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SULFUR ISOTOPE RELATIVE RATIOS
DETERMINED BY MASS SPECTROMETRY

O. H. Howard

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OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
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Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Oak Ridge, Tennessee

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ABSTRACT

The ratio of the sulfur isotope ratio, $^{34}\text{S}/(^{32}\text{S} + ^{33}\text{S})$, in a sample of sulfur hexafluoride to that in an isotopically different sample (relative ratio) is determined to ± 0.00003 (standard deviation) at relative ratios of 1.003-1.007 and near-natural isotopic abundances.

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SULFUR ISOTOPE RELATIVE RATIOS DETERMINED BY MASS SPECTROMETRY

INTRODUCTION

Isotope separation studies using sulfur hexafluoride (SF_6) necessitate measurement of ratios of sulfur isotope ratios (relative ratios). A mass spectrometer is used to obtain $R = A/B$, where R is the relative ratio and A and B are the isotope ratios, $^{34}\text{S}/(^{32}\text{S} + ^{33}\text{S})$, of samples A and B . Sample A is either of natural isotopic composition (95.1% ^{32}S , 0.7% ^{33}S , 4.2% ^{34}S) or slightly enriched in ^{34}S , while sample B is slightly enriched in ^{32}S . Typical relative ratios of interest in this work range between 1.003 and 1.007.

SUMMARY

Sulfur isotope relative ratios are determined in SF_6 with a 5-in. radius, Dempster-type, automatic, ratio mass spectrometer. Determinations are sequenced and relative ratios are calculated with a computer. Relative ratios in the range of 1.003-1.007 are determined to ± 0.00003 standard deviation, with four determinations, in one hour.

APPARATUS AND REAGENTS

MASS SPECTROMETER

A Dempster-type mass spectrometer with 5-in. radius of curvature, Nier ion source, dual collector, and ratiometer is used (Consolidated Electrodynamics Corporation, Model 21-320A, modified).^{*} The width of the ion-source exit slit is 0.008 in. The $^{32}\text{SF}_5^+$ and $^{33}\text{SF}_5^+$ ions (m/e 127 and 128) are collected on a plate (high-current collector). The $^{34}\text{SF}_5^+$ ions pass through a 0.020-in. slit in the high-current collector, and are collected in a Faraday cup (low-current collector). A beam positioner¹ keeps the $^{34}\text{SF}_5^+$ ion beam centered in the slit; approximately 95% of the beam passes through the slit.

The signals from the two collectors are amplified and fed to a ratiometer whose output is proportional to the isotope ratio. Input resistors of 5×10^{10} and 1×10^{11} ohms are used in the high- and low-current amplifiers, respectively.

The mass spectrometer operates automatically², after the two samples have been attached to the sample inlet manifold shown in figure 1. The samples are admitted alternately to the mass spectrometer according to the sequence of steps shown in figure 2.

^{*}Brand names mentioned in this report are intended to be descriptive, not limiting. Another brand of comparable characteristics could perform equally well.

Figure 1
SAMPLE INLET MANIFOLD

MANUAL	{	Attach Samples	
		Evacuate Connectors	
		Start Sequence	
			<u>MINUTES</u>
AUTOMATIC	{	Sample B (No data taken in this step)	1.0
		Pump Out	0.5
		Sample A ₁	2.0
		Pump Out	0.5
		Sample B ₁	2.0
		Pump Out	0.5
		Sample A ₂	2.0
		Pump Out	0.5
		Sample B ₂	2.0
		Pump Out	0.5
		Sample A ₃	2.0
		Standby	—
Total			13.5

$$\frac{\frac{A_1 + A_2 + A_3}{3}}{\frac{B_1 + B_2}{2}}$$

= R =

$$\frac{\left(\frac{34s}{32s + 33s}\right)_A}{\left(\frac{34s}{32s + 33s}\right)_B}$$

Figure 2
STEPS IN DETERMINATION OF RATIO A/B

COMPUTER

The steps of a determination are sequenced and the relative ratios are calculated and printed out with a computer, which the spectrometer shares with fourteen other mass spectrometers³.

SAMPLE CONTAINERS

Valved Monel sample cylinders of 150-cc volume have proved satisfactory.

Two control-sample cylinders, also of Monel, have a volume of 1500 cc to enable several replicate analyses to be made on the same sample pair over an extended time. The control-sample containers have a second valve in series with the cylinder valve to minimize the likelihood of atmospheric inleakage during the relatively long life of the control samples.

CONTROL SAMPLES

A pair of control samples is obtained in the same manner as regular samples, except that a volume ten times larger is collected at a pressure of 100 torr.

PROCEDURE

Two samples, A and B, consisting of equal volumes of SF_6 of 100 cc or more, at a pressure of 100 torr, are attached to the sample inlet manifold (figure 1) and the connectors are evacuated. The spectrometer leak is closed before the start of the first determination on a sample. (Having progressively opened during the analysis of the preceding sample, the leak is too large for the relatively high pressure of a fresh sample during the few seconds before the automatic leak control is actuated.)

Four determinations are scheduled on the computer and are run automatically, following the steps shown in figure 2. If a pressure difference between the two samples is indicated by a difference in the high-current signals for the same leak aperture, some of the higher pressure sample is exhausted to the manifold pumps until the signals are equal.

For each determination the computer averages the ratiometer outputs for each sample, divides the A average by the B average, as indicated in figure 2, and prints the result. The results from the four determinations are averaged to obtain the relative ratio.

The last sample analyzed during the day is left attached to the spectrometer, and one or more additional determinations is run on it at the start of the next day to ensure that the system is functioning correctly.

A pair of control samples is analyzed once a day, interspersed with regular samples.

SAMPLE PRESSURE

An initial SF_6 pressure of 100 torr in the 150-cc sample containers is sufficient sample (approximately 0.1 g of SF_6) for up to ten determinations.

The pressures in the two samples to be compared must be approximately equal. The effect of pressure differences is shown in table 1. A difference of 10% causes an error of 0.0001 in the measured relative ratio.

It is postulated that the effect is due to a difference in ion-beam distortion caused by a higher SF_6 pressure, though not discerned on the gage, in the mass spectrometer analyzer during the higher-pressure sample measurement. The automatic leak control is not actuated for the first few seconds of a sample entry. During that time the leak aperture is the same as for the previous sample. Consequently, an excess of the higher-pressure sample is admitted initially, resulting in a generally higher analyzer pressure and an isotopic ratio measurement that is biased high.

Table 1

EFFECT OF SAMPLE-PRESSURE DIFFERENCE

Initial Pressure, torr		Relative Ratio, Sample A/Sample B*
Sample A	Sample B	
100	100	1.0000
100	90	1.0001
100	80	1.0002

*For this test, samples A and B had the same isotopic composition.

The sample pressures are generally adjusted to within 10% of the specified 100 torr at time of sampling. Then, the pressures are equalized at the start of the analysis as described under PROCEDURE. With the sample pressures equal, the leak aperture is the same for both samples and, thus, no difference in isotopic fractionation across the leak, or in amount of sample admitted to the mass spectrometer, is expected.

SAMPLE PURITY

Air in the samples causes an error in the measured relative ratio, particularly if the samples contain different amounts of air, as shown in table 2. The error is approximately 0.0001 per 3% (absolute) air difference. The error is positive if there is more air in the A sample, negative if

more in the B sample, as would be expected from ion beam distortion by gaseous impurities⁴.

To avoid interference, the air is reduced to less than 0.1% at time of sampling by pumping after freezing the SF₆ in liquid nitrogen. The precision of the method improved after special care was taken to eliminate air from the samples.

Table 2
EFFECT OF AIR IN SAMPLE

Air in Sample, %		Relative Ratio, Sample A/Sample B
<u>Sample A₁</u>	<u>Sample B₁</u>	
0.1	0.1	1.0057
21	7	1.0061
<u>Sample A₂</u>	<u>Sample B₂</u>	
0.1	0.1	1.0061
0.4	35	1.0050

PRECISION AND ACCURACY

The relative ratios obtained from twenty analyses on a pair of control samples analyzed at the rate of no more than once a day, interspersed with regular samples, are presented in table 3. An analysis consists of four determinations. The mean of the twenty analyses is 1.00645 and the standard deviation is ± 0.00003 for a single analysis. (This precision is an order of magnitude better than was obtained before special care was taken to eliminate air from the samples.) The time required to complete one analysis is approximately one hour.

No attempt has been made to determine possible bias or memory since no SF₆ of known isotopic composition is on hand for use as a standard. Any bias or memory is expected to be small in view of the small relative ratios being measured and the inertness and volatility of SF₆.

An additional determination at the start of the day on the last sample analyzed the previous day, plus a daily analysis on a control sample, minimize the likelihood of undetected bias resulting from instrument malfunction.

Table 3

PRECISION OF RELATIVE RATIO MEASUREMENT

<u>Analysis*</u> <u>No.</u>	<u>Relative Ratio,**</u> <u>Sample A/Sample B</u>
1	1.00647
2	1.00648
3	1.00641
4	1.00650
5	1.00650
6	1.00648
7	1.00645
8	1.00647
9	1.00648
10	1.00642
11	1.00643
12	1.00646
13	1.00646
14	1.00642
15	1.00647
16	1.00646
17	1.00642
18	1.00642
19	1.00645
20	1.00644
Mean	1.00645
Standard Deviation	± 0.00003

*No more than one analysis was run on any one day.

**Each ratio is the average of four determinations.

RELIABILITY

The method has been in use for two years during which time nearly 7000 determinations have been run. No maintenance has been performed on the ion source, the spectrometer vacuum has not been interrupted and only minor electronic and manifold maintenance have been required.

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