280
6-29-65

IDO-14656

May 1965

MASTER

**BURNUP DETERMINATION OF NUCLEAR FUELS:
1964 ANNUAL REPORT**

Edited By

W. J. Maeck and J. E. Rein

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US 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 USA. PRICE \$2.00. AVAILABLE FROM THE CLEARINGHOUSE FOR FEDERAL
SCIENTIFIC AND TECHNICAL INFORMATION, NATIONAL BUREAU OF STANDARDS
U. S. DEPARTMENT OF COMMERCE, SPRINGFIELD, VIRGINIA

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.

IDO-14656
AEC Research and Development Report
Chemistry
TID-4500 (40th Ed.)
Issued: May 1965

BURNUP DETERMINATION OF NUCLEAR FUELS:
1964 ANNUAL REPORT

Edited By
W. J. Maeck and J. E. Rein

PHILLIPS
PETROLEUM
COMPANY

Atomic Energy Division
Contract AT(10-1)-205
Idaho Operations Office
U. S. ATOMIC ENERGY COMMISSION

BURNUP DETERMINATION OF NUCLEAR FUELS:

1964 ANNUAL REPORT

Edited By

W. J. Maeck and J. E. Rein

Contributing Personnel

Analytical Development Section

F. W. Dykes	K. L. McMillan
R. E. Foster	M. A. Wade
M. E. Kussy	S. S. Yamamura
S. F. Marsh	

Mass Spectrometry Group

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

Nuclear Chemistry Section (MTR)

W. H. Burgus
R. N. Chanda
K. T. Faler

Operations Analysis (Statistics)

F. W. Spraktes

BURNUP DETERMINATION OF NUCLEAR FUELS:

1964 ANNUAL REPORT

Edited By

W. J. Maeck and J. E. Rein

ABSTRACT

This annual report for 1964 describes the status of the project to develop methods for the determination of burnup of nuclear fuels. The major analytical technique being investigated is stable fission product analysis. The preparation of standard burnup and fission yield samples is presented. Chemical separations, the evaluation of several methods for stable fission product analysis, the preparation of standards for mass spectrometric analysis, and the dissolution of fuel samples are discussed.

BURNUP DETERMINATION OF NUCLEAR FUELS:

1964 ANNUAL REPORT

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
SUMMARY	1
INTRODUCTION	2
PREPARATION OF STANDARD BURNUP AND FISSION YIELD SAMPLES	3
EVALUATION OF CHEMICAL SEPARATION METHODS FOR FISSION PRODUCT ANALYSIS	10
<u>Dissolution Behavior of Irradiated Uranium-235 Capsules</u> . .	10
<u>Separation of Cesium-137 and Calculation of Number of Fissions</u>	10
<u>Separation, Analysis, and Fission Yields of Krypton and Xenon</u>	15
Separation and Collection of Krypton and Xenon from Dissolver Off-Gas	15
Gas Chromatographic Analysis of Krypton and Xenon . .	18
Fission Yields of the Stable Isotopes of Krypton and Xenon	20
<u>Separation of Lanthanides</u>	20
<u>Separation of Trivalent Actinides and Lanthanides</u>	25
<u>Separation of Zirconium</u>	25
<u>Separation of Barium and Strontium</u>	27
<u>Separation of Ruthenium</u>	27
<u>Separation of Molybdenum</u>	28
PREPARATION OF STANDARDS FOR MASS SPECTROMETRIC ANALYSIS	29
DISSOLUTION OF FUEL SAMPLES	30

TABLE OF CONTENTS

	<u>Page</u>
<u>Uranium Dioxide-Stainless Steel</u>	30
<u>Plutonium Dioxide-Aluminum</u>	30
MEASUREMENT OF STABLE FISSION PRODUCT NUCLIDE CROSS SECTIONS .	32
PROPOSED DETERMINATION OF NUCLEAR FUEL BURNUP BASED ON THE RATIO OF TWO STABLE FISSION PRODUCTS OF THE SAME ELEMENT . .	33
APPENDIX - A. PROCEDURE FOR THE ANALYSIS OF CESIUM-137 . . .	34
APPENDIX - B. PROCEDURE FOR GAS CHROMATOGRAPHIC SEPARATION AND ANALYSIS OF KRYPTON AND XENON	36
APPENDIX - C. PROCEDURE FOR THE SEPARATION OF NEODYMIUM . . .	40
APPENDIX - D. PROCEDURE FOR THE SEPARATION OF ZIRCONIUM . . .	42

LIST OF TABLES

<u>Table</u>		
I	STANDARD BURNUP CAPSULES: CONTENTS AND IRRADIATION HISTORY.	8,9
II	ATOMS CESIUM-137 IN IRRADIATED URANIUM-235 CAPSULES AND CALCULATED NUMBER OF FISSIONS	14
III	RECOVERY OF KRYPTON AND XENON FROM A SIMULATED DISSOLUTION.	18
IV	URANIUM-235 THERMAL FISSION YIELDS FOR THE STABLE ISOTOPES OF KRYPTON AND XENON	21
V	ISOTOPIC DISTRIBUTION OF THE ISOTOPES OF NEODYMIUM IN THERMALLY IRRADIATED URANIUM-235	24
VI	RELATIVE URANIUM-235 THERMAL FISSION YIELDS OF NEODYMIUM ISOTOPES	24
VII	ISOTOPIC DISTRIBUTION OF THE ISOTOPES OF ZIRCONIUM IN THERMALLY-IRRADIATED URANIUM-235	27
VIII	INTERLABORATORY COMPARISONS OF LANTHANIDE STANDARD SOLUTIONS	29

<u>Figure</u>		<u>Page</u>
1	APPARATUS FOR MIXING OF FISSIONABLE MATERIAL AND ALUMINUM POWDER FOR STANDARD BURNUP CAPSULES	5
2	EXPLODED VIEW OF STANDARD BURNUP CAPSULE AND ASSEMBLY . .	6
3	ASSEMBLED VIEW OF STANDARD BURNUP CAPSULE ASSEMBLY CON- TAINING SIX CAPSULES	7
4	APPARATUS FOR CAPSULE DISSOLUTION AND COLLECTION OF KRYPTON AND XENON	11
5	RELEASE OF KRYPTON AND XENON DURING CAPSULE DISSOLUTION AS A FUNCTION OF DISSOLUTION TIME	17
6	CHROMATOGRAM OF KRYPTON-XENON-NITROGEN MIXTURE	19
7	APPARATUS FOR AUTOMATIC pH-GRADIENT ELUTION FOR CHROMATOGRAPHY.	23
8	APPARATUS FOR THE CHROMATOGRAPHIC ANALYSIS OF KRYPTON AND XENON AND THEIR COLLECTION FOR MASS ISOTOPIC DISTRIBUTION ANALYSIS	39

SUMMARY

The objective of this project is to develop reliable methods for the determination of burnup of nuclear fuels. Fuels of high burnup, mainly power reactor types, are of prime interest. The major analytical technique being investigated is stable fission product analysis.

The reliability of a burnup determination based on the determined abundance of a stable fission product nuclide depends on three main factors; the accuracy of the fission yield value, the buildup and burnout of the particular nuclide during reactor operation, and the reliability of the analysis procedure.

The major effort during the past year has been two-fold; the fabrication and irradiation of standard burnup capsules to provide samples for the accurate determination of fission yields, and the development and evaluation of chemical separation methods for stable fission product analysis.

Capsules containing known amounts of U-233, U-235, Pu-239 and Pu-241 were irradiated in the MTR to various levels of burnup which produced milligram quantities of the stable fission products. The number of fissions will be calculated from accurately-determined pre-irradiation and post-irradiation heavy element concentrations.

Chemical separation methods have been developed for the stable isotopes of krypton, xenon, the lanthanides, barium, strontium, ruthenium, and molybdenum. The analysis technique for the stable fission product nuclides is isotope dilution mass spectrometry. Standards of the lanthanide elements were prepared and the standardization was verified by interlaboratory comparison.

The technique for burnup determination based on an analysis for the total atoms of a fission product requires a complete dissolution of the fuel sample. Methods were developed for the dissolution of UO_2 -stainless steel and the PuO_2 -aluminum samples.

The analysis of the MTR-irradiated capsules for the thermal fission yields of the stable fission products for U-233, U-235, Pu-239, and Pu-241 will start early in 1965 with an expected rapid accumulation of data. Therefore, reports covering this project will in the future be issued on a quarterly basis rather than an annual basis. The first quarterly report will cover the period January 1 through March 31, 1965, and will be issued as an IDO report. Prior annual reports of this program are TID-17385 for 1962 and IDO-14649 for 1963.

INTRODUCTION

In December, 1961, the Division of Reactor Development, USAEC, awarded contracts to the Atomic Energy Division of Phillips Petroleum Company and the Vallecitos Atomic Laboratory of the General Electric Company for a joint project with the objective to develop accurate methods for the determination of burnup of nuclear fuels. The emphasis of this project is on power reactor fuels having long-term reactor residence time and high burnup rather than on short-term, experimental irradiations.

The general trend in power reactor technology is to larger cores, higher temperatures, and higher burnup with burnup levels of 10^5 Mwd/T envisioned. The commonly used method of burnup analysis based on changes in the isotopic distribution of the heavy elements, determined by mass spectrometry, loses effectiveness for power reactor fuels for two major reasons. First, matched pre-irradiation and post-irradiation samples are extremely difficult to obtain and second, at high burnup levels, the calculations are adversely affected by the buildup and burnout of the higher transuranic isotopes. Therefore, the method selected is that based on measuring the atoms of selected fission products and computing the number of fissions from their fission yields. This method has long been used for short-term irradiations because a variety of useful radioactive nuclides are available. Only two radioactive fission products, Cs-137 and Sr-90, have sufficiently long half lives to be considered for power reactor fuels and even then the uncertainties in the in-pile decay corrections become intolerably large. Due to uncertainties in their physical constants such as half life and decay scheme, high precision measurements are not possible. Another detracting feature to their use is their relatively low boiling points and hence migration in the fuels. Many stable products do not have these limitations and are therefore a better choice for burnup monitors.

The degree of reliability obtainable in a burnup determination based on stable fission product analysis depends on two factors; the accuracy of the values used for the fission yields of the selected fission products and the linearity between the number of fissions and the number of atoms of the particular fission product present at the end of the irradiation. The latter requires that the cross section values of the fission products and their parents be small.

Specific goals of this project are the accurate measurement of the fission yields of selected fission product nuclides, the selection of the nuclides to be used as burnup monitors for the various fuel types, and the development of analysis methods for these nuclides.

The best analyses technique for determining the yields of stable fission products is isotope dilution mass spectrometry following their chemical separation. Such methods are being developed, with consideration given to applicability to a wide variety of reactor fuels. The initial emphasis is the thermal fission yields for U-233, U-235, Pu-239, and Pu-241.

PREPARATION OF STANDARD BURNUP AND FISSION YIELD SAMPLES

R. N. Chanda, F. W. Dykes, M. E. Kussy

One specific goal of this project is the preparation of a series of standard samples with accurately known burnup values. Two purposes will be served by these standards. One is to provide accurate fission yields with emphasis on the stable fission products. The other is to evaluate new proposals for the determination of burnup.

Two different techniques, in-pile fission counting and high-burnup capsule irradiations, had been selected at the beginning of the project for the preparation of the standard samples. Solid-state silicon diodes had been selected for use as the detectors in the in-pile counter. Extensive research has now shown that deterioration of these diodes sets in when 10^8 fission fragments have been collected. Calculations show that even with a 10^4 ratio of uranium on the heavy foil (50 mg) to uranium on the lighter foil (5 μ g) the quantities of stable fission product nuclides produced would be insufficient for reliable mass spectrometric measurement. Consequently, the in-pile fission counter as a means of preparing standard burnup samples has been abandoned in favor of the high-burnup capsule irradiation method.

In the high-burnup capsule irradiation method, a known quantity of fissionable material in a welded capsule is irradiated, dissolved, and accurately analyzed both for the heavy elements and the fission products. In the case of highly-enriched U-235, the loss of uranium is equal to the atoms of U-235 fissioned.

A series of irradiation capsules have been prepared containing weighed amounts of the oxides of highly-enriched U-233, U-235, Pu-239, and Pu-241. Because of heat transfer problems, these oxides had to be mixed with high-purity aluminum powder prior to loading into the capsule. The capsules were fabricated from 99.999% pure aluminum.

A weighed amount of the oxide of one of the four isotopes was placed into a tared glass tube (Fig. 1). Approximately 1 g of 99.99% pure aluminum powder was added and the tube was stoppered with the flat-top glass stopper (Fig. 1). The contents were mixed by holding the tube against the rubber bumper of a rapidly-rotating "Vortex Mixer". After mixing, the funnel type stopper (Fig. 1) was placed on the tube and the tube was inverted over the capsule. The stem of the funnel was inserted into the capsule and the contents were transferred to the capsule by tapping the glass tube. After transfer, the glass tube was reweighed to insure that the transfer was complete. The filled capsule then was placed in a vacuum desiccator which was evacuated and filled with helium several times. The aluminum plug was then inserted and fused to the capsule by heli-arc welding in a helium atmosphere.

An exploded view of the capsule and assembly is shown in Fig. 2 and the completed assembly containing six capsules is shown in Fig. 3.

Six assemblies (36 capsules) were fabricated. The contents and irradiation history of the capsules are given in Table I.

The assemblies were irradiated in the A-28 SE position of the MTR. At this point the average unperturbed neutron flux was 0.6×10^{14} n/cm²sec and the cadmium ratio for cobalt was 15.

The purpose of the series of graded exposures is two-fold; to provide multiply samples to increase the validity of the data, and to verify the usefulness of certain nuclides and relationships which have been proposed for burnup monitors as a function of flux and irradiation time.

All these samples have been irradiated and are currently cooling. Dissolution and analysis will start early in 1965.

Figure 1. APPARATUS FOR MIXING OF FISSIONABLE MATERIAL AND ALUMINUM
POWDER FOR STANDARD BURNUP CAPSULES

Figure 2. EXPLODED VIEW OF STANDARD BURNUP CAPSULE AND ASSEMBLY

Figure 3. ASSEMBLED VIEW OF STANDARD BURNUP CAPSULE ASSEMBLY CONTAINING SIX CAPSULES

Table I. STANDARD BURNUP CAPSULES: CONTENTS AND IRRADIATION HISTORY

Assembly	Capsule	Fissionable Isotope	mg Fuel Weighed into Capsule	Weighed Form	% Major Isotope(a)	Accumulated nvt x 10 ²⁰	MTR Cycles	Estimated Mwd	Discharge Date
CPP-6-2	1	U-235	53.5	U ₃ O ₈	99.22	5.8	8	4994	8-30-64
	2	U-235	61.4	"	99.22				
	3	U-233	66.1	"	99.92				
	4	U-233	58.8	"	99.92				
	5	Pu-239	49.1	PuO ₂	99.18				
	6	Pu-239	56.4	PuO ₂	99.18				
CPP-6-3	1	U-235	106.6	U ₃ O ₈	99.22	0.7	1	527	4-6-64
	2	U-235	98.2	"	99.22				
	3	U-233	139.4	"	99.92				
	4	U-233	136.3	"	99.92				
	5	Pu-239	99.6	PuO ₂	99.18				
	6	Pu-239	89.6	PuO ₂	99.18				
CPP-6-4	1	U-235	115.2	U ₃ C ₈	99.22	2.4	3	1848	6-8-64
	2	U-233	152.1	"	99.92				
	3	U-233	126.5	"	99.92				
	4	Pu-239	93.2	PuC ₂	99.18				
	5	Pu-239	77.2	PuC ₂	99.18				
	6	Pu-241	77.1	PuC ₂	95.46				
CPP-6-5	1	U-233	144.4	U ₃ C ₈	99.92	1.7	2	1290	7-20-64
	2	U-235	109.6	"	99.22				
	3	U-235	121.8	"	99.22				
	4	Pu-239	97.9	PuC ₂	99.18				
	5	Pu-239	95.2	"	99.18				
	6	Pu-241	76.0	"	95.46				

Table I. STANDARD BURNUP CAPSULES: CONTENTS AND IRRADIATION HISTORY (Continued)

<u>Assembly</u>	<u>Capsule</u>	<u>Fissionable Isotope</u>	<u>mg Fuel Weighed into Capsule</u>	<u>Weighed Form</u>	<u>% Major Isotope(a)</u>	<u>Accumulated nvt x 10²⁰</u>	<u>MTR Cycles</u>	<u>Estimated Mwd</u>	<u>Discharge Date</u>
CPP-6-6	1	U-235	84.8	U ₃ O ₈	99.22	2.4	3	1908	9-15-64
	2	U-235	82.0	"	99.22				
	3	U-233	92.8	"	99.92				
	4	Pu-239	92.8	PuO ₂	99.18				
	5	Pu-241	59.9	"	95.46				
	6	Pu-241	53.7	"	95.46				
CPP-6-7	1	U-235	82.2	U ₃ O ₈	99.22	0.6	1	589	9 15-64
	2	U-235	84.1	"	99.22				
	3	U-233	91.7	"	99.92				
	4	U-233	88.0	"	99.92				
	5	Pu-239	85.8	PuO ₂	99.18				
	6	Pu-239	83.0	PuO ₂	99.18				

(a) Isotopic composition supplied by ORNL:

<u>Isotope</u>	<u>ORNL Batch No.</u>	<u>U-233</u>	<u>U-234</u>	<u>U-235</u>	<u>U-236</u>	<u>U-238</u>
U-233	UP-91-2	99.92	< 0.02	< 0.02	< 0.02	0.06
U-235	235-F2S-22(K)	0	0.415	99.22	0.044	0.321
		<u>Pu-239</u>	<u>Pu-240</u>	<u>Pu-241</u>	<u>Pu-242</u>	
Pu-239	P-5-49	99.18	0.81	0.01	< 0.01	
Pu-241	Pu-241-102-B	0.81	2.89	95.46	0.84	

Date of assay for Pu-241 was not supplied.

EVALUATION OF CHEMICAL SEPARATION METHODS FOR FISSION PRODUCT ANALYSIS

Eighteen months prior to the standard burnup capsules described above, two similar capsules containing U-235-enriched U_3O_8 had been prepared and irradiated. The purpose was to provide trial samples to evaluate dissolver equipment, dissolution behavior, and separation and analysis methods. These high-purity aluminum capsules, containing approximately 115 mg of U_3O_8 , had been irradiated at a flux of 7.4×10^{13} n/cm²sec for three cycles ($nvt = 2.5 \times 10^{20}$) in the MTR.

Dissolution Behavior of Irradiated Uranium-235 Capsules, R. E. Foster, S. F. Marsh

From previous dissolution experiments, an acid mixture of 6M HCl-1.6M HNO_3 was selected on the basis of complete solubility and stability of the fission products and a satisfactory dissolution rate. The dissolutions were carried out in a 4-inch lead shielded facility. A sketch of the dissolution apparatus is shown in Fig. 4.

A water-cooled reflux condenser reduced the loss of acid and volatile fission products, except krypton and xenon. During dissolution, the krypton and xenon were continuously swept from the system with helium and were collected for subsequent analysis.

The dissolution proceeded smoothly and was complete in about 5 hr. Based on visual observation, approximately 2.5 hr were required to dissolve the cladding and 1.5 hr to dissolve the U_3O_8 . The dissolution process was continued for an additional hour to insure complete dissolution and removal of all the krypton and xenon. The final solution (about 350 ml) was water clear and contained no residue.

After cooling, the dissolver solution was transferred to a 500-ml class "A" volumetric flask. The dissolver flask was washed several times with 6M HCl-1.6M HNO_3 and the washes were transferred to the volumetric flask. The same acid mixture was added to the volumetric flask just short of the mark. The solution was cooled and diluted to volume with water. A Teflon-coated stirring bar was admitted and the contents were stirred for 1 hr.

Separation of Cesium-137 and Calculation of Number of Fissions, M. E. Kussy

Cesium-137 was separated from aliquots of the dissolver solutions by a cesium perchlorate method (Appendix A). The number of Cs-137 atoms was determined by two different gamma counting techniques. The first was based on using a 3 x 3 in. NaI(Tl) crystal as the standard with the crystal parameters taken from Heath(1). The comparison technique was

(1) Heath, R. L., Scintillation Spectrometry Gamma Ray Spectrum Catalogue, 2nd Ed., Vol. 1 of 2, IDO-16880 (1964).

1. 1500 - ml quartz 3-NECK DISSOLUTION FLASK WITH HEATING MANTLE.	6.-7. GAMMA MONITOR AND RECORDER
2. QUARTZ SPIRAL REFLUX CONDENSER.	8. CuO IN QUARTZ TUBE AT 550°C.
3. DRY POLYETHYLENE BEAD SURGE TRAP.	9. WATER - COLLECTION TRAP
4. DRY MIXTURE, ASCARITE-DRIERITE TRAP.	10. Ti SPONGE IN STAINLESS STEEL AT 850°C.
5. CHARCOAL IN COPPER U-TUBE AT 175°C.	11. MOLECULAR SIEVE 5A AT -190°C
	12. OUTLET FLOWMETER AND VENT.

Figure 4. APPARATUS FOR CAPSULE DISSOLUTION AND COLLECTION OF KRYPTON AND XENON

the second used. The area under the 661-kev Cs-137 peak, after correction for Cs-134, was compared to that of a certified standard sample of Cs-137. The certified standard (RS-137-ASTM-Nuclear Chicago Corp.) contained 1.72×10^{14} atoms (reliability = $\pm 3\%$) of Cs-137 per ml on Aug. 8, 1962. The results between these two techniques agreed within 3%. The number of Cs-137 atoms determined for each of the two capsules is given in Table II. Each value is the average of six analyses.

The number of fissions in each capsule was obtained by dividing the number of Cs-137 atoms by the U-235 thermal fission yield value of Cs-137. The fission yield value used was $0.0622 \pm 0.0014(2)$.

A sample calculation of the number of Cs-137 atoms and the error propagation follows.

Constants for Cs-137 Counting

$$\begin{aligned}
 \text{Source} &= 3/4\text{-in. disk} \\
 \text{Distance} &= 10 \text{ cm} \\
 T &= \text{detector efficiency} = 0.02012 \\
 P &= \text{photopeak efficiency} = 0.536 \\
 A &= \text{absorber (1.18 mg/cm}^2 \text{ Be)} = 0.934 \\
 q &= r's/dis = 0.826 \text{ (estimated std dev} = 1.0\%) \\
 \frac{1}{\text{TPAq}} &= 120.2 \pm 2.2 (1.8\%) \\
 t_{1/2} &= 30.0 \text{ yr (estimated std dev} = 2.0\%)
 \end{aligned}
 \left. \begin{array}{l} T \\ P \\ A \end{array} \right\} \text{Estimated std dev} = 1.5\%$$

Sample Calculation and Error Propagation (Capsule A)

3 x 3 in. NaI(Tl) Crystal as the Standard

cpm under 661-kev photopeak (corrected for chemical yield)

Replicate	1	12,909
	2	12,682
	3	12,582
	4	12,824
	5	12,648
	6	<u>12,595</u>

$$\bar{X}_6 = 12,707$$

$$\sigma_i = 132 (1.04\%)$$

$$\sigma_{\bar{X}} = \sigma_i / \sqrt{6} = 54 (0.42\%)$$

- (2) Maeck, W. J., Rein, J. E., Editors, Burnup Determination of Nuclear Fuels: Project Report for the Quarter January 1-March 31, 1965, IDO-14660 (to be published).

cpm Cs-137 per sample aliquot corrected for 1.583-yr decay

$$= \frac{12,707 \pm 54}{e^{-\frac{0.693(1.583)}{30 \pm 1}}} = 13,180 \pm 57 \text{ (0.43\%)}$$

dpm Cs-137 per sample aliquot

$$= (13,180 \pm 57)(120.2 \pm 2.2) = (1.584 \pm 0.029) \times 10^6 \text{ (1.85\%)}$$

Atom Cs-137 per sample aliquot

$$= \frac{(1.584 \pm 0.029) \times 10^6}{(0.693)} = (3.604 \pm 0.127) \times 10^{13} \text{ (3.53\%)}$$
$$\frac{(30 \pm 1)(5.256 \times 10^5)}{(30 \pm 1)(5.256 \times 10^5)}$$

Atom Cs-137 per capsule

error of dilution factor (4×10^4) with calibrated glassware
considered negligible

$$= (4 \times 10^4)(3.604 \pm 0.127)(10^{13}) = (1.442 \pm 0.050) \times 10^{18} \text{ (3.5\%)}$$

Comparison Technique

Seven 0.100-ml aliquots of the RS-137-ASTM standard were counted on October 26, 1964 (analysis time of samples). The cpm per 0.100 ml under 661-kev photopeak

$$= 6180 \pm 30 \text{ (0.48\%)}$$

Atoms Cs-137 per 0.100 ml of RS-137-ASTM standard on August 8, 1962,

$$= (1.72 \pm 0.05) \times 10^{13} \text{ (3\%)}$$

Atoms Cs-137 per 0.100 ml of RS-137-ASTM standard corrected to October 26, 1964 (analysis time of samples).

$$= (e^{-\frac{0.693(2.217)}{30 \pm 1}})(1.72 \pm 0.05) \times 10^{13}$$

$$= (1.63 \pm 0.05) \times 10^{13} \text{ (3.1\%)}$$

cpm Cs-137 per sample aliquot

$$= 12,707 \pm 54 \text{ (0.42\%)}$$

Ratio of sample activity to standard activity

$$= \frac{12,707 \pm 54}{6,180 \pm 30} = 2.056 \pm 0.0013 \text{ (0.64\%)}$$

Atoms Cs-137 per sample aliquot

$$\begin{aligned} &= (2.056 \pm 0.0013)(1.63 \pm 0.05) \times 10^{13} \\ &= (3.35 \pm 0.11) \times 10^{13} \quad (3.2\%) \end{aligned}$$

Atoms Cs-137 per sample aliquot corrected for 1.583-yr decay

$$\begin{aligned} &= \frac{(3.35 \pm 0.11) \times 10^{13}}{e^{-\frac{0.693(1.583)}{30+1}}} = (3.47 \pm 0.11) \times 10^{13} \quad (3.2\%) \end{aligned}$$

Atoms Cs-137 per capsule

error of dilution factor (4×10^4) with calibrated glassware considered negligible

$$= (4 \times 10^4)(3.47 \pm 0.11) \times 10^{13} = (1.39 \pm 0.04) \times 10^{18} \quad (3.2\%)$$

Table II. ATOMS Cs-137 IN IRRADIATED U-235 CAPSULES
AND CALCULATED NUMBER OF FISSIONS

	Capsule A	Capsule B
Atoms Cs-137 Using Crystal as Standard	$(1.442 \pm 0.050) \times 10^{18} \quad (3.5\%)$	$(1.605 \pm 0.058) \times 10^{18} \quad (3.6\%)$
Atoms Cs-137 by Comparison Technique	$(1.39 \pm 0.04) \times 10^{18} \quad (3.2\%)$	$(1.56 \pm 0.05) \times 10^{18} \quad (3.2\%)$
Atoms Cs-137 Pooled from Both Methods	$(1.416 \pm 0.03) \times 10^{18} \quad (2.4\%)$	$(1.58 \pm 0.04) \times 10^{18} \quad (2.4\%)$
Number of Fissions	$(2.27 \pm 0.08) \times 10^{19} \quad (3.5\%)$	$(2.54 \pm 0.09) \times 10^{19} \quad (3.5\%)$

The uncertainty of 3.5% for the gamma spectrometric determination of the atoms of Cs-137 is, we believe, the best that can be expected by this technique with the present knowledge of the nuclear constants for this nuclide and for the sodium iodide crystal constants.

The separation procedure initially used for the Cs-137 was that recommended by ASTM(3). The procedure produced erratic results which were traced to coprecipitation of sodium perchlorate with resultant high yields.

- (3) ASTM Designation E 198-62T, Tentative Method for Radiochemical Determination of Cesium-137 in Aqueous Solutions, ASTM, Philadelphia, 1962.

Recommended modifications are: (a) reduce the amount of sodium hydroxide added for the subsequent removal of ammonia to two drops of 6M NaOH, (b) reduce the volume for the volatilization of the ammonia to a final 2 ml, and (c) agitate-wash the second (final) cesium perchlorate precipitate with 20 ml of ethanol in an ultrasonic mixer. The details of the Cs-137 procedure used in this work are given in Appendix A.

The number of fissions, based on the Cs-137 analysis for the two preliminary capsules; was used to calculate the fission yields of the stable isotopes of krypton and xenon reported in the next section.

Separation, Analysis, and Fission Yields of Krypton and Xenon, R. E. Foster, L. L. Dickerson

The stable isotopes of krypton and xenon comprise a major fraction of the total isotopes formed in fission and an accurate measurement of their yields is essential. In addition, this laboratory has suggested a new proposal for the determination of burnup⁽⁴⁾ based upon a ratio measurement of the stable isotopes of krypton and xenon which requires accurate fission yield data for a critical evaluation.

The development of a method for the analysis of fission product krypton and xenon to obtain fission yields required two studies. One was the separation and collection of krypton and xenon from the dissolver off-gas. The other was the development of a gas chromatographic method for the determination of the total amounts of each element followed by a mass spectrometric analysis for the isotopic composition.

Separation and Collection of Krypton and Xenon from Dissolver Off-Gas

The apparatus shown in Fig. 4 gave complete recovery of the krypton and xenon from the dissolver off-gas and a sample of adequate purity for analysis by gas chromatography and mass spectrometry.

Helium carrier gas was introduced into the dissolver flask at a rate of 50-100 cc/min to sweep the off-gas through the collection train. The dry polyethylene-bead trap served to remove any spray carried past the condenser and the Ascarite-Drierite mixture removed NO₂, water vapor, and > 99% of the iodine. The small remainder of iodine was removed on the 175°C charcoal bed at which temperature neither krypton nor xenon was adsorbed.

-
- (4) Maeck, W. J., Proposed Determination of Nuclear Fuel Burnup Report Based on the Ratio of Two Stable Fission Products of the Same Element, IDO-14642 (1965). Also presented at the Eighth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct., 1964.

The gamma-monitoring device established when the fission gases were first released from the capsule and when they had completely passed through the system. The concentration of Kr-85 was sufficient to give a signal several hundred times above background when passed through the 2 x 2 in. NaI(Tl) flow-through scintillation crystal. The detector output was recorded on a strip-chart recorder.

Hydrogen and any organic vapors present in the off-gas were converted to water vapor as the gases flowed over the heated, 550°C, bed of copper oxide. Approximately 2 ml of water were collected in the bulb at the outlet of the copper oxide chamber. The most stable oxide of nitrogen, N₂O, had to be removed from the off-gas. Otherwise it would have collected with the krypton and xenon and interfered with their gas chromatographic determination. The best means of reducing the N₂O level was found to be to pass the gas over a heated, 850°C, bed of titanium metal sponge. Complete catalytic thermal reduction of the N₂O was obtained.

At this point in the collection train, the only gas components remaining were helium, nitrogen, krypton, and xenon. The krypton and xenon were completely adsorbed on the Molecular Sieve trap maintained at -190°C. Helium and nitrogen also were adsorbed at this temperature.

Several hours of dissolution time were required before the krypton and xenon appeared in the off-gas. As the cladding dissolved, small amounts of these two gases were released. They were rapidly released when the cladding completely dissolved and vigorous dissolution of the U₃O₈ was started. Following this rapid release, the rate slowed but continued for nearly an hour after the dissolution was visually complete. The rate of release of the krypton and xenon as a function of dissolution time is shown in Fig. 5.

To decrease the amount of nitrogen adsorbed on the Molecular Sieve trap, the off-gas was vented through a by-pass valve until the first appearance of the fission gases indicated by the gamma monitor. The krypton and xenon were released together with no apparent segregation as determined by monitoring the crystal output with a multichannel analyzer.

The effectiveness of the collection train was evaluated by dissolving unirradiated aluminum capsules with known amounts of krypton and xenon spiked into the dissolution flask. Complete recovery was obtained compared to standards introduced directly into the gas chromatograph (Table III).

Figure 5. RELEASE OF KRYPTON AND XENON DURING CAPSULE DISSOLUTION AS A FUNCTION OF DISSOLUTION TIME

Table III. RECOVERY OF KRYPTON AND XENON FROM A SIMULATED DISSOLUTION

	DIRECT STANDARD		STANDARD THROUGH DISSOLUTION	
	Integrator Counts/cc		Integrator Counts/cc	
	<u>Kr</u>	<u>Xe</u>	<u>Kr</u>	<u>Xe</u>
$\bar{X}$	21,783	27,509	21,761	27,179
σ	371	562	269	473
n	8	8	6	6
% Recovery $\pm$ std dev = 99.9 $\pm$ 2.1(Kr); 98.9 $\pm$ 2.7(Xe)				
Statistical "t" test for Kr = 0.12(t_{12df}^{95} = 2.2)				
Statistical "t" test for Xe = 1.2(t_{12df}^{95} = 2.2)				

Gas Chromatographic Analysis of Krypton and Xenon

As previously stated, the krypton and xenon collected on the Molecular Sieve trap were determined by gas chromatography. The trap was connected to a manifold which was in turn connected to a Model 500, F and M gas chromatograph. The trap was heated to at least 150°C and the gases were flashed onto a 5-ft charcoal column. With temperature programming, the krypton was eluted from the column at 60°C and the xenon at 150°C with a flow rate of helium carrier gas of 95 cc/min. The absolute volumes, in std cc, of krypton and xenon were determined by comparing peak areas to standards analyzed just prior to and after the analysis of the sample. A typical chromatogram of a mixture of krypton, xenon, and nitrogen is shown in Fig. 6. A diagram of the chromatographic analysis apparatus and a detailed procedure for the chromatographic separation and analysis of krypton and xenon is given in Appendix B.

The response for krypton and xenon was linear over the range of 0.052 to 0.24 std cc of krypton and 0.19 to 1.18 std cc of xenon. The standard deviations of the slopes of the least squares fit for xenon and krypton were 1.9% and 2.2% respectively.

The krypton and xenon, upon exit from the chromatographic column, were trapped in tubes of charcoal at -80°C. The krypton and xenon were then analyzed for isotopic composition in a Consolidated gas mass spectrometer.

Figure 6. CHROMATOGRAM OF KRYPTON-XENON-NITROGEN MIXTURE

Fission Yields of the Stable Isotopes of Krypton and Xenon

The computed fission yields of the stable isotopes of krypton and xenon for the thermal fission of U-235 from the two experimental capsules are presented in Table IV. These yields are relative to the fission yield, 6.22% of Cs-137.

The experimentally determined isotopic composition of krypton was corrected for the decay of Kr-85. The corrections for capture on Kr-83 and Xe-131, which amounted to less than 3%, were based on computer data which simulated the irradiation with respect to the buildup and burnout of the individual isotopes of krypton and xenon.

Separation of Lanthanides, S. F. Marsh

The lanthanide fission product elements, which comprise about one-half of the isotopes in the heavy mass peak, are separated as a group from the dissolved fuel solution and then are individually separated by cation exchange with α -hydroxyisobutyric acid, at controlled pH, as the elutriant(6).

Another technique commonly used for the individual separation of the lanthanides is reversed phase partition chromatography at an elevated temperature. Our experience is that the cation exchange technique has advantages of higher capacity and room temperature operation. The major advantage of the reversed phase column technique is that the lower lanthanides are eluted first so that neodymium is obtained in an early fraction. This is not an advantage when heavier lanthanides are also sought. The over-all procedure described below, including both the group separation of the lanthanides and the individual separation of neodymium, requires only 4 hours, 2.5 hours of which is required for the individual cation exchange separation.

In our procedure, the first step in the group separation is a double precipitation of the lanthanide hydroxides (carried on 1 mg of high-purity lanthanum) from 6M NaOH containing sodium hypochlorite. Aluminum remains in solution as aluminate and ruthenium is oxidized to a soluble species. The hydroxide precipitate is dissolved in dilute nitric acid and transferred to a column of silver periodate (80-120 mesh). The trivalent lanthanides pass through while cerium, zirconium, most of the remaining ruthenium, and plutonium remain on the column. The trivalent lanthanides, now essentially free of other activity, are precipitated with ammonium hydroxide, dissolved in dilute hydrochloric acid, and transferred to the cation exchange column for their chromatographic separation. This procedure is detailed in Appendix C.

(6) Smith, L., Hoffman, D. C., J. Inorg. Nucl. Chem. 3, 243 (1956).

Table IV. U-235 THERMAL FISSION YIELDS FOR THE STABLE
ISOTOPES OF KRYPTON AND XENON

Experimental Data			Fission Yields			
	Capsule A	Capsule B	Isotope	Capsule A	Capsule B	Literature(5)
Std cc Kr	0.0303	0.0357	Kr-83	0.51	0.53	0.54
Std cc Xe	0.225	0.264	Kr-84	0.97	1.01	1.00
Isotopic Composition	Atom %	Atom %	Kr-85	0.27	0.29	0.29
Kr-83	13.96	13.92	Kr-86	1.88	1.98	2.02
Kr-84	26.70	26.57	Xe-131	2.93	3.04	2.93
Kr-85	7.52	7.54	Xe-132	4.40	4.58	4.38
Kr-86	51.82	51.97	Xe-134	7.92	8.27	8.06
Xe-131	10.88	10.79	Xe-136	-	-	-
Xe-132	16.36	16.25				
Xe-134	29.45	29.35				
Xe-136(a)	43.31	43.61				
No. of Fissions						
Based on Cs-137 $(2.27 \pm 0.08) \times 10^{19}$ $(2.54 \pm 0.09) \times 10^{19}$						

(a) Includes that fraction of Xe-135 which
captured to Xe-136.

(5) Katcoff, S., Nucleonics 18, No. 11, 201 (1960).

The cation exchange separation of the individual lanthanides has been automated. The column effluent is monitored by a flow-through type NaI(Tl) scintillation crystal. The exact position of most of the fission product lanthanides are identifiable by their own activity or that of their immediate neighbors. This technique of gamma monitoring the chromatographic ion-exchange column effluent has proven satisfactory for separating neodymium from even several-year cooled samples. Sufficient Pm-147 and Pr-144 activity is monitored to identify the position of the stable neodymium fraction which falls between them.

A photocell-actuated drop counter has been fabricated and coupled to a commercial fraction collector. The fraction collector was modified to increase the capacity from 60 to 90 individual fractions.

Near-optimum eluting conditions for neodymium have been established for the 0.5M α -hydroxyisobutyric acid-Dowex 50-X⁴ cation exchange column approach. The previously-used continuous pH-gradient elution technique has been replaced by two portions of elutrient; 10 ml of pH 3.50 followed by 15 ml of pH 3.90. A coil of tubing, which connects the reservoir and the column, permits initial loading of both portions with no intermixing.

For the individual separation of all lanthanides, the pH-gradient approach is necessary. An apparatus has been designed and successfully tested which automatically provides a continuously-varying pH elutrient. As shown in Fig. 7, it consists of two flasks, each with a stopcock, and with magnetic stirring in the lower flask. As the elutrient drains from the lower flask, the higher pH solution from the upper flask replaces it to provide the continuously-increasing pH. With an arrangement such as this, the pH can be changed either up or down and at any desired rate by controlling the pH of the two elutriants and their respective volumes.

Modifications were investigated to improve the separation of the individual lanthanides. Amberlite 200, a "macroreticular" high-porosity cation resin, was evaluated as a substitute for Dowex 50 and pyridine- α -hydroxyisobutyrate was investigated as an elutrient. Neither improved the original procedure.

The procedure (detailed in Appendix C) was evaluated with three samples of the dissolved U-235 capsules. Each sample contained ~ 3 μ g of neodymium and the separated neodymium fractions were mass analyzed for isotopic distribution. Although untreated Analytical Reagent grade chemicals were used, the level of natural neodymium contamination was found to be minor (Table V). The shielded Nd-142 isotope, with a natural abundance of 27.11%, accounts for less than 0.15% of the separated fission product neodymium. With zero natural contamination, the expected level is ~0.01%.

Figure 7. APPARATUS FOR AUTOMATIC pH-GRADIENT ELUTION FOR CHROMATOGRAPHY

Table V. ISOTOPIC DISTRIBUTION OF THE ISOTOPES OF NEODYMIUM IN
THERMALLY IRRADIATED U-235

Sample	Neodymium Isotope, Atom % (a)						
	142	143	144	145	146	148	150
1	0.14	30.02	22.49	19.96	15.39	8.71	3.31
2	0.11	30.11	22.45	19.98	15.37	8.68	3.30
3	0.13	30.11	22.59	20.03	15.38	8.45	3.32
$\bar{X}$	0.13	30.08	22.51	19.99	15.38	8.61	3.31
σ_1	0.016	0.052	0.072	0.036	0.032	0.140	0.010
$\sigma_{\bar{x}}$	0.009	0.030	0.042	0.021	0.018	0.081	0.058

(a) Mass analyses by R. E. McAtee and G. D. Workman

The U-235 thermal fission yields for Nd-143, Nd-144, Nd-145, Nd-146, and Nd-150 were calculated relative to Nd-148 for both capsules (Table VI). The mass-spectrometrically measured isotope distribution was corrected for traces of natural neodymium contamination by the amount of Nd-142 present in excess of 0.01%. Corrections for the thermal neutron capture on Nd-143, Nd-144, Nd-146, and Nd-148 were made, based on a computer program which simulated the irradiation. These corrections were 1.5% or less. A correction also was made for the holdup in the 144-chain due to 285-day Ce-144.

A comparison of the relative fission yields from these data to an independent foil irradiation and analysis by the G. E. Vallecitos Laboratory and to literature data is included in Table VI. The agreement is excellent.

Table VI. RELATIVE U-235 THERMAL FISSION YIELDS OF NEODYMIUM ISOTOPES

Isotope	Phillips	G. E. Vallecitos(7)	Literature(8)
143	3.515±0.023	3.571±0.029	3.53
144	3.136±0.018	3.194±0.029	3.29
145	2.331±0.017	2.330±0.019	2.33
146	1.758±0.010	1.758±0.014	1.79
148	1.000	1.000	1.00
150	0.380±0.002	0.382±0.006	0.391

(7) Rider, B. F., Ruiz, C. P., Peterson, J. P., Smith, F. R., Accurate Nuclear Fuel Burnup Analyses, Eleventh Quarterly Progress Report, GEAP-4716 (1964).

(8) Katcoff, S., Nucleonics 18, No. 11, 201 (1960).

Another technique being evaluated for the group separation of the lanthanides from gross fission product mixtures is the Talspeak process(9). The main advantage is that the lanthanides are separated both from the trivalent actinides and gross fission products which makes it attractive for plutonium fuels. Further information is presented in the next section.

Separation of Trivalent Actinides and Lanthanides, S. F. Marsh

When the method described in the preceding section is used for samples containing transplutonium elements (such as irradiated plutonium), the trivalent actinides (especially americium and curium) accompany the lower lanthanides. This constitutes a serious biological hazard, especially to the mass laboratory personnel.

The Talspeak process(9) was evaluated for the separation of lanthanides from the trivalent actinides as well as from gross fission products.

Chromosorb-P(acid washed and ignited at 700°C for 18 hours) was saturated with 0.3M di-2-ethylhexylphosphoric acid (D2EHP) in diisopropyl benzene. The resulting material was air-dried for use in a reversed-phase partition chromatography column.

A sample containing gross fission products and Am-241 was evaporated, taken up in 1M glycine·HNO₃-0.05M diethylenetriaminepentaacetic acid (DTPA), and passed through the column. Most of the non-lanthanide fission products and 99.5% of the americium were eluted in six column volumes of 1M glycine·HNO₃-0.05M DTPA. The lanthanides then were eluted, nearly free of extraneous activity, with two column volumes of 2M HNO₃. Curium is expected to behave similarly to americium.

The procedure is rapid and promising for use prior to the α-hydroxy-isobutyric acid cation exchange column separation of the individual lanthanides.

Separation of Zirconium, S. F. Marsh

In most zirconium analyses, a pretreatment is required to insure conversion of all sample and carrier atoms to the same chemical form. However, in the dissolution of the irradiated U-235 capsules

-
- (9) Weaver, B., Kappelman, F. A., Talspeak: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacidic Organophosphate or Phosphonate, ORNL-3559(1964).

described above, the dissolution conditions were sufficiently acid that polymerization of zirconium was unlikely and pretreatment was not considered necessary.

Omission of the pretreatment so simplifies subsequent chemistry that it was likely that a batch extraction separation would give a product sufficiently pure for mass spectrometric analysis. The 2-thenoyltrifluoroacetone (TTA) extraction procedure (10), while satisfactory for radiochemical analysis, resulted in large amounts of solids which hindered the mass spectrometric analysis. Attempts to separate zirconium from these solids by anion exchange were unsuccessful. TTA and two other extractants, dibutylphosphate (DBP) and Primene-JMT, which are known to extract zirconium, were evaluated by reversed-phase chromatography. Fluoropak was used as the inert support. The TTA column was unsuitable because of poor packing characteristics. Primene-JMT gave a low yield and a product contaminated with other fission products. The DBP column was satisfactory with respect to zirconium retention and decontamination from other fission products; however, the zirconium was not elutable without also eluting the DBP. The DBP interfered with mass spectrometry.

Another carrier-free separation method for zirconium, coprecipitation with thorium iodate(11), was evaluated. The thorium iodate precipitate was washed with $2M\ HNO_3$ - $0.04M\ HIO_3$, dissolved in a concentrated hydrochloric acid-hydrogen peroxide mixture, and passed through an anion exchange column in the concentrated hydrochloric acid form. The column was washed with concentrated hydrochloric acid and the adsorbed zirconium was eluted with $4M\ HCl$.

An aliquot of the dissolved U-235 capsule solution was processed through the iodate procedure and was mass spectrometrically analyzed. The theoretical isotopic composition of zirconium in 20.7-month cooled fission products was calculated from the fission yield compilation of Katcoff(12). Because Zr-90 is partially shielded by 28-year Sr-90 and its natural abundance is 51.5%, it serves as a sensitive indicator for natural zirconium contamination. The total amount of natural contamination in the sample analyzed was 3 atom %. This is believed to have been introduced as an impurity in the thorium carrier.

-
- (10) Moore, F. L., Anal. Chem. 28, 997 (1956).
- (11) Ballou, N. E., Radiochemical Studies: The Fission Products, Coryell, C. D., Sugarman, N., Eds., NNES, Vol. 9, paper 249, McGraw-Hill, New York, 1951.
- (12) Katcoff, S., Nucleonics 18, No. 11, 201(1960). (Corrected for holdup of Sr-90).

The mass spectrometric data were corrected for this level of natural contamination and the results agreed closely with the expected data (Table VII). Eight additional zirconium-separated fractions, in which the thorium carrier used was of high purity, have been submitted for mass analysis. The procedure appears satisfactory with regard to speed, simplicity, specificity, natural contamination, and mass analysis compatibility.

The detailed procedure is given in Appendix D.

Table VII. ISOTOPIC DISTRIBUTION OF THE ISOTOPES OF ZIRCONIUM IN THERMALLY IRRADIATED U-235(a)

	<u>Actual Atom %</u>	<u>Corrected Atom %</u>	<u>Literature Atom %</u>
Zr-90	2.41	0.78	0.78
Zr-91	18.44	18.68	18.66
Zr-92	19.08	19.14	19.27
Zr-93	19.86	20.52	20.61
Zr-94	20.54	20.64	20.45
Zr-96	19.69	20.25	20.23

(a) Mass analyses by R. M. Abernathey, R. E. McAtee and G. D. Workman.

Separation of Barium and Strontium, S. F. Marsh, R. A. Nielsen

Preliminary experiments have shown that barium and strontium need not be separated prior to mass spectrometric analysis and that both may be determined from the same filament loading. This resulted in simplifying the chemistry to an alkaline earth group separation.

The two elements were homogeneously coprecipitated as the sulfate with 5 mg of high-purity lead by controlled hydrolysis of dimethyl sulfate. After dissolving the precipitate in dilute nitric acid, fuming nitric acid was added to precipitate the nitrate salts. Finally, lead was eluted as the EDTA complex on a cation exchange column at pH 4.0 while barium and strontium were retained on the column. The column was washed with water and the alkaline earths were eluted with 5M HCl. Separation from all other fission products appeared satisfactory. Due to contamination of presently available filament material with the alkaline earths, mass evaluation has not been possible.

Separation of Ruthenium, S. F. Marsh

Two techniques, distillation and solvent extraction, were investigated for the carrier-free separation of ruthenium from fission product mixtures.

The experience of this and other laboratories indicates that a drastic pretreatment of fission product ruthenium is necessary to insure complete dissociation of the highly-stable nitrate and nitrosyl complexes of ruthenium and to insure exchange between the fission product ruthenium and the isotopic spike. For these reasons, RuO_4 was selected as the separable chemical species.

In the distillation method, the usual absorbant for the RuO_4 distillate is chilled sodium hydroxide. This, however, is not practical for subsequent mass spectrometric analysis because of the high salt concentration. Distillation from a mixture of 9M H_2SO_4 - PbO_2 and collection in chilled sulfurous acid was evaluated. Recovery, established by tracer Ru-103, was greater than 95% and the distillate could be concentrated by evaporation without loss of ruthenium.

Solvent extraction procedures for ruthenium, after oxidation to RuO_4 with nitric acid-periodic acid, were investigated for three organic solvents; benzene, carbon tetrachloride, and toluene. In all cases the extracted ruthenium was rapidly reduced to insoluble RuO_2 . Of the two techniques, the distillation approach appears superior. Conditions for the mass analysis of ruthenium are being investigated.

Separation of Molybdenum, S. F. Marsh

Three procedures for the separation of carrier-free fission product molybdenum are being evaluated. One is the extraction of molybdenum as the α -benzoinoxime complex, a routinely-used method for the radiochemical determination of molybdenum. Another is the extraction of molybdenum from 6M HBr into amyl acetate. After either extraction the molybdenum is back extracted into water, made 6M in hydrochloric acid, and passed through an anion exchange column. The adsorbed molybdenum is eluted with 4M HNO_3 . The third procedure, similar to the first, was suggested by Fudge(13). It consists of a preliminary extraction of uranium with TBP, followed by extraction of molybdenum as the α -benzoinoxime complex, back-extraction with concentrated hydrochloric acid, and two iron hydroxide scavenges of foreign activities.

All three methods gave adequate decontamination of other fission products. The difficulty of obtaining filament material sufficiently low in molybdenum is hindering the mass spectrometric evaluation.

(13) Fudge, A. J., Private Communication, June, 1964.

PREPARATION OF STANDARDS FOR MASS SPECTROMETRIC ANALYSIS

M. E. Kussy, M. A. Wade, S. S. Yamamura

The success of the program to measure the fission yields of the stable fission products by isotope dilution mass spectrometry depends upon the calibration accuracy of the isotope spike solutions. Because of the low concentration of the spike solutions ($\sim 1 \mu\text{g/g}$) used in the isotope dilution mass spectrometric analysis of the stable fission products, the standardization of the spike solutions must be made mass spectrometrically against a $1 \mu\text{g/g}$ standard solution of the natural element. This natural element standard is prepared by weight dilution of a 1 mg/g solution which has been independently standardized.

Solutions ($\sim 1 \text{ mg/g}$) of six lanthanide elements have been prepared and standardized by EDTA titrations. Because fission yield measurements are being done in both the General Electric and Phillips Laboratories, the standard solutions are being exchanged. The Phillips standardization results for the six Phillips-prepared solutions and results from both laboratories on three exchanged standards are summarized in Table VIII. Agreement within 0.1% was obtained on these three standards.

Table VIII. INTERLABORATORY COMPARISONS OF LANTHANIDE STANDARD SOLUTIONS

<u>Lanthanide Solution</u>	<u>Laboratory Where Prepared</u>	<u>Phillips</u>		<u>GE Vallecitos</u>
		<u>mg/g</u>	<u>Molarity</u>	<u>Molarity</u>
La	GE Vallecitos	1.4714	0.01103	0.01103 ₆
Nd	GE Vallecitos	1.1856	0.00870 ₀	0.00869 ₄
La	Phillips	0.9780	0.00714 ₂	
Nd	Phillips	1.0313	0.00725 ₈	0.007263
Ce	Phillips	0.980 ₃	0.00710 ₅	
Sm	Phillips	0.978 ₁	0.00600 ₀	
Eu	Phillips	0.9792	0.00653 ₆	
Gd	Phillips	0.9787	0.00633 ₂	

DISSOLUTION OF FUEL SAMPLES

K. L. McMillan, S. F. Marsh

The method of burnup determination, based on an analysis for fission products, requires complete dissolution of the fuel samples with no plateout loss of the fission products. Dissolution conditions for uranium and plutonium fuel samples are being evaluated with this objective. Satisfactory dissolution conditions for uranium metal, uranium-aluminum alloys, and uranium-zircaloy fuel samples have been reported previously(14).

Uranium Dioxide-Stainless Steel

Dissolution of irradiated UO_2 -stainless steel fuel was attained with a mixture of 5M HNO_3 -2M HCl -0.3M HF . To establish that dissolution was complete, Mo-99 and Ce-143 were analyzed on aliquots of the dissolver solutions. The determined Mo-99/Ce-143 ratio was 1.05 ± 0.05 (standard deviation) for the seven samples. This ratio was not significantly different than the value of 1.04 ± 0.01 previously obtained for irradiated uranium-aluminum alloys(14).

Plutonium Dioxide-Aluminum

The aluminum capsules which have been irradiated for the determination of the fission yields of Pu-239 and Pu-241 contain a blend of PuO_2 and aluminum metal powder. Aqua regia, which successfully dissolved the similar uranium-containing capsules, did not dissolve the plutonium dioxide.

Several methods for the dissolution of plutonium dioxide were studied. The plutonium dioxide used for this study was prepared by converting plutonium oxalate to plutonium dioxide at 800°C for 6 hr. Ammonium bifluoride fusion, fluoride-catalyzed nitric acid, and prolonged fuming with perchloric acid were found to successfully dissolve PuO_2 . Because the aluminum capsule and its contents must be dissolved together to insure complete recovery of fission products, the dissolution medium must tolerate aluminum. Only the fuming perchloric acid dissolution met this requirement. Although aluminum precipitates as the perchlorate salt from fuming perchloric acid, the PuO_2 satisfactorily dissolves.

The perchloric acid dissolution system was evaluated with an unirradiated aluminum capsule containing PuO_2 . Complete dissolution was achieved by an aqua regia dissolution of the aluminum, followed by the addition of perchloric acid, and prolonged fuming.

(14) Rein, J. E., Maeck, W. J., Burnup Determination of Nuclear Fuels: 1963 Annual Progress Report, IDO-14649(1964).

Aluminum also was found to dissolve at a satisfactory rate in 6M HClO_4 . The dissolution must be done under reflux to prevent concentration of the perchloric acid, otherwise insoluble aluminum perchlorate forms on the sample surface. When the aluminum dissolution is complete, the reflux is removed and the PuO_2 dissolves as the perchloric acid becomes concentrated. Both the aqua regia-perchloric acid dissolution and this method have the same disadvantage. The volatile fission products, especially ruthenium, may be lost.

MEASUREMENT OF STABLE FISSION PRODUCT NUCLIDE CROSS SECTIONS

K. T. Faler

The magnitude of this program has been reduced for the present. Cross section measurements will only be made for those nuclides which show promise as fission monitors. To obtain both thermal and epithermal cross section values, bare and cadmium-covered irradiations are planned.

An important variable is the thickness of the cadmium shield so that thermal neutron leakage is negligible. Calculating burn-through rate as a function of neutron exposure is straightforward if the neutrons are a beam and if the sample is a simple geometric shape; but in a reactor in which the neutrons exist in a spherical flux (usually approximately isotropic) the situation is more complex. The most difficult variable to calculate or measure is flux depression in the vicinity of the shield. It was felt, therefore, that it would be useful to measure the change in transmission of thermal neutrons as a function of exposure for a particular frequently used experimental arrangement.

Cylindrical cadmium shields, 20 mm in height and 8 mm in diameter with a 0.040-in. wall thickness, were fabricated, and their initial sub-cadmium neutron transmissions were checked. All transmission checks were carried out by irradiating matched pairs of sodium and gold samples both inside a cadmium shield and with no shield present. Ratios of activities produced in the monitor pairs permit calculation of subcadmium neutron transmission changes with a sensitivity of the order of 0.01%. (The sodium monitor is very sensitive to thermal neutrons and the gold monitor to epicadmium neutrons, so that the ratio of induced sodium to gold activities provides a very sensitive indication of subcadmium leak-through).

The cadmium test shield and a control shield were checked for thermal neutron transmission; neither was found to have measurable leaks due to mechanical defects. Following this check, the test shield was irradiated in the L-45 position of the MTR to an unperturbed exposure (that is, the exposure to which a sample would be subjected in the absence of flux depression as measured by external monitors) of 4.8×10^{20} thermal n/cm². Following removal from the reactor and time allowed for "cooling", the shield was checked again by comparison with the control shield using the same set of matched Au-Na samples. The change in sample activity ratios indicated that the increased transmission of thermal neutrons amounted to 0.032%. A calculated value for transmission at this exposure, based on a conservative estimate of flux depression which, therefore, is expected to give a somewhat low value, less than 10⁻³%. The cadmium shield was then reinserted into the reactor for a second irradiation in the burn-through measurement program.

Following the second cycle of neutron irradiation, the "unperturbed" integrated flux was found to have reached a total value of 1.24×10^{21} thermal n/cm².

After allowing the shield to "cool" by decay, the transmission was again checked and found to be 0.46%. This value again falls above the calculated value based on an assumed flux depression due to the cadmium, and by the same amount as found for the value previously determined at an nvt of 4.8×10^{20} . This gives added evidence to the idea that the estimated flux depression value was too high.

The cadmium test shield was re-capsulated and is being irradiated for another cycle.

PROPOSED DETERMINATION OF NUCLEAR FUEL BURNUP BASED ON THE RATIO OF TWO STABLE FISSION PRODUCTS OF THE SAME ELEMENT

The following is the abstract of the paper which will be published as a separate report(15).

"A new method is proposed for the determination of nuclear fuel burnup based on the ratio of selected pairs of two fission product nuclides of the same element. The ratios Kr-83/Kr-84, Xe-131/Xe-132, and Nd-143/Nd-144, which change with irradiation, are useful as fission monitors. With this method, many problems associated with the conventional fission product analysis for burnup are eliminated."

-
- (15) Maeck, W. J., Proposed Determination of Nuclear Fuel Burnup Report Based on the Ratio of Two Stable Fission Products of the Same Element, IDO-14642(1965). Also presented at the Eighth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct., 1964.

APPENDIX - A

Procedure for the Analysis of Cesium-137 (For samples low in potassium, sodium, and ammonium ions). CATUTION: For safety reasons, alcohol-perchloric acids mixtures should be diluted well with H₂O and discarded immediately ²

1. Pipet the sample into a 50-ml centrifuge tube and add the cesium carrier (30-35 mg).
2. Add 5 ml of 70% HClO₄ and evaporate until dense white fumes are evolved.
3. Cool the tube in an ice bath, then cautiously add 15 ml of absolute ethyl alcohol. Mix and let stand in the ice bath for 10 minutes.
4. After standing, stir the precipitate for 1 to 2 minutes, centrifuge, decant, and wash the precipitate with 10 ml of absolute alcohol. Centrifuge and decant.
5. Dissolve the cesium perchlorate precipitate in 10 ml of water, add 5 mg of iron holdback carrier, and heat to near boiling. Dropwise add 6M NH₄OH until the ferric hydroxide precipitate coagulates.
6. Centrifuge and decant the supernatant solution to a clean 50-ml centrifuge tube. Repeat the iron scavenge, centrifuge, and filter the supernatant solution into a clean 50-ml centrifuge tube.
7. Add 2 drops of 6M NaOH and evaporate to about 2 ml.
8. Add 5 ml of 70% HClO₄ and evaporate to dense fumes.
9. Cool the tube in an ice bath, then cautiously add 15 ml of absolute ethyl alcohol. Mix and let stand 10 minutes. Centrifuge and discard the supernatant solution.
10. Add 15 ml of absolute ethyl alcohol, stir, and hold the tube in an ultrasonic mixer for 1 to 2 minutes. Centrifuge and decant the supernatant solution.
11. Add 5 ml of absolute ethyl alcohol and swirl until the cesium perchlorate is suspended in solution. Filter onto a tared 1-in. glass-fiber filter.
12. Wash the precipitate three times with 5-ml portions of absolute ethyl alcohol, followed by 5 ml of diethyl ether.
13. Dry the precipitate in a vacuum desiccator, reweigh for a yield determination, and mount the sample for counting.

14. Count with a gamma spectrometer (remove the Cs-134 and Cs-136 contribution by instrumental complement nullification) and determine the area under the 661-kev photopeak of Cs-137.

APPENDIX - B

Procedure for Gas Chromatographic Separation and Analysis of Krypton and Xenon

The krypton and xenon collected on the Molecular Sieve 5A adsorption trap is contaminated with nitrogen. Because large amounts of nitrogen interfere in the chromatographic measurement of krypton, it is desorbed from the trap by warming the trap from -190°C to -80°C and expanding into an evacuated tube containing Molecular Sieve 5A at -190°C .

Procedure

Refer to Fig. 8 for identification of equipment and parts.

1. Open stopcocks 4 and 11 which bypasses the lower portion of the manifold and purge the gas chromatographic column (B) and the charcoal trap (C) with helium. During the purge, heat the column to 150°C for 1 hr, and heat the charcoal trap (C) at $> 100^{\circ}\text{C}$ with a heat gun for 5 to 10 min.
2. Close stopcocks 1 and 2 and immediately open stopcock 3 through the bubble-o-meter.
3. Measure and adjust the flow rate at 95 cc/min. The minimum pressure of helium on the flow regulator should be 60 psi.
4. Cool the chromatographic column to room temperature and the charcoal trap at the chromatograph outlet to -80°C .
5. Attach the Molecular Sieve 5A trap containing the krypton and xenon (after desorption of the nitrogen) to the manifold of the chromatograph.
6. Turn on the chromatograph recorder and integrator (D) and set to zero.
7. Set the temperature programmer at $11^{\circ}\text{C}/\text{min}$.
8. Turn on the gamma monitoring equipment (E).
9. With stopcocks 7, 8, and 9 closed, and 5 and 10 open across the manifold, evacuate the manifold through stopcock 6.
10. Close stopcock 6 and turn 5 and 10 180° to direct purge gas into the Molecular Sieve trap.
11. Open stopcocks 7 and 8 and turn stopcock 4 and 11 90° to sweep the helium purge gas through the Molecular Sieve 5A trap into the chromatographic column.

12. Remove the Molecular Sieve 5A trap from the dry ice-acetone bath and immediately heat with a heat gun for 4 min. The nitrogen, krypton, and xenon have now been removed from the Molecular Sieve 5A trap and transferred to the chromatographic column.
13. After the chromatograph recorder has indicated that the elution of nitrogen has been completed from the column (which takes 2 to 3 min), turn on the programmer.
14. Choose an attenuator setting dependent on the approximate krypton concentration.
15. Again set the chromatographic recorder and integrator to zero.
16. When radioactivity is first indicated by the gamma monitor recorder, turn stopcock 3 to by-pass the bubble-o-meter and open stopcock 2 and 1. Krypton is eluted from the column at 60°C.
17. After the gamma monitor recorder has returned to the baseline, close stopcocks 1 and 2 and open stopcock 3.
18. Disconnect the charcoal tube containing the krypton and replace it with another charcoal tube which has been previously purged and cooled to -80°C.
19. Choose an attenuator setting dependent on the approximate concentration of xenon.
20. Again set the chromatographic recorder and integrator to zero.
21. When radioactivity is first indicated by the gamma monitor, turn stopcock 3 to by-pass the bubble-o-meter and open stopcocks 2 and 1. Xenon is eluted from the column at 150°C.
22. After the gamma monitor recorder has returned to the baseline, close stopcocks 1 and 2 and open stopcock 3.
23. Transfer the two tubes containing the separated krypton and xenon to the mass laboratory for isotopic measurement.

A typical chromatogram for a mixture of nitrogen, krypton, and xenon is shown in Fig. 6.

Calibration

Process natural krypton and xenon standards through the chromatograph just prior to and after the sample analysis for calibration. The elution and retention times for krypton and xenon, indicated on these standard chromatograms, can be used in lieu of gamma monitoring to indicate when to open and close stopcocks 1, 2 and 3 in steps 16 and 21 respectively.

Preparation of Gas Chromatographic Column and Charcoal Trap

Activated coconut charcoal (-30+50) mesh is used for the chromatographic column and for the charcoal trap. Place the charcoal overnight in a drying oven at 110°C before use.

Prepare the gas chromatographic column (B) by packing 5 ft of 0.25-in. OD copper tubing with the activated charcoal. After packing, turn the tubing in the form of a spiral.

The charcoal trap (C) is a glass tube, 11-cm long and 2.2-cm OD, equipped with a fritted-glass joint cap and stopcocks. The tube contains 4.5 g of the -30+50 mesh activated charcoal.

Figure 8. APPARATUS FOR THE CHROMATOGRAPHIC ANALYSIS OF KRYPTON AND XENON AND THEIR COLLECTION FOR MASS ISOTOPIC DISTRIBUTION ANALYSIS

APPENDIX - C

Procedure for the Separation of Neodymium

1. To an aliquot of sample which contains several micrograms of fission product neodymium, add 1 mg of high-purity lanthanum carrier, 1 ml of 5% sodium hypochlorite, and sufficient 6M NaOH to solubilize the aluminum. Add the neodymium isotopic spike (and thoroughly mix) before the sodium hydroxide is added if a quantitative measurement is sought.
2. Centrifuge and decant the solution. Dissolve the precipitate in a minimum amount of 1M HNO_3 . Add 1 ml of 5% sodium hypochlorite and excess 6M NaOH.
3. Centrifuge and decant the solution. Wash the precipitate with water. Centrifuge and again decant the solution.
4. Dissolve the precipitate in 1 ml of 0.1M HNO_3 . Dilute to 3 ml with water and pass the resulting solution through a 4- x 40-mm column of silver periodate (80-120 mesh).
5. Collect the eluted lanthanide fraction. Wash the column with 1 ml of water and collect it also.
6. Add excess ammonium hydroxide to the collected effluent. Heat to coagulate, then centrifuge. Decant the solution.
7. Dissolve the precipitate in a few drops of nitric acid. Dilute with water and again add excess ammonium hydroxide. Heat to coagulate the precipitate. Centrifuge and decant the solution.
8. Dissolve the precipitate in 1 ml of 0.2M HCl.

NOTE: The most critical part of an efficient chromatographic separation is the initial loading of the column. It is essential that the total lanthanide group is adsorbed on a minimum amount of Dowex 50-X₄ (325-400 mesh, ammonium form) resin to form a narrow, uniform band. From this initial band at the top of the column, the chromatographic resolution into individual element bands takes place.

9. Add a small portion of Dowex 50-X₄ (325-400 mesh, ammonium form) resin to the separated lanthanide fraction solution. Wait several minutes for equilibration and allow the resin to settle. Withdraw the resin with a transfer pipet, taking as little solution as possible, and transfer it to the top of an 8-by 150-mm column of Dowex 50-X₄ (325-400 mesh, ammonium form). Repeat this adsorption and transfer with additional small portions of resin until the remaining activity level indicates a sufficient fraction of the lanthanide activity has been transferred to the column.

10. Drain the column liquid just to the level of the resin. Add 0.5 ml of 0.50M α -hydroxyisobutyric acid, pH 3.50, to the column. Insert a glass wool plug, carefully, to avoid disturbing the resin bed by further additions of elutriant. Add another 10 ml of 0.50M α -hydroxyisobutyric acid, pH 3.50, to the column.
11. Connect the air pressure line to the column and adjust the air pressure to maintain an effluent flow rate of 10 ml per hr.
12. Gamma monitor the effluent to indicate the position of the various lanthanide activities as they are eluted. Set the automatic fraction collector to collect approximately 0.5-ml fractions.
13. When the pH 3.50 eluting solution is nearly through the column, add 15 ml of pH 3.90, 0.50M α -hydroxyisobutyric acid. (A provision is included in the apparatus design to automatically deliver the pH 3.90 solution at the appropriate time.)
14. When the neodymium fraction has been eluted (as indicated by gamma monitoring), quickly examine the subsequent tubes for praseodymium activity by gamma spectrometry. Likewise, examine the tubes showing adjacent element activities and retain the two or three center tubes of the remaining neodymium fraction.
15. Combine the contents of these tubes, dilute twofold with water, and add 2 drops of 12M HCl. This solution is passed through a micro ion exchange column of Dowex 50-X8 (100-200 mesh). Rinse the column with several column volumes of 0.1M HCl.
16. Elute the neodymium with 6M HCl. Evaporate the effluent under a heat lamp to a small volume and transfer it to the mass laboratory.

APPENDIX - D

Procedure for the Separation of Zirconium

1. To the sample add 1 mg of high-purity thorium carrier, one drop of 30% H_2O_2 , 2 ml of 15.7M HNO_3 , and 10 ml of 0.35M HIO_3 . Allow 5 min for thorium iodate to precipitate.

If a quantitative measurement is desired, add the enriched isotope spike and mix thoroughly before adding the thorium carrier.

2. Centrifuge and discard the supernatant solution. Dissolve the precipitate in a few drops of 12M HCl and one drop of 30% H_2O_2 . Heat until free iodine has been expelled.
3. Add 2 ml of 15.7M HNO_3 and continue to heat briefly to destroy the hydrochloric acid. Cool, then add one drop of 30% H_2O_2 and 10 ml of 0.35M HIO_3 . Again allow 5 min for thorium iodate to precipitate.
4. Centrifuge and decant the supernatant solution. Dissolve the precipitate in a few drops of 12M HCl and one drop of 30% H_2O_2 . Heat until free iodine has been expelled.
5. Add 1 ml of 12M HCl and pass this solution through a small Dowex 1-X8 (100-200 mesh) column. Thoroughly wash the column with 12M HCl and elute the adsorbed zirconium with 4M HCl . Evaporate the effluent to a small volume and transfer it to the mass laboratory.

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION