key
501
11/7

**BURNUP DETERMINATION OF NUCLEAR FUELS
PROJECT REPORT
FOR THE QUARTER OCTOBER 1 - DECEMBER 31, 1966**

Edited by

Frederick L. Lisman, William J. Maeck, and James E. Rein

MASTER

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U. S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

IN-1113
Issued: October 1967
Chemistry
TID-4500

BURNUP DETERMINATION OF NUCLEAR FUELS

PROJECT REPORT
FOR THE QUARTER OCTOBER 1 - DECEMBER 31, 1966

Edited By

Frederick L. Lisman, William J. Maeck, and James E. Rein

IDAHO NUCLEAR CORPORATION

A JOINTLY OWNED SUBSIDIARY OF
AEROJET ALLIED
GENERAL CHEMICAL
CORPORATION CORPORATION

U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

gcy

BURNUP DETERMINATION
OF NUCLEAR FUELS

PROJECT REPORT
FOR THE QUARTER OCTOBER 1 - DECEMBER 31, 1966

Edited by

Frederick L. Lisman, William J. Maeck, and James E. Rein

Contributing Personnel

Analytical Development Section

W. A. Emel
R. E. Foster
M. E. Kussy
S. F. Marsh

Mass Spectrometry Group

R. M. Abernathey
L. W. Buttars
L. L. Dickerson
R. E. McAtee
R. A. Nielsen
A. H. Toepfer
G. D. Workman

Operations Analysis (Statistics)

F. W. Spraktes

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 measurement of the absolute, thermal fission yields of stable Cs-133, 30.3y Cs-137 and the stable Zr-91, -92, -93, -94, and -96 isotopes for U-233 and U-235 by isotope dilution mass spectrometry. These values, determined on each of four dissolved U-233 capsules and three U-235 capsules, are:

Fission Yields for U-233

<u>Isotope</u>	<u>Capsule</u>			
	<u>6-2-4</u>	<u>6-4-2</u>	<u>6-4-3</u>	<u>6-5-1</u>
Cs-133	6.10±0.09	6.08±0.10	5.81±0.11	6.45±0.16
Cs-137	6.94±0.09	6.90±0.11	6.67±0.13	7.33±0.16
Zr-91	6.56±0.08	6.68±0.11	6.38±0.12	6.96±0.15
Zr-92	6.66±0.08	6.76±0.11	6.44±0.12	7.08±0.15
Zr-93	7.06±0.08	7.16±0.12	6.81±0.13	7.53±0.16
Zr-94	6.91±0.08	6.95±0.11	6.65±0.12	7.31±0.16
Zr-96	5.88±0.07	5.85±0.10	5.57±0.10	6.16±0.13

Fission Yields for U-235

<u>Isotope</u>	<u>Capsule</u>		
	<u>6-2-2</u>	<u>6-4-1</u>	<u>6-6-2</u>
Cs-133	6.72±0.04	6.71±0.08	6.83±0.13
Cs-137	6.27±0.04	6.22±0.14	6.32±0.09
Zr-91	5.90±0.04	5.90±0.08	5.90±0.09
Zr-92	5.96±0.04	5.92±0.08	5.97±0.09
Zr-93	6.35±0.05	6.31±0.08	6.34±0.09
Zr-94	6.40±0.05	6.45±0.08	6.42±0.09
Zr-96	6.24±0.04	6.23±0.08	6.22±0.09

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

Previous project reports are:

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
Quarter, October-December, 1965	IDO-14676
Quarter, January-March, 1966	IDO-14678
Quarter, April-June, 1966	IDO-14681
Quarter, July-September, 1966	IN-1064

CONTENTS

SUMMARY	iii
INTRODUCTION	1
ABSOLUTE THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233 AND U-235	2
<u>IRRADIATION HISTORY OF CAPSULES</u>	2
<u>DISSOLUTION OF CAPSULES</u>	2
<u>CHEMICAL SEPARATION OF CESIUM</u>	2
<u>MASS SPECTROMETRIC ANALYSIS OF CESIUM</u>	4
<u>FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233.</u>	4
<u>FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-235</u>	.6
ABSOLUTE THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-233 AND U-235	.16
<u>CHEMICAL SEPARATION OF ZIRCONIUM</u>	.16
<u>MASS SPECTROMETRIC ANALYSIS OF ZIRCONIUM</u>	.16
<u>FISSION YIELDS OF THE ZIRCONIUM ISOTOPES FOR U-233</u>	.16
<u>FISSION YIELDS OF THE ZIRCONIUM ISOTOPES FOR U-235</u>	18
REFERENCES	.27
APPENDIX I - PROCEDURE FOR THE SEPARATION AND MASS SPECTROMETRIC ANALYSIS OF FISSION PRODUCT CESIUM	29
APPENDIX II - PROCEDURE FOR THE SEPARATION AND MASS SPECTROMETRIC ANALYSIS OF FISSION PRODUCT ZIRCONIUM	.41
FIGURES	
I. COMPUTER PROGRAM SCHEMATIC FOR BUILDUP AND BURNOUT OF FISSION PRODUCT CESIUM	8
II. COMPUTER PROGRAM SCHEMATIC FOR BUILDUP AND BURNOUT OF FISSION PRODUCT ZIRCONIUM	.19

TABLES

I.	COMPOSITION AND IRRADIATION HISTORY OF STANDARD BURNUP CAPSULES.	3
II.	PRECISION OF OVERALL PROCEDURE	5
III.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233 FROM CAPSULE 6-2-4	9
IV.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233 FROM CAPSULE 6-4-2	10
V.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233 FROM CAPSULE 6-4-3	11
VI.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233 FROM CAPSULE 6-5-1.	12
VII.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-235 FROM CAPSULE 6-2-2	13
VIII.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-235 FROM CAPSULE 6-4-1	14
IX.	THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-235 FROM CAPSULE 6-6-2	15
X.	COMPARISON OF ISOTOPIC DISTRIBUTION OF NATURAL ZIRCONIUM	17
XI.	THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-233 FROM CAPSULE 6-2-4	20
XII.	THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-233 FROM CAPSULE 6-4-2	21
XIII.	THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-233 FROM CAPSULE 6-4-3	22
XIV.	THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-233 FROM CAPSULE 6-5-1	23
XV.	THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-235 FROM CAPSULE 6-2-2	24

XVI. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-235 FROM CAPSULE 6-4-1	25
XVII. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM ISOTOPES FOR U-235 FROM CAPSULE 6-6-2	26

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. The use of stable fission product nuclides, determined by isotope dilution mass spectrometry, has therefore been selected. The degree of reliability of a burnup determination based on stable fission product analysis 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 fission product atoms 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 spectrometric 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, fast fission yields will be measured.

Initial values for many U-233 and U-235 thermal fission yields have been reported in previous reports IDO-14660, IDO-14663, IDO-14667, IDO-14676, IDO-14678, IDO-14681, and IN-1064.

ABSOLUTE THERMAL FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233 AND U-235

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 Cs-133 and Cs-137 for U-233 and U-235 were determined by isotope dilution mass spectrometry for four U-233 and three U-235 capsules.

IRRADIATION HISTORY OF 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 I.

DISSOLUTION OF CAPSULES, R. E. Foster, Jr., S. F. Marsh

Dissolution of the capsules was carried out in a 4-in. lead-shielded facility. The dissolution apparatus has been previously described (1, 2). The dissolver flask and reflux condenser were fabricated from high-purity quartz and an acid mixture of 6M HCl-1.6M HNO₃, prepared from quartz-distilled reagents, was the dissolution reagent (1).

The dissolutions proceeded smoothly and were usually complete in 3.5 hr. The fission gases, krypton and xenon, appeared approximately 1 hr after the start of dissolution and their evolution continued for about 2 hr. The final solutions (about 200 ml) were water clear and contained no residue.

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

CHEMICAL SEPARATION OF CESIUM, R. E. Foster, Jr., F. L. Lisman

Cesium is separated carrier-free for analysis by isotope dilution mass spectrometry by scavenging most other fission products and uranium by

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>
6-2-4	U-233	99.908	58.8±0.2	8	32.40±0.37	August 30, 1964
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
6-5-1	U-233	99.908	144.4±0.2	2	8.33±0.17	July 20, 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	81.9±0.1	3	12.54±0.18	September 15, 1964
6-2-2	U-235	99.1633	61.2±0.1	8	31.57±0.19	August 30, 1964

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

an aluminum hydroxide precipitation. Barium is effectively removed by adding a drop of sulfuric acid to the solution prior to the hydroxide precipitation.

Because natural cesium is monoisotopic (Cs-133), contamination with natural cesium must be prevented as Cs-133 is both a fission product and the isotope dilution "spike". For these separations, quartz-distilled reagents were used, all reagents were tested for natural cesium contamination by isotope dilution mass spectrometry using Cs-137 as the "spike", and only quartz or polypropylene ware was used.

The separation procedure is detailed in Appendix I as is the preparation and standardization of the natural cesium "spike".

MASS SPECTROMETRIC ANALYSIS OF CESIUM, R. M. Abernathcy, L. W. Buttars, R. A. Nielsen, R. E. McAtee, G. D. Workman

The mass spectrometer used for this work was a Nuclide Corporation TDD-1, tandem, 12-in., 90° instrument with three ion detection systems. For the cesium analysis, the Faraday Cage, electrometer, strip chart detection system was used. Details of this instrument and the various detection systems available have been previously reported (2).

Cesium samples, as the chloride, were mounted on a single rhenium filament.

The procedure for the mass analysis of fission product cesium is detailed in Appendix I. 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 II.

FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-233, F. L. Lisman, F. W. Spraktes

The absolute thermal fission yields of Cs-133 and Cs-137 were determined on each of the four, dissolved, U-233 standard burnup capsules. Eight 1-ml aliquots (four spiked with known amounts of Cs-133 and four without spike) were analyzed for each dissolved capsule solution. The analysis results and calculated fission yields are summarized in Tables III through VI. Included are the previously determined radiometric results for Cs-137. Methods of calculation and the error propagation for the determined number of Cs-133 and Cs-137 atoms are given in Appendix I.

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 analysis 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:

$$F_3 = U^0 - U$$

Table II. PRECISION OF OVERALL PROCEDURE

<u>Aliquot</u>	Cesium Isotope (atoms/ml x 10 ⁻¹⁵)	
	<u>133</u>	<u>137</u>
1	9.912	8.805
2	9.943	8.832
3	9.889	8.785
Avg	9.915	8.807
Std Dev	0.027	0.024
% Std Dev ^(a)	0.27	0.27

^a Standard deviation for an individual result.

where

F_3 = number of U-233 fissions

U^0 = total preirradiated atoms of uranium

U = total postirradiated atoms of uranium

To effectively use this relationship, one must account for those atoms of U-235 and U-238 lost by fission and neutron capture. This was done with data obtained from a computer program which simulated the history of the irradiation. The determined number of fissions for each of the U-233 capsules, along with the appropriate references, are given in Tables III thru VI.

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 (5).

In the case of Cs-133 and Cs-137, corrections for buildup and burnout by neutron capture and β decay are moderate being from 2 to 6%. A schematic diagram of the buildup and burnout program for cesium is given in Figure 1.

FISSION YIELDS OF Cs-133 AND Cs-137 FOR U-235, F. L. Lisman, F. W. Sprakles

The absolute thermal fission yields of Cs-133 and Cs-137 were determined on each of the three, dissolved, U-235 capsules.

Eight 1-ml aliquots (four spiked with known amounts of Cs-133 and four without spike) were analyzed from each dissolved capsule solution. The analysis results and calculated fission yields are summarized in Tables VII thru IX. Included are the previously determined radiometric results for Cs-137. Methods of calculation and the error propagation for the determined number of Cs-133 and Cs-137 atoms are given in Appendix I.

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

U = total postirradiation atoms of uranium

The use of this relationship requires corrections for those atoms of U-236 and U-238 lost by neutron capture and subsequent decay to nonuranium isotopes. This was done with data obtained from a computer program which simulated the irradiation history of the various capsules. The determined number of fissions for each of the U-235 capsules, along with the references, are given in Tables VII thru IX.

As in the case of the U-233 thermal fission yields of Cs-133 and Cs-137, correction for the buildup and burnout by neutron capture and β^- decay were based on a computer program which simulated the irradiation history of the capsules.

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

Table III. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-233 FROM CAPSULE 6-2-4

Number of Fissions = $(4.138 \pm 0.045) \times 10^{19}$ (Ref 3)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137</u> <u>(radiometric)(Ref 3)</u>
Determined number of atoms	2.470×10^{18}	2.693×10^{18}	2.801×10^{18}
Std Dev _{avg} (n=3)	0.022×10^{18}	0.010×10^{18}	0.056×10^{18}
Atoms after correction for neutron capture and decay	2.523×10^{18}	2.873×10^{18}	2.882×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.94	0.63	2.00
<hr/>			
Percent fission yield	6.10	6.94	6.96
Std Dev	0.08 ₈	0.08 ₇	0.16
Std Dev, %	1.4	1.2	2.3

Table IV. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-233 FROM CAPSULE 6-4-2

Number of Fission = $(3.786 \pm 0.059) \times 10^{19}$ (Ref 4)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137 (radiometric)(Ref 4)</u>
Determined number of atoms	2.283×10^{18}	2.445×10^{18}	2.482×10^{18}
Std Dev _{avg} (n=4)	0.004×10^{18}	0.010×10^{18}	0.049×10^{18}
Atoms after correction for neutron capture and decay	2.302×10^{18}	2.611×10^{18}	2.532×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.35	0.50	1.97
<hr/>			
Percent fission yield	6.08	6.90	6.69
Std Dev	0.09 ₈	0.11	0.17
Std Dev, %	1.6	1.6	2.5

Table V. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-233 FROM CAPSULE 6-4-3

Number of Fissions = $(3.390 \pm 0.062) \times 10^{19}$ (Ref 5)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137</u> (radiometric)(Ref 5)
Determined number of atoms	1.954×10^{18}	2.117×10^{18}	2.188×10^{18}
Std Dev _{avg} (n=4)	0.010×10^{18}	0.013×10^{18}	0.043×10^{18}
Atoms after correction for neutron capture and decay	1.968×10^{18}	2.262×10^{18}	2.239×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.59	0.69	1.95
<hr/>			
Percent fission yield	5.81	6.67	6.60
Std Dev	0.11	0.13	0.17
Std Dev, %	1.9	1.9	2.6

Table VI. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-233 FROM CAPSULE 6-5-1

Number of Fissions = $(2.614 \pm 0.055) \times 10^{19}$ (Ref 3)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137</u> <u>(radiometric)(Ref 3)</u>
Determined number of atoms	1.676×10^{18}	1.798×10^{18}	1.795×10^{18}
Std Dev _{avg} (n=4)	0.022×10^{18}	0.014×10^{18}	0.036×10^{18}
Atoms after correction for neutron capture and decay	1.686×10^{18}	1.916×10^{18}	1.857×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	1.35	0.82	2.00
<hr/>			
Percent fission yield	6.45	7.33	7.03
Std Dev	0.16	0.16	0.20
Std Dev, %	2.5	2.2	2.9

Table VII. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-235 FROM CAPSULE 6-2-2

Number of Fissions = $(4.142 \pm 0.022) \times 10^{19}$ (Ref 6)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137</u> <u>(radiometric)(Ref 6)</u>
Determined number of atoms	2.739×10^{18}	2.433×10^{18}	2.477×10^{18}
Std Dev _{avg} (n=3) ^a	0.008×10^{18}	$0.007_6 \times 10^{18}$	$0.049_5 \times 10^{18}$
Atoms after correction for neutron capture and decay	2.782×10^{18}	2.595×10^{18}	2.601×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.41	0.43	2.00
<hr/>			
Percent fission yield	6.72	6.27	6.28
Std Dev	0.04 ₅	0.04 ₃	0.13
Std Dev, %	0.7	0.7	2.1

^a One sample was inadvertently lost during the chemical separation.

Table VIII. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-235 FROM CAPSULE 6-4-1

Number of Fissions = $(2.839 \pm 0.032) \times 10^{19}$ (Ref 7)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137 (radiometric)(Ref 7)</u>
Determined number of atoms	1.889×10^{18}	1.668×10^{18}	1.738×10^{18}
Std Dev _{avg} (n=4)	0.006×10^{18}	$0.006_6 \times 10^{18}$	0.034×10^{18}
Atoms after correction for neutron capture and decay	1.905×10^{18}	1.782×10^{18}	1.765×10^{18}
Std Dev, % (includes estimated uncertainties in correciton factors for neutron capture and radioactive decay)	0.44	0.50	1.98
<hr/>			
Percent fission yield	6.71	6.28	6.22
Std Dev	0.08 ₁	0.07 ₈	0.14
Std Dev, %	1.2	1.2	2.2

Table IX. THERMAL FISSION YIELDS OF Cs-133 AND
Cs-137 FOR U-235 FROM CAPSULE 6-6-2

Number of Fissions = $(2.201 \pm 0.030) \times 10^{19}$ (Ref 5)

	<u>Cs-133</u>	<u>Cs-137</u>	<u>Cs-137 (radiometric)(Ref 5)</u>
Determined number of atoms	1.493×10^{18}	1.311×10^{18}	1.340×10^{18}
Std Dev _{avg} (n=3)	0.019×10^{18}	$0.005_8 \times 10^{18}$	0.026×10^{18}
Atoms after correction for neutron capture and decay	1.504×10^{18}	1.391×10^{18}	1.365×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	1.28	0.53	1.95
<hr/>			
Percent fission yield	6.83	6.32	6.20
Std Dev	0.13	0.09	0.15
Std Dev, %	1.9	1.5	2.4

ABSOLUTE THERMAL FISSION YIELDS
OF STABLE ZIRCONIUM ISOTOPES FOR U-233 AND U-235

The absolute thermal fission yields of Zr-91, -92, -93, -94, and -96 were determined for four U-233 and three U-235 capsules.

The irradiation histories and dissolution of the U-233 and U-235 capsules were the same as discussed in the previous section.

CHEMICAL SEPARATION OF ZIRCONIUM, S. F. Marsh, M. E. Kussy

The zirconium was separated carrier-free by a thorium iodate coprecipitation method (1). Potassium, leached from glassware, interferes with the mass spectrometric measurement. For this reason, a polyethylene tube is used for the final, anion exchange separation step, and polypropylene ware is used for the final evaporation just prior to the mass spectrometer measurement. The procedure is detailed in Appendix II.

MASS SPECTROMETRIC ANALYSIS OF ZIRCONIUM, R. M. Abernathey, L. W. Buttars, R. E. McAtee, R. A. Nielsen, G. D. Workman

Evaporation of the zirconium samples from dilute hydrochloric acid onto a rhenium filament proved satisfactory for a triple filament source. The measured ion species was ZrO^+ .

The mass spectrometer was a Nuclide Corporation, TDD-1, tandem, 12-in., 90° instrument. Details of the instrument and its various detection systems have been reported (2). For zirconium, the 20-stage electron multiplier, electrometer, strip chart detection system was used. Mass discrimination was established by comparing results from a synthetic mixture of Zr-90 and Zr-96 to those obtained from the same samples with the nondiscriminating Faraday Cage detection system. The Faraday Cage results are compared to Nuclear Data Sheets (8) values in Table X.

The procedure for the mass spectrometric analysis of zirconium is detailed in Appendix II.

FISSION YIELDS OF THE ZIRCONIUM ISOTOPES FOR U-233, M. E. Kussy, F. L. Lisman, F. W. Spraktes

The absolute thermal fission yields of Zr-91, -92, -93, -94, and -96 were determined on each of the four irradiated U-233 capsules.

Table X. COMPARISON OF ISOTOPIC
DISTRIBUTION OF NATURAL ZIRCONIUM

<u>Isotope</u>	<u>Value, Atom Percent</u>	
	<u>This Work</u> ^(a)	<u>NDS</u>
90	51.427±0.002	51.46
91	11.208±0.008	11.23
92	17.130±0.009	17.11
94	17.431±0.002	17.40
96	2.804±0.005	2.80

(a) Error is expressed as the standard deviation of the average for duplicate determinations.

Eight 1-ml aliquots (four spiked with known amounts of Zr-90 and four without spike) were analyzed from each dissolver solution. The results and calculated fission yields are summarized in Tables XI thru XIV. The calculation of the number of atoms of each zirconium isotope is detailed in Appendix II. The number of U-233 fissions was calculated as described in the previous section. The determined number of fissions for each U-233 capsule and the appropriate references are given in Tables XI through XIV.

As in the case of the thermal fission yields of the cesium isotopes, corrections for the buildup and burnout of the zirconium isotopes were based on a computer program which simulated the irradiation history of the samples. A schematic diagram of the program for the buildup and burnout of zirconium is given in Figure 2.

FISSION YIELDS OF THE ZIRCONIUM ISOTOPES FOR U-235, M. E. Kussy,
F. L. Lisman, F. W. Spraktes

The absolute thermal fission yields of Zr-91, -92, -93, -94, and -96 were determined on each of the three irradiated U-235 capsules.

Eight 1-ml aliquots (four spiked with known amounts of Zr-90 and four without spike) were analyzed from each dissolver solution. The analysis results and calculated fission yields are summarized in Tables XV through XVII.

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

Figure 2. COMPUTER PROGRAM SCHEMATIC FOR BUILDUP
AND BURNOUT OF FISSION PRODUCT ZIRCONIUM

Table XI. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPES FOR U-233 FROM CAPSULE 6-2-1

Number of Fissions = $(4.138 \pm 0.045) \times 10^{19}$ (Ref 3)

	<u>Zr-91</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	2.715×10^{18}	2.756×10^{18}	2.921×10^{18}	2.863×10^{18}	2.434×10^{18}
Std Dev _{avg} (n=4)	0.013×10^{18}	0.013×10^{18}	0.014×10^{18}	0.014×10^{18}	0.012×10^{18}
Atoms after correction for neutron capture and decay	2.714×10^{18}	2.756×10^{18}	2.924×10^{18}	2.861×10^{18}	2.433×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.49	0.49	0.49	0.49	0.52
<hr/>					
Percent fission yield	6.56	6.66	7.06	6.91	5.88
Std Dev	0.07 ₈	0.07 ₉	0.08 ₄	0.08 ₃	0.07 ₁
Std Dev, %	1.19	1.19	1.19	1.19	1.21

Table XII. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPEs FOR U-233 FROM CAPSULE 6-4-2

Number of Fissions = $(3.786 \pm 0.059) \times 10^{19}$ (Ref 4)

	<u>Zr-91</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	2.494×10^{18}	2.561×10^{18}	2.711×10^{18}	2.632×10^{18}	2.215×10^{18}
Std Dev _{avg} (n=4)	0.011×10^{18}	0.011×10^{18}	0.012×10^{18}	0.011×10^{18}	0.010×10^{18}
Atoms after correction for neutron capture and decay	2.529×10^{18}	2.561×10^{18}	2.712×10^{18}	2.632×10^{18}	2.215×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.53	0.43	0.43	0.43	0.46
<hr/>					
Percent fission yield	6.68	6.76	71.6	6.95	5.85
Std Dev	0.11	0.11	0.12	0.11	0.09 ₆
Std Dev, %	1.7	1.6	1.6	1.6	1.6

Table XIII. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPES FOR U-233 FROM CAPSULE 6-4-3

Number of Fissions = $(3.390 \pm 0.062) \times 10^{19}$ (Ref 5)

	<u>Zr-91</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	2.150×10^{18}	2.183×10^{18}	2.308×10^{18}	2.256×10^{18}	1.888×10^{18}
Std Dev _{avg} (n=3)	0.010×10^{18}	0.010×10^{18}	0.011×10^{18}	0.012×10^{18}	0.009×10^{18}
Atoms after correction for neutron capture and decay	2.165×10^{18}	2.183×10^{18}	2.308×10^{18}	2.256×10^{18}	1.887×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.49	0.47	0.47	0.52	0.47
Percent fission yield	6.38	6.44	6.81	6.65	5.57
Std Dev	0.12	0.12	0.13	0.12	0.10
Std Dev, %	1.9	1.9	1.9	1.9	1.9

Table XIV. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPES FOR U-233 FROM CAPSULE 6-5-1

Number of Fissions = $(2.614 \pm 0.055) \times 10^{19}$ (Ref 3)

	<u>Zr-91</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	1.820×10^{18}	1.850×10^{18}	1.969×10^{18}	1.913×10^{18}	1.611×10^{18}
Std Dev _{avg} (n=3) ^a	0.012×10^{18}	0.012×10^{18}	0.013×10^{18}	0.012×10^{18}	0.010×10^{18}
Atoms after correction for neutron capture and decay	1.820×10^{18}	1.850×10^{18}	1.969×10^{18}	1.912×10^{18}	1.611×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.64	0.64	0.65	0.64	0.64
<hr/>					
Percent fission yield	6.96	7.07	7.53	7.31	6.16
Std Dev	0.15	0.15	0.16	0.16	0.13
Std Dev, %	2.2	2.2	2.2	2.2	2.2
<hr/>					

^a One sample was inadvertently lost during the chemical separation.

Table XV. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPES FOR U-235 FROM CAPSULE 6-2-2

Number of Fissions = $(4.142 \pm 0.022) \times 10^{19}$ (Ref 6)

	<u>Zr-91</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	2.445×10^{18}	2.469×10^{18}	2.629×10^{18}	2.652×10^{18}	2.584×10^{18}
Std Dev _{avg} (n=4)	0.012×10^{18}	0.012×10^{18}	0.013×10^{18}	0.013×10^{18}	0.013×10^{18}
Atoms after correction for neutron capture and decay	2.444×10^{18}	2.469×10^{18}	2.631×10^{18}	2.650×10^{18}	2.584×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.49	0.49	0.49	0.49	0.49
<hr/>					
Percent fission yield	5.90	5.96	6.35	6.40	6.24
Std Dev	0.04 ₂	0.04 ₃	0.04 ₆	0.04 ₆	0.04 ₅
Std Dev, %	0.7	0.7	0.7	0.7	0.7

Table XVI. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPES FOR U-235 FROM CAPSULE 6-4-1

Number of Fissions = $(2.839 \pm 0.032) \times 10^{19}$ (Ref 7)

	<u>Zr-91</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	1.653×10^{18}	1.682×10^{18}	1.791×10^{18}	1.832×10^{18}	1.769×10^{18}
Std Dev _{avg} (n=4)	0.010×10^{18}	0.010×10^{18}	0.011×10^{18}	0.011×10^{18}	0.013×10^{18}
Atoms after correction for neutron capture and decay	1.675×10^{18}	1.682×10^{18}	1.792×10^{18}	1.831×10^{18}	1.768×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.66	0.62	0.62	0.59	0.76
<hr/>					
Percent fission yield	5.90	5.92	6.31	6.45	6.23
Std Dev	0.07 ₇	0.07 ₆	0.08 ₁	0.08 ₂	0.08 ₅
Std Dev, %	1.3	1.3	1.3	1.3	1.4

Table XVII. THERMAL FISSION YIELDS OF STABLE ZIRCONIUM
ISOTOPES FOR U-235 FROM CAPSULE 6-6-2

Number of fissions = $(2.201 \pm 0.030) \times 10^{19}$ (Ref 5)

	<u>Zr-90</u>	<u>Zr-92</u>	<u>Zr-93</u>	<u>Zr-94</u>	<u>Zr-96</u>
Determined number of atoms	1.269×10^{18}	1.313×10^{18}	1.396×10^{18}	1.412×10^{18}	1.370×10^{18}
Std Dev _{avg} (n=3) ^a	0.006×10^{18}	0.006×10^{18}	0.006×10^{18}	0.006×10^{18}	0.006×10^{18}
Atoms after correction for neutron capture and decay	1.298×10^{18}	1.313×10^{18}	1.396×10^{18}	1.412×10^{18}	1.370×10^{18}
Std Dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.55	0.43	0.43	0.45	0.47
<hr/>					
Percent fission yield	5.90	5.97	6.34	6.42	6.22
Std Dev	0.08 ₇	0.08 ₇	0.09 ₂	0.09 ₃	0.09 ₁
Std Dev, %	1.5	1.4	1.4	1.4	1.5

^a One sample was inadvertently lost during the chemical separation.

REFERENCES

1. Maeck, W. J., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: 1964 Annual Report, IDO-14656 (1965).
2. Maeck, W. J., Abernathey, R. M., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: Project Report for the Quarter October 1 - December 31, 1965, IDO-14676 (1966).
3. Maeck, W. J., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: Project Report for the Quarter April 1 - June 30, 1966, IDO-14681 (1967).
4. Maeck, W. J., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: Project Report for the Quarter April 1 - June 30, 1965, IDO-14663 (1965).
5. Maeck, W. J., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: Project Report for the Quarter July 1 - September 30, 1965, IDO-14667 (1965).
6. Lisman, F. L., Maeck, W. J., Foster, R. E., Jr., Rein, J. E., Burnup Determination of Nuclear Fuels: Project Report for the Quarter July 1 - September 30, 1966, IN-1064 (1967).
7. Maeck, W. J., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: Project Report for the Quarter January 1 - March 31, 1965, IDO-14660 (1965).
8. Nuclear Data Sheets, Appendix 2, Relative Isotopic Abundances, National Academy of Sciences - National Research Council, Washington, D. C.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX I

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

R. E. Foster, Jr., R. M. Abernathey, F. L. Lisman

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

PREPARATION AND STANDARDIZATION OF NATURAL CESIUM SPIKE

Approximately 1 g of "Specpure" cesium chloride was heated in a muffle furnace at 500°C for 16 hr, then weighed and dissolved in approximately 1 liter (by weight) of quartz-distilled water. Three 100-g aliquots were gravimetrically analyzed by fuming to the sulfate with sulfuric acid. The determined concentration was 1.0094 mg Cs/g solution with a relative standard deviation for the average of 0.18%.

Weight aliquots containing approximately 5 mg of Cs were transferred to glass ampoules which were flame sealed. When used, the entire contents of an ampoule were diluted approximately 1000 fold (by weight) and weight aliquots were taken.

CHEMICAL SEPARATION

1. Pipet approximately 1 ml of Cs-133 spike solution into a tared 15-ml polypropylene tube and reweigh the tube.	This establishes the amount of Cs-133 spike.
2. Accurately pipet a 1-ml aliquot of the dissolver solution into the 15-ml polypropylene tube.	Use a calibrated pipet.
3. Add one drop of quartz-distilled 4.5M H_2SO_4 and stir the solution.	A vortex mixer is satisfactory.
4. Add one drop of methyl red indicator solution.	
5. Add quartz-distilled NH_4OH dropwise until the solution turns yellow.	
6. Centrifuge.	
7. Transfer the supernatant solution to a clean 15-ml polypropylene tube.	Discard any precipitate which usually is a metal hydroxide(s) forming from fuel components.
8. Add 1 ml of conc quartz-distilled HNO_3 .	
9. Evaporate to approximately 0.1 ml with a heat lamp.	During the evaporation, NH_4Cl may precipitate, If so, add an additional drop of conc HNO_3 and continue the evaporation.

MASS SPECTROMETRIC ANALYSIS

1. Prepare a canoe-shaped filament from high purity, 1- x 30-mil rhenium ribbon, and vacuum bake it for 1 hr at 4 A at a pressure of 1×10^{-6} torr. Assemble the sample filament in the center (ionizing) position.

Most of the trace cesium and barium impurities are volatilized
2. Using a new, freshly cleaned, disposable glass pipet, transfer the solution from step 9 (previous section) to the filament. Evaporate the solution by passing 1.2 A through the filament.
3. Mount the filament holder on the ion source carriage and insert the carriage into the vacuum lock.

Allow about 1-min pumping time at each lock stage.
4. Adjust the filament current to 0.6 to 0.8 A and locate the major isotope beam by reference to the mass-vs-DVM (accelerating voltage) curve for the magnetic field in use. Adjust the source voltage divider controls for the maximum beam. Make a rapid voltage scan in both directions to verify the mass identification.

Use the electron multiplier. Keep the J2 setting low, the J10 setting maximum, and the J4-J5 setting near center. The source may need to be rotated to get J4-J5 centered with the maximum beam.
5. Insert the Faraday Cage collector and increase the filament current to obtain an ion current of 3×10^{-11} A. Scan the spectrum magnetically in both directions, recording the sensitivity settings used to give near full-scale peak heights. Obtain three charts of $4\frac{1}{2}$ double scans.

6. 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. If the atom percent of an individual isotope is desired, it is given by:

$$\text{atom \% Cs}^A =$$

$$100 \frac{\sum \text{peak heights}^A}{\sum (\sum \text{peak heights})}$$

CALCULATIONS

Let R_{sf} be the atom ratio of Cs-133 to Cs-137 in the spiked fission product sample. Then:

$$R_{sf} = \frac{N_s^3 + N_f^3}{N_f^7} \quad (I)$$

where: N_s^3 = number of spike Cs-133 atoms in the sample.

N_f^3 = number of fission product Cs-133 atoms in the sample.

N_f^7 = number of fission product Cs-137 atoms in the sample.

To eliminate the N_f^3 term from equation (I), let R_f be the atom ratio of fission product Cs-133 to Cs-137 in an unspiked fission product sample. Then:

$$R_f = \frac{N_f^3}{N_f^7}$$

and

$$N_f^3 = R_f N_f^7$$

Substituting for N_f^3 in equation (I) yields

$$R_{sf} = \frac{N_s^3 + R_f N_f^7}{N_f^7}$$

and

$$N_f^7 = \frac{N_s^3 V_d}{(R_{sf} - R_f) V_x} \quad (II)$$

where: V_d = volume of the dissolver solution

V_x = volume of sample aliquot

Normally R_f is obtained on four unspiked aliquots and the average ($\bar{R}_f$) is used to calculate N_f^7 . Thus:

$$N_f^7 = \frac{N_s^3 V_d}{(R_{sf} - \bar{R}_f) V_x} \quad (III)$$

The number of fission product Cs-133 atoms is:

$$N_f^3 = \bar{R}_f N_f^7 \quad (IV)$$

ERROR PROPAGATION FOR Cs-137

The number of Cs-137 atoms, by equation III of the previous section is:

$$N_f^7 = \frac{N_s^3 V_d}{(R_{sf} - \bar{R}_f) V_x} \quad (III)$$

Reported values are the average of several determinations:

$$\bar{N}_f^7 = \frac{\sum_{i=1}^n N_{f_i}^7}{n}$$

where: $\overline{N}_f^7$ = average number of Cs-137 atoms

$N_{f_i}^7$ = number of Cs-137 atoms in the i^{th} sample.

n = number of determinations.

or:

$$\overline{N}_f^7 = \sum_{i=1}^n \frac{N_{s_i}^3 V_d}{(R_{sf_i} - R_{f_i}) V_x}$$

V_d and usually V_x are the same for all samples. Also $\overline{R}_f$ is the same for all determinations on a given capsule. Thus:

$$\overline{N}_f^7 = \frac{\left(\sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \overline{R}_f)} \right) \frac{V_d}{V_x}}{n}$$

The variance of $\overline{N}_f^7$ is then given approximately by:

$$\begin{aligned} \sigma^2 \overline{N}_f^7 = & \sum_{i=1}^n \left(\frac{\partial \overline{N}_f^7}{\partial N_{s_i}^3} \right)^2 \sigma^2 N_{s_i}^3 + \sum_{i=1}^n \left(\frac{\partial \overline{N}_f^7}{\partial R_{sf_i}} \right)^2 \sigma^2 R_{sf_i} + \left(\frac{\partial \overline{N}_f^7}{\partial \overline{R}_f} \right)^2 \sigma^2 \overline{R}_f \\ & + \left(\frac{\partial \overline{N}_f^7}{\partial V_d} \right)^2 \sigma^2 V_d + \left(\frac{\partial \overline{N}_f^7}{\partial V_x} \right)^2 \sigma^2 V_x + (\text{covariance terms}) \end{aligned}$$

The covariance terms are negligible.

and

$$\frac{\partial \overline{N}_f^7}{\partial N_{s_i}^3} = \frac{V_d}{n V_x} \left(\frac{1}{(R_{sf_i} - \overline{R}_f)} \right)$$

$$\frac{\partial \bar{N}_f^7}{\partial R_{sf_i}} = \frac{V_d}{nV_x} \left[\frac{-N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)^2} \right]$$

$$\frac{\partial \bar{N}_f^7}{\partial R_f} = \frac{V_d}{nV_x} \left[\sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)^2} \right]$$

$$\frac{\partial \bar{N}_f^7}{\partial V_d} = \frac{1}{nV_x} \left[\sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)} \right]$$

$$\frac{\partial \bar{N}_f^7}{\partial V_x} = -\frac{V_d}{nV_x^2} \left[\sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)} \right]$$

or

$$\begin{aligned} \sigma^2 \bar{N}_f^7 &= \frac{1}{n^2 V_x^2} \left\{ V_d^2 \left[\sum_{i=1}^n \left[\frac{1}{(R_{sf_i} - \bar{R}_f)} \right]^2 \right] \sigma^2 N_{s_i}^3 \right. \\ &+ \sum_{i=1}^n \left[\frac{-N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)^2} \right]^2 \sigma^2 R_{sf_i} \\ &+ \left[\sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)^2} \right]^2 \sigma^2 \bar{R}_f \end{aligned}$$

$$+ \frac{1}{y_x^2} \left[\sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)} \right]^2 \sigma^2 V_x \Bigg]$$

$$+ \left\{ \sum_{i=1}^n \frac{N_{s_i}^3}{(R_{sf_i} - \bar{R}_f)} \right\}^2 \sigma^2 V_d \Bigg\}$$

The variance $\sigma^2 \bar{R}_f$ is obtained from multiple determinations on unspiked samples. The variance $\sigma^2 R_{sf_i}$ is obtained by averaging the values of

$\frac{\sigma^2 R_{sf_i}}{R_{sf_i}}$ determined from multiple scans on several spiked samples and

then assumed to be the same from all samples from a given capsule.

ERROR PROPAGATION FOR Cs-133

The number of Cs-133 atoms present is given by:

$$N_{f_i}^3 = N_{s_i}^7 \bar{R}_f$$

Reported values are the average of several determinations and:

$$\bar{N}_f^3 = \frac{\sum_{i=1}^n N_{f_i}^7 \bar{R}_f}{n}$$

$$\bar{N}_f^3 = \frac{V_d}{nV_x} \left[\sum_{i=1}^n \frac{\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]} \right]$$

The variance of N_f^3 is given approximately by:

$$\begin{aligned} \sigma^2 \bar{N}_f^3 &= \sum_{i=1}^n \left(\frac{\partial \bar{N}_f^3}{\partial R_{sf_i}} \right)^2 \sigma^2 R_{sf_i} + \sum_{i=1}^n \left(\frac{\partial \bar{N}_f^3}{\partial N_{s_i}^3} \right)^2 \sigma^2 N_{s_i}^3 \\ &+ \left(\frac{\partial \bar{N}_f^3}{\partial R_f} \right)^2 \sigma^2 R_f + \left(\frac{\partial \bar{N}_f^3}{\partial V_d} \right)^2 \sigma^2 V_d + \left(\frac{\partial \bar{N}_f^3}{\partial V_x} \right)^2 \sigma^2 V_x \\ &+ (\text{covariance terms}) \end{aligned}$$

The covariance terms are negligible.

and:

$$\frac{\partial \bar{N}_f^3}{\partial R_{sf_i}} = \frac{V_d}{nV_x} \left(\frac{-\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]^2} \right)$$

$$\frac{\partial \bar{N}_f^3}{\partial N_{s_i}^3} = \frac{V_d^2}{nV_x} \left(\frac{\bar{R}_f}{[R_{sf_i} - \bar{R}_f]} \right)$$

$$\frac{\partial \bar{N}_f^3}{\partial R_f} = \frac{V_d}{nV_x} \left[\sum_{i=1}^n \frac{R_{sf_i} N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]^2} \right]$$

$$\frac{\partial \bar{N}_f^3}{\partial V_d} = \frac{1}{nV_x} \left[\sum_{i=1}^n \frac{\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]} \right]$$

$$\frac{\partial \bar{N}_f^3}{\partial V_x} = \frac{-V_d}{nV_x} \left[\sum_{i=1}^n \frac{\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]} \right]$$

and:

$$\begin{aligned} \sigma^2 \bar{N}_f = & \frac{1}{n^2} \left\{ \frac{V_d}{V_x^2} \left(\sum_{i=1}^n \left[\left(\frac{\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]^2} \right)^2 \sigma^2 R_{sf_i} \right] \right. \right. \\ & + \sum_{i=1}^n \left[\left(\frac{\bar{R}_f}{[R_{sf_i} - \bar{R}_f]} \right)^2 \sigma^2 N_{s_i}^3 \right] + \left[\sum_{i=1}^n \left(\frac{R_{sf_i} N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]^2} \right)^2 \sigma^2 \bar{R}_f \right. \\ & + \left. \frac{1}{V_x^2} \left[\sum_{i=1}^n \frac{\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]} \right]^2 \sigma^2 V_x \right) \\ & \left. + \frac{1}{V_x^2} \left[\sum_{i=1}^n \frac{\bar{R}_f N_{s_i}^3}{[R_{sf_i} - \bar{R}_f]} \right]^2 \sigma^2 V_d \right\} \end{aligned}$$

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX II

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

R. M. Abernathey, F. L. Lisman, S. F. Marsh, R. E. McAtee, G. D. Workman
M. E. Kussy

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

PREPARATION OF Zr-90 SPIKE

A 1.6-mg sample of isotopically enriched Zr-90, obtained from ORNL as the oxide, was fused with potassium pyrosulfate.

The melt was dissolved in sulfuric acid and diluted to approximately 1 liter with 6M HCl. Weighed 3-ml aliquots were transferred to glass ampoules which were flame sealed.

CALIBRATION OF Zr-90 SPIKE

The calibration technique was isotope dilution mass spectrometry with natural zirconium as the primary standard. The natural zirconium standard was prepared from high purity zirconium metal. The metal was dissolved with bromine-methanol, then diluted with 6M HCl to an approximate concentration of 3.5 mg Zr/g solution. Five ~ 25-g aliquots were gravimetrically analyzed by mandelate precipitation followed by ignition to the oxide at 1000°C to constant weight. The relative standard deviation of the average was better than 0.2%. Weight aliquots of approximately 1 g of the standardized solution were transferred to glass ampoules which were flame sealed. One 1-g weight aliquot of the standardized solution was diluted 1000-fold on a weight basis with 6M HCl from which eight 1-g weight aliquots were individually combined with eight weight aliquots of the Zr-90 spike solution. The eight mixtures then were analyzed by isotope dilution mass spectrometry. The determined concentration of the Zr-90 "spike" was 6.7642×10^{15} atom/g with a relative standard deviation for the average of 0.40%.

CHEMICAL SEPARATION

1. To a 40-ml centrifuge tube, add the enriched Zr-90 spike, 1 mg of high purity thorium carrier, one drop of 30% H₂O₂, 2 ml of 15.7M HNO₃, and 10 ml of 0.35M HIO₃.
A borosilicate glass centrifuge tube may be used. If only isotopic distribution results are desired, omit the Zr-90 spike.
2. Allow 5 min for thorium iodate to precipitate.
3. Centrifuge and discard the supernatant solution.

4. Dissolve the precipitate in a few drops of 12M HCl , add 1 drop of 30% H_2O_2 , and heat to expel the free iodine.
5. Add 2 ml of 15.7M HNO_3 and heat to destroy the HCl .
6. Add 1 drop of 30% H_2O_2 and 10 ml of 0.35M HIO_3 .
7. Allow 5 min for thorium iodate to precipitate.
8. Centrifuge and discard the supernatant solution.
9. Dissolve the precipitate in a few drops of 12M HCl and add 1 drop of 30% H_2O_2 .
10. Evaporate the sample to dryness.
11. Dissolve the residue in 1 ml of quartz-distilled (QD) 10.6M HCl .
12. Pass the dissolved residue through a small Dowex 1 x 8 (100 to 200 mesh) column.
13. Thoroughly wash the column with QD 10.6M HCl . Discard the washings.
14. Elute the adsorbed zirconium with QD 4M HCl .
15. Evaporate the effluent to approximately 0.1 ml and transfer it to the mass laboratory.

The evolution of free iodine may be tested with moistened starch paper held above the tube.

Fill a 2-ml polyethylene medicine dropper with approximately 1 in. of Dowex 1 x 8 resin. Do not use glassware for the column nor in any subsequent steps. Polypropylene ware is recommended for the subsequent steps.

MASS SPECTROMETRIC ANALYSIS

1. Prepare a triple filament assembly from high purity, 1- x 30-ml rhenium ribbon and vacuum bake it for 1 hr at 4 A at a pressure of 1×10^{-6} torr.
2. Using a new, freshly washed, transfer pipet, transfer the solution from step 15 (previous section) to the sample filaments. Evaporate the solution by passing 1.5 A through the filament.
3. Mount the filament holder on the ion source carriage and insert the carriage in the vacuum lock. Allow about 1-min pumping time at each lock stage.
4. Adjust the center filament current to 3.5 A and the sample filament currents to 2.5 A. Locate the major isotope beam by reference to the mass- vs-DVM (accelerating voltage) curve for the magnetic field in use. Adjust the source voltage divider controls for the maximum beam. Make a rapid voltage scan in both directions to verify the mass identification. Use the electron multiplier. Keep the J2 setting low, the J10 setting maximum and the J4-J5 setting near center. The source may need to be rotated to get J4-J5 centered with the maximum beam.
5. Increase the filament current to obtain a multiplier output current of 3×10^{-9} A. Scan the spectrum magnetically in both directions, recording the sensitivity settings used to give near full-scale peak heights. Obtain 3 charts of $4\frac{1}{2}$ double scans.
6. 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 turnaround in the scans, and take peak

height readings at the intersection of these lines with those connecting the peak tops. Sum the readings for each isotope.

7. Correct for mass discrimination. Because the detected beam is ZrO^+ , corrections must be made for the O^{17} and O^{18} contributions at the $Zr^{(A+1)}$ and $Zr^{(A+2)}$ peaks.

If atom percent of an individual isotope is desired, it is given by:

$$\text{atom \% } Zr^A =$$

$$100 \frac{\sum \text{corr peak heights}^A}{\sum (\sum \text{corr peak heights})}$$

CALCULATIONS

The isotopic distribution of the various zirconium fission product isotopes is obtained from unspiked samples.

To correct for natural zirconium contamination,

let:

A_o = relative atom abundance of Zr-90 to total zirconium in sample.

B_o = relative atom abundance of fission product Zr-90 in total fission product zirconium. (This is obtained by a computer calculation and is less than 1.5%).

C_o = natural abundance of Zr-90.

Z = relative atom abundance of total fission product zirconium to total zirconium in the sample.

X_n = relative atom abundance of natural zirconium to total zirconium in the sample.

Then:

$$A_o - C_o X_n = B_o Z$$

assuming that the zirconium in the sample is composed only of fission product zirconium and natural zirconium.

Then:

$$X_n + Z = 1$$

or

$$Z = 1 - X_n$$

The relative atom abundance of natural zirconium to total zirconium in the unspiked sample is:

$$X_n = \frac{(A_o - B_o)}{(C_o - B_o)}$$

Let B_i = relative atom abundance of a particular fission product zirconium isotope to the total zirconium in the sample.

and:

$$B_i = A_i - C_i X_n$$

The atom ratio of two fission product zirconium isotopes $R_{f(i/j)}$ is:

$$R_{f(i/j)} = \frac{B_i}{B_j}$$

or

$$R_{f(i/j)} = \frac{A_i - C_i X_n}{A_j - C_j X_n}$$

where:

A_i, A_j = relative atom abundance of a particular zirconium isotope, to the total zirconium in the sample.

C_i, C_j = natural atom abundance of the i^{th} or j^{th} zirconium isotope.

To calculate the number of atoms of each fission product zirconium isotope the spiked samples are used.

To calculate the number of fission product zirconium atoms in the sample.

Let:

$R_{sf(i/j)}$ = atom ratio of i^{th} zirconium isotope to the j^{th} zirconium isotope in the spiked fission product sample.

N_s^i = number of "spike" atoms of the i^{th} fission product zirconium isotope in the sample.

N_f^i = number of atoms of the i^{th} fission product zirconium isotope in the sample.

N_n^i = number of atoms of the i^{th} zirconium isotope in the sample due to natural zirconium contamination.

$\bar{R}_{f(i/j)}$ = fission product atom ratio of the i^{th} zirconium isotope to the j^{th} zirconium isotope. (This ratio is an average obtained from several unspiked samples.)

$R_{n(i/j)}$ = ratio of the natural atom abundances of the i^{th} to j^{th} zirconium isotopes.

To calculate the number of fission product Zr-91 atoms in the sample:

$$R_{sf}(91/93) = \frac{N_s^{91} + N_f^{91} + N_n^{91}}{N_f^{93}}$$

or

$$R_{sf}(91/93) = \frac{R_{s(91/93)} N_s^{90} + N_f^{91} + R_{n(91/90)} N_n^{90}}{R_{f(93/91)} N_f^{91}} \quad (1)$$

now

$$R_{sf}(90/93) = \frac{N_s^{90} + N_f^{90} + N_n^{90}}{N_f^{93}}$$

or

$$N_n^{90} = N_f^{93} R_{sf}(90/93) - N_s^{90} - N_f^{90}$$

or

$$N_n^{90} = R_{f(93/91)} N_f^{91} R_{sf}(90/93) - N_s^{90} - R_{f(90/91)} N_f^{91}$$

substituting for N_n^{90} in equation (1) yields:

$$N_f^{91} = \frac{N_s^{90} [R_{s(91/90)} - R_{n(91/90)}]}{[R_{f(93/91)} [R_{sf(91/93)} - R_{n(91/90)} R_{sf(90/93)}] + R_{n(91/90)} R_{f(90/91)} - 1}$$

To calculate the number of fission product atoms of Zr-92, Zr-93, Zr-94, and Zr-96 in the sample:

$$N_f^{92} = \bar{R}_{f(92/91)} N_f^{91}$$

$$N_f^{93} = \bar{R}_{f(93/91)} N_f^{91}$$

$$N_f^{94} = \bar{R}_{f(94/91)} N_f^{91}$$

$$N_f^{96} = \bar{R}_{f(96/91)} N_f^{91}$$

where:

$$N_f^{91} = \text{number of fission product Zr-91 atoms in the sample.}$$