfur compounds from it has prevented Mound from making sales from their inventory. Hydrogen sulfide is a cheap ($10/kg) feed stock, and its normal isotope effect is at least the equal of the other two compounds. Toxicity and reactivity of H_2S are problems which are routinely dealt with by industry, and H_2S is a good starting material from which many labeled compounds can be made.

An example of practical enrichment of ^{34}S may be demonstrated by considering six distillation columns at Los Alamos which are presently not used. These columns were used previously for separating nitrogen and oxygen isotopes by distillation of nitric oxide (14). Each column is made of stainless steel with a heat-pipe style condenser capable of obtaining temperatures appropriate to H_2S distillation. No firm plans have been made for the columns, and they could be rapidly converted to H_2S service. Depending upon desired enrichments and production scale, the columns could be configured a number of ways. Column details are given in Table 4. Column boilup is expressed in mole/day (M/D) of H_2S.

Table 4. Production Column Specifications

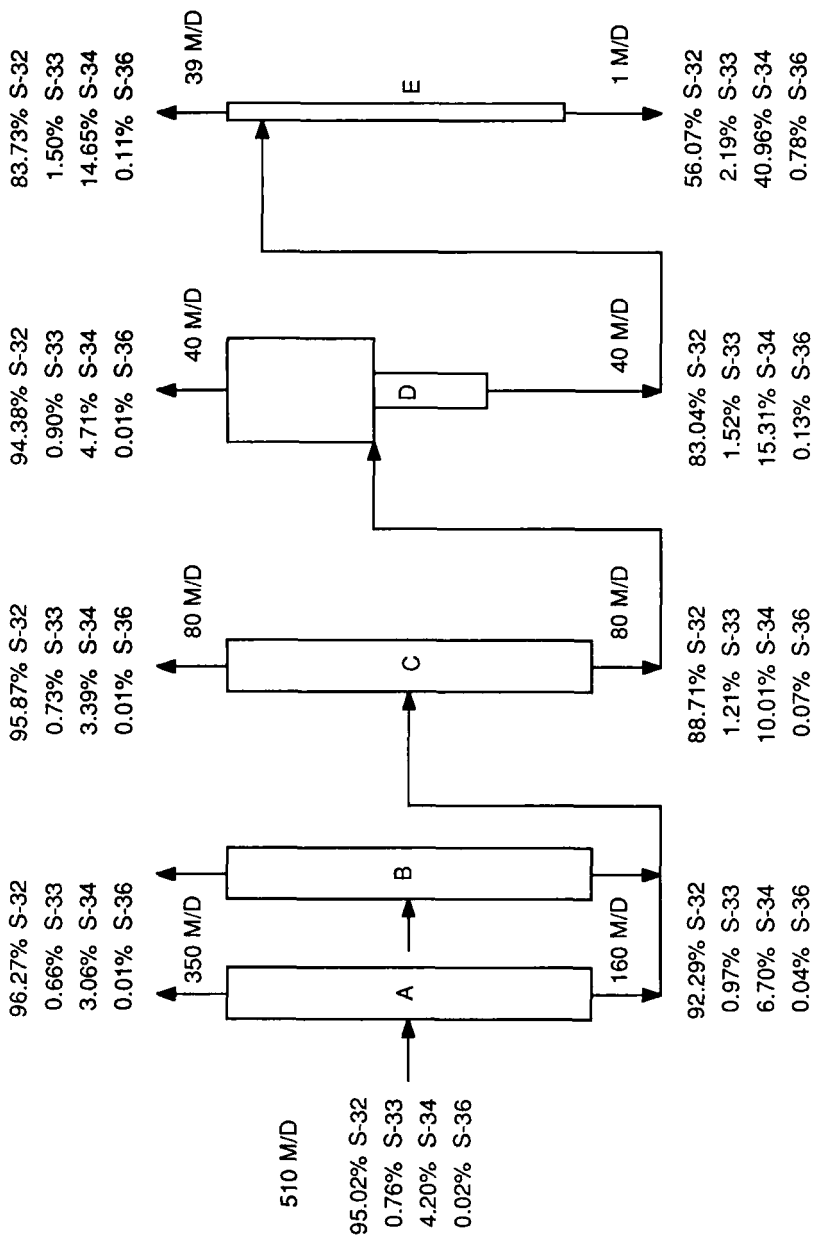| Column	Cross-Section (cm^3)	Boilup (M/D)	Above Feed (plates)	Below Feed (plates)
A	42	22500	600	600
B	42	22500	600	600
C	42	22500	600	600
D	113	36000	500	
	19	9000		250
E	6	1350	72	1008
F	6	1350	72	864

Figure 1. Large-Scale Separation of Sulfur Isotopes using Five-Column Network for H2S Distillation

One possible mode of operation is to produce large amounts of ^{34}S at moderate enrichment. Calculations have been made for a network of five columns as shown in Fig. 1. Columns A and B are operated in parallel with equal flows. All columns have bottom boilers. Column D has a greater cross-sectional area above the feed location, and an additional boiler is located at this point. The relative volatility of $^{32}S/^{34}S$ is 1.0023 at 196 K (Table 3), and α's for $^{32}S/^{33}S$ and $^{32}S/^{36}S$ separation are taken to be 1.00115 and 1.0046, respectively. Flows are M/D of H_2S.

This operational scheme enables production of some 6 moles of contained ^{34}S per day (40 M/D @ 15% enrichment) from Column D. Use of Column E gives the variant of a small amount of significantly higher enrichment product with minimal effect on the enrichment of the remaining material. Assuming a 250 day year, the annual production capacity of this cascade is 1500 moles or 51 kg of contained ^{34}S. Based upon previous operating experience with NO, the total operating cost would be about $1.5M, giving a unit cost of about $30/g of ^{34}S. Raw material would contribute less than $1/g to the cost, and the major costs would be cryogenic refrigeration and operating personnel.

As an alternative approach, small amounts of relatively high enrichment heavy isotopes could be separated. Using only Column E and a nearly identical column (Column F) would reduce the cost of LN_2 consumption and staffing to perhaps $200K per year. These columns could be operated to produce enriched ^{34}S under a wide variety of operating conditions. For example, they could produce either 1 M/D of gas containing 14% ^{34}S and 0.11% ^{36}S or 0.05 M/D at 52% ^{34}S and 1.3% ^{36}S, depending upon location of the withdrawal stream (Fig. 2). If the columns were operated in parallel, 2 M/D of 16% ^{34}S could be produced. These isotopic compositions could be of interest if only limited amounts of isotope were needed for experiments. This product could also be used as an enriched feed stock for other separation processes which inherently have low throughput (e.g., liquid thermal diffusion or calutrons).

CONCLUSIONS

The magnitude of the basic $^{32}S/^{34}S$ vapor pressure isotope effect is about 1.002 for distillation of SF_4, SF_6, and H_2S. Smaller sulfur isotope separations occur for COS and CH_3SH. The $^{32}S/^{33}S$ separation is approximately the square root of that for $^{32}S/^{34}S$, as expected. These separations are sufficiently large for use in practical separation of sulfur isotopes. A combination of availability, reactivity, and a normal isotope effect make H_2S the preferable compound for sulfur isotope separation. Some existing distillation columns could be configured to provide $H_2^{34}S$ at varying enrichments and production rates.

Reverse isotope effects were found in distillation of several compounds. A rule for predicting the existence of the reverse effect has been formulated: the reverse isotope effect occurs for a central atom in poly-
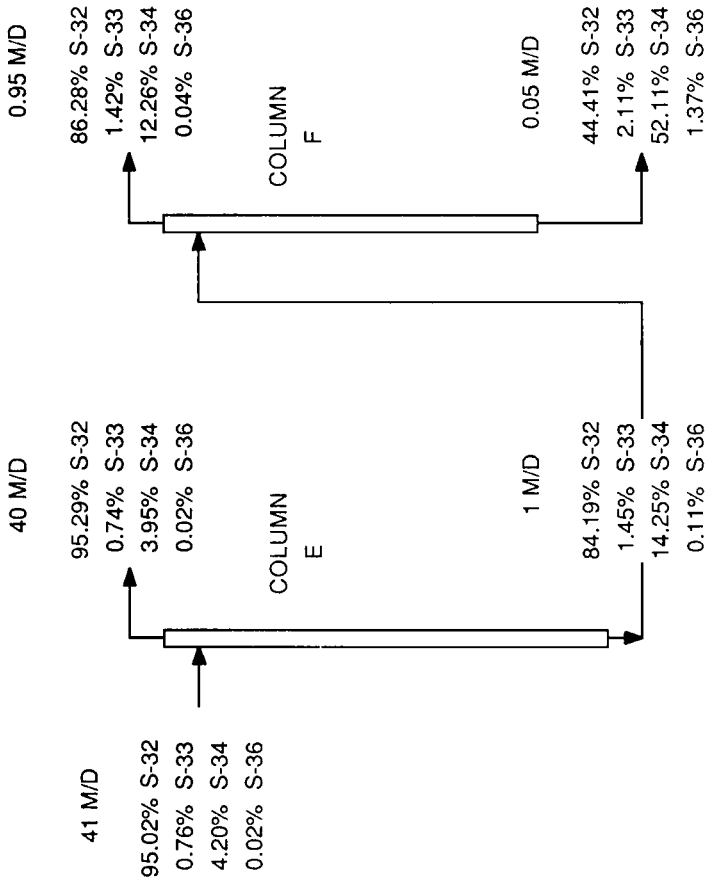
0.95 M/D

86.28% S-32
1.42% S-33
12.26% S-34
0.04% S-36

COLUMN
F

0.05 M/D

44.41% S-32
2.11% S-33
52.11% S-34
1.37% S-36

40 M/D

95.29% S-32
0.74% S-33
3.95% S-34
0.02% S-36

COLUMN
E

1 M/D

84.19% S-32
1.45% S-33
14.25% S-34
0.11% S-36

41 M/D

95.02% S-32
0.76% S-33
4.20% S-34
0.02% S-36

Figure 2. Small-Scale Separation of Sulfur Isotopes using Two-Column Network for H2S Distillation

atomic compounds when the central atom accounts for a minor fraction of the molecular weight. This rule holds true for the reverse effects found in the present work and in that of several other investigators.

ACKNOWLEDGEMENT

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