UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Selenium isotope analysis

By

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Open-File Report 81-992
1981

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Abstract

The isotope ratio of selenium-80 to selenium-74 was determined on an isotope ratio mass spectrometer. Samples of 2 to 4 mg of selenium were fluorinated with CoF_3 in a small disposable copper bomb. The product, SeF_6, was purified in a vacuum line by distillation. The $^{80}Se/^{74}Se$ ratio was determined on a double-collector mass spectrometer that was modified to collect either $^{82}Se-^{80}Se$ or $^{80}Se-^{74}Se$ ion pairs. The standard deviation of the difference between two individually fluorinated samples was about 1 per mil. Because essentially all the error was associated with the fluorination step, comparisons between a standard of SeF_6 and individually fluorinated samples can be expected to have a standard deviation of about 0.5 per mil.

Introduction

The need for selenium isotope analysis was recognized during studies of sulfur isotopes Wyoming uranium deposits (Warren, 1972). In that study, it would have been desirable to obtain samples for sulfur isotope analysis all the way across a uranium roll into the undisturbed pre-ore pyrite. Because mining operations are restricted to the ore zone, we were never able to obtain a complete sample suite. Selenium, however, is highly compressed spatially when compared to sulfur (Granger and others, 1961). Thus it is possible to obtain a complete sample suite for selenium in the zone normally mined. The problem then arose that selenium isotope analysis is not a routine

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procedure. The pur-pose of the work reported here (Webster, 1972) was to gain experience and to deetermine whether selenium isotope analysis is feasible.

The occurrence of selenium in sedimentary roll type uranium deposits (Granger, 1966; Har-shman, 1966) suggests that an isotope analysis of selenium would be interestingg and informative. Isotope abundances of sulfur has been used to identify thee source of the sulfur (Goldhaber and others, 1979), supply informtion about thee genetic geochemistry of the deposit (Warren, 1972), and determine the temperrature of hydrothermal deposits (Sakai, 1958). Selenium isotope abundances aelso have the potential to provide the same kind of valuable informatiorn.

The first recorded selenium isotope analysis was conducted by Aston (1931) who used the newly developed mass spectrograph to survey the relative abundances of the scable isotopes of many of the elements. For selenium isotope analysis, the element was plated on the inside of the glass ionization chamber of the mass spectrometer. White and Cameron (1948) redetermined the previously measured isotope abundances of 26 elements, including selenium, with a scanning mass spectrometer. For selenium they used both the element and selenium hexafluoride. The average difference in the abundances of the six selenium isotopes for the two forms of selenium was about ±1.7 percent. Hibbs and Herndon (1949) also included selenium in a survey of natural isotope abundances of 18 elements. Thode and his coworkers (Krouse and Thode, 1962; Rees and Thode, 1966), after studying sulfur isotopes for many years, turned briefly to selenium isotopes. They used an isotope ratio mass spectrometer equipped with a dual inlet system and a double collector. Only gases can be used with this type of instrument, and as a result, they used the gaseous compound SeF_6. Thode's group compared the relative abundance of ^{82}Se and ^{76}Se

from 15 different sources with the selenium in the Canyon Diablo meteorite. Ratios of the two isotope abundances were reported to about ±0.7 per mil and appear to represent an average of several determinations.

Although a selenium isotope analysis has been previously described, numerous difficulties were encountered in applying the procedure in this laboratory. The synthesis of selenium hexafluoride was the principal chemical problem that was encountered in developing a procedure for selenium isotope analysis. The only authors (Klemm and Henkel, 1932; Brauer, 1963; Stacey and others, 1965; Yost, 1939; Yost and Claussen, 1933) who had described SeF_6 syntheses in any detail were primarily interested in its chemical properties. These authors reported that direct combination of selenium and fluorine yielded Se_2F_2, SeF_4, SeF_6, and various minor impurities. Pure SeF_6 was obtained from this mixture by fractional distillations with yields that were variable but never exceeded 70 percent. Other authors (Bagnall, 1966; Emele'us and Woolf, 1950; Pitts and Jache, 1968) reported that selenium and fluorinating agents such as BrF_3, BrF_5, and ClF produced numerous impurities along with the SeF_6. Yields were not reported. White and Cameron (1948) as well as Hibbs and Herndon (1949) used CoF_3 as a fluorinating agent, but they did not describe the synthesis of SeF_6. Thode and coworkers synthesized SeF_6 by a method developed by R. H. Farquhar. Unfortunately, this synthesis does not appear to have been published.

Isotopically enriched selenium

The procedure for selenium isotope analysis was tested by using samples of enriched selenium that were prepared in our laboratory. Three samples were prepared and labled L, LL and H. The L and LL samples were enriched in the light isotopes while the H sample was enriched in the heavy isotopes. The
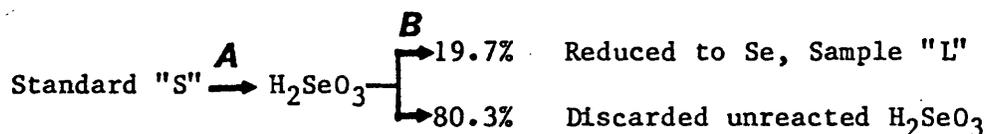
isotopically enriched samples were prepared by reducing selenous acid to elemental selenium with hydroxylamine in an acid solution according to the following reaction.

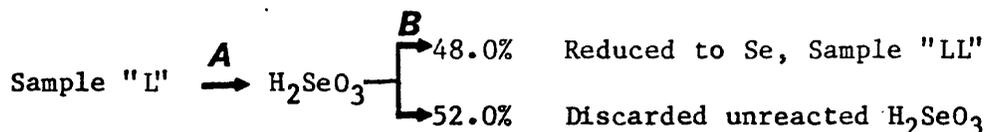$$H_2SeO_3 + 4H^+ + 4e^- = Se + 3H_2O$$
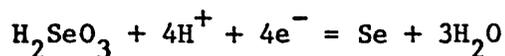
Because a limited amount of hydroxylamine was used, only part of the selenous acid was reduced. The light isotopes were slightly enriched in the elemental selenium that was produced. The excess selenous acid that was not reduced remained in solution. It contained a slight excess of the heavier isotopes. A flow chart for producing enriched samples is shown below.
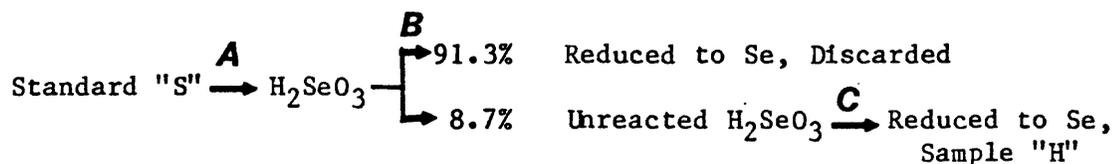
Flow Chart for Enriched Selenium

Sample L

Standard "S" $\xrightarrow{A}$ H₂SeO₃ $\begin{array}{l} \xrightarrow{B} 19.7\% \quad \text{Reduced to Se, Sample "L"} \\ \longrightarrow 80.3\% \quad \text{Discarded unreacted } H_2SeO_3 \end{array}$

Sample LL

Sample "L" $\xrightarrow{A}$ H₂SeO₃ $\begin{array}{l} \xrightarrow{B} 48.0\% \quad \text{Reduced to Se, Sample "LL"} \\ \longrightarrow 52.0\% \quad \text{Discarded unreacted } H_2SeO_3 \end{array}$

Sample H

Standard "S" $\xrightarrow{A}$ H₂SeO₃ $\begin{array}{l} \xrightarrow{B} 91.3\% \quad \text{Reduced to Se, Discarded} \\ \longrightarrow 8.7\% \quad \text{Unreacted } H_2SeO_3 \xrightarrow{C} \text{Reduced to Se,} \\ \text{Sample "H"} \end{array}$

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Step B of the flow chart represents selenous acid reductions in which isotope enrichment occurred. The H_2SeO_3 was dissolved in 100 ml of 4 M HCl. A limited amount of hydroxylamine hydrochloride was added and the solution digested for three days at $25^{\circ}C$. The elemental selenium was separated from the solution by centrifuging and decanting. The elemental Se was washed with distilled water and acetone. It was dried at $70^{\circ}C$ for 25 minutes and then weighed. The percent recovery was based on the weight of Se recovered and is shown in the flow chart.

The percent recovery is not shown on the flow chart for quantitative reactions of steps A and C. These include the last step for sample H and the first step for samples L, LL, and H. Step A of the three preparations consisted of a quantitative conversion of elemental selenium to selenous acid with an excess of concentrated nitric acid. The excess nitric acid was removed by ta$\langle$ ..g the H_2SeO_3 to dryness at $70^{\circ}C$. Step C in the production of sample "H" was a quantitative reduction of selenous acid. The H_2SeO_3 that remained in solution after discarding the light isotopes was reduced with sulfur dioxide. The solution was saturated with SO_2 and allowed to stand for four hours. The elemental selenium was recovered by centrifuging, washing and drying.

Generation of selenium hexafluoride

Elemental selenium was converted to selenium hexafluoride with cobalt(III) fluoride in a disposable copper bomb. Between 2 and 4 mg of Se and 400 mg CoF_3 were weighed and placed in the bomb (internal volume 3 ml) which was then purged with pre-purified nitrogen and sealed with a thin copper diaphragm. The copper bombs were heated for 20 hours at $300\pm10^{\circ}$ C under an

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inert atmosphere. The inert atmosphere prevented external oxidation of the thin copper diaphragm used in sealing the bomb. At the end of the heating period the copper bombs were rapidly cooled in a stream of compressed air. The bomb was placed on a vacuum line and the copper diaphragm was ruptured.

Figure 1 is a schematic of the major features of the vacuum line. The copper diaphragm in the bomb was ruptured by the extended thrust of a modified stainless steel valve. With all valves open, the SeF_6 and impurities were collected in a liquid-nitrogen-cooled trap. During collection the pressure in the vacuum system remained at approximately 100 microns pressure. Valve A was then closed and the system was evacuated to 15 microns. Valve C was then closed. After cooling the sample container with liquid nitrogen, the trap was warmed with a carbon tetrachloride slush that had been previously cooled with liquid nitrogen. The SeF_6 volatilized and was transferred while most of the impurities remained frozen. Transfer was allowed to continue for 4 minutes at which time the pressure returned to 15 microns and valves D and E were closed. After warming the sample container to 25° C the sample was ready to place on the mass spectrometer inlet system.

Two samples were simultaneously placed on the dual inlets of the mass spectrometer. For each sample the approximate yield of SeF_6 was measured by the volume and the total pressure in the inlet system. The relative purity of the two samples was measured by the $^{80}SeF_5^+$ ion current. The samples were occasionally scanned to identify the impurities which included SeF_4, SiF_4 and carbon fluorides. Impure samples and samples with unusually high or low yields were discarded.

COPPER 14/20 ⚡

STANDARD 45° BRASS FLARE UNION

.01" COPPER DIAPHRAM

COPPER TUBING

14/20 ⚡

A

TRAP

B

A

VACUUM GUAGE

C

24/40 ⚡

VACUUM PUMP

D

10/30 ⚡

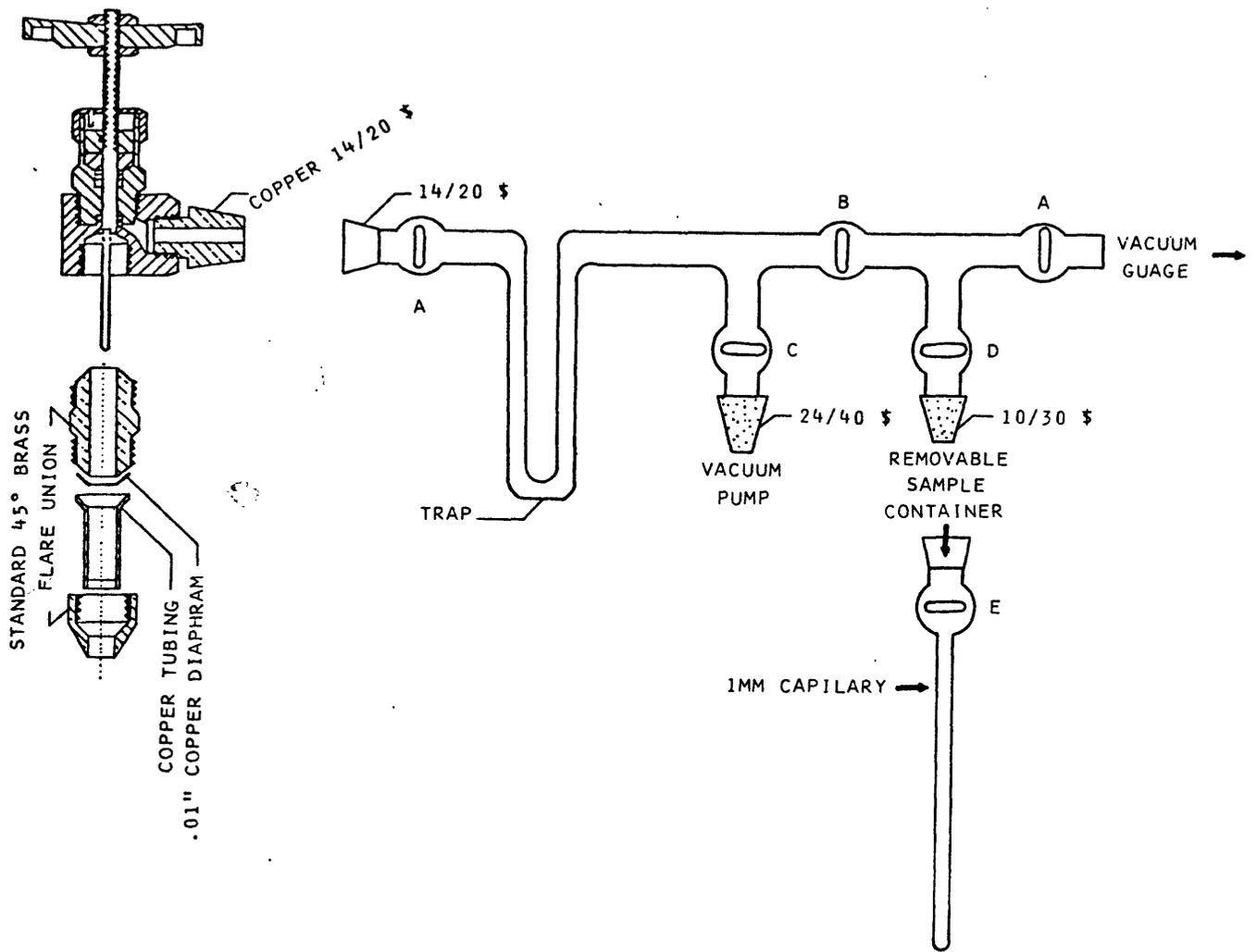REMOVABLE SAMPLE CONTAINER

E

1MM CAPILARY

Figure 1.--Vacuum line used in sample preparation.

Mass spectrometer procedures

The mass spectrometer was conditioned daily before sample analyses. The entire inlet system was routinely baked overnight at 150° C. After cooling the inlet system to ambient temperature, identical samples of commercial SeF_6 were placed on both sides of the inlet system. The inlet system was automatically cycled from one side to the other at 1-minute intervals until identical isotope ratios were obtained for both right- and left-hand sides. The conditioning procedure usually took about 2 hours. However, when the entire vacuum system was baked at 300° C for 2 days, the conditioning required about 6 hours. The mass spectrometer response remained constant after conditioning was completed.

Instrumentation

All isotope ratios were determined on a modified 180° deflection A.E.I. MS-20 isotope mass spectrometer. It was equipped with a permanent 4.5 kilogauss magnet and an automatic valving inlet system. The isotope mass spectrometer was fitted with a double collector system that consisted of three separate plates. The first plate was a masking plate held at ground potential. The second plate was the major isotope collector. The third plate was the minor isotope collector. The standard collector assembly was modified to accommodate the distribution and abundance of selenium isotopes. In determining an isotope ratio, the minor isotope was focused through the slit in the major plate onto the third plate. The major isotope then collected on the second plate. The remaining isotopes were removed by the masking plate.

The minor isotope was focused on the minor collector plate by adjusting the accelerating voltage. When ^{74}Se was focused on the minor plate, ^{80}Se collected on the major plate and ^{82}Se, ^{78}Se, ^{77}Se, and ^{76}Se were removed by the masking plate. When ^{82}Se was focused on the minor plate, ^{80}Se collected on the major plate and ^{78}Se, ^{77}Se, ^{76}Se, and ^{74}Se were removed by the masking plate. The major features of the collector system is shown in figure 2.

Results and discussion

Quantitative yields of SeF_6 were not obtained from elemental selenium and CoF_3. In a series of 30 consecutive fluorinations the yield of SeF_6 for the first 10 averaged 57 percent, the yield for the second 10 averaged 79 percent, and the last 10 averaged 90 percent. The major impurity was SeF_4. Although a quantitative method for making SeF_6 was preferable, a workable procedure for selenium isotope analysis was needed. Therefore, it was decided to test the entire procedure without further improvements in the fluorination of selenium.

Isotope fractionations generally occur whenever a chemical reaction is incomplete. The amount of fractionation is governed by the extent of the reaction. However, the isotope analysis used in this study was a comparative procedure, and where identical fractionations occurred in both samples, the potential error was automatically eliminated. The average for all the fluorinations was near 80 percent, and this yield was chosen as the most representative for the experiments recorded in this paper. Where the fluorination yield deviated from 80 percent, a correction was applied to the observed isotope content. The correction was based on the assumption that an intermediate form of selenium (possibly SeF_4) was quickly and quantitatively produced. This intermediate form of selenium was then slowly fluorinated to
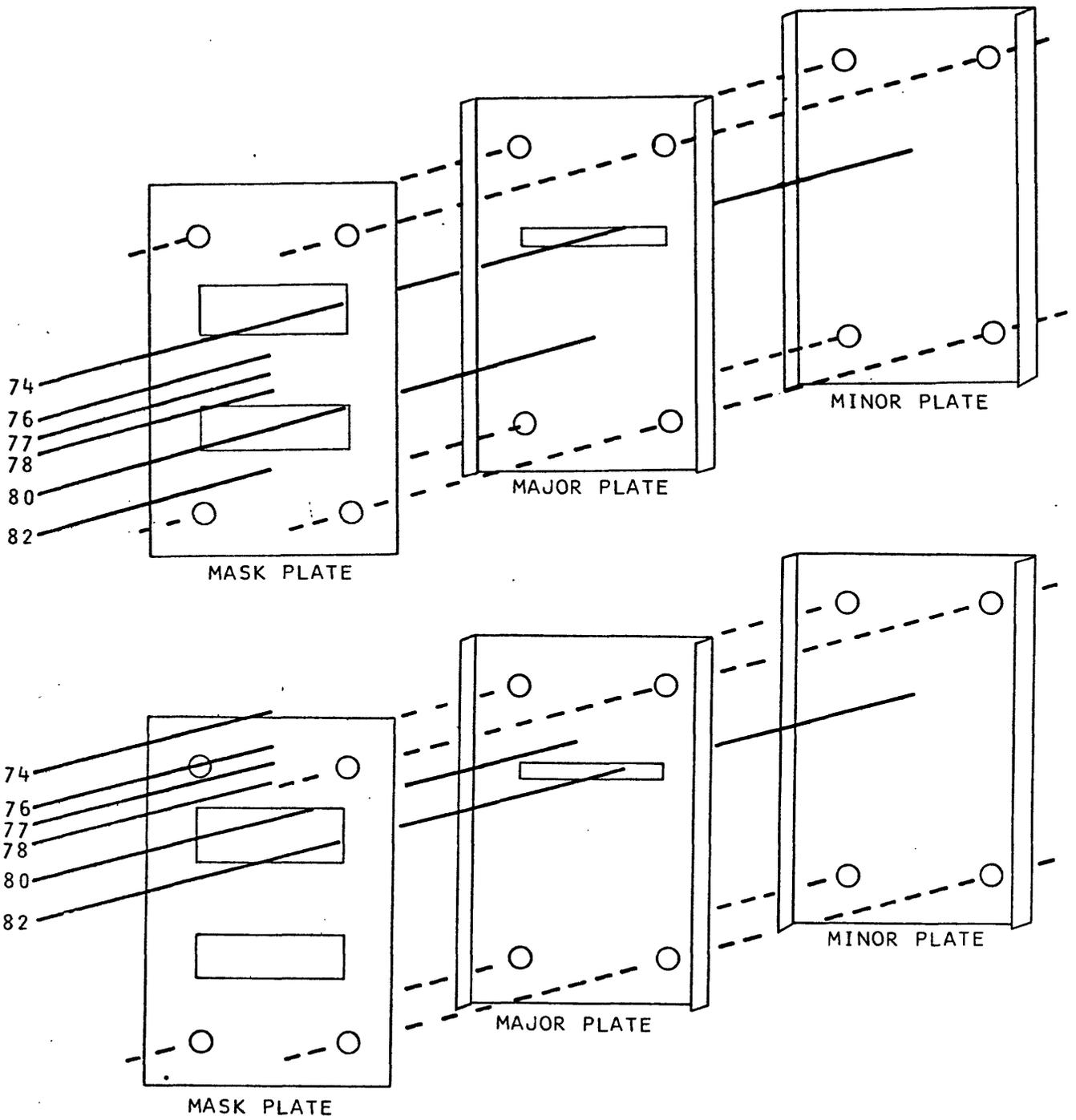
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Figure 2.--Collector system. The solid lines indicate ion beams. Dotted
lines show the position and method of connecting plates.

SeF_6. The light isotopes were assumed to have reacted slightly faster than the heavy isotopes. The correction was provided by equation 1 (Melander, 1960).

$$\frac{k_{74}}{k_{80}} = \frac{\ln(1 - rx)}{\ln(1 - x)} \qquad (1)$$

where k_{74} and k_{80} are the isotope rates of reaction

x is the extent of the reaction and

r is $(^{74}Se/^{80}Se)$ product/$(^{74}Se/^{80}Se)$ reactant

Equation (1) is applicable to reactions that are incomplete and where two isotopes react at different rates. The value of x represents the yield of SeF_6 in this particular application. The yield was obtained experimentally from the weight of Se used and the volume-pressure of SeF_6 obtained. The value of r is a measure of the fractionation that occurs in incomplete reactions. An algebric rearrangement of equation (1), replacing r with δ^{74}, results in equation (2).

$$\delta^{74}_x = 1 - x - (1-x)^{k_{74}/k_{80}} \qquad (2)$$

This equation compares δ^{74}_x for the product of an incomplete reaction with $\delta^{74} = 0$ for the starting material. The value of δ^{74} between two different reactions of the same starting material with different yields is shown in equation (3).

$$\delta^{74} = \delta_x^{74} - \delta_y^{74} \qquad (3)$$

where x and y represent two different fluorinations.

δ_x and δ_y are defined by equation (2).

Fluorinations of identical samples of Se with differing yields indicated that k_{74}/k_{80} should be about 1.02. The system of equations (2) and (3) was then used to prepare the following corrections that were applied to all samples. The corrections were as follows: Yield 70 percent, correction δ = +2.3 per mil; 75 percent, 1.2 per mil; 80 percent, 0.0 per mil; 85 percent, -1.3 per mil; and 90 percent, -2.9 per mil.

The differences between two randomly chosen samples were established by the mass spectrometer according to the following equation:

$$\delta^{74} = \frac{(^{80}Se/^{74}Se) \text{ right} - (^{80}Se/^{74}Se) \text{ left}}{(^{80}Se/^{74}Se) \text{ left}} \times 1000 \qquad (4)$$

The experimental data for isotope analyses are given in Table 1. The value of X in Table 1 indicates the position of the sample on the mass spectrometer. The values of X have the following meanings: X = -1 sample on the right inlet, X = +1 sample on the left inlet, X = 0 sample not used and +X - X=0 identical samples used on left and right sides. A least squares analysis of the data of Table 1 gave the isotope contents of samples H, L, and LL versus the laboratory standard S. The relationship of the constants and variables is shown by equation (5).

Table 1.-- δ^{74}Se and position parameters on the mass spectrometer.
[+1 denotes left hand side; -1 denotes right side; 0 denotes absence;
+1-1=0 denotes same sample used on left- and right-hand side]

δ^{74}Se per mil		X H	X S	X L	X LL
0.00	0	+1-1=0	0	0	
0.00	0	+1-1=0	0	0	
0.00	0	+1-1=0	0	0	
-9.40	0	0	+1	-1	
+30.75	-1	0	+1	0	
+24.46	-1	+1	0	0	
-0.39	0	0	+1-1=0	0	
-9.45	0	+1	-1	0	
-14.73	0	+1	0	-1	
+24.25	-1	+1	0	0	
0.00	0	0	0	+1-1=0	
-23.91	+1	-1	0	0	
-38.77	+1	0	0	-1	
+39.56	-1	0	0	+1	
+15.50	0	-1	0	+1	
0.00	+1-1=0	0	0	0	
+9.56	0	0	-1	+1	
-30.65	+1	0	-1	0	
+9.50	0	-1	+1	0	
0.00	0	0	+1-1=0	0	
+9.36	0	-1	+1	0	
-9.24	0	+1	-1	0	
0.21	0	+1-1=0	0	0	

$$\delta^{74} = \delta_H^{74} X_H + \delta_L^{74} X_L + \delta^{74} X_{LL} + \delta_S^{74} X_S \qquad (5)$$

where δ_H^{74}, δ_S^{74}, δ_L^{74} and δ_{LL}^{74} are constants that are equal to the isotope contents of samples H, S, L, and LL. By definition $\delta_S^{74} = 0.00$ and X_H, X_S, X_L, and X_{LL} are variables that represent the position of the sample on the mass spectrometer. δ^{74} is defined in equations (3) or (4).

The results of the least–squares analysis gave the following results:

$$\delta_H^{74} = 23.33 \pm 0.42 \qquad \delta_L^{74} = 8.22 \pm 0.19 \quad \text{and} \quad \delta_{LL}^{74} = 16.22 \pm 0.44.$$

The δ_H^{74}, δ_L^{74}, and δ_{LL}^{74} were converted to r of equation (1) by the manipulations shown below. For sample L that is represented by reaction 1 of the flow cha... the observed $\delta^{74} = 8.22$ parts per thousand converts to r = 1.00822. The starting material for sample LL was sample L and is represented by reaction 2 of the flow chart. The difference between their observed δ^{74} values gives the δ^{74} for the reaction which is 16.22 − 8.22 = 8.00 parts per thousand. This converts to r = 1.00800. The conversion for sample H, represented by reaction 3 of the flow chart is particularly complicated and needs a special word of explanation. The primary product was discarded in the preparation of H. The selenium saved had a $\delta_H^{74} = -23.33$. The yield for the discarded material was 0.911 and for the selenium saved 0.089. The conservation of mass requires that the sum of the isotope contents of the two products equal the starting material. In terms of δ^{74} this means $-23.33 \times 0.089 + \delta_{PP}^{74} \times .911 = 0$, where PP is the primary product. δ_{PP}^{74} for the primary product was calculated to be 2.22 parts per

thousand. This converts to an r value of 1.00222 for a reaction that is 91.1 percent complete. These conversions are summarized in the footnotes of Table 2.

Substitution of the values of r and x into equation (1) provided the three independent determinations of k_{74}/k_{80} that are shown in column 2 of Table 2. The value of k_{74}/k_{80} is the relative rate at which the two isotopes of selenium in H_2SeO_3 are reduced. Ideally k_{74}/k_{80} should be identical for all three determinations. The agreement of k_{74}/k_{80} provides a check on the linearity of the isotope analysis. If the analytical precedure responded abnormally it would be reflected in an abnormal k^{74}/k^{80} value. The fact that the three determinations of k^{74}/k^{80} are 1.0095, 1.0092 and 1.0113 suggest that the procedure was linear from $\delta^{74} = +39$ to $\delta^{74} = -39$ parts per thousand.

Conclusions

As shown in Table 2, the isotope contents of the four samples (H, S, L, and LL) were related by equation (1). The agreement between the values of k_{74}/k_{80} for H, L, and LL in Table 2 indicates that the responses of the mass spectrometer is essentially linear from $\delta^{74}Se = 0$ to $\delta^{74}Se = \pm40$ per mil. The method could not be tested for accuracy because established standards were not available. The standard deviation for two randomly chosen fluorinated samples was about 1 per mil. In practice, however, samples are compared to a standard of accepted isotope composition. If this standard was a large reservoir of SeF_6 of known isotope composition, the standard deviation would be 0.5 per mil.

Table 2.—Isotope fractionation in reduction of selenious acid

Sample	k_{74}/k_{80}	r of equation 1	x of equation 1	δ^{74} per mil
H	[4]1.0095	[1]1.00222	0.911	[2]-23.33
L	[4]1.0092	[2]1.00822	0.197	[2] +8.22
LL	[4]1.0113	[3]1.00800	0.480	[2]+16.22
Average	1.0100 ± 0.0009			

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[1]Calculated from isotope ratio of the selenious acid remaining in solution [23.33 (0.089/0.911) = 2.22 per mil].

[2]Observed value.

[3]Starting material was sample L. (16.22-8.22=8.00 per mil).

[4]Values for k_{74}/k_{80} in column 2 were calculated from the data of columns 3 and 4 with equation (1).

The major difficulty and source of error in the procedure was the fluorination of selenium. By-products or impurities fouled the viscous flow inlets and made it necessary to bake the inlet system frequently. Variable yields of SeF_6 introduced extraneous isotope fractionations. However, the overall procedure was reasonably reliable and convenient and did not consume an excessive amount of operator time.

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