MASTER

BURNUP DETERMINATION OF NUCLEAR FUELS
PROJECT REPORT
FOR THE QUARTER JULY 1-SEPTEMBER 30, 1966

Edited By
Frederick L. Lisman, William J. Maeck
Robert E. Foster, Jr., and James E. Rein

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

U. S. ATOMIC ENERGY COMMISSION

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IDAHO NUCLEAR CORPORATION

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PROJECT REPORT
FOR THE QUARTER JULY 1 - SEPTEMBER 30, 1966

Edited by

Frederick L. Lisman, William J. Maeck,
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SUMMARY

In this continuing program to develop methods for the accurate determination of the burnup of nuclear fuels, the main emphasis this quarter was the additional measurement of U-235 thermal fission yields for many stable and long-lived fission products and the development of an extraction, in-situ spectrophotometric method for the determination of the Tc-99 fission yields for U-233 and U-235. A capsule containing a weighed quantity of highly enriched U-235, irradiated to 31.6 atom percent fission, was dissolved and analyzed for the number of atoms of each uranium isotope and various stable and long-lived fission product nuclides. From these data, the capture-to-fission ratio (α) and absolute fission yields were determined. The value for α_0 is 0.1752 ± 0.0028 . The fission yield values are:

<u>Mass Number</u>	<u>Element</u>	<u>Fission Yield</u>	<u>Mass Number</u>	<u>Element</u>	<u>Fission Yield</u>
137 (30.3y)	Cs	6.28 ± 0.13	146	Nd	2.95 ± 0.02
140	Ce	6.31 ± 0.04	147	Sm	2.15 ± 0.06
142	Ce	5.88 ± 0.04	148	Nd	1.70 ± 0.01
143	Nd	5.90 ± 0.04	149	Sm	1.02 ± 0.01
144	Nd	5.43 ± 0.06	150	Nd	0.637 ± 0.004
144	Ce	5.43 ± 0.06			
144	Nd+Ce	5.43 ± 0.03	151	Sm	0.456 ± 0.023
145	Nd	3.85 ± 0.03	152	Sm	0.231 ± 0.007

The absolute thermal fission yields of Tc-99 for U-233 and U-235 were determined on each of four previously dissolved U-233 capsules and three U-235 capsules. The Tc-99 was separated from the dissolved capsule solutions by extraction of the tetrapropylammonium pertechnetate ion-association complex and was determined spectrophotometrically as the Tc(V) thiocyanate complex. The determined fission yields are:

<u>U-233</u>		<u>U-235</u>	
<u>Capsule</u>	<u>Fission Yield</u>	<u>Capsule</u>	<u>Fission Yield</u>
6-2-4	5.36±0.14	6-2-2	6.06±0.13
6-4-2	5.03±0.13	6-4-1	6.20±0.20
6-4-3	5.23±0.18	6-6-2	6.37±0.25
6-5-1	5.05±0.15		

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

Previous project reports are:

<u>Period</u>	<u>Report</u>
Annual - 1962	TID-17385
Annual - 1963	IDO-14649
Annual - 1964	IDO-14656
Quarter, January-March, 1965	IDO-14660
Quarter, April-June, 1965	IDO-14663
Quarter, July-September, 1965	IDO-14667
Quarter, October-December, 1965	IDO-14676
Quarter, January-March, 1966	IDO-14678
Quarter, April-June, 1966	IDO-14681

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BURNUP DETERMINATION OF NUCLEAR FUELS

INTRODUCTION

The objective of this project is the development of methods for the accurate determination of burnup of nuclear fuels. The emphasis is on power reactor fuels having long residence time and high burnup rather than on short term, experimental irradiations. The principal measurement technique under study is chemical analysis for fission products. The use of long-lived, radiochemically determined fission products is not applicable because the errors of the in-pile decay corrections are magnified with long term irradiations, the nuclear constants are not known with sufficient accuracy, and the few available nuclides, Cs-137 and Sr-90, are volatile. 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 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, and IDO-14681.

ABSOLUTE U-235 THERMAL FISSION YIELDS OF LONG-LIVED AND STABLE FISSION PRODUCTS

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 a third U-235 capsule was dissolved and the absolute fission yields were measured for many lanthanides, Tc-99, and Cs-137. Also measured was α_0 , the thermal capture-to-fission ratio for U-235.

Irradiation History of U-235 Capsule

Standard burnup capsule CPP-6-2-2, which contained 61.2 mg of highly-enriched U_3O_8 mixed with high-purity aluminum powder and welded in a high-purity aluminum tube, was irradiated for eight fuel cycles (4994 Mwd) in the MTR at an estimated unperturbed flux of 6×10^{13} n/cm²-sec (accumulated nvt = 5.8×10^{20}). The cadmium ratio for cobalt for this irradiation was 15. The capsule was discharged from the reactor August 30, 1964, and allowed to cool for about two years before dissolution.

Dissolution of U-235 Capsule, R. E. Foster, Jr., S. F. Marsh

The dissolution of the capsule 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 used for the dissolution (1).

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

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

Determination of Number of U-235 Fissions, R. M. Abernathy, L. W. Buttars, M. E. Kussy, F. L. Lisman, W. J. Maeck, R. A. Nielsen, F. W. Sprakles.

The accuracy of the absolute fission yield measurements directly depends on the accuracy of the determined number of fissions in the irradiated U-235 capsule. 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.

The U_3O_8 (obtained from ORNL) that was weighed into the capsule was analyzed both for weight percent uranium content and isotopic distribution. For the former, samples of the U_3O_8 were weighed on a microbalance and dissolved in nitric acid, weight aliquots were mixed with weight aliquots of a standard U-233 solution, and the mixtures were analyzed by isotope dilution mass spectrometry. Isotopic distribution was determined on unspiked samples. The calculated atoms of each uranium isotope (in the capsule charge of 61.2 ± 0.1 mg U_3O_8) are summarized in Table I. Of interest was the finding that the uranium content of the U_3O_8 corresponded to 99.62% of theoretical.

The postirradiation atoms of each uranium isotope were determined in a similar manner with unspiked and U-233 spiked aliquots of the dissolver solution. The aliquots of the dissolver solution were delivered with a calibrated 1000- μ l pipet. The calculated atoms are presented in Table I.

To accurately compute the number of U-235 fissions by the relationship:

$$F_5 = U^O - U$$

in which:

$$F_5 = \text{number of U-235 fissions}$$

$$U^O = \text{total preirradiated atoms of uranium}$$

$$U = \text{total postirradiated atoms of uranium}$$

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

From the results:

$$U^O = (1.3229 \pm 0.0021) \times 10^{20}$$

$$U = (0.9087 \pm 0.0007) \times 10^{20}$$

$$\text{The number of fissions} = F_5 = (0.4142 \pm 0.0022) \times 10^{20}$$

The propagated standard deviation error of 0.0022×10^{20} for the computed number of fissions corresponds to a relative error of 0.53%. The atom percent U-235 fissioned (defined as atoms of U-235 fissioned per 100 initial atoms of U-235) is:

Table I. ANALYSIS RESULTS OF IRRADIATED U-235 CAPSULE AND
CALCULATED NUMBERS OF ATOMS

<u>Preirradiation Data</u>				
Initial Loading	61.2±0.1 mg U ₃ O ₈			
mg U-235/mg U ₃ O ₈	0.8361±0.0007			
mg U-235 in capsule	51.17±0.08 (0.16%)			
	<u>U-234</u>	<u>U-235</u>	<u>U-236</u>	<u>U-238</u>
Isotopic distribution, wt%	0.4677	99.1633	0.0603	0.3087
Std dev _{ind}	0.0025	0.0032	0.0015	0.0006
Std dev _{avg} (n=3)	0.0015	0.0019	0.0009	0.0004
Number of atoms	6.2151x10 ¹⁷	1.3119x10 ²⁰	7.9455x10 ¹⁶	4.0336x10 ¹⁷
Std dev _{avg}	0.0224x10 ¹⁷	0.0021x10 ²⁰	0.1192x10 ¹⁶	0.0085x10 ¹⁷
Total atoms of uranium	(1.3229±0.0021)x10 ²⁰ (0.16%)			
<u>Postirradiation Data</u>				
mg U determined in dissolved sample (n=8)	35.486±0.028 (0.08%)			
	<u>U-234</u>	<u>U-235</u>	<u>U-236</u>	<u>U-238</u>
Isotopic distribution, wt%	0.621	90.631	8.296	0.452
Std dev _{ind}	0.002	0.009	0.007	0.002
Std dev _{avg} (n=6)	0.001	0.004	0.003	0.001
Number of atoms	5.667x10 ¹⁷	8.2335x10 ¹⁹	7.505x10 ¹⁸	4.050x10 ¹⁷
Std dev _{avg}	0.010x10 ¹⁷	0.0071x10 ¹⁹	0.007x10 ¹⁸	0.010x10 ¹⁷
Total atoms of uranium	(9.0812±0.0071)x10 ¹⁹ (0.08%)			
Atoms of uranium lost during irradiation by capture on U-236 and U-238	0.0006x10 ²⁰			
Total atoms of uranium corrected for capture loss of U-236 and U-238	(0.9087±0.0007)x10 ²⁰ (0.08%)			

$$\begin{aligned} \%F_5 &= \frac{100 (0.4142 \pm 0.0022) \times 10^{20}}{(1.3119 \pm 0.0021) \times 10^{20}} \\ &= 31.57 \pm 0.19 \end{aligned}$$

in which the value of 0.19 is the propagated standard deviation error and corresponds to a relative error of 0.60%.

Capture-to-Fission Ratio for U-235, F. L. Lisman, W. J. Maeck, F. W. Spraktes

The effective capture-to-fission ratio, $\hat{\alpha}$, is calculated from the data of Table I. The number of U-235 atoms captured to form U-236 equals the postirradiation number of U-236 atoms plus those lost by capture to U-237 (and β^- decay to Np-237) less those atoms of U-236 initially present in the loading. As stated previously, the number of U-236 atoms lost by capture was calculated from a computer program.

Calculation of $\hat{\alpha}$ for U-235

- (1) atoms U_6 present at end of irradiation $= (7.505 \pm 0.007) \times 10^{18}$
 - (2) atoms U_6 lost by capture $= 0.054 \times 10^{18}$
 - (3) (1) + (2) $= (7.559 \pm 0.007) \times 10^{18}$
 - (4) atoms U_6^0 , initial atoms loaded into capsule $= (0.079 \pm 0.001) \times 10^{18}$
 - (5) atoms U_5^0 captured to U_6 , (3)-(4) $= (7.480 \pm 0.007) \times 10^{18}$
 - (6) atoms U_5^0 fissioned (see previous section) $= (41.42 \pm 0.22) \times 10^{18}$
 - (7) $\hat{\alpha}$, (atoms U_5^0 captured/atoms U_5^0 fissioned) $= \frac{(7.480 \pm 0.007) \times 10^{18}}{(41.42 \pm 0.22) \times 10^{18}}$
- $$\hat{\alpha} = 0.1806 \pm 0.0011$$

The propagated standard deviation value of 0.0011 corresponds to a relative error of 0.61%.

The capsule was irradiated in the MTR in a location near the beryllium reflector where the cadmium ratio for cobalt is 15. The Westcott "r" value corresponding to $R_{Cd}^{Co} = 15$ is 0.031, computed from the relationship (3):

$$r = \frac{s_{Co}}{R_{Cd}^{Co} \left[s_{Co} + \frac{1}{K} \sqrt{\frac{T}{T_0}} \right] - s_{Co}}$$

in which:

$$g_{Co} = 1$$

$$R_{Cd}^{Co} = \text{cadmium ratio for cobalt} = 15 \pm 3$$

$$s_{Co} = 1.795 \text{ (ref. 4)}$$

$$K = 2.2931 \text{ (for 0.040 in. of Cd) (ref. 4)}$$

$$T = 313^{\circ}\text{K}$$

$$T_o = 293.6^{\circ}\text{K}$$

to convert $\hat{\alpha}$ to α_o , the 2200 m/sec. value, the relationship:

$$1 + \alpha_o = (1 + \hat{\alpha})(g_f + rs_f)/(g_a + rsa)$$

applies (4). For a neutron temperature of 40°C (313°K) the values are:

$$g_f = 0.9735 \pm 0.006 \text{ (ref 5)} \quad g_a = 0.9723 \pm 0.0012 \text{ (ref 5)}$$

$$s_f = -0.0316 \text{ (ref 5)} \quad s_a = 0.1501 \text{ (ref 5)}$$

$$r = 0.031 \pm 0.006 \quad \hat{\alpha} = 0.1805 \pm 0.001_1$$

Therefore:

$$\alpha_o \text{ for U-235} = 0.1752 \pm 0.0028 \text{ (1.6\%)}$$

The quoted error (standard deviation) 0.0028 includes errors in the measured $\hat{\alpha}$, epithermal parameter "r", and Westcott's quoted uncertainties for the g values (6). This value of α_o agrees closely with our previously determined values of 0.1717 and 0.1715 (7).

Fission Yields of the Lanthanides for U-235, F. L. Lisman, S. F. Marsh, W. J. Maeck, F. W. Spraktes

The absolute fission yields of neodymium, samarium, and cerium were determined. Four 1000- μl aliquots of the irradiated U-235 dissolver solution were spiked with known amounts of Nd-150, Sm-144, and Ce-136. The preparation and standardization of the spike solutions has been described previously (1,2). A three-column sequential procedure is used for the separation of the individual lanthanides. The first column separates the lanthanides from the actinides and most fission products. Cerium is separated from the other lanthanides on a second column. On the third column, the lanthanides are chromatographically separated with α -hydroxyisobutyric acid at controlled pH as the elutriant. Details of the procedure have been previously reported (2).

The analysis results and calculated U-235 thermal fission yields for neodymium, cerium, and samarium are summarized in Tables II, III, and IV respectively.

To accurately calculate the fission yields of the lanthanide isotopes, the atoms of each nuclide must be corrected for buildup and burnout due to neutron capture. These corrections were obtained from a computer program which simulated the actual irradiation conditions of the experimental capsule. A detailed discussion of the determination of these correction factors has been previously reported (8).

The yield of the mass 144 chain was calculated three different ways: from the neodymium analysis, from the cerium analysis, and from the combination of the two. In the case of the neodymium analysis, the determined number of Nd-144 atoms was corrected, by a computer calculation, for the undecayed Ce-144 atoms giving a percent thermal fission yield of 5.43 ± 0.06 . The yield of the 144 chain calculated only from the mass spectrometrically determined number of Ce-144 atoms, with the appropriate decay corrections applied, was 5.43 ± 0.06 . The most accurate fission yield value is considered to be the sum of the determined Nd-144 and Ce-144 atoms. This value also is 5.43 ± 0.04 .

The determined number of atoms of each samarium isotope in the capsule, the computer-corrected number of atoms, and the calculated fission yields are summarized in Table IV. Due to the large capture cross sections on some of the samarium isotopes, corrections for neutron capture buildup and burnout are much greater than for cerium and neodymium and hence the errors associated with the fission yields are larger.

Most of the Sm-149, due to its very large cross section, is converted to Sm-150. Rather than apply a large correction factor, it is possible to sum the determined atoms of Sm-149 and Sm-150 because Sm-150 is a shielded nuclide and is not directly formed in fission. Small corrections were required however for the loss of Sm-150 by neutron capture. This correction factor was determined from the computer program.

Fission Yield of Cs-137 for U-235, M. E. Kussy, F. L. Lisman, W. J. Maeck

The number of Cs-137 atoms in the capsule dissolver solution was determined by gamma counting after a radiochemical separation. An additional measurement of the number of Cs-137 atoms by isotope dilution mass spectrometry is planned.

Three 1000- μ l aliquots of the dissolved capsule solution were diluted to 50.00-ml volumes. Duplicate 1000- μ l aliquots from each dilution were then analyzed by a modified ASTM perchlorate procedure (1). Two different gamma counting techniques were used. One was based on using a 3 x 3 in. NaI(Tl) crystal as the standard with the crystal parameters recommended by Heath (9). The other was a comparison method in which

Table II. DETERMINED ATOMS OF EACH NEODYMIUM ISOTOPE AND
CALCULATED NEODYMIUM THERMAL FISSION YIELDS FOR U-235

$$\text{Number of Fissions} = (4.142 \pm 0.022) \times 10^{19} \text{ } (\pm 0.53\%)$$

	Nd-143	Nd-144	Nd-145	Nd-146	Nd-148	Nd-150
Determined number of atoms	2.2090×10^{18}	2.2118×10^{18}	1.5666×10^{18}	1.2503×10^{18}	7.0733×10^{17}	2.6386×10^{17}
Std dev _{avg} (n=4)	0.0088×10^{18}	0.0082×10^{18}	0.0058×10^{18}	0.0046×10^{18}	0.0276×10^{17}	0.0124×10^{17}
Atoms after correction for neutron capture	2.4438×10^{18}	2.2509×10^{18}	1.5956×10^{18}	1.2210×10^{18}	7.0528×10^{17}	2.6402×10^{17}
Std dev, % (includes estimated uncertainties in correction factors)	0.50	1.07	0.48	0.48	0.49	0.47
Percent fission yield	5.90	5.43	3.85	2.95	1.70	0.637
Std dev	0.04 ₃	0.06 ₅	0.02 ₇	0.02 ₁	0.01 ₂	0.004 ₅
Std dev, %	0.73	1.19	0.71	0.71	0.72	0.71

Table III. DETERMINED ATOMS OF EACH CERIUM ISOTOPE AND
CALCULATED CERIUM THERMAL FISSION YIELDS FOR U-235

Number of Fissions = $(4.142 \pm 0.022) \times 10^{19}$ (0.53%)

	Ce-140	Ce-142	Ce-144
Determined number of atoms	2.6214×10^{18}	2.4466×10^{18}	2.7630×10^{17}
Std dev _{avg} (n=4)	0.0097×10^{18}	0.0056×10^{18}	0.0075×10^{17}
Atoms after correction for neutron capture	2.6127×10^{18}	2.4368×10^{18}	$2.2477 \times 10^{18}{}^a$
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	0.48	0.38	1.03
Percent fission yield	6.31	5.88	5.43
Std dev	0.045	0.038	0.063
Std dev, %	0.71	0.65	1.16

^aInclude in-pile decay corrections

Table IV. DETERMINED ATOMS OF EACH SAMARIUM ISOTOPE AND
CALCULATED SAMARIUM THERMAL FISSION YIELDS FOR U-235

$$\text{Number of Fissions} = (4.142 \pm 0.022) \times 10^{19} \text{ (0.53\%)}$$

	Sm-147	Sm-148	Sm-149	Sm-150	Sm-151	Sm-152
Determined number of atoms	3.7024×10^{17}	4.9734×10^{16}	1.6854×10^{16}	4.1376×10^{17}	1.9617×10^{16}	2.3002×10^{17}
Std dev _{avg} (n=4)	0.0085×10^{17}	0.0140×10^{16}	0.0047×10^{16}	0.0157×10^{17}	0.0125×10^{16}	0.0083×10^{17}
Atoms after correction for neutron capture and radio- active decay	8.9017×10^{17}	None	4.2187×10^{17}	None	1.8908×10^{17}	9.5695×10^{16}
Std dev, % (include estimated uncertainties in correction factors for neutron capture and radioactive decay)	3.00		0.47		5.04	3.02
Percent fission yield	2.15		1.02		0.456	0.231
Std dev	0.06 ₅		0.00 ₇		0.023	0.00 ₇ ₁
Std dev, %	3.05		0.71		5.07	3.06

the area under the 661-Kev photopeak, after correction for Cs-134, was compared to that of a certified standard (RC-137-ASTM, Nuclear Chicago Corp.). The details of the analysis and computations for the two methods have been previously discussed (2).

The determined numbers of Cs-137 atoms by both methods and the U-235 thermal fission yield are given in Table V.

Table V. DETERMINED ATOMS OF Cs-137 AND
CALCULATED U-235 FISSION YIELD

Atoms Cs-137 using crystal as standard	
= $(2.628 \pm 0.068) \times 10^{18}$	(2.6%)
Atoms Cs-137 by comparison method	
= $(2.559 \pm 0.084) \times 10^{18}$	(3.3%)
Weighted value, atoms Cs-137 ^a	
= $(2.601 \pm 0.052) \times 10^{18}$	(2.0%)
Number of fissions	
= $(4.142 \pm 0.022) \times 10^{19}$	(0.53%)
Fission Yield Cs-137	
= 6.28 ± 0.13	(2.1%)

^aValues were averaged by weighting the reciprocal of the variances.

ABSOLUTE THERMAL FISSION YIELDS OF Tc-99 FOR U-233 AND U-235

The absolute thermal fission yield of Tc-99 was determined 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 VI.

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

The dissolution of the capsules and treatment of the dissolver solution were the same as described in the previous section.

Determination of Tc-99, R. E. Foster, Jr.

The Tc-99 was determined by a carrier-free extraction followed by an in-situ spectrophotometric method. Aliquots of the dissolved capsule solutions were made 3M in sodium hydroxide and the Tc-99 was doubly extracted as the tetrapropylammonium pertechnetate ion-association complex into chloroform. The combined chloroform phases were contacted with potassium thiocyanate, sulfuric acid, and tetrapropylammonium hydroxide. The red-colored Tc(V)-thiocyanate complex that formed extracted into the chloroform. The absorbance was measured at 513 mμ.

The initial extraction is >99% from 2.6 to 3.5M NaOH and no fission products extract that form colored thiocyanate complexes. The color development is complete within 7 min and the color is stable for several hours. The molar absorptivity at the 513-mμ peak is 46,000. The linear range is 1 to 20 μg of technetium and the standard deviation is 0.09 μg of technetium.

This method is faster and more specific than existing methods for the determination of microgram amounts of technetium. Of 57 metallic ions studied, only those of Au, Hg, Os, Pd, and Re coextract. Of these, only gold and osmium form colored complexes but with such weak intensities as to be tolerated at 120 to 1 mole ratios to technetium. Chloride, fluoride, sulfate, phosphate, oxalate, citrate, and ethylenediaminetetraacetic acid do not interfere. The tolerance for nitrate is 3.2 mmole and for perchlorate is 0.12 mmole.

Table VI. COMPOSITION AND IRRADIATION HISTORY OF STANDARD BURNUP CAPSULES

Capsule	Fissionable Isotope	Enrichment wt %	mg U ₃ O ₈ in capsule	MTR cycles	% Burnup ^a	Discharge Date
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

^aDefined as atoms of major isotope fissioned per 100 initial atoms of major isotope.

The procedure is presented in detail as an appendix to this report.

A manuscript concerning this method has been submitted for publication in ANALYTICAL CHEMISTRY.

Fission Yield of Tc-99 for U-233, R. E. Foster, Jr., M. E. Kussy,
F. L. Lisman, W. J. Maeck, F. W. Sprakes

The absolute thermal fission yield of Tc-99 was determined on each of the four, dissolved, U-233 standard burnup capsules. Four aliquots (either 1000 or 2000- μ l depending on the estimated amount of technetium present) were analyzed from each dissolved capsule solution. The results and calculated fission yields are summarized in Table VII.

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:

$$F_3 = U^0 - U$$

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 Table VII.

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

Table VII. U-233 THERMAL FISSION YIELD OF Tc-99

	Capsule 6-2-4	Capsule 6-4-2	Capsule 6-4-3	Capsule 6-5-1
Determined number of atoms	2.198×10^{18}	1.900×10^{18}	1.769×10^{18}	1.320×10^{18}
Std Dev _{avg} (n=4)	0.055	0.042	0.053	0.028
Atoms after correction for neutron capture and decay	2.215×10^{18}	1.904×10^{18}	1.772×10^{18}	1.321×10^{18}
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	2.5	2.2	3.0	2.1
Determined number of fissions	$(4.138 \pm 0.045) \times 10^{19}$ (Ref 11)	$(3.786 \pm 0.059) \times 10^{19}$ (Ref 10)	$(3.390 \pm 0.062) \times 10^{19}$ (Ref 8)	$(2.614 \pm 0.055) \times 10^{19}$ (Ref 11)
Percent fission yield	5.35	5.03	5.23	5.05
Std dev	0.14	0.13	0.18	0.15
Std dev, %	2.6	2.6	3.4	3.0

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 (8).

In the case of Tc-99, corrections for buildup and burnout by neutron capture are small ($<1\%$). A schematic diagram of the buildup and burnout of technetium is given in Figure 1.

Fission Yield of Tc-99 for U-235, R. E. Foster, Jr., M. E. Kussy, F. L. Lisman, W. J. Maeck, F. W. Spraktes.

The absolute thermal fission yield of Tc-99 was determined on each of the three U-235 capsules.

Four aliquots (either 1000 or 2000- μ l depending on the estimated amount of technetium present) were analyzed from each dissolved capsule solution. The analysis results and calculated fission yields are summarized in Table VIII. The number of U-235 fissions was calculated as described in the previous section for the absolute thermal fission yields of U-235. The determined number of fissions for the irradiated U-235 capsules, along with the appropriate references, are given in Table VIII.

As in the case of the U-233 thermal fission yield of Tc-99, corrections for the buildup and burnout of Tc-99 were based on computer program which simulated the irradiation history of the samples.

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

Table VIII. U-235 THERMAL FISSION YIELD OF Tc-99

	6-2-2	6-4-1	6-6-2
Determined number of atoms	2.492×10^{18}	1.756×10^{18}	1.400×10^{18}
Std dev _{avg} (n=4)	0.052	0.053	0.053
Atoms after correction for neutron capture and decay	2.512×10^{18}	1.759×10^{18}	1.403×10^{18}
Std dev, % (includes estimated uncertainties in correction factors for neutron capture and radioactive decay)	2.1	3.0	3.8
Determined number of fissions	$(4.142 \pm 0.022) \times 10^{19}$ (this report)	$(2.839 \pm 0.030) \times 10^{19}$ (Ref 2)	$(2.201 \pm 0.030) \times 10^{19}$ (Ref 8)
Percent fission yield	6.06	6.20	6.37
Std dev	0.13	0.20	0.25
Std dev, %	2.2	3.2	4.0

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APPENDIX

PROCEDURE FOR THE SOLVENT EXTRACTION SEPARATION
AND IN-SITU SPECTROPHOTOMETRIC DETERMINATION
OF TECHNETIUM

R. E. Foster, Jr.

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CALIBRATION AND STANDARDIZATION

Two standard solutions of Tc-99, one containing 162.6 $\mu\text{g/ml}$ and the other containing 203.3 $\mu\text{g/ml}$, both in 4.5M H_2SO_4 were used. These solutions were provided by R.P. Larsen of the Argonne National Laboratory and he has described their preparation and standardization (12).

1. Preparation of Standard Curve.

Process five standards, in duplicate, in the concentration range of the samples as described in the section PROCEDURE.

When a previously prepared curve is used, a single standard in the concentration range of the samples is processed before analyzing a series of samples to ensure that the reagents and apparatus are satisfactory.

2. Calibration by the Method of Internal Standards

Process two standards that bracket the concentration range of the samples as described in the section PROCEDURE.

This method of calibration replaces the standard curve.

3. Preparation of Blank

Substitute 0.5 ml of 4.5M H_2SO_4 for the sample and process with the samples.

CELL MATCHING

Absorption cells should be matched or have correction factors determined to within 0.001 absorbance unit at the working wavelength of 513 $\text{m}\mu$.

1. Fill two clean cells with a solution prepared by processing a technetium standard as described in the previous section and measure their absorbance at 513 $\text{m}\mu$.

2. Designate the cell with the lowest absorbance reading the reference cell.
3. Adjust the instrument to 0.000 absorbance reading with the reference cell.
4. Determine the absorbance value for the other cell.

This absorbance value is the cell correction. Subtract this from the sample absorbance readings to give corrected readings.

Determine these corrections each time samples are analyzed.

PROCEDURE

1. Quantitatively pipet a sample aliquot of 2 ml or less with a calibrated pipet into a 60-ml separatory funnel.

The sample aliquot must contain from 1 to 20 μg of technetium and less than 16 meq of acid.

2. Dilute to 4 ml with water and add 10 drops of 30% H_2O_2 . Swirl to mix.

3. Add 10M NaOH dropwise until $\text{Al}(\text{OH})_3$ precipitates.

Record the approximate volume of NaOH solution added.

The aluminum is present from the capsule material. For other sample types, also add 10M NaOH until metal hydroxides completely precipitate.

4. Add additional 10M NaOH solution dropwise until the $\text{Al}(\text{OH})_3$ dissolves.

Record the approximate volume of NaOH solution added.

5. Pipet an additional 3-ml of 10M NaOH into the separatory funnel.

6. Add 2 drops of 0.47M tetrapropylammonium hydroxide solution and swirl to mix.

7. Add water to a total volume of 10 ml. Sum the volumes of all preceeding reagent additions to determine the volume of water to be added.
8. Pipet 3 ml of chloroform into the separatory funnel.
9. Extract for 5 min by stirring with an electrically driven, glass, propeller stirrer. A glass, propeller stirrer is recommended.
10. Raise the stirrer above the surface of the solution. Rinse it with a small volume of chloroform from a polyethylene squeeze bottle.
11. Place a wad of glass wool in the stem of the separatory funnel to serve as a filter.
12. Let the two phases separate. Carefully transfer the organic (lower) phase into a clean 60-ml separatory funnel.
13. Wash the aqueous phase three times with 0.5-ml squirts of chloroform. Transfer the chloroform washes to the separatory funnel containing the initial chloroform extract. After each addition of chloroform, gently shake the mixture.
14. Pipet 3 ml of chloroform into the separatory funnel that contains the once extracted aqueous phase.
15. Extract as before. The time of the second extraction can be decreased to 2 min.
16. Raise the stirrer above the surface of the solution. Rinse it with a small volume of chloroform from a polyethylene squeeze bottle.
17. Let the two phases separate. Carefully transfer the organic (lower) phase to the separatory funnel containing the initial chloroform extract.

18. Wash the aqueous phase three times with 0.5-ml volumes of chloroform from a polyethylene squeeze bottle. Transfer the chloroform washes to the separatory funnel containing the initial chloroform extract.
19. Add 8 ml of 4.5M H_2SO_4 to the chloroform extract.
20. Add 5 drops of 0.47M tetrapropylammonium hydroxide.
21. Add 10 drops of 2M KSCN.
22. Stir for 7 min with an electrically driven stirrer. The glass, propeller stirrer should be rinsed with 4.5M H_2SO_4 , water, and acetone before use.
23. Raise the stirrer above the surface of the solution. Rinse it with a small volume of chloroform from a polyethylene squeeze bottle.
24. Let the two phases separate and transfer the organic (lower) phase to a 10-ml volumetric flask.
25. Wash the aqueous phase with small volumes of chloroform, using these washes to dilute the chloroform in the volumetric flask to 10 ml.
26. Stopper the flask and mix the solution by repeated inversion until homogeneous. Prevent any leak of solution.
27. Transfer the solution to a 5-cm absorbance cell and measure the absorbance at 513 m μ against the reagent blank.
28. Determine the micrograms of technetium in the sample from the standard reference curve or by the method of internal standards.

CALCULATIONS

1. Calculate the corrected absorbance of the sample by:

$$E = C - D$$

in which:

E = corrected sample absorbance.

C = total sample absorbance

D = cell correction absorbance

See section CELL MATCHING.

2. Method of Standard Reference Curve

Calculate the concentration of technetium in the sample by:

$$I = \frac{B}{A}$$

in which:

I = concentration, $\mu\text{g/ml}$, of technetium in the sample.

B = micrograms of technetium from the reference curve.

A = milliliters of sample aliquot taken for the extraction.

3. Method of Internal Standards.

Calculate the calibration factor as follows:

$$F = 0.5 \left[\frac{H}{J} + \frac{H^*}{J^*} \right]$$

in which:

F = calibration factor.

H = corrected absorbance
of the lower calibration
standard.

J = micrograms of technetium
in the lower calibration
standard.

H' = corrected absorbance of
the higher calibration
standard.

J' = micrograms of technetium
in the higher calibration
standard.

Calculate the concentration of
technetium in the sample by:

$$I = \frac{E}{FA}$$

in which:

I = $\mu\text{g/ml}$ of technetium in
the sample.

E = corrected absorbance
of the sample.

F = calibration factor

A = milliliters of sample
aliquot taken for
extraction.