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BURNUP DETERMINATION OF NUCLEAR FUELS
PROJECT REPORT
FOR THE QUARTER OCTOBER 1-DECEMBER 31, 1965

Edited By

William J. Maeck, Robert M. Abernathey, and James E. Rein

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
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PROJECT REPORT
FOR THE QUARTER OCTOBER 1 - DECEMBER 31, 1965

Edited by

William J. Maeck, Robert M. Abernathey, and James E. Rein

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SUMMARY

In this continuing program to develop methods for the accurate determination of the burnup of nuclear fuels, the main emphasis this quarter was the development of an isotope dilution, mass spectrometric analysis method for ruthenium and the determination of the absolute thermal fission yields of stable and long lived isotopes of ruthenium for U-233 and U-235. The average values, determined on two each of dissolved, standard U-233 and U-235 burnup capsules, are:

<u>Isotope</u>	<u>Fission Yield, %</u>	
	<u>U-233</u>	<u>U-235</u>
Ru-101	3.19±0.06	5.03±0.06
Ru-102	2.40±0.04	4.18±0.05
Ru-104	0.998±0.019	1.81±0.02
Ru-106	0.255±0.006	0.385±0.007

These values are tentative. As additional capsules are analyzed, refined data will be reported.

Previous project reports are:

<u>Period</u>	<u>Report</u>
Annual - 1962	TID-17385
Annual - 1963	IDO-14649
Annual - 1964	IDO-14656
Quarter, January-March, 1965	IDO-14660
Quarter, April-June, 1965	IDO-14663
Quarter, July-September, 1965	IDO-14667

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BURNUP DETERMINATION OF NUCLEAR FUELS

INTRODUCTION

The objective of this project is the development of methods for the accurate determination of burnup of nuclear fuels. The emphasis is on power reactor fuels having long residence time and high burnup rather than on short term, experimental irradiations. The principal measurement technique under study is chemical analysis for fission products. The use of long lived, radiochemically determined fission products is not applicable because the errors of the in-pile decay corrections are magnified with long term irradiations, the nuclear constants are not known with sufficient accuracy, and the few available nuclides, Cs-137 and Sr-90, are volatile. Therefore the use of stable fission product nuclides, determined by isotope dilution mass spectrometry, has been selected. The degree of reliability of a burnup determination based on stable fission product analyses depends on three factors; the accuracy of the values used for the fission yields, the linearity between the number of fissions and the number of atoms of the fission product present at the end of the irradiation, and the reliability of the analysis methods.

Specific goals of this project are the accurate measurement of the fission yields of selected nuclides for various fissioning isotopes, the selection of fission product nuclides for use as fission monitors for various fuel types, and the development of separation and mass analysis methods for these nuclides. Presently, experiments are in progress to measure the absolute thermal fission yields for U-233, U-235, Pu-239, and Pu-241 to a high degree of accuracy. Later in the program, epithermal and fast fission yields will be measured.

Initial values for many U-235 and U-233 thermal fission yields have been reported in previous quarterly reports IDO-14660, IDO-14663, and IDO-14667.

ABSOLUTE U-233 AND U-235 THERMAL FISSION YIELDS OF RUTHENIUM ISOTOPES

A major goal of the burnup project is the accurate determination of the thermal fission yields of long lived and stable fission products. A series of capsules containing weighed amounts of the oxides of highly enriched U-233, U-235, Pu-239, and Pu-241 was prepared and irradiated in the MTR(1). During this quarter, the absolute thermal fission yields of Ru-101, -102, -104, and -106 were determined for two U-233 and two U-235 capsules by carrier-free chemical separations and isotope dilution mass spectrometry. The Ru-106 yield also was determined by radiometric counting.

Irradiation History of U-233 and U-235 Capsules

The U-233 and U-235 standard burnup capsules, which contained weighed amounts of U_3O_8 (highly enriched in the respective isotopes) blended with high purity aluminum powder and weld-sealed in aluminum tubes, were irradiated in the MTR at a position where the unperturbed flux was 6×10^{13} n/cm²/sec and the cadmium ratio for cobalt was 15. The irradiation histories of these capsules are given in Table 1.

Dissolution of Irradiated Capsules, R. E. Foster, S. F. Marsh

The capsules were dissolved in special apparatus located in a 4-in. lead-shielded facility. The dissolution apparatus and downstream apparatus for the collection of krypton and xenon have been described(1,2). The dissolver flask and reflux condenser were fabricated from high purity quartz. An acid mixture of 6M HCl-1.6M HNO₃, prepared from quartz distilled reagents, was used for the dissolutions(1).

The dissolutions proceeded smoothly and were complete in 3.5 hr. The fission gases, krypton and xenon, appeared 1.5 hr after the start of the dissolutions and their evolutions continued for 2 hr. The final solutions (about 200 ml) were water clear and contained no residue.

After cooling, each dissolver solution was quantitatively transferred to a 250-ml class "A" volumetric flask with the aid of 6M HCl-1.6M HNO₃ rinses. The solution was cooled and diluted to volume with quartz distilled water. A Teflon-coated stirring bar was introduced and the contents were stirred for 1 hr.

A survey of the condenser and components of the gas collection train showed no significant amounts of ruthenium, indicative that no ruthenium was volatilized during any of the four dissolutions. After the dissolver solution was transferred to the volumetric flask, the dissolver flask was surveyed for ruthenium activity. None was found, indicative that all the ruthenium had dissolved with no plating on the flask surfaces.

Table I. COMPOSITION AND IRRADIATION HISTORY OF STANDARD BURNUP CAPSULES

<u>Capsule</u>	<u>Fissionable Isotope</u>	<u>Enrichment, wt %</u>	<u>mg U₃O₈ in Capsule</u>	<u>MTR Cycles</u>	<u>% Burnup^a</u>	<u>Reactor Discharge Date</u>
6-4-2	U-233	99.908	152.4±0.2	3	11.44±0.18	June 8, 1964
6-4-3	U-233	99.908	126.0±0.2	3	12.39±0.23	June 8, 1964
6-4-1	U-235	99.1633	115.2±0.1	3	11.50±0.13	June 8, 1964
6-6-2	U-235	99.1633	81.94±0.10	3	12.54±0.18	Sept. 15, 1964

^a Defined as atoms of major isotope fissioned per 100 initial atoms of major isotope.

Chemical Separation of Ruthenium, R. E. Foster

An earlier method(2) for the carrier-free separation of stable fission product ruthenium was modified to improve the subsequent analysis in a surface ionization mass spectrometer. The RuO_4 distillate is now collected in 6M HCl rather than in sulfurous acid. The thermal emission of ruthenium is steady when the ruthenium is evaporated on the filaments as the chloride. Information pertaining to mass spectrometry studies is given in the following section, "Mass Spectrometric Analysis."

The ruthenium-6M HCl solution is evaporated to a volume of 0.1 ml, before transfer to the mass laboratory, with no detectable loss of ruthenium. Also, no loss of ruthenium was detected (based on counting of Ru-106) upon evaporation of the ruthenium solution to dryness on the mass spectrometer filament.

The procedure for the carrier-free separation of ruthenium is detailed in the Appendix.

Mass Spectrometric Analysis of Ruthenium, R. M. Abernathey, R. E. McAtee, A. H. Toepfer, G. D. Workman

Various procedures have been used for the mass spectrometric determination of ruthenium. White, Collins, and Rourke(3) loaded the sample as a suspension of ruthenium metal in amyl acetate on a rhenium filament for single filament, surface ionization excitation. Friedman and Irsa(4) used gas phase, electron bombardment of ruthenocene, a metallo-organic compound. Both Baldock(5) and Sites(6) load a sample of ruthenium metal powder in a water slurry on a heavy iridium filament for surface ionization excitation. We have found that evaporation of an aqueous slurry of ruthenium sulfide on a rhenium filament is satisfactory for a single filament, surface ionization source.

None of the above procedures is readily useful for a highly radioactive (fission product) sample in which the radiation level restricts the amount of ruthenium to a maximum of 5 μg . Of various soluble salts of ruthenium investigated, the chloride gave the most intense, stable ion beam for a single rhenium filament, surface ionization source.

The mass spectrometer used for this work was a Nuclide Associates, TDD-1, tandem, 12-in., -90° instrument with three ion detection systems. These systems are a Faraday Cage, electrometer, strip chart; a 20-stage electron multiplier, electrometer, strip chart; and the multiplier with a pulse counter substituted for the electrometer and strip chart. The Faraday Cage system was preferred because it was linear in its response and had no mass discrimination, verified by the analysis of NBS-certified uranium isotopic standards U-500 and U-750.

Two different lots of natural ruthenium chloride were repeatedly mass analyzed for isotopic distribution with the Faraday Cage system. The results, compared to data from the Nuclear Data Sheets(7) are summarized

in Table II. A substantial disagreement is noted for which no explanation is offered at this time. Additional work is planned on natural ruthenium compounds from a wide variety of sources.

The 20-stage electron multiplier, electrometer, strip chart system had to be used for some of the ruthenium fission product samples in which the total amount of ruthenium was less than $\sim 3 \mu\text{g}$. The mass discrimination of this system was established by comparing results of several natural ruthenium samples to results on the same samples obtained with the nondiscrimination Faraday Cage system.

The procedure for the chemical separation and mass analysis of fission product ruthenium is detailed in the Appendix. Typical data showing the degree of precision obtained for the isotope dilution analysis of three 1-ml aliquots of a dissolved, irradiated U-235 sample are summarized in Table III.

Ruthenium Fission Yields of U-233, R. E. Foster, F. L. Lisman, W. J. Maeck, F. W. Sprakles

The absolute thermal fission yields of ruthenium were determined on each of the two, dissolved, U-233, standard burnup capsules (6-4-2 and 6-4-3). Four 1000- μl aliquots from each dissolver solution were spiked with known amounts of Ru-96 (see Appendix for details of preparation and calibration) and carried through the separation and analysis procedure, also described in the Appendix. The analysis results and calculated fission yields for ruthenium are summarized in Tables IV and V respectively.

The accuracy of the absolute fission yield measurements directly depends on the accuracy of the determined number of fissions in the irradiated U-233 capsules. For this reason, a large effort was placed on the pre- and postirradiation analyses for the atoms of the various uranium isotopes from which the number of fissions was calculated.

To accurately compute the number of U-233 fissions, the following relationship was used.

$$F_3 = U^0 - U$$

where

F_3 = number of U-233 fissions

U^0 = total preirradiated atoms of uranium

and

U = total postirradiated atoms of uranium.

Table II. COMPARISON OF ISOTOPIC DISTRIBUTION
OF NATURAL RUTHENIUM

Isotope	Value, atom percent	
	This Work ^a	NDS
96	5.38±0.02	5.51
98	1.82±0.01	1.87
99	12.58±0.03	12.72
100	12.46±0.02	12.62
101	17.02±0.02	17.07
102	31.76±0.01	31.61
104	18.98±0.04	18.58

^a Error is expressed as standard deviation of the average.

Table III. PRECISION OF OVERALL PROCEDURE

Isotope	Result, Atoms/ml $\times 10^{-15}$					
	Aliquot			Avg	Std Dev ^a	% Std Dev ^a
	1	2	3			
101	5.69	5.72	5.73	5.71 ₃	0.02 ₁	0.37
102	4.73	4.75	4.75	4.74 ₃	0.01 ₂	0.24
104	2.05	2.07	2.05	2.05 ₇	0.01 ₂	0.56
106	0.14	0.14	0.14	0.14	---	---

^a Standard deviation of an individual result.

Table IV. U-233 THERMAL FISSION YIELDS OF LONG-LIVED AND STABLE
RUTHENIUM ISOTOPES FROM CAPSULE 6-4-2

Number of Fissions = $(3.7863 \pm 0.0588) \times 10^{19}$

	Ru-101	Ru-102	Ru-104	Ru-106
Determined number of atoms	1.2306×10^{18}	9.2500×10^{17}	3.8563×10^{17}	3.5000×10^{16}
Std dev _{avg} (n=4)	0.0025×10^{18}	0.0204×10^{17}	0.0119×10^{17}	0.0100×10^{16}
Atoms after correction for neutron capture and decay	1.2307×10^{18}	9.2500×10^{17}	3.8555×10^{17}	9.7815×10^{16} ^a
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.20	0.22	0.30	1.1
Percent fission yield	3.25	2.44	1.02	0.258
Std dev	0.05	0.04	0.02	0.005
Std dev, %	1.54	1.64	1.96	1.94

^a Includes in-pile and out-pile decay corrections.

Table V. U-233 THERMAL FISSION YIELDS OF LONG-LIVED AND STABLE
RUTHENIUM ISOTOPES FROM CAPSULE 6-4-3

$$\text{Number of Fissions} = (3.3904 \pm 0.0616) \times 10^{19}$$

	Ru-101	Ru-102	Ru-104	Ru-106
Determined number of atoms	1.0618×10^{18}	7.9650×10^{17}	3.3094×10^{17}	3.0187×10^{16}
Std dev _{avg} (n=4)	0.0012×10^{18}	0.0098×10^{17}	0.0135×10^{17}	0.0213×10^{16}
Atoms after correction for neutron capture and decay	1.0620×10^{18}	7.9650×10^{17}	3.3086×10^{17}	$8.5325 \times 10^{16}^a$
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.11	0.12	0.41	1.22
Percent fission yield	3.13	2.35	0.976	0.252
Std dev	0.06	0.04	0.018	0.006
Std dev, %	1.92	1.70	1.84	2.38

^a Includes in-pile and out-pile decay corrections.

To effectively use this relationship, one must account for those atoms of U-235 and U-238 lost by fission and capture. This was done with data obtained from a computer program which simulated the history of the irradiation. For these irradiated U-233 samples, the loss of U-235 and U-238 during the irradiation amounted to less than 0.002% of the total uranium measured at the end of the irradiation. The determined number of fissions for the irradiated U-233 capsules are $(3.7863 \pm 0.0588) \times 10^{19}$ for capsule 6-4-2 and $(3.3904 \pm 0.0616) \times 10^{17}$ for capsule 6-4-3 where the propagated standard deviation errors for the computed number of fissions correspond to a relative error of 1.55% and 1.82% respectively. Details of these calculations are given in references 8 and 9.

The accurate determination of absolute fission yields, for samples which have undergone long term irradiations, requires corrections for the buildup and burnout of the various fission products due to neutron capture. Also required are corrections for the decay of radioactive nuclides.

The method of correcting for buildup and burnout of the fission products is based on a series of computer programs which simulate the irradiation history of the samples. These programs yield the number of individual fission product atoms formed during the irradiation and their manner of formation. In addition, the programs consider the decay of any radioactive nuclides for the time period between termination of the irradiation and sample analysis. Details of these programs have been previously reported(9).

In the case of ruthenium, corrections for the buildup and burnout of the stable isotopes are small (< 1%), because of the small capture cross sections. A schematic diagram of the buildup and burnout of ruthenium is given in Figure 1.

Ruthenium Fission Yields of U-235, R. E. Foster, F. L. Lisman, W. J. Maeck, F. W. Spraktes

The absolute thermal fission yields of ruthenium were determined on each of the two, dissolved, U-235, standard burnup capsules (6-4-1 and 6-6-2). Three 1000- μ l aliquots of the dissolver solution from capsule 6-4-1 and four 1000- μ l aliquots of the dissolver solution from capsule 6-6-2 were spiked with known amounts of Ru-96 and carried through the separation and analysis procedure described in the Appendix. The analysis results and calculated fission yields for the ruthenium isotopes are summarized in Tables VI and VII respectively. The number of U-235 fissions was calculated from the following relationship:

$$F_5 = U^0 - U$$

in which: F_5 = number of U-235 fissions

U^0 = total preirradiated atoms of uranium

and U = total postirradiation atoms of uranium

Figure 1. COMPUTER PROGRAM SCHEMATIC FOR BUILDUP AND BURNOUT OF FISSION PRODUCT RUTHENIUM

Table VI. U-235 THERMAL FISSION YIELDS OF LONG-LIVED AND STABLE
RUTHENIUM ISOTOPES FROM CAPSULE 6-4-1

$$\text{Number of Fissions} = (2.8389 \pm 0.0321) \times 10^{19}$$

	Ru-101	Ru-102	Ru-104	Ru-106
Determined number of atoms	1.4283×10^{18}	1.1858×10^{18}	5.1417×10^{17}	3.5333×10^{16}
Std dev _{avg} (n=3)	0.0030×10^{18}	0.0017×10^{18}	0.0167×10^{17}	0.0221×10^{16}
Atoms after correction for neutron capture and decay	1.4284×10^{18}	0.1858×10^{18}	5.1408×10^{17}	10.597×10^{16a}
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.21	0.14	0.32	1.17
Percent Fission Yield	5.03	4.18	1.81	0.373
Std dev	0.06	0.05	0.02	0.006
Std dev, %	1.19	1.20	1.10	1.61

^a Includes in-pile and out-pile decay corrections.

Table VII. U-235 THERMAL FISSION YIELDS OF LONG-LIVED AND STABLE RUTHENIUM ISOTOPES FROM CAPSULE 6-6-2

$$\text{Number of Fissions} = (2.2010 \pm 0.0305) \times 10^{19}$$

	Ru-101	Ru-102	Ru-104	Ru-106
Determined number of atoms	1.105×10^{18}	9.1772×10^{17}	3.9925×10^{17}	3.5469×10^{16}
Std dev _{avg} (n=4)	0.0025×10^{18}	0.0147×10^{17}	0.0204×10^{17}	0.0316×10^{16}
Atoms after correction for neutron capture and decay	1.1052×10^{18}	9.1773×10^{17}	3.9917×10^{17}	$8.7640 \times 10^{16}{}^a$
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.23	0.16	0.51	1.34
Percent fission yield	5.02	4.17	1.81	0.398
Std dev	0.07	0.06	0.03	0.008
Std dev, %	1.39	1.44	1.66	2.01

^a Includes in-pile and out-pile decay corrections.

The use of this relationship requires correction for those atoms of U-236 and U-238 lost by capture and subsequent decay to nonuranium isotopes. This was done with data obtained from a computer program which simulated the history of the irradiation. Discussion and details of the buildup and burnout calculations have been reported previously(2).

The determined number of fissions for the irradiated U-235 capsules are $(2.839 \pm 0.032) \times 10^{19}$ for capsule 6-4-1 and $(2.2010 \pm 0.0305) \times 10^{19}$ for capsule 6-6-2 where the propagated standard deviation errors for the computed number of fissions correspond to a relative error of 1.13% and 1.38% respectively. Details of these calculations are given in references 2 and 9.

As in the case of the U-233 thermal fission yields for ruthenium, corrections for the buildup and burnout of the various ruthenium isotopes were based on a series of computer programs which simulated the irradiation history of the samples.

Radiometric Determined Thermal Fission Yield of 1.0-yr Ru-106 for U-233 and U-235 and Comparison to Mass Spectrometric Data, R. E. Foster, W. J. Maeck

The thermal fission yields of 1.0-yr Ru-106 for U-233 and U-235 were determined by radiochemical counting, as well as mass spectrometry reported in the previous section.

For the carrier free radiochemical determination, four 1000- μ l or less aliquots of the four dissolver solutions were carried through the ruthenium distillation procedure described in the Appendix. For these analyses, the distillate was collected in 5 ml of sulfurous acid (50% by vol). After collection, the ruthenium distillate was transferred to a 50-ml volumetric flask and diluted to volume with water. The entire flask was counted 10-cm above a 3 x 3-in. NaI(Tl) scintillation detector and the area under the 620-Kev photopeak was measured. The counting geometry was calibrated with a standard Ru-106 solution in a 50-ml volumetric flask at 10 cm. The Ru-106 solution was standardized by pipetting 100- μ l aliquots onto 1-in. filter paper discs and counting at 10-cm.

Gamma ray spectrometry factors for detector efficiency, peak-to-total ratio, and absorption were taken from Heath(10). The gamma branching ratio for the 620-Kev photopeak of Ru-106 was estimated to be 0.1061. This value is an average of six quoted in the Nuclear Data Sheets(11).

Corrections for the small Ru-103 contribution to the 620-Kev photopeak of Ru-106 were obtained by overlaying a standard Ru-103 gamma ray spectrum on a standard Ru-106 spectrum. The amount of Ru-103 removed from the Ru-106 spectrum was based on decay corrections and relative fission yields. The corrections ranged from 3.5 to 5%.

The experimental radiometric data and calculated Ru-106 fission yields for the four capsules are given in Table VIII. Comparison of the radiometrically determined fission yields and those determined by mass spectrometry are given in Table IX. There are no significant differences between the Ru-106 yields determined by both methods. The precision of the mass spectrometric data is better.

The largest uncertainty in the radiometric method is associated with the branching ratio of the 620-Kev gamma transition. By using mass spectrometry to measure the number of Ru-106 atoms and γ -ray spectrometry to measure the number of events resulting in a 620-Kev photon, an accurate measure of the total 620-Kev gamma ray branching ratio can be obtained. This technique circumvents decay scheme errors and is currently being evaluated to obtain working data for Ru-106 as well as other long lived radionuclides.

Table VIII. RADIOMETRICALLY DETERMINED FISSION YIELD OF Ru-106
FOR THE THERMAL FISSION OF U-233 AND U-235

	U-233		U-235	
	Capsule 6-4-2	Capsule 6-4-3	Capsule 6-4-1	Capsule 6-6-2
Measured c/min under 620-Kev photopeak for entire sample (n=4)	5.080×10^7	3.915×10^7	5.847×10^7	5.130×10^7
c/min corrected for Ru-103	4.908×10^7	3.847×10^7	5.678×10^7	4.870×10^7
d/min	6.844×10^{10}	5.365×10^{10}	7.921×10^{10}	6.791×10^{10}
Atoms Ru-106 at $t = 0$	9.518×10^{16}	8.094×10^{16}	1.086×10^{17}	9.066×10^{16}
No. of Fissions	3.786×10^{19}	3.390×10^{19}	2.839×10^{19}	2.201×10^{19}

Percent Fission Yield	0.251	0.239	0.382	0.412
Std dev ^a	0.009	0.009	0.013	0.015
Std dev, %	3.7	3.8	3.5	3.6

^a Propagated error calculated based on the estimated errors for the following:

Half-life; 1.1%

1/TPA; 2.3%

Branching ratio; 2.1%

The determined number of fissions for each capsule; usually 1-2%

Method reproducibility; usually < 1%.

Table IX. COMPARISON OF RADIOMETRICALLY AND MASS SPECTROMETRICALLY
DETERMINED FISSION YIELDS OF Ru-106

	<u>Thermal Fission Yield, Percent</u>	
	<u>Radiometric</u>	<u>Mass Spectrometric</u>
<u>U-233</u>		
Capsule 6-4-2	0.251±0.009	0.258±0.005
Capsule 6-4-3	0.239±0.009	0.252±0.006
<u>U-235</u>		
Capsule 6-4-1	0.382±0.013	0.373±0.006
Capsule 6-6-2	0.412±0.015	0.398±0.008

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APPENDIX

PROCEDURE FOR THE SEPARATION AND MASS SPECTROMETRIC ANALYSIS OF FISSION PRODUCT RUTHENIUM

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A-1

PREPARATION OF Ru-96 SPIKE

One milligram of isotopically enriched Ru-96 metal, obtained from ORNL, was placed in a distillation flask, then dissolved in 8 ml of boiling 1.25% sodium hypochlorite - 4.5M NaOH mixture. The solution was neutralized with 6 ml of 6M HCl, cooled, and 10 ml of conc H₂SO₄ was slowly added. The mixture was heated to SO₃ fumes, then fumed for 10 min. After cooling to room temperature, 50 ml of distilled water was added followed by a slurry of 1 g sodium bismuthate in 20 ml of water. The ruthenium was distilled as RuO₄ by heating for 10 min after boiling started. The distillate was collected in 5 ml of chilled 50% sulfurous acid and transferred to a 1-liter volumetric flask with 2M HCl. The final concentration was ~ 1 µg Ru-96/ml. Weighed 3-ml aliquots were transferred to glass ampoules which were flame sealed.

CALIBRATION OF Ru-96 SPIKE

The calibration technique used was isotope dilution mass spectrometry with natural ruthenium as the primary standard. The natural ruthenium standard was prepared by hydrogen reduction of the trichloride salt to the metal in a tube furnace. Three equal weight aliquots of a weighed RuCl₃ solution (~ 1 mg Ru/g) were separately reduced. The precision of the weight of ruthenium metal obtained was better than 0.3%. A weight aliquot of the standardized solution was diluted 1000-fold on a weight basis with 2M HCl. Weight aliquots containing ~ 4 µg of ruthenium were transferred to glass ampoules which were flame sealed.

Five mixtures of the Ru-96 and the standard natural ruthenium, each consisting of the total contents of one ampoule of each, were carried through the chemical separation procedure and the mass spectrometric analysis described in the next two sections. The reason for the chemical separation was to ensure isotopic exchange and to remove any traces of diverse impurities, such as zirconium, which may leach from the glass ampoules. The determined concentration of the Ru-96 was 5.420×10^{15} atoms/g with a relative standard deviation for the average of 0.14%.

CHEMICAL SEPARATION

1. To a distillation flask (Fig A-1), add an aliquot of the dissolver solution containing 1 to 3 µg of fission product ruthenium. The apparatus must be scrupulously clean. To clean, distill a mixture of 5% sodium hypochlorite through the apparatus for 20 min, then rinse with distilled water.

2. Add a known amount ($\sim 3 \mu\text{g}$) of Ru-96.

In this laboratory, standardized Ru-96 is packaged in sealed ampoules with $\sim 3 \mu\text{g}$ /per ampoule (see previous section). Add the entire amount of one ampoule with the aid of 2M HCl rinsings.
3. Add 10 ml of conc H_2SO_4 . Mix by swirling.

Carefully add the conc H_2SO_4 to avoid spattering.
4. Assemble the distillation apparatus.
5. Place 5 ml of 6M HCl in the collection tube.
6. Start the air purge at a flow rate of 60 cc/min.
7. Heat to strong fumes of SO_3 and continue heating for 5 min after aluminum sulfate forms.

If the samples do not contain aluminum, heat for a total of 5 min after SO_3 fumes appear.
8. Cool the distillation flask.

Immerse in a beaker of cold water to hasten the cooling.
9. Remove the collection tube and count it for ruthenium activity. If none, discard the solution.

In this digestion, the objective is to obtain chemical identify of sample and spike ruthenium. If ruthenium distills, reject and start over.
10. Attach a new collection tube, containing 5 ml of 6M HCl, to the apparatus.
11. Add 50 ml of distilled water to the distillation flask.

Do carefully with continuous swirling. Water is being added to conc H_2SO_4 .
12. Add a slurry of 0.5 g of sodium bismuthate in 20 ml of distilled water to the distillation flask.

Prepare the slurry fresh before use.
13. Heat to boiling and continue the boiling for 10 min.

The ruthenium distills as RuO_4 .
14. Remove the collection tube, then evaporate the distillate to near dryness ($\sim 0.1 \text{ ml}$) under an infrared lamp.

The evaporation can be accelerated by directing a fine stream of air into the tube.

MASS SPECTROMETRIC ANALYSIS

1. Prepare a canoe-shaped filament from high purity, 1-x30-mil rhenium ribbon and vacuum bake for 1 hr by passing 4 amp through it at a pressure of 1×10^{-6} torr. Assemble in center (ionizing filament) position. This removes most of the residual molybdenum impurities which interfere.
2. Using a new, disposable boro-silicate glass pipet, transfer the solution from step 14 (previous section) to the filament. Dry by passing 1.5 amp through the filament.
3. Mount the filament holder on the ion source carriage and insert in the vacuum lock. Allow about 1-min pumping time at each lock stage.
4. Degas for about 5 min at 1 amp. Then increase the filament current to 2.5 to 3 amp and locate the major isotope beam by reference to the mass-vs-DVM reading (accelerating voltage) curve for the magnetic field in use. Adjust the source voltage divider controls for maximum beam. Make a rapid voltage scan in both directions to verify the mass identification. Use electron multiplier. Keep J2 setting low, J10 max, and J4-J5 near center. It may be necessary to rotate the source to get J4-J5 centered with the maximum beam.
5. Increase the filament current to obtain a multiplier output current of 3×10^{-10} amp. Scan the spectrum magnetically in both directions, recording the sensitivity settings used to give near full-scale peak heights. Obtain at least six double scans.
6. Insert the Faraday cup collector and increase the filament current to obtain an ion current of 3×10^{-12} amp. Record the spectrum as above. Obtain 8 to 12 double scans. If unable to obtain the desired ion current with a filament current of 4 amps, reduce the filament current and record additional data with the multiplier.

7. Graphically interpolate by drawing lines on the chart which connect the tops of the successive peaks of each isotope. Draw vertical lines on the chart at each turn-around in the scans, and take peak height readings at the intersections of these lines with those connecting the peak tops. Sum the readings for each isotope.

Use the same number of readings in each sum.

8. Using the known isotopic composition of the Ru-96 spike and m/e 96 peak height, subtract the spike contribution from the rest of the spectrum. Check for molybdenum contamination at m/e 95 and correct the spectrum, if necessary.

If using multiplier data, correct for mass discrimination. If atom percent of an individual isotope is desired, it is given by:

$$\text{atom \% Ru}^A = 100 \frac{(\text{corr peak ht}^A)}{\Sigma(\text{corr peak ht})}$$

9. Obtain the ratio of each corrected peak height to the m/e 96 peak. These ratios multiplied by the known number of Ru-96 atoms gives the number of atoms of each isotope present in the sample.

$$\text{wt \% Ru}^A = 100 \frac{(\text{corr peak ht}^A)(\text{at wt}^A)}{\Sigma(\text{corr peak ht})(\text{at wt})}$$

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Fig. A-1 Ruthenium Distillation Apparatus

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