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MASS SPECTROMETER WITH DUAL-APERTURE
COLLECTION OF URANIUM ISOTOPES

C. Sulfridge
A. Langdon

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OAK RIDGE GASEOUS DIFFUSION PLANT
P. O. Box P
Oak Ridge, Tennessee 37830

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MASS SPECTROMETER WITH DUAL-APERTURE
COLLECTION OF URANIUM ISOTOPES

C. Sulfridge and A. Langdon

Isotopic Analysis Department
Laboratory Division

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ABSTRACT

A mass spectrometer with a dual-aperture collector assembly is described which simultaneously resolves two uranium isotopes from all others and permits the measurement of the ratio of two specific isotopes. Precise relative measurements of uranium isotopes have been made to assist the Oak Ridge National Laboratory in the analysis of the performance of a molten salt reactor.

CONTENTS

	<u>Page</u>
INTRODUCTION AND SUMMARY	4
INSTRUMENTATION.	4
SAMPLE ANALYSIS PROCEDURE.	8
SPECTROMETER MEMORY.	9
PRECISION OF RATIOS.	10
CONCLUSIONS.	11
ACKNOWLEDGMENTS.	11
REFERENCES	11

MASS SPECTROMETER WITH DUAL-APERTURE COLLECTION OF URANIUM ISOTOPES

INTRODUCTION AND SUMMARY

The advantages of making a relative type mass spectrometer measurement, where two samples are rapidly alternated into the spectrometer and their isotopic ratios are observed, are well known. Such measurements were considered, by The Reactor Analysis Department*, for the analysis of samples taken from the fuel of a molten salt reactor during experiments to determine the relation of neutron capture for uranium-235 (^{235}U) and uranium-233 (^{233}U) fuels. In order to measure this ratio of cross sections in ^{235}U fuel, for example, a precise determination of the uranium-236 (^{236}U) resulting from neutron capture by ^{235}U during a period of reactor operation was required. Each of these two isotopes had to be compared to the uranium-238 (^{238}U) isotope which undergoes only a slight change for which a correction can be applied. Similarly with ^{233}U fuel, the precise determination of the ratio of uranium-234 (^{234}U) generated to the ^{233}U burned during a period of operation was required.

In conventional relative mass spectrometry, a single uranium isotope is resolved from all other isotopes and the ion current generated by that resolved isotope is measured concurrently with the sum of the currents from all other isotopes. For the cross-sectional determinations, however, it was necessary to resolve simultaneously two isotopes from all others in order to measure the ratio of two specific isotopes.

INSTRUMENTATION

In designing the collection system, consideration was given to using as much of the existing equipment as possible on a 12-in.-radius, 90° sector type uranium hexafluoride (UF_6) instrument in our laboratory. This instrument is equipped with a simplified molecular beam ion source¹ operating at 5000 volts.

The final version of the collection system is shown in figure 1. The movable aperture plate is coupled through a bellows assembly to the spindle of a micrometer to permit accurate positioning of the movable aperture, S1, in relation to the fixed aperture, S2.

The Faraday cup beneath the movable aperture plate is attached to the aperture plate to insure that ions strike the same *conditioned* area in the cup regardless of the aperture position. This was found necessary due to collector surface *spotting* or contamination from ion bombardment.

*Reactor Division, Oak Ridge National Laboratory.

SECTION A-A
Figure 1
COLLECTION SYSTEM

The accuracy requirements for the determinations were such that an abundance sensitivity² of 100,000 or better at m/e 333 had to be maintained. Ion beam width measurements were made which showed that the required abundance sensitivity could be obtained by using a source defining aperture width of 0.005 in. and collector apertures 0.012 in. wide. This allowed greater than 99% beam transmission through the collector apertures. Analyzer tube pressures were kept below 10^{-8} torr in order to meet these requirements.

The collector entrance apertures, 0.008 in. wide, were cut in the nichrome plates by an electrical discharge process. The entrance edges were bevelled 20° . The electrical discharge process was used to prevent deformation of the aperture which would result from other machining methods. Final finishing of the apertures was done manually with the aid of a measuring microscope. The two apertures finally used were finished to $0.0120 \text{ in.} \pm 0.0002 \text{ in.}$ along their entire 0.5-in. length. Several apertures were fabricated before obtaining the desired dimensions. Since the separation between centers of UF_5^+ ion beams one mass unit apart is only 0.036 in., the overlap region of the two aperture plates was limited to about 0.045 in. It was found that ions falling through a gap between the aperture plates, and/or secondaries generated by the ions, were detected on the Faraday cups positioned below each aperture. This limited the mass range that could be covered by the movable aperture to two mass units (0.072 in.) while still maintaining plate overlap. The ^{235}U and ^{236}U could be compared to the ^{238}U without collector removal for modification but when ^{233}U and ^{234}U were compared to ^{238}U , a filler approximately 0.072 in. wide was required in the overlap region as shown by the shaded area in figure 1.

A partition was installed between the Faraday cups in a manner similar to that used by Hayatsu and Farquhar³ in their dual-aperture system for strontium isotope measurements. A magnet positioned around the outside of the collector housing provided suppression of secondary particles emitted from the bombarded surfaces. The field strength was approximately 300 gauss at the center of the collector apertures. An ion beam was swept slowly across either of the apertures and the zero ion current condition was monitored on the signal amplifier for the other aperture. The suppressor magnet was then positioned to reduce amplifier zero disturbance to an insignificant level at the amplifier current gain being used for a particular isotope. Best results were obtained by operating the aperture plates at a positive potential of up to 30 volts.

The ion currents were amplified by two identical electrometers with feedback resistors ranging from 2×10^{10} to 2×10^{11} ohms, depending upon the concentrations of the two isotopes being compared. The outputs of the two electrometers were compared on a ratio recording system with a recorder slidewire sensitivity of 9 mv full scale. The recorder balance point was recorded on chart paper 10 in. wide, with 110 divisions.

A small-volume sample inlet system, arranged as in figure 2, was designed to allow the maximum amount of data to be obtained from the small samples received for analysis. The inlet system volume was 4.2 cc which allowed approximately 36 determinations to be made per gram of UF_6 .

Figure 2
SAMPLE INLET MANIFOLD

SAMPLE ANALYSIS PROCEDURE

Generally, UF_6 samples at three isotopic concentrations were received for analysis; one sample from starting fuel, one sample at an intermediate point of reactor operation, and one sample at the end of the period of operation. These are referred to as samples, A, B, and C, respectively. A ratio-of-ratios type determination, R, was made for each isotope, such as

$$R(^i\text{U}) = \frac{(^i\text{U}/^{238}\text{U})_C}{(^i\text{U}/^{238}\text{U})_A}, \quad (1)$$

where ^iU = the individual isotope of interest.

A single determination consisted of alternately valving each of two samples into the spectrometer three times in a closely timed sequence lasting 15 minutes. No data were taken on the first introduction of sample to minimize the drift effect. A 40-second pump-out period was allowed between introductions of samples, and data were taken during the last half of the 2-minute period in which the sample was in the spectrometer.

The $^{238}\text{UF}_5^+$ beam was carefully centered in the fixed aperture by adjusting the accelerating voltage. The movable aperture was then positioned with the micrometer adjusting mechanism to center the other isotope of interest in the movable aperture. A null point was detectable on the ratio recorder when the signals from both ion beams *peaked* simultaneously as the beams were swept across the apertures. All ratio measurements were made at the null point.

Samples from two sealed capsules of material which had been irradiated in the core of the reactor during the ^{233}U fuel operation were also analyzed. This material was especially blended isotopically to enhance the accuracy of subsequent calculations of capture-to-fission ratios. Table 1 lists the average isotopic compositions of all four types of material received for analysis.

Table 1

AVERAGE COMPOSITION OF SAMPLES
Expressed in Mol Percent

Sample Type	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
^{235}U Fuel	< 0.01	0.36	33.50	0.40	65.74
^{233}U Fuel	84.25	7.18	2.51	0.09	5.97
Capsule S	0.79	2.64	5.50	0.40	90.67
Capsule L	9.29	0.48	0.86	0.05	89.32

SPECTROMETER MEMORY

A large degree of cancellation of errors in the calculations of the capture-to-absorption ratios could be expected only if the spectrometer memory effect was constant during the time ^{235}U and ^{236}U determinations were being made and during the time ^{233}U and ^{234}U determinations were being made.

To check for differences in the spectrometer memory effect between isotopes and/or the two aperture positions, standards of known composition were prepared from high purity uranium oxide by a gravimetric dilution technique⁴. Using these standards, a memory factor, M , was obtained by making a relative determination, R_0 , of the ratio of the isotope of interest to the ^{238}U in the standards and comparing it to the true ratio, R , in the following relationship:

$$M = \frac{R - 1}{R_0 - 1} \quad (2)$$

The ^{235}U and ^{236}U memory factors were measured independently and were consistent within 0.0003, and the ^{233}U and ^{234}U were consistent within 0.004.

The use of M which is measured at a particular R_0 value can obviously lead to significant errors when used to correct observed ratios differing by large amounts from R_0 . A method used by G. L. Ragan* to relate an M factor to a particular R value involves the approximation,

$$M \approx 1 + Q(R_0 + 1) \quad (3)$$

where $Q = \frac{V}{(1 - V)^2}$

and V = the fraction of the gas pressure in the ionization chamber contributed by remnants of the previous sample. The parameter Q is obtained from measurements made with the memory standards, and the memory factor applicable to any measured ratio can be obtained from equation 3.

The following procedures were observed to minimize variations in the memory effect during the analysis of samples:

1. The ion source and sample inlet system were cleaned prior to running each type of sample material.
2. Sample flow into the ion source was maintained at the same rate for all samples by monitoring and adjusting flow according to isotopic concentrations of the samples being analyzed.

*Reactor Analysis Department, Reactor Division, Oak Ridge National Laboratory.

3. Determinations were made with minimum time lapse between determinations on the isotopes primarily involved in fission and capture.

PRECISION OF RATIOS

Table 2 lists the range of sample ratios for each type of sample and the standard deviation of a single determination. Enough duplicate analyses were made with the sample material available to reduce the standard deviation of the mean to ± 0.0001 on all isotopes except the ^{236}U in the ^{235}U fuel and the capsule L samples. The lower precision for the ^{236}U isotope was attributed to the low ^{236}U concentrations and to the close proximity of the two apertures when comparing the ^{236}U to the ^{238}U .

Table 2

RATIO RANGE AND STANDARD DEVIATION OF SAMPLE TYPES

Sample Type	Ratio(^iU)	Ratio Range	Standard Deviation of a Single Determination
^{235}U Fuel	^{234}U	0.9944 - 0.9974	± 0.0003
	^{235}U	0.9850 - 0.9920	± 0.0002
	^{236}U	1.1708 - 1.3117	± 0.0021
^{233}U Fuel	^{233}U	0.9712 - 0.9878	± 0.0003
	^{234}U	1.0044 - 1.0190	± 0.0003
	^{235}U	0.9957 - 1.0027	± 0.0003
	^{236}U	1.0362 - 1.1038	± 0.0003
Capsule S	^{233}U	0.9057 - 0.9205	± 0.0002
	^{234}U	0.9810 - 0.9824	± 0.0002
	^{235}U	0.9345 - 0.9392	± 0.0002
	^{236}U	1.2312 - 1.2510	± 0.0002
Capsule L	^{233}U	0.9157 - 0.9296	± 0.0002
	^{234}U	1.1633 - 1.1950	± 0.0002
	^{235}U	0.9387 - 0.9495	± 0.0002
	^{236}U	1.2358 - 1.2840	± 0.0006

The initial evaluation of the analyses as they pertain to capture-to-fission measurements and to reactor power level measurements is reported by G. L. Ragan^{5,6,7}.

CONCLUSIONS

It has been shown that rather precise relative isotopic ratio measurements involving only two isotopes of a species can be made. It may be possible to apply a similar system to studies of the distribution of all isotopes in an isotope separation system, supplementing separation tests which have previously defined only the change in one isotope relative to the sum of all the others.

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REFERENCES

1. Smith, L. A. and Langdon, Aubrey, "Performance of Simplified Molecular Beam Ion Sources for Uranium Isotope Mass Spectrometers," *Recent Developments in Mass Spectroscopy*, United Park Press, Baltimore, p.450 (1970).
2. Roboz, John, "Introduction to Mass Spectrometry," *Instrumentation and Techniques*, John Wiley and Sons, New York, 1968.
3. Hayatsu, A. and Farquhar, R. M., "A Mass Spectrometric Dual Collector for Precise Strontium Isotope Abundance Ratio Measurements," *J. Sci. Inst.*, 44, p.141-145 (1967).
4. Petit, G. S. and Kienberger, C. A., "Preparation of Stoichiometric U_3O_8 ," *Analytica Chimica ACTA*, 25, No. 6, p.579-586 (1961).
5. Molten Salt Reactor Program Semiannual Progress Report for Period Ending August 31, 1969, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, ORNL-4449, p.70-72.
6. Molten Salt Reactor Program Semiannual Progress Report for Period Ending February 28, 1970, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, ORNL-4548, p.65-66.
7. Molten Salt Reactor Program Semiannual Progress Report for Period Ending August 31, 1970, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, ORNL-4622, p.31-34.