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URANIUM AND THORIUM LOADINGS DETERMINED BY CHEMICAL AND NONDESTRUCTIVE METHODS IN HTGR FUEL RODS FOR THE FORT ST. VRAIN EARLY VALIDATION IRRADIATION EXPERIMENT

P. Angelini and J. E. Rushton

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ABSTRACT

The Fort St. Vrain Early Validation Irradiation Experiment is an irradiation test of reference and of improved High-Temperature Gas-Cooled Reactor fuels in the Fort St. Vrain Reactor. The irradiation test includes fuel rods fabricated at ORNL on an engineering scale fuel rod molding machine. Fuel rods were nondestructively assayed for ^{235}U content by a technique based on the detection of prompt-fission neutrons induced by thermal-neutron interrogation and were later chemically assayed by using the modified Davies Gray potentiometric titration method. The chemical analysis of the thorium content was determined by a volumetric titration method.

The chemical assay method for uranium was evaluated and the results from the as-molded fuel rods agree with those from (1) large samples of Triso-coated fissile particles, (2) physical mixtures of the three particle types, and (3) standard solutions to within 0.05%. Standard fuel rods were fabricated in order to evaluate and calibrate the nondestructive assay device. The agreement of the results from calibration methods was within 0.6%. The precision of the nondestructive assay device was established as approximately 0.6% by repeated measurements of standard rods. The precision was comparable to that estimated by Poisson statistics.

A relative difference of 0.77 to 1.5% was found between the nondestructive and chemical determinations on the reactor grade fuel rods. The difference was comparable to the combined uncertainties of single measurements for the respective methods. The analysis of the assay data did not allow rejection of the hypothesis that the data followed the normal statistical distribution using the 5% significance level. Thus the normal distribution statistics could be used in determining fuel contents of many rods in fuel elements. The assay data were analyzed to determine whether a correlation existed between heavy-metal content and the order in which the fuel rods were produced. The linear correlation was minimal. Thus, volumetric particle dispensing yielded acceptable heavy-metal loading in fuel rods, as required by the product specifications.

INTRODUCTION

The Fort St. Vrain-Early Validation Irradiation Experiment (FSV-EVIE) is an irradiation test of reference and of improved HTGR fuels in the Fort St. Vrain Reactor. The irradiation test includes fuel rods fabricated at ORNL[1] on an engineering scale fuel rod molding machine[2] by the matrix slug-injection process.[3] These fuel rods will be included in test elements FTE-2, FTE-4, and FTE-6 of reload 1. The quality control assurance and experimental plan for the experiment were developed before fuel rod fabrication. Some of the materials used in fabricating the fuel rods were received from General Atomic Company. These materials included the Biso-fertile particles, carbon shim particles, and matrix. The matrix was fabricated into matrix pellets at ORNL. The Triso-fissile particles were produced at ORNL. These included fissile batches A-611 and A-601. Fissile particle batch A-611 was used in fabricating fuel rods for Campaigns I and III; batch A-601 was used for Campaigns II and IV. The characteristics of the Triso-fissile particles are presented in Table A.1 of Appendix A. The fuel rods fabricated at ORNL were required to meet Large High Temperature Gas Cooled Reactor (LHTGR) fuel product specifications, where appropriate. A sampling plan was developed for the rods before fabrication. After fabrication, the fuel rods from each production campaign required for the various tests were chosen by a random selection procedure and assigned to the various tests.

The philosophy for fabrication of each of the four campaigns was to first determine the proper fuel rod machine operating conditions such as particle dispenser and air blender settings by analyzing a limited number of fuel rods. If the test fuel rods were within specifications, then the fabrication of the campaign would start and continue uninterrupted until the required number of fuel rods was produced. This was the case for Campaigns I, II, and IV. The rods for Campaign III were produced during a two-day period. The number of rods produced on a per day basis is nearly the same. In the analyses that follow, tests on each part of Campaign III are identified by the suffix 1D or 2D, corresponding to first-day production and second-day production.

In this report, we describe and analyze the measurement of uranium and thorium loadings in fuel rods fabricated at ORNL for this test. The uranium loadings were obtained by chemical and nondestructive assay (NDA) methods. The thorium determinations were performed by chemical analysis only. A total of 48 rods were analyzed for uranium by a modified Davies-Gray potentiometric titration method, and for thorium by the volumetric EDTA titration method. The chemical procedures used for the analyses are presented in Appendix B. Thirty-two of the rods were also nondestructively assayed for ^{235}U content by a technique based on the detection of prompt-fission neutrons induced by thermal-neutron interrogation. The NDA procedure is presented in Appendix B. Analyses of the measured data were completed to (1) compare chemical and NDA assays for uranium, (2) to determine the single-measurement precision of the methods, (3) to investigate the normality of the data, and (4) to investigate correlations between heavy-metal content and the order of fuel rod production.

EVALUATION OF SAMPLE PREPARATION AND CHEMICAL ANALYSIS PROCEDURE

A series of chemical analyses were performed of uranium and thorium to determine whether chemical determinations were affected by the nature or amount of starting material. Replicate samples of (1) each separate particle type, (2) a physical mixture of the three particle types, and (3) the green fuel rods were analyzed. The amount of material used for samples was determined from that required of fuel rods produced for the FSV-EVI experiment. Particles of each specific type were obtained by riffling down to the required amount from respective batches. This assured that the final charge was a representative sample of the initial batch. The mass of each sample, as well as the results of the chemical analyses, are presented in Table 1. The chemical assay for uranium revealed a lower value for its content in small samples of loose particles than either the physical mixture of each particle type or of green fuel rods. The results of the assay for uranium in the physical mixture of particles agreed with those for the green fuel rods. This indicate that the preparation of small samples of Triso particles

Table 1. Uranium and Thorium Analyses for Triso and Biso Particles, Physical Mixtures, and Green Fuel Rods

Sample Set	Mass of Fissile	Mass of Fertile	Shim Particles Mass (g)	Uranium Content (wt %)	Thorium Content (wt %)	Fuel Rod Length (cm)	Fuel Rod Mass (g)
				Particles			
I	1.004			19.40			
	1.022			19.71			
	1.024			19.82			
	1.007			19.74			
	1.015			19.76			
	1.023			19.65			
Mean				19.68			
Standard deviation				0.15			
Relative standard deviation				0.76%			
II		7.030			57.78		
		6.998					
		7.018			57.59		
		7.002			57.76		
		7.014			57.51		
		7.009			57.51		
Mean					57.66		
Standard deviation					0.12		
Relative standard deviation					0.21%		
				Physical Mixtures			
III	1.013	7.006	1.574	19.98	57.29		
	1.009	7.015	1.525	19.96	57.41		
	1.015	6.979	1.543	19.98	57.14		
	1.022	7.025	1.549	20.05	57.49		
	1.016	7.019	1.582	20.11	57.64		
	1.020	7.005	1.530	20.19	57.42		
Mean				20.04	57.40		
Standard deviation				0.09	0.17		
Relative standard deviation				0.45%	0.30%		
				Green Fuel Rods			
IV	1.027	7.029	1.577	19.74	57.52	4.475	12.525
	1.010	7.013	1.569	19.93	57.49	4.432	12.425
	1.013	7.009	1.548	19.93	57.86	4.407	12.391
	1.018	7.000	1.575	20.08	57.76	4.453	12.528
	1.006	6.985	1.557	20.23	57.57	4.425	12.451
	1.011	7.012	1.552	20.00	57.66	4.463	12.490
Mean				19.99	57.65		
Standard deviation				0.16	0.14		
Relative standard deviation				0.80%	0.24%		

before chemical analysis was affecting the results. Additional experiments were performed with Triso particle samples to improve the sample preparation techniques. Two initial sample sizes (1 and 10 g) of Triso particles, as well as a physical mixture of Triso particles and graphite shim were analyzed. These data are listed in Table 2. The results again show that the smaller samples of Triso particles had a lower uranium content than the 10-g samples of Triso particles. The results from the physical mixture agreed with those from the 10-g sample of Triso particles. These results support the hypothesis that preparation of small samples of Triso-coated fissile particles affects the chemical analysis.

In comparing the results of Tables 1 and 2, one notes the consistency in the data. The results from the analyses of 1-g samples of Triso particles (Table 1) agree very well with the values for the 1-g samples in Table 2. Also, the results of the physical mixture of particles agree with each other.

The results from these tests show that the uranium analyses of green fuel rods agree with the uranium analyses of (1) large samples of Triso particles, (2) a physical mixture of the three types of particles, and (3) physical mixtures of Triso and shim particles. The same improvements in sample preparation and analysis were used for the chemical analysis of heavy metal in fuel rods produced during the FSV-EVIE campaigns.

DESCRIPTION OF NONDESTRUCTIVE METHOD

The nondestructive assay (NDA) system[4] determines the fissile material loading in a fuel rod by counting the number of prompt-fission neutrons emitted from the rod during irradiation with thermal neutrons. The assay system consists of three units — an irradiator, a sample positioning mechanism, and a neutron detector system. These components have been assembled in a test assay device, shown in Fig. 1. A cross section of the assay system is shown in Fig. 2. A brief description of each component is given below.

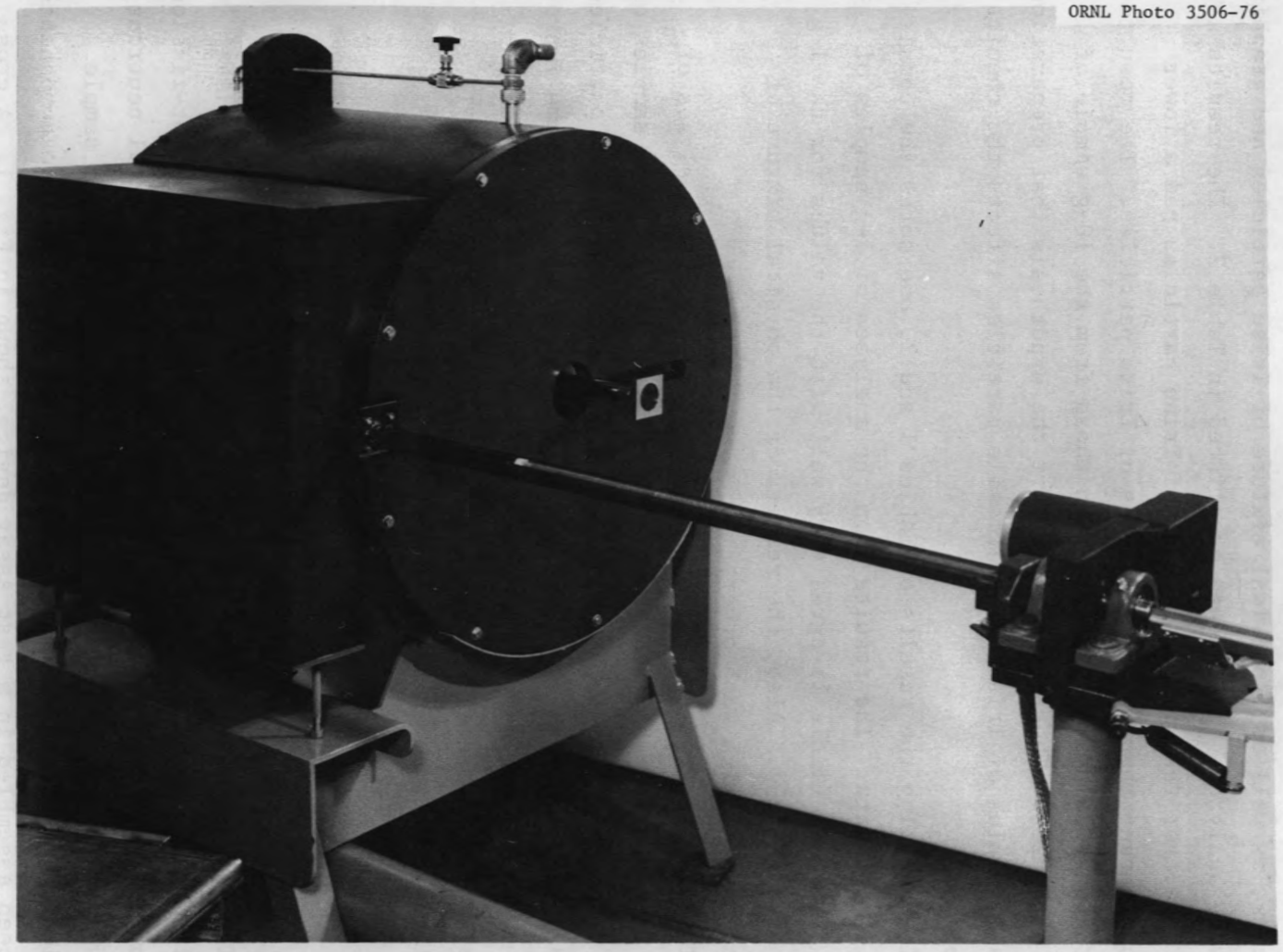

Fig. 1. Irradiator and Fuel Rod Translator Components of the HTGR Fuel Rod Assay Device.

Table 2. Analyses for Uranium in Triso Particles

Sample Set	Mass of Fissile Particles, Batch A-673 (g)	Shim Weight, Batch H-451 (g)	Uranium Content (wt %)
	Particles		
I	1.0543		19.722
	1.0865		19.774
	1.0306		19.816
	1.0481		19.721
Mean			19.758
Standard deviation			0.046
Relative standard deviation			0.23%
II	10.6281		20.050
	9.8787		19.947
Mean			20.00
Standard deviation			0.07
Relative standard deviation			0.36%
	Physical Mixtures		
III	1.2079	9.0037	19.936
	1.2784	9.0005	20.018
Mean			19.98
Standard deviation			0.06
Relative standard deviation			0.29%

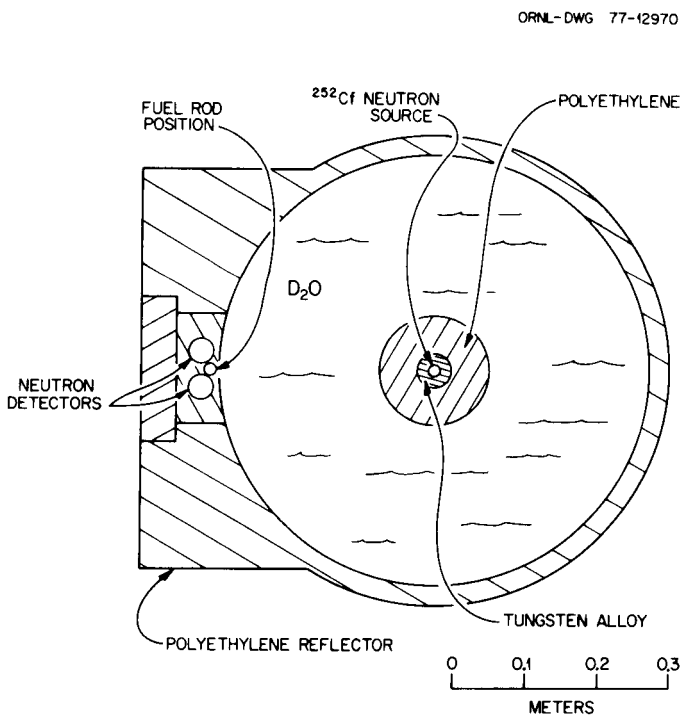

Fig. 2. Cross-Section View of Fuel Rod Nondestructive Assay Device.

Irradiator

The fuel rod irradiator consists of a ^{252}Cf isotopic neutron source surrounded by a moderator assembly to produce a thermal-neutron flux with a high thermal-neutron to fast-neutron ratio. The moderator assembly is composed of an aluminum tank containing D_2O that surrounds an inner moderator thimble containing polyethylene, tungsten, and the ^{252}Cf source. The irradiator was designed to allow experimental optimization of the moderator configuration by changing the dimensions of the D_2O and polyethylene moderators. For the measurements of the FSV-EVIE rods, the irradiator configuration and the ^{252}Cf neutron source intensity are recorded in Table 3.

Table 3. Irradiator and ^{252}Cf Neutron Source Parameters for the Nondestructive Assay of the FSV-EVIE Rods

^{252}Cf neutron source intensity (9/15/76)	2.23×10^9 n/sec
Irradiator geometry	
Tungsten alloy thickness	18.2 mm
Polyethylene thickness	47.4 mm
D_2O thickness	223.3 mm
^{252}Cf centerline to sample centerline distance	314.0 mm
Mechanical properties	
Tungsten alloy	94% W-4% Ni-2% Fe
Density of tungsten alloy	18.0 g/cm^3
Density of polyethylene	0.95 g/cm^3

Sample Positioner/Translator

The sample positioner/translator is designed to accurately locate samples in the irradiation position or to translate samples through the irradiator at a constant rate. The positioner/translator is actuated by a stepping motor coupled by reducing gears to a drive nut which rotates

in a fixed position and moves a threaded push rod along a guide track for the sample. The threaded rod is keyed to prevent rotation. Precise positioning is achieved by referencing the push rod to a fixed position at the end of the irradiator assembly. For the FSV-EVIE assays, each fuel rod was placed between two uncarbonized rods loaded with Biso-coated thoria and shim particles (3.52 g Th/rod). This three-rod combination was moved to the center of the irradiation channel with the sample positioner. The two thorium loaded end rods were used to minimize end effects. The fuel rods were stationary during the measurement.

Detectors

The prompt-fission neutron detectors are ^{4}He-filled proportional counters. The counter and instrumentation characteristics are listed in Table 4. Figure 3 shows a block diagram of the electronic modules used in the detector system. The two counters are located in a polyethylene assembly which also contains the sample irradiation position. Figure 4 is a detailed cross section of the sample and detector positions relative to the D_2O moderator assembly.

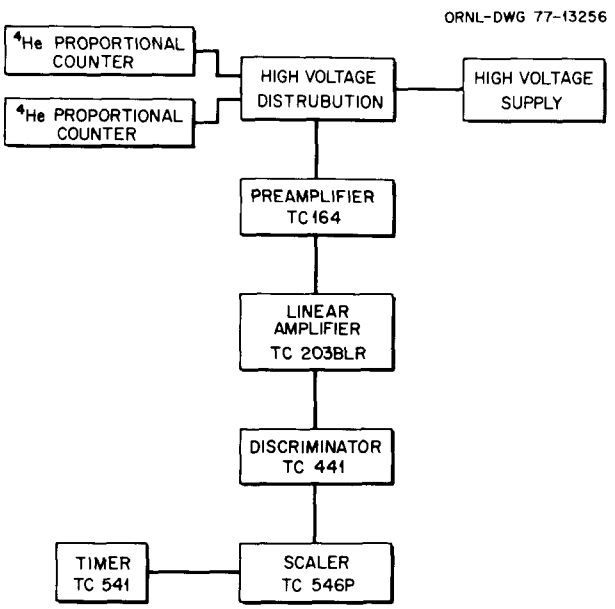

Fig. 3. Block Diagram of Neutron Detection Instrumentation for the Nondestructive Assay System.

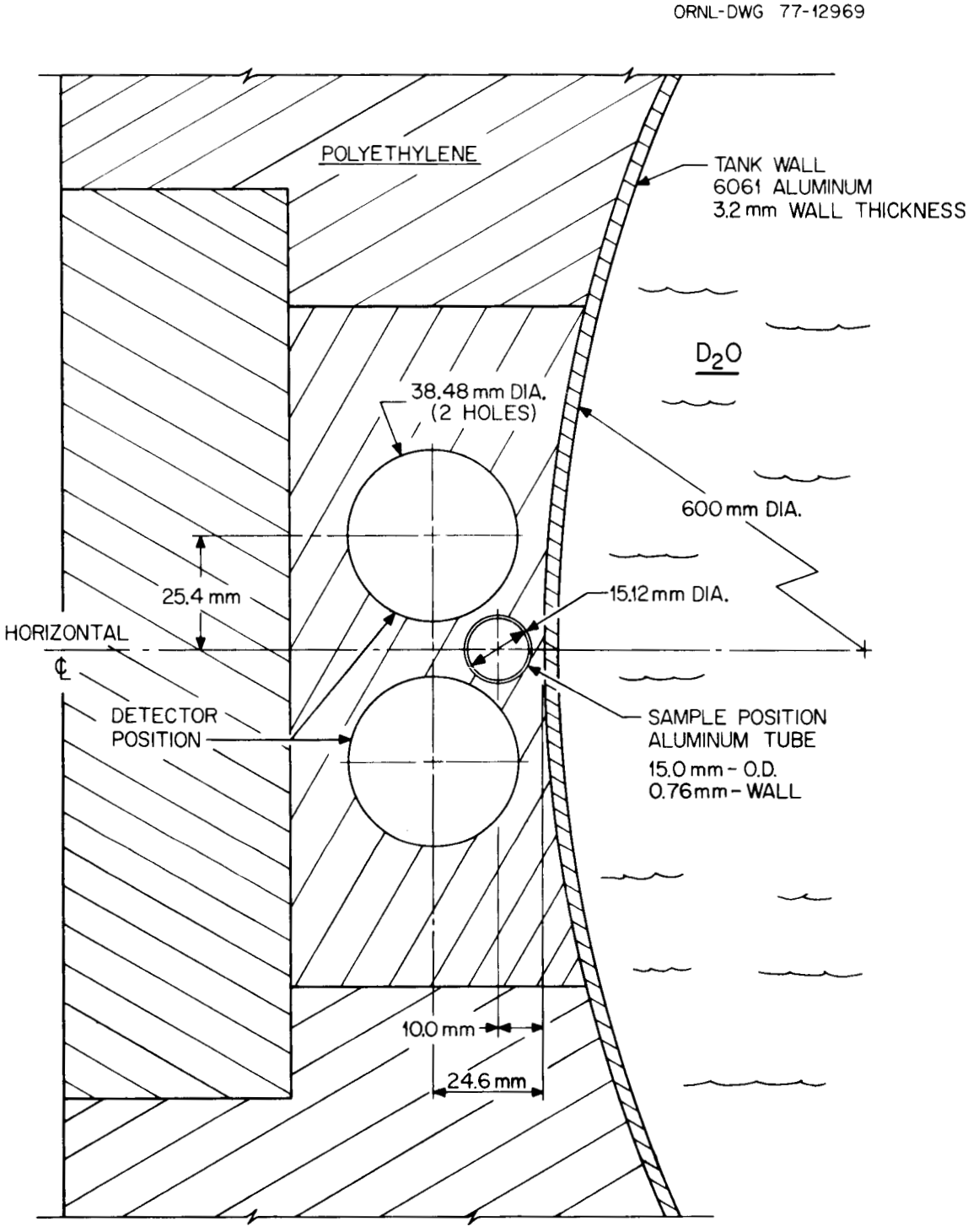

Fig. 4. Cross-Section View of Fuel Rod and Detector Positions in the Fuel Rod Assay System.

Table 4. Specifications and Operating Parameters for Neutron Detector and Instrumentation

Neutron detector make	Reuter stokes proportional counter
Model	RS-Pt-SK801
Series	S2934 and S2935
Active length, mm (in.)	152.0 (6.0)
Cathode diameter, mm (in.)	38.0 (1.5)
Anode diameter, mm (in.)	0.051 (0.0020)
Fill gas, MPa (psig)	
Helium	2.07 (300)
Carbon dioxide	0.207 (30)
Voltage supply	Tennelec TC 945
Voltage, V	+3550
Charge-sensitive preamplifier	Tennelec TC 164
Linear amplifier	Tennelec TC 203 BLR
Gain	
Coarse	100.0
Fine	0.80
Shaping time constant, μs	0.25
Single-channel analyzer	Tennelec TC 441
Lower level discriminator, V	1.4
Timer	Tennelec TC 541
Scaler	Tennelec TC 546P

DESCRIPTION OF STANDARDS FOR NONDESTRUCTIVE ASSAY OF FUEL RODS

Fuel rods were fabricated in July 1976 to evaluate NDA methods. Four of these fuel rods were selected as standards for determining an absolute level of ^{235}U in the FSV-EVIE rods. The standard rods were fabricated with Triso-coated, weak-acid resin derived kernels containing 93% enriched uranium (Batch J-501R) and with Biso-coated thoria microspheres (Batch J-483). The fissile particle Batch J-501R is an annealed portion of the A-601 fissile particle batch used in the FSV-EVIE rods fabricated in Campaigns II and IV. Characteristics of the A-601 and

J-483 particles are given in Table A.1 of Appendix A. The uranium loadings of the standard rods were determined from the total weight of the fissile particles in each rod and a determination of the weight fraction of uranium in the particles. The uranium weight fraction of J-501R particles was determined by destructively chemically analyzing four riffled samples. These sample weights and percent uranium (corrected for 93% ^{235}U enrichment) are listed in Table 5. The average uranium content is 17.41 ± 0.015 wt %.

The detailed procedure used to fabricate the standard rods is presented in Appendix B. The measured characteristics of the four standard rods are listed in Table 6.

DETERMINATION OF THE PRECISION OF A SINGLE NONDESTRUCTIVE ASSAY MEASUREMENT

The precision of the NDA technique was determined by repetitive assay of two standard fuel rods using the three-week period in which the FSV-EVT rods were measured. Tables 7 and 8 list this assay data for standards ND1001 and ND1201. Because the ^{252}Cf neutron source strength decreases with a 2.646-year half-life, the net count for each measurement in the tables is listed with and without a source intensity correction. The average response and its standard deviation for each standard are shown in these tables for each day and for the entire test period. The measured standard deviation for a single measurement on each day is comparable to that expected from Poisson counting statistics; however, the standard deviation of the responses of standard rod ND1201 over the three-week period is higher than would be calculated. The measured relative standard deviations on a single measurement were 0.58 and 0.52% for rods ND1001 and ND1201, respectively.

NONDESTRUCTIVE ASSAY DETERMINATION AND CALIBRATION METHOD

A set of measurements of the four standard rods was made initially to establish the relative responses of the standards. Then fuel rods

Table 5. Chemical Determination of Uranium Weight Percent for J-501R Particles

Sample	Sample Weight (g)	Uranium Content (wt %)
AC 5004	5.0274	17.42
AC 5005	5.0140	17.40
AC 5006	5.1116	17.43
AC 5007	5.0119	17.40

Table 6. Characteristics of Standards for FSV-EVIE Nondestructive Assay

Identification Number of Standard Rod	ND1001	ND1101	ND1201	ND1301
Uranium particle mass, g	0.9316	1.6766	1.8630	2.7947
Uranium mass,[a] g	0.1622	0.2919	0.3244	0.4866
Uranium mass,[b] g	0.1619	0.2901	0.3188	0.4765
^{235}U mass,[c] g	0.1508	0.2714	0.3016	0.4524
^{235}U mass,[d] g	0.1505	0.2697	0.2964	0.4430
Thorium particle mass, g	6.0070	6.0094	6.0072	6.0080
Thorium mass,[e] g	3.513	3.515	3.513	3.514
Thorium mass,[b] g	3.5107	3.5429	3.4918	3.5388
Shim mass, g	3.327	2.560	2.530	1.943
Matrix mass (by difference), g	3.160	3.140	3.034	2.665
Total rod mass, g	13.426	13.386	13.434	13.411
Rod length, mm	50.98	50.80	50.70	50.42
Rod outside diameter, mm	12.40	12.40	12.40	12.40

[a]Determined from U mass fraction of particle mass.

[b]Determined by chemical analysis of the fuel rod. The chemical analysis was performed after all data were obtained for the standard and campaign II, III, and IV fuel rods.

[c]0.9297 × Uranium mass, as determined from U mass fraction of particle mass.

[d]0.9297 × Uranium mass, as determined by chemical analysis of fuel rod.

[e]Determined by the mass fraction of particle mass.

Table 7. Nondestructive Measurement Data for Standard Rod ND1001

Date	Gross Count	Background Count	Net Count	Relative ^{252}Cf Intensity	Average Net Count	Standard Deviation (%)
9/16/77	220,537	157,537	63,331	1.0000	63,331	0.56
	220,544		63,338		63,338	
	219,931		62,725		62,725	
9/22/76	219,632	156,714	62,918	0.99552	63,201	0.61
	219,510		62,796		63,079	
	219,627		62,913		63,196	
	220,473		63,759		64,046	
	219,849		63,135		63,419	
10/8/76	217,118	155,301	61,817	0.98416	62,812	0.69
	217,766		62,465		63,470	
	217,937		62,636		63,644	
Overall Average Value for Single Measurements:					63,296	0.58
Standard Deviation of Single Measurement Predicted by Poisson Statistics:						0.74

Table 8. Nondestructive Measurement Data for Standard Rod ND1201

Date	Gross Count	Background Count	Net Count	Relative ^{252}Cf Intensity	Average Net Count	Standard Deviation (%)
9/15/76	276,588	157,362	119,226	1.00054	119,162	0.52
	277,824		120,462		120,397	
	277,273		119,911		119,846	
9/16/76	277,314	157,206	120,108	1.00000	120,108	0.59
	278,135		120,929		120,929	
	276,396		119,190		119,190	
	277,323		120,117		120,117	
9/22/76	276,305	156,714	119,591	0.99552	120,129	0.16
	275,956		119,242		119,779	
	275,846		119,132		119,668	
	276,255		119,541		120,079	
	276,119		119,405		119,942	
10/8/76	274,338	155,301	119,037	0.98416	120,973	0.40
	273,893		118,592		120,500	
	274,835		119,534		121,458	
Overall Average Value for Single Measurements:					120,150	0.52
Standard Deviation of Single Measurement Predicted by Poisson Statistics:						0.44

from Campaigns II, III, and IV were nondestructively assayed for ^{235}U content. The set of samples from each campaign was assayed separately and at least one of the standard rods was analyzed with each set of sample rods.

Data for each campaign were analyzed by two methods. First, a linear calibration curve based on the two standard fuel rods that bracketed the loadings of the test rods was established and used to determine the ^{235}U content of each rod from the counts corrected for background. The ^{235}U content of each standard fuel rod was based on the knowledge of the uranium isotopics and on the uranium mass fraction for the particle batch. These data were reported in the FSV-EVIE data package[1] and are reproduced in Appendix A.

The second method, developed after the data package had been assembled, uses a nonlinear calibration curve to convert the neutron detector net counts to ^{235}U masses. The calibration curve is given by

$$C = a(1 - e^{+bU5}) ,$$

where C and U5 are the net detector counts and the ^{235}U mass of the sample, respectively. The calibration coefficients a and b are determined by a nonlinear least squares fit of the calibration equation to the data from the rod standards. This procedure resembles that recommended in ANSI Standard N15.20-1975, "American National Standard Guide to Calibrating Nondestructive Assay Systems."

Standards ND1001, ND1101, and ND1201 were used to determine the coefficients for the nonlinear calibration. Standard ND1301 was not used because its ^{235}U content was 50% higher than any of the assayed rods. Each of the standard rods ND1001, ND1101, and ND1201 were counted in the NDA device. Then these standard rods were chemically assayed for ^{235}U content. The counts from the nondestructive assay device and the results of the chemical assay were used in the nonlinear calibration method to obtain the coefficients a and b. The results of the nonlinear calibration are shown in Table 9, which includes the gross and net counts of the standards, the nonlinear calibration coefficients a and b, and the identification of the calibration standards.

Table 9. Calibration Data for Fuel Rod NDA

	Standard Rod Identification Number		
	ND1001	ND1101	ND1201
^{235}U Mass, g[a]	0.1505	0.2697	0.2964
Gross Counts[b]	220,337	266,476	277,292
Net Counts[b]	63,131	109,270	120,086

Nonlinear Calibration Coefficients

Standards used: ND1001, ND1101, ND1201

a = 881,770

b = -0.49254

[a] ^{235}U mass of rods obtained by (0.9297 × chemical analysis of U mass in the standard rod).

[b] Counts are for a 100-sec counting period.

The nondestructive assay results for ^{235}U are shown in Table 10 for each calibration technique. The differences in ^{235}U masses due to the type of calibration are shown in this table for each campaign. The masses determined with the linear calibration have been compared with the chemical assay results in the remainder of this report.

COMPARISON OF NDA AND CHEMICAL ASSAY DETERMINATION

The NDA based on the linear calibration method and chemical assay determinations for the four campaigns are shown in Tables A.2, A.3, A.4, and A.5 of Appendix A. The average uranium content per rod, standard deviation of uranium contents, 95% confidence intervals about the mean, and the difference between NDA based on the linear calibration method and chemical assay are shown in Table 11 for each fuel rod production campaign. The average NDA determinations vary from 0.77 to 1.55% less than the chemical assays. This difference has not yet been explained.

Although the difference between NDA and chemical determinations is comparable to the combined uncertainties of single NDA and chemical

Table 10. Comparison of Linear and Nonlinear Calibration Methods on the ^{235}U Masses Measured with the Nondestructive Assay System

Run	^{235}U Mass, g	
	Linear Calibration	Nonlinear Calibration
2M5	0.2874	0.2837
2M30	0.2869	0.2832
2M61	0.2881	0.2844
2M92	0.2874	0.2837
2M114	0.2872	0.2835
2M134	0.2853	0.2816
2M155	0.2879	0.2842
2M170	0.2839	0.2802
Average Relative Difference 1.2%		
4M9	0.1620	0.1616
4M35	0.1655	0.1649
4M52	0.1654	0.1648
4M74	0.1658	0.1652
4M110	0.1655	0.1649
4M128	0.1648	0.1642
4M166	0.1685	0.1677
4M184	0.1678	0.1670
Average Relative Difference 0.35%		

Run	^{235}U Mass, g	
	Linear Calibration Type A	Nonlinear Calibration
3M7	0.1669	0.1662
3M44	0.1660	0.1653
3M67	0.1697	0.1689
3M77	0.1686	0.1678
3M83	0.1683	0.1675
3M109	0.1699	0.1690
3M128	0.1678	0.1670
3M147	0.1696	0.1688
3M158	0.1706	0.1697
3M172	0.1651	0.1645
3M204	0.1667	0.1660
3M220	0.1645	0.1639
3M234	0.1666	0.1659
3M250	0.1685	0.1677
3M280	0.1683	0.1675
3M291	0.1695	0.1687
Average Relative Difference 0.57%		

Table 11. Comparison of NDA Linear Calibration and Chemical Assay of Fuel Rods from Production Campaigns II, III, and IV

	Campaign					
	II		III		IV	
	NDA	Chemical	NDA	Chemical	NDA	Chemical
Average Uranium Content per Fuel Rod	0.3085	0.3109	0.1806	0.1822	0.1782	0.1810
Standard Deviation	0.0016	0.0014	0.0019	0.0015	0.0021	0.0010
95% Confidence Interval of Mean	0.018	0.0011	0.0010	0.0008	0.0017	0.0008
Number of Samples	8	8	16	16	8	8
Difference, NDA-Chemical	-0.0024		-0.0016		-0.0028	
Difference, %	-0.77		-0.88		-1.55	

measurements, a possible correlation between chemical and NDA values within each campaign was investigated. Figure 5 is a plot of the measured uranium masses for the 16 rods in Campaign III. The NDA value is plotted versus the chemical determination. The solid line represents loci of equal values for the two assay methods. All but one of the points lie below this line and demonstrate the negative bias of the NDA results or the positive bias of chemical assay. A straight line was fitted by the method of least squares to the 16 data points. This line and the 95% confidence limits on the line are also shown in Fig. 5. The fitted line shows excellent correlation with close to the expected slope. Correlations were also investigated for the uranium assays of

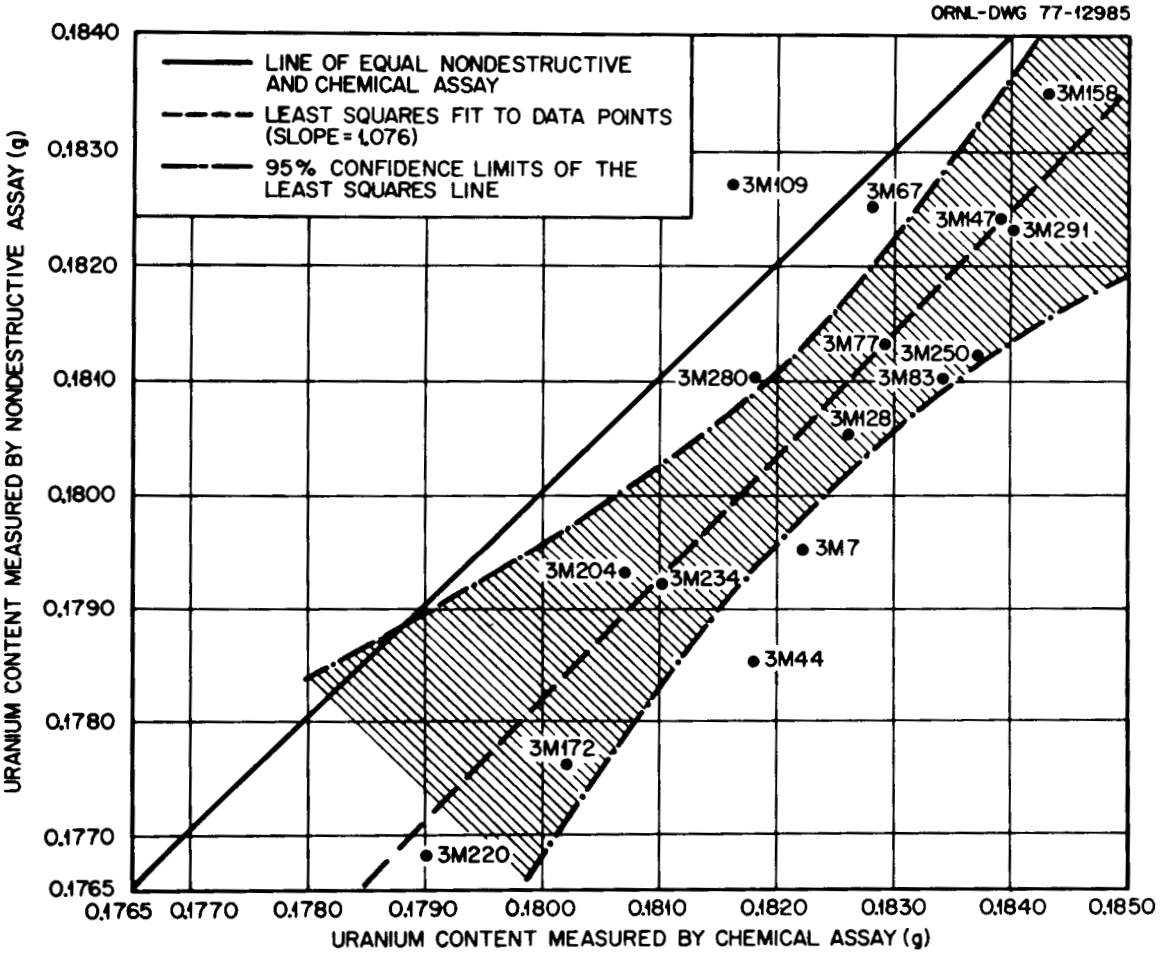

Fig. 5. Comparison of Nondestructive and Chemical Assay for Uranium in Fuel Rods from Campaign III.

Campaigns II and IV. Because only eight data points were available for each of these campaigns and because the range of uranium loadings was less than 2%, no significant results could be deduced.

NORMALITY TESTS FOR THE HEAVY-METAL MEASUREMENTS

The heavy metal determinations from each campaign were tested statistically in three ways to obtain an index to evaluate the normality of the data. It is important to determine the statistical distribution for the fissile content of many fuel rods since the calculation of the mean, standard deviation and confidence intervals for the total fissile content of a fuel element depends on such knowledge. Such calculations determine the acceptance or rejection of a loaded fuel element. The assay measurements evaluated were:

1. thorium determination by chemical method (T-C),
2. uranium determination by chemical method (U-C), and
3. uranium determination by nondestructive method (U-N).

The data were evaluated by the Bowman-Shenton test for Normality,[5] in which kurtosis and skewness are calculated. The results are then compared with a contour based on the 5% significance level. The results of the Bowman-Shenton test for the various data sets are presented in Table 12. The results for all except the 1U-C series were within the 95% contour. The Bowman-Shenton test on each set of data does not reject the hypothesis that the data are normal at the 5% significance level for all but 1U-C.

The W-test or Wilk-Shapiro test[6] was also used to evaluate the assumed Normality of the data. This test is more sensitive than the Bowman-Shenton test to the detection of non-normality for small sample size (less than 20). The results for the W-test are presented in Table 13. The W-test does not allow rejection of the hypothesis that the data of every case considered are Normal using the 5% significance level. The results of the W-test agree with those from the Bowman-Shenton except for the Case 1U-C.

Table 12. Bowman-Shenton Test for Normality of Heavy-Metal Measurements of FSV-EVT

Fuel Rod Production Campaign	Heavy Metal Analysis	Data Points	Skewness Magnitude	Kurtosis Magnitude	Within 95% Contour as Specified
I	1 T-C	16	0.49	2.03	Yes
	1 U-C	16	0.34	1.48	No
II	2 T-C	8	0.36	1.79	Yes
	2 U-C	8	1.21	3.49	Yes
	2 U-N	8	1.08	2.85	Yes
III	3 T-C	16	0.54	2.81	Yes
	3 U-C	16	0.41	2.45	Yes
	3 U-N	16	0.43	2.21	Yes
	3 T-C-1D	9	0.00	1.85	Yes
	3 U-C-1D	9	0.31	2.00	Yes
	3 U-N-1D	9	0.36	2.06	Yes
	3 T-C-2D	7	0.52	1.97	Yes
	3 U-C-2D	7	0.22	1.83	Yes
	3 U-N-2D	7	0.08	1.73	Yes
IV	4 T-C	8	0.42	1.69	Yes
	4 U-C	8	0.48	1.69	Yes
	4 U-N	8	0.36	2.96	Yes

Table 13. Analysis of Variance for Normality W-Test Method for the FSV-EVT Heavy-Metal Measurements

Fuel Rod Production Campaign	Heavy Metal Analysis	Data Points	W Parameter[a]	Percentage Points for W Test[b]
I	1 T-C	16	0.919	0.887
	1 U-C	16	0.893	0.887
II	2 T-C	8	0.931	0.818
	2 U-C	8	0.950	0.818
	2 U-N	8	0.834	0.818
III	3 T-C	16	0.953	0.887
	3 U-C	16	0.955	0.887
	3 U-N	16	0.965	0.887
	3 T-C-1D	9	0.933	0.829
	3 U-C-1D	9	0.968	0.829
	3 U-N-1D	9	0.897	0.829
	3 T-C-2D	7	0.938	0.803
	3 U-C-2D	7	0.942	0.803
	3 U-N-2D	7	0.957	0.803
IV	4 T-C	8	0.948	0.818
	3 U-C	8	0.917	0.818
	4 U-N	8	0.918	0.818

[a]W parameter is from S. S. Shapiro and M. B. Wilk, "An Analysis of Variance Test for Normality (Complete Samples)," *Biometrika* 52(4): 591-607 (1965).

[b]Significance level = 0.05.

The third test for Normality[7] involved ranking the data from the lowest to the highest value for each data set and calculating the value

$$\frac{8i - 3}{8n + 1},$$

where

i = ranking of data, and

n = total number of data points.

These results were then plotted on probability paper. A straight-line fit through the data would then indicate Normality. There was general correspondence between the plots and the two tests previously mentioned. Thus Normal statistics can be used for the calculation of the fissile content of loaded fuel elements.

CORRELATION TESTS FOR HEAVY-METAL CONTENT VERSUS ORDER OF FUEL ROD PRODUCTION

An analysis of the assay data from each fuel rod production campaign was performed to determine whether a correlation existed between the respective heavy-metal content and the order in which fuel rods were made. A correlation would result if there were a systematic change with time of the quantity of particles dispensed by the volumetric dispenser on the fuel rod molding machine. The changes could be caused by the changes in the dispenser settings or by particle segregation in the supply hoppers. The heavy-metal assay data versus order for each of the campaigns are presented in Figs. 6-9. The first-day production schedule for Campaign III, Fig. 8, occurred through fuel rod 3-168. In observing these figures, one may conclude subjectively that a linear correlation exists for some of the data sets; however, quantitative tests were performed.

A linear function was fitted to the data by a least-squares procedure in the SAS-76 computer code[8]

$$y = mx + b ,$$

where

y = heavy-metal measurement,
x = order of fuel rod production,
m = slope, and
b = intercept.

Correlation between the heavy-metal measurement and the order of fuel rod production depends on the value and on the significance level of the value fitted to the slope m. The F-test at the 5% significance level was used to determine the significance of the slope. A second analysis

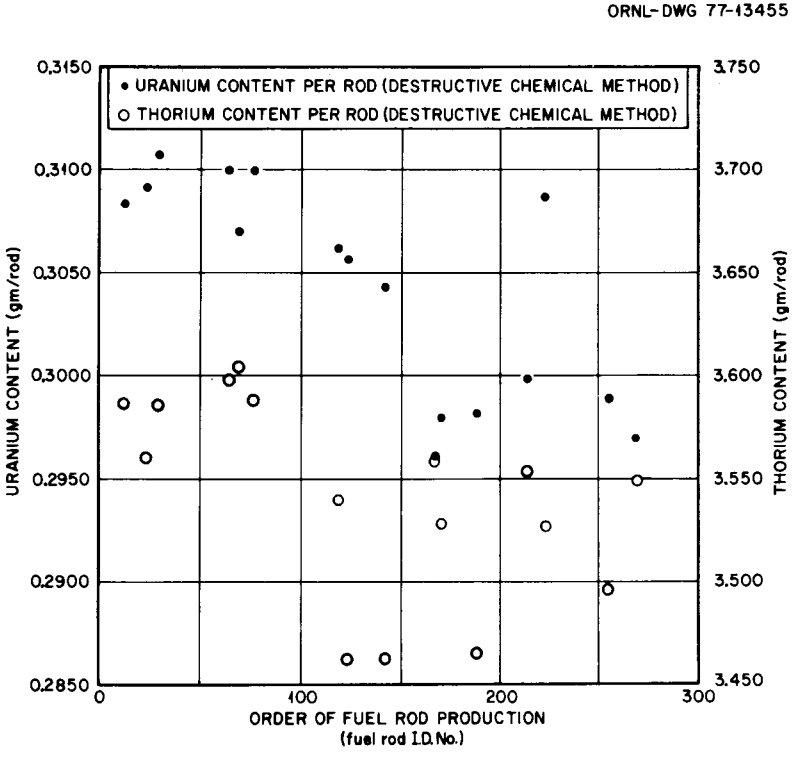

Fig. 6. Uranium and Thorium Content Versus the Order of Fuel Rod Production for Campaign I.

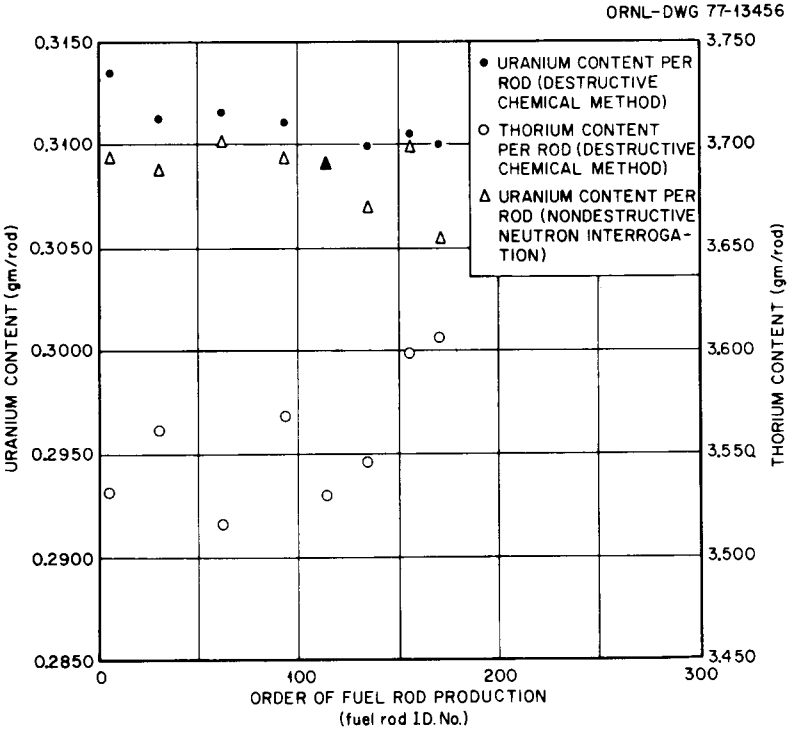

Fig. 7. Uranium and Thorium Content Versus the Order of Fuel Rod Production of Campaign II.

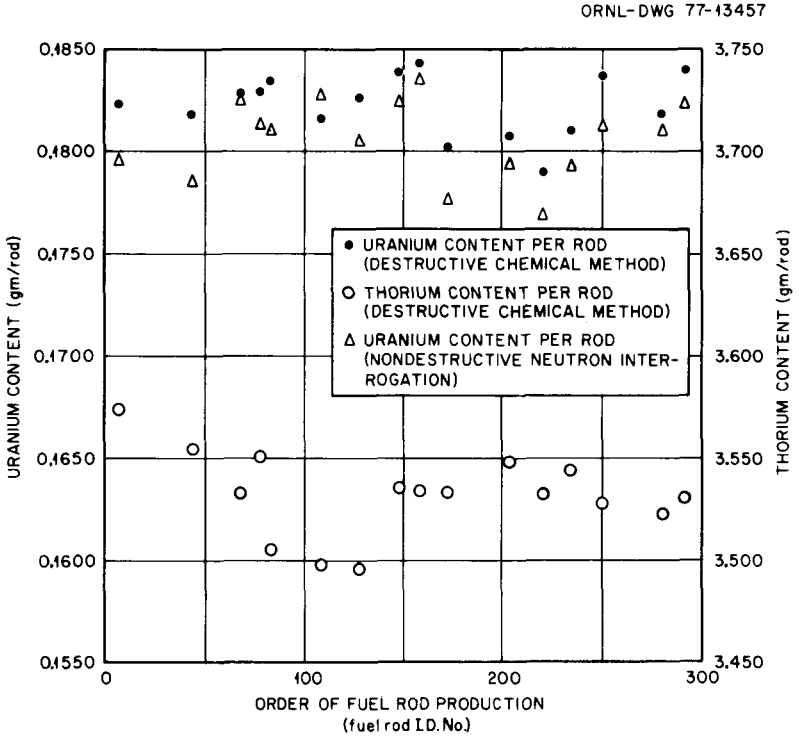

Fig. 8. Uranium and Thorium Content Versus the Order of Fuel Rod Production of Campaign III.

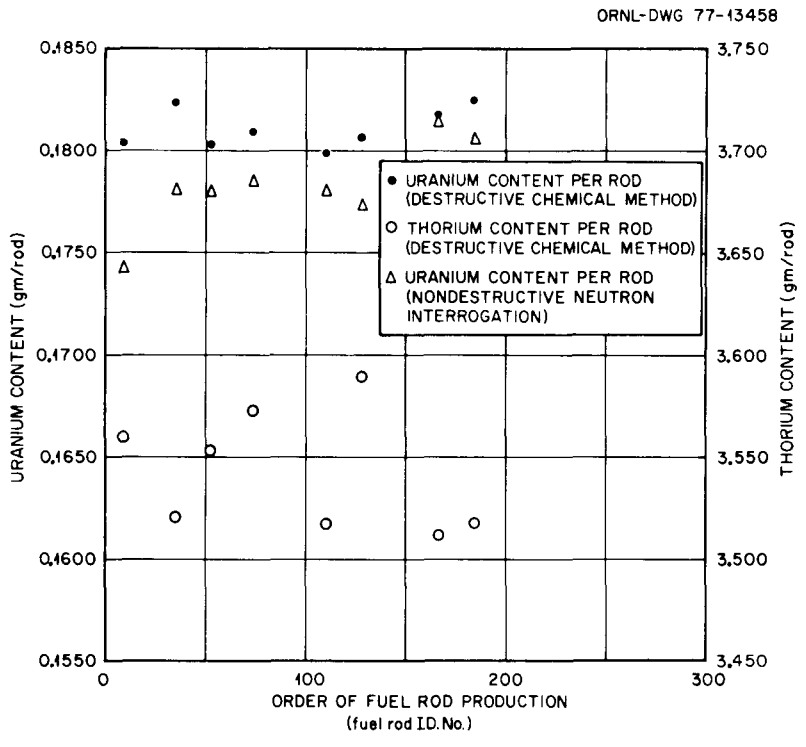

Fig. 9. Uranium and Thorium Content Versus the Order of Fuel Rod Production of Campaign IV.

for linear correlation was obtained by calculating the correlation coefficient for each case,

$$C_F = \frac{\sigma_x}{\sigma_y} m ,$$

where

C_F = linear correlation coefficient,

σ_x = standard deviation of the x variable,

σ_y = standard deviation of the y variable, and

m = slope.

The closer the value of C_F is to unity, the greater the linear correlation between the y and x variables. The results of the analysis are presented in Table 14. The F-test results indicate that a slope exists at the 5% significance level for five of 17 data sets. This indicates that a linear correlation existed between the heavy-metal content and the order of fuel rod production for those five data sets. The five data sets are identified in the column of Table 14 labeled "PR > F."

Another indication of the linear correlation is the value of the linear correlation coefficient (C_F). The results of the calculations for this parameter are also presented in Table 14. These results correspond closely with the results from the F-test. The value of the C_F parameter is much less than unity for all of the data sets considered, including those data sets for which the F-test showed a statistically significant slope. Thus, there does not appear to be a strong correlation between the heavy-metal content and the order of fuel rod production for the data sets considered.

Table 14. Results of Statistical Tests for Correlation Between Fuel Content Versus Order of Fuel Rod Production

Fuel Rod Production Campaign	Heavy Metal Analysis	Mean Value for Heavy Metal	Standard Deviation of Mean for Heavy Metal (σ_y) Analysis	Standard Error of Mean for Heavy Metal Analysis	Slope	Standard Error of Slope	F Value	PR>F	Standard Deviation of Order for Fuel Rod ID (σ_x)	Correlation Coefficient (σ_x/σ_y)*m
I	1 T-C	3.5408	0.0481	0.0120	-3.04 E-4	1.31 E-4	5.35	0.036[a]	83.106	0.526
	1 U-C	0.3042	0.0055	0.0013	-4.96 E-5	1.09 E-5	20.41	0.000[a]	83.106	0.770
II	2 T-C	3.5567	0.0328	0.0116	3.51 E-4	1.75 E-4	4.02	0.092	59.277	0.634
	2 U-C	0.3109	0.0014	0.0005	-1.78 E-5	0.59 E-5	9.26	0.023[a]	59.277	0.753
	2 U-N	0.3085	0.0016	0.0006	-1.37 E-5	0.93 E-5	2.16	0.192	59.277	0.5075
III	3 T-C	3.5327	0.0209	0.0052	-5.38 E-5	6.28 E-5	0.74	0.406	86.584	0.222
	3 U-C	0.1822	0.0015	0.0004	-1.89 E-6	4.61 E-6	0.17	0.488	86.584	0.109
	3 U-N	0.1806	0.0019	0.0005	-7.90 E-7	5.98 E-7	0.02	0.897	86.584	0.360
	3 T-C-1D	3.5315	0.0273	0.0091	-3.27 E-4	1.69 E-4	3.74	0.094	49.27	0.590
	3 U-C-1D	0.1828	0.0009	0.0003	1.12 E-5	0.55 E-5	4.45	0.073	49.27	0.613
	3 U-N-1D	0.1813	0.0016	0.0005	2.37 E-5	0.87 E-5	7.43	0.030[a]	49.27	0.730
	3 T-C-2D	3.5342	0.0093	0.0035	-1.14 E-4	0.85 E-4	1.80	0.237	41.900	0.511
	3 U-C-2D	0.1815	0.0018	0.0007	3.14 E-5	1.35 E-5	5.43	0.067	41.900	0.730
	3 U-N-2D	0.1796	0.0020	0.0008	3.94 E-5	1.19 E-5	10.95	0.021[a]	41.900	0.826
IV	4 T-C	3.5423	0.0293	0.0103	-1.47 E-4	1.81 E-4	0.66	0.446	62.748	0.315
	4 U-C	0.1810	0.0010	0.0004	6.20 E-6	6.07 E-6	1.04	0.347	62.748	0.389
	4 U-N	0.1782	0.0021	0.0008	2.75 E-5	0.82 E-5	11.19	0.016	62.748	

[a]Significant at the 95% confidence level.

CONCLUSIONS

The analyses of the uranium and thorium determinations for the FSV-EVIE yielded the following conclusions:

1. The nondestructive and chemical assays for uranium exhibited a relative difference of 0.8 to 1.6%. The cause of the difference has not been determined.

2. The precision of a single NDA measurement was established as approximately 0.6% by repeated measurements of two standards. This precision is comparable to that estimated by Poisson statistics; therefore, precision can be improved by repeated measurements, longer measurement time, or an increase in neutron source strength.

3. The procedure for fabricating fuel rod standards for nondestructive assay calibration has been confirmed and demonstrated.

4. The procedure for fuel rod chemical assay determination was evaluated. The results show that the uranium analyses of green fuel rods agree with both the uranium analysis of large samples of Triso-coated particles as well as with the uranium analysis of physical mixtures of the three types of particles. However, the analysis of small samples of fissile particles indicated lower uranium contents.

5. The assay data were tested to provide an index to evaluate the assumed Normality of the heavy-metal measurements. Neither the Bowman-Shenton nor the Wilk-Shapiro test on each data set allows rejection of the hypothesis that the data are Normal at the 5% significance level. Thus, Normal statistics can be used in estimating the total fissile content of loaded fuel elements.

6. The linear correlation between heavy-metal content and the order of fuel rod production was analyzed. A correlation between heavy-metal content and the order of fuel rod production would be due to a bias with time of the volumetric dispensers or to particle segregation during drainage from the storage hoppers on the fuel rod molding machine. Results from the F-test showed that a correlation did exist at the 5% significance level for a few of the data sets. Calculation of the linear correlation coefficient for the data sets showed that linear correlation was minimal.

ACKNOWLEDGMENTS

The authors would like to thank A. J. Caputo and D. R. Johnson for their aid in fabricating the fuel rods and review of the manuscript; D. A. Costanzo and F. Layton for chemical procedure development and chemical assay of fuel rods; S. W. Cook, J. C. McLaughlin, and W. B. Stines in the fabrication of the fuel rods; A. G. Mason for fabricating NDA standards and NDA measurements on the samples; E. J. Allen, W. J. Lackey, and E. L. Long for their review of the manuscript; C. K. Bayne for his assistance in statistical interpretations and review of the manuscript; and Brenda Johnson for typing the manuscript and Nancy Richards for editing the report.

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APPENDIX A

APPENDIX A

This appendix contains the data summaries for fuel rod heavy-metal assay. These summaries were reproduced from the data package.[1]

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[1]P. Angelini et al., *Data Package for Fort St. Vrain Early Validation Test Irradiation Experiment FSV-EVT*, March 28, 1977 (unpublished work).

Table A.1. Characteristics of A-601, A-611, and J-483 Fuel Particles

	Triso Coated Fissile						Biso Coated Thoria Batch No. J-483		
	Batch No. A-601			Batch No. A-611					
	Mean ± 95% C.I.	Standard Deviation	Number Measured	Mean ± 95% C.I.	Standard Deviation	Number Measured	Mean ± 95% C.I.	Standard Deviation	Number Measured
Kernel	Run No. V-40			Run No. V-44			Run No. J-211		
Diameter, μm	354.2 ± 1.9	15.0	250	366.4 ± 2.1	15.0	200	495.9 ± 0.8	2.8	50
Density, g/cm^3	3.034		2	3.102		2	9.95		
Uranium analysis, wt %	79.02 ± 0.24	0.23	6	71.57 ± 0.19	0.18	6			
Carbon analysis, wt %	17.70 ± 0.05	0.05	6	19.92 ± 0.19	0.18	6			
Oxygen analysis, wt %	3.07 ± 0.56	0.45	5	8.59 ± 0.41	0.23	6			
Oxygen by difference, wt %	3.29 ± 0.21	0.20	6	8.51 ± 0.23	0.22	6			
Percent conversion by oxygen difference	69.4 ± 2.1	2.0	6	12.6 ± 2.5	2.5	6	NA		
Shape ratio	1.006 ± 0.001	0.005	50	1.009 0.002	0.007	50	NA		
Isotope, wt % as received									
^{233}U	<0.001			<0.001					
^{234}U	0.990			0.988					
^{235}U	92.97			93.00					
^{236}U	0.440			0.440					
^{238}U	5.60			5.57					
Buffer Coat	Run No. A-599			Run No. A-609			Run No. A-577		
Thickness, μm	58.8 ± 2.9	10.1	50	47.6 ± 2.9	10.2	50	80.2 ± 3.0	15.2	50
Shape ratio	1.062 ± 0.018	0.065	50	1.090 ± 0.022	0.078	50	1.103 ± 0.080	0.08	50
Density after sealing, g/cm^3	NA			NA			NA		
Density after ILTI, g/cm^3	1.217			1.159			1.221		
Inner LTI Coat	Run No. A-599			Run No. A-609			Run No. A-577		
Thickness, μm	35.4 ± 0.9	3.1	50	36.8 ± 0.9	3.0	50	74.7 ± 1.5	5.2	50
Shape ratio	1.057 ± 0.016	0.056	50	1.060 ± 0.016	0.058	50	1.102 ± 0.020	0.072	50
Observed gradient density, g/cm^3	1.999 ± 0.006	0.014	22	1.986 ± 0.012	0.023	17	1.963 ± 0.003	0.006	23
Corrected gradient density, g/cm^3	1.713 ± 0.006	0.012	22	1.753 ± 0.010	0.020	17	1.832 ± 0.003	0.006	23
Volume percent open porosity	14.3			11.7					
Deposition rate, μm/min	5.2			5.2					
Defective fraction by Cl_2 leach (1500°C, 2 hr)	2.05×10^{-3}			1.84×10^{-4}					

Table A.1. (Continued)

	Triso Coated Fissile						Biso Coated Thoria Batch No. J-483		
	Batch No. A-601			Batch No. A-611					
	Mean ± 95% C.I.	Standard Deviation	Number Measured	Mean ± 95% C.I.	Standard Deviation	Number Measured	Mean ± 95% C.I.	Standard Deviation	Number Measured
Silicon Carbide Coat	Run No. A-600			Run No. A-610			NA		
Thickness, μm	30.0 ± 0.4	1.4	50	30.5 ± 0.4	1.4	50			
Shape ratio	1.035 ± 0.014	0.049	50	1.032 ± 0.016	0.057	50			
Gradient density, g/cm^3	3.206 ± 0.0004	0.001	19	3.204 ± 0.0001	0.0003	20			
Deposition rate, μm/min	0.159			0.143					
Defective fraction by burn and aqueous leach	2.2×10^{-4}			4.4×10^{-5}					
Outer LTI Coat	Run No. A-601			Run No. A-611			NA		
Thickness, μm	35.8 ± 1.0	3.4	50	35.5 ± 1.1	3.9	50			
Shape ratio	1.087 ± 0.018	0.062	50	1.105 ± 0.024	0.085	50			
Observed gradient density, g/cm^3	1.903 ± 0.003	0.008	30	1.908 ± 0.003	0.007	25			
Corrected gradient density, g/cm^3	1.724 ± 0.003	0.008	30	1.696 ± 0.002	0.006	25			
Volume percent open porosity	9.4			11.1					
Deposition rate, μm/min	4.8			5.1					
Fully-Coated Particle									
Diameter, μm	652.6 ± 7.9	27.8	50	653.9 ± 8.5	30.0	50			
Total coating shape ratio	1.034 ± 0.008	0.028	50	1.036 ± 0.007	0.025	50			
Particle shape ratio	1.014 ± 0.004	0.013	50	1.013 ± 0.003	0.009	50	1.088 ± 0.019	0.067	50
Mercury density at 250 psi, g/cm^3	2.080		2	2.130		2			
Uranium analysis, wt %	17.32		2	17.39		2			
Alpha probe, d/m/g	19.5			11.5					
Defective fraction by burn and aqueous leach	2.1×10^{-5}			4.0×10^{-4}					
Crush strength, lb	4.24 ± 0.16	0.55	50	4.56 ± 0.15	0.52	47			
Thorium analysis, wt %							58.26		
Carbon analysis, wt %							33.72		
Oxygen analysis, wt %							8.02		

Fuel Cycle Technology
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Procedure No. MET-FCT-DS-2
Revision No.
Date March 17, 1977
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DATA SUMMARY FOR FUEL ROD HEAVY METAL ASSAY

Type of Specimen Fuel Rod Machine, Slug Injected

Fuel Rod Production Campaign I

Irradiation Experiment FSV-EVT

Heavy Metal Assay						
Specimen Identification						
Fuel Rod Production Campaign	Specimen Number	Uranium[a] Content (g/specimen)	^{235}U[a] Content (g/specimen)	Uranium[b] Content (g/specimen)	^{235}U[b] Content (g/specimen)	Thorium[b] Content (g/specimen)
1	12	N/D	N/D	0.3083	0.2867	3.5862
1	23	N/D	N/D	0.3091	0.2875	3.5597
1	29	N/D	N/D	0.3107	0.2890	3.5853
1	64	N/D	N/D	0.3099	0.2882	3.5954
1	69	N/D	N/D	0.3069	0.2854	3.6042
1	76	N/D	N/D	0.3099	0.2882	3.5877
1	117	N/D	N/D	0.3061	0.2847	3.5359
1	123	N/D	N/D	0.3056	0.2842	3.4619
1	141	N/D	N/D	0.3042	0.2829	3.4626
1	166	N/D	N/D	0.2961	0.2754	3.5592
1	170	N/D	N/D	0.2979	0.2770	3.5271
1	188	N/D	N/D	0.2981	0.2772	3.4649
1	214	N/D	N/D	0.2998	0.2788	3.5539
1	223	N/D	N/D	0.3086	0.2870	3.5269
1	255	N/D	N/D	0.2988	0.2779	3.4960
1	269	N/D	N/D	0.2966	0.2758	3.5459

Average uranium content per fuel rod[a] = N/D
Standard deviation =
95% confidence interval about the mean =
Number of samples =

Average uranium content per fuel rod[b] = 0.3042 g
Standard deviation = ±0.0054 g
95% confidence interval about the mean = ±0.0029 g
Number of samples = 16

Average thorium content per fuel rod[b] = 3.5408 g
Standard deviation = ±0.0481 g
95% confidence interval about the mean = ±0.0256 g
Number of samples = 16

[a]Nondestructive — prompt neutron method

[b]Destructive — chemical method.

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DATA SUMMARY FOR FUEL ROD HEAVY METAL ASSAY

Type of Specimen Fuel Rod Machine, Slug Injected
Fuel Rod Production Campaign II
Irradiation Experiment FSV-EVT

Heavy Metal Assay						
Specimen Identification		Uranium[a] Content (g/specimen)	^{235}U[a] Content (g/specimen)	Uranium[b] Content (g/specimen)	^{235}U[b] Content (g/specimen)	Thorium[b] Content (g/specimen)
Fuel Rod Production Campaign	Specimen Number					
2	5	0.3092	0.2874	0.3135	0.2915	3.5304
2	30	0.3087	0.2869	0.3112	0.2893	3.5614
2	61	0.3100	0.2881	0.3116	0.2897	3.5159
2	92	0.3092	0.2874	0.3111	0.2892	3.5675
2	114	0.3090	0.2872	0.3090	0.2873	3.5291
2	134	0.3069	0.2853	0.3099	0.2881	3.5451
2	155	0.3098	0.2879	0.3106	0.2888	3.5981
2	170	0.3054	0.2839	0.3100	0.2882	3.6061

Average uranium content per fuel rod[a] = 0.3085 g
Standard deviation = ±0.0016 g
95% confidence interval about the mean = ±0.0013 g
Number of samples = 8

Average uranium content per fuel rod[b] = 0.3109 g
Standard deviation = ±0.0014 g
95% confidence interval about the mean = ±0.0011 g
Number of samples = 8

Average thorium content per fuel rod[b] = 3.5567 g
Standard deviation = 0.0328 g
95% confidence interval about the mean = ±0.0274 g
Number of samples = 8

[a]Nondestructive — prompt neutron method

[b]Destructive — chemical method.

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DATA SUMMARY FOR FUEL ROD HEAVY METAL ASSAY

Type of Specimen Fuel Rod Machine, Slug Injected

Fuel Rod Production Campaign III

Irradiation Experiment FSV-EVT

Heavy Metal Assay						
Specimen Identification						
Fuel Rod Production Campaign	Specimen Number	Uranium[a] Content (g/specimen)	^{235}U[a] Content (g/specimen)	Uranium[b] Content (g/specimen)	^{235}U[b] Content (g/specimen)	Thorium[b] Content (g/specimen)
3	7	0.1795	0.1669	0.1822	0.1694	3.5744
3	44	0.1785	0.1660	0.1818	0.1691	3.5569
3	67	0.1825	0.1697	0.1828	0.1700	3.5323
3	77	0.1813	0.1686	0.1829	0.1701	3.5506
3	83	0.1810	0.1683	0.1834	0.1706	3.5056
3	109	0.1827	0.1699	0.1816	0.1689	3.4974
3	128	0.1805	0.1678	0.1826	0.1698	3.4959
3	147	0.1824	0.1696	0.1839	0.1710	3.5357
3	158	0.1835	0.1706	0.1843	0.1714	3.5347
3	172	0.1776	0.1651	0.1802	0.1676	3.5330
3	204	0.1793	0.1667	0.1807	0.1680	3.5488
3	220	0.1768	0.1645	0.1790	0.1665	3.5326
3	234	0.1792	0.1666	0.1810	0.1683	3.5447
3	250	0.1812	0.1685	0.1837	0.1708	3.5270
3	280	0.1810	0.1683	0.1818	0.1691	3.5229
3	291	0.1823	0.1695	0.1840	0.1711	3.5301

Average uranium content per fuel rod[a] = 0.1806 g
Standard deviation = ±0.0019 g
95% confidence interval about the mean = ±0.0010 g
Number of samples = 16

Average uranium content per fuel rod[b] = 0.1822 g
Standard deviation = 0.0015 g
95% confidence interval about the mean = ±0.0008 g
Number of samples = 16

Average thorium content per fuel rod[b] = 3.5327 g
Standard deviation = 0.0209 g
95% confidence interval about the mean = ±0.0111 g
Number of samples = 16

[a]Nondestructive — prompt neutron method

[b]Destructive — chemical method.

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DATA SUMMARY FOR FUEL ROD HEAVY METAL ASSAY

Type of Specimen Fuel Rod Machine, Slug Injected
Fuel Rod Production Campaign IV
Irradiation Experiment FSV-EVT

Heavy Metal Assay						
Specimen Identification		Uranium[a] Content (g/specimen)	^{235}U[a] Content (g/specimen)	Uranium[b] Content (g/specimen)	^{235}U[b] Content (g/specimen)	Thorium[b] Content (g/specimen)
Fuel Rod Production Campaign	Specimen Number					
4	9	0.1742	0.1620	0.1803	0.1676	3.5556
4	35	0.1780	0.1655	0.1823	0.1695	3.5205
4	52	0.1779	0.1654	0.1802	0.1675	3.5530
4	74	0.1784	0.1658	0.1809	0.1682	3.5721
4	110	0.1780	0.1655	0.1798	0.1672	3.5178
4	128	0.1773	0.1648	0.1806	0.1679	3.5895
4	166	0.1813	0.1685	0.1817	0.1689	3.5122
4	184	0.1805	0.1678	0.1825	0.1697	3.5177

Average uranium content per fuel rod[a] = 0.1782 g
Standard deviation = ±0.0021 g
95% confidence interval about the mean = ±0.0017 g
Number of samples = 8

Average uranium content per fuel rod[b] = 0.1810 g
Standard deviation = 0.0010 g
95% confidence interval about the mean = ±0.0008 g
Number of samples = 8

Average thorium content per fuel rod[b] = 3.5423 g
Standard deviation = 0.0293 g
95% confidence interval about the mean = ±0.0245 g
Number of samples = 8

[a]Nondestructive — prompt neutron method

[b]Destructive — chemical method.

APPENDIX B

APPENDIX B

In this appendix are reported the procedures used for the preparation of sample and standard fuel rods, as well as the chemical and NDA analysis procedures for heavy-metal assay.[1]

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[1]P. Angelini et al., *Data Package for Fort St. Vrain Early Validation Test Irradiation Experiment FSV-EVT*, March 28, 1977 (unpublished work).

FABRICATION PROCEDURE FOR STANDARD FUEL RODS FOR THE NDA DEVICE

The standard fuel rods for calibrating the NDA device were individually fabricated with the following procedure:

1. determine the uranium and thorium coated particle weights to achieve rod loading values,
2. obtain uranium particles for each rod by repeated separation of the particle batch with a two-way splitter until the particle sample is nominally 10 mg less than the desired value,
3. add uranium particles to the sample until the weight is within ±0.4 mg of the desired particle weight,
4. obtain thorium particles for each rod by repeated two-way splits and a final addition of particles until the sample weight is within ±1 mg of the rod loading,
5. measure the bulk volume of the fissile particles in a 10 ml graduated cylinder,
6. measure the bulk volume of the fertile particles in a 10 ml graduated cylinder,
7. measure out shim particles in a 10 ml graduated cylinder so that the shim volume is equal to 6.35 ml minus the bulk volumes of the fertile and fissile particles,
8. weigh the shim particles,
9. level the benchtop 10-way splitter,
10. pour fissile particles in the 10-way splitter,
11. pour fertile particles in the 10-way splitter,
12. pour shim particles in the 10-way splitter,
13. take each one-tenth portion from the splitter and pour it through a 2-way splitter,
14. insert bottom end punch in die,
15. load each one-twentieth portion in buret tube with stopcock, mix portion by shaking, and unload through stopcock into die,
16. repeat step 15 for each one-twentieth portion,
17. measure matrix slug length,
18. insert matrix slug and top punch,

19. measure distance from top of die to top punch and calculate height of particle bed; if height is within tolerance (2.020-2.045 in.), inject; if out of tolerance, remove particles, add or subtract weighed amount of shim, and repeat above procedure from step 10; note that steps 10, 11, and 12 must be done simultaneously in this case,
20. parameters for the single mold injection are as follows:

    temperature: 185°C
    pressure: 4.3 E + 2 kPa (63 psig)
    preheat time: 120 sec.

21. end injection after top punch hits particle bed (observed by change in rate of travel on dial indicator),
22. cool mold, remove rod, and measure length.

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TEST SPECIFICATION

Title: Analysis of Uranium in HTGR Uncarbonized Fuel Rods by Prompt Neutron Emission Technique

Prepared by: J. E. Rushton J. E. Rushton

Approved by: W. J. Lackey W. J. Lackey 3-3-77

QA Approval: R. J. Beaver R J Beaver 3/4/77

1. Scope

This preliminary procedure covers the determination of uranium in uncarbonized HTGR fuel rods by the measurement of prompt neutron emission from fissions induced by thermal neutrons obtained from a moderated ^{252}Cf neutron source. The method is specific to fissile material. Total uranium is determined by prior knowledge of the uranium isotopics.

2. Equipment

2.1 Fuel rod irradiator with a ^{252}Cf source greater than 800 μg, a moderator assembly of polyethylene, tungsten, and D_2O, and a fuel rod positioning system.

2.2 Neutron detectors consisting of two proportional counters, with diameters of 3.81 cm and filled with ^4He-CO_2 mixture.

2.3 Scale-timer, power supply, and linear electronics for signal processing including (1) H.V. power supply 0—5000 V, (2) proportional counter preamplifier, (3) pulse shaping amplifier, (4) integral discriminator, and (5) scale-timer.

3. General Analysis Technique

3.1 Standards

Fuel rod standards are fabricated with weighed quantities of fissile, fertile, and shim particles. Each type of particles is subjected to a 20-way split, and the particles are added to the mold in 20 increments to assure homogeneity. Rod length is controlled to ±0.05 cm and diameter to ±0.003 cm. Standards should contain a range of uranium loadings that bracket the sample loadings. Thorium loadings

of the standards should be within 15% of sample thorium content. The standard rods are measured with this technique to calibrate the assay system. In each set of measurements, at least one standard is remeasured to establish a normalization for neutron source intensity on the day of measurement.

The procedure for analysis of the standards is identical to the procedure outlined in 3.2.

3.2 Samples

3.2.1 Remove sample from storage container or tray and position on rod transfer mechanism with a master-slave manipulator. Locate one thorium rod at each end of sample.

3.2.2 Set transfer position control to irradiation position. Start transfer system to move rod into irradiator-counter.

3.2.3 Start timer scaler. At end of counting period, reverse transfer mechanism direction to remove sample. Record scaler datum.

3.2.4 Repeat 3.2.2 and 3.2.3 so that the rod is measured a total of three times.

3.2.5 Remove rod from transfer track. Measure background count rate.

4. Detailed Analysis Procedure

4.1 Preparation of Samples and Standards for Analysis

4.1.1 Prepare sample and standard tray with labels showing the identification number of each rod.

4.1.2 Remove samples and standards from storage containers and position on sample and standard tray.

4.2 Preparation of Analysis Equipment

4.2.1 Determine home position of transfer mechanism. Insert position calibrator onto track. Step transfer position control until calibrator indicator lights. Zero transfer position controller.

4.2.2 Clear personnel from cell area. Close main cell door.

4.2.3 Insert ^{252}Cf source into irradiator.

4.2.4 Check electronic instrument settings against previous records.

4.3 Measurement Procedure

4.3.1 Measure background neutron count three times. For each measurement, set timer to 100 sec and then start scaler-timer. Record background data in databook as follows: "Background Count/100 sec"; "Time-of-Day".

4.3.2 Set transfer mechanism controller to +5000 on thumbwheel switches and start transfer mechanism.

4.3.3 Select sample or standard. Position sample or standard on the transfer track. Position a thorium loaded rod at each end of the sample.

4.3.4 Enter irradiation position on transfer controller thumbwheel switches. Set direction switch to minus (—). Initiate transfer to position rod in irradiator.

4.3.5 Set timer to 100 sec and start scaler-timer.

4.3.6 Record data in databook as follows: "Sample Identification"; "Counts/100 sec".

4.3.7 Set direction of position controller to plus (+). Initiate transfer to remove sample and thorium rods from irradiator.

4.3.8 Repeat Steps 4.3.4 to 4.3.7 until a total of three counts is obtained for the rod.

4.3.9 Remove sample or standard from transfer track and return rod to tray with master-slave manipulator.

4.3.10 Measure and record neutron background in one 100-sec counting time.

4.3.11 Repeat from Step 4.3.3 for each rod.

5. Data Handling

5.1 Determine the mean background count by simple averaging of all background measurements.

5.2 Determine the mean total count for each rod by averaging the three total counts for that rod.

5.3 Determine net count for each sample or standard as follows: Net count — Average total count — Average background count.

5.4 For each sample, identify two standards whose net count rates bracket the count rate of the sample. The two standards are referred to as Standard A and Standard B. Note: If these standards were not measured on the day of analysis of the sample, normalize the Standard A and Standard B net count rate by using the net count rate of a standard measured on the day of analysis.

5.5 Determine the ^{235}U mass of each sample using the normalized count rates of Standards A and B as follows:

Define: A = net counts per 100 sec from Standard A,

B = net counts per 100 sec from Standard B,

S = net counts per 100 sec from sample,

M_A = ^{235}U mass of Standard A,

M_B = ^{235}U mass of Standard B,

M_S = ^{235}U mass of sample,

then

$$M_S = M_A + \frac{(M_B - M_A)}{(B - A)} (S - A)$$

5.6 Determine the total uranium mass per rod by dividing the result of 5.5 by the ^{235}U isotopic weight fraction.

5.7 Record identification number, ^{235}U mass, and total uranium mass.

6. References

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OPERATOR PROCEDURE

Title: Debonding of a Green Fuel Rod and Separation of Particles for Physical Measurements

Prepared by: F. L. Layton F. L. Layton

Approved by: D. A. Costanzo D. A. Costanzo

QA Approval: R. J. Beaver R J Beaver 3/18/77

1. Scope

This specification outlines the procedures to be followed for the debonding of a green (unfired) fuel rod and preparation of the particles for physical measurements.

2. Request

Request for control analysis shall be submitted on sample request forms MET-CER-D-16 and UCN-1910. The original investigator shall indicate on form UNC-1910 any special precautions to be taken with the sample (e.g., fertile and/or fissile particles, enrichment, Biso- and/or Triso-coated particles, accountability, disposition of samples, etc.).

3. Sampling

A fuel rod shall be selected at random from a batch of green (unfired) fuel rods.

4. Debonding of Fuel Rod and Separation of Particles

4.1 Equipment

4.1.1 Hotplate.

4.1.2 Water bath, controlled at ∿75°C.

4.1.3 U.S. Standard Sieve, 60 mesh.

4.1.4 Erlenmeyer flasks, 250 ml capacity.

4.2 Reagents

4.2.1 Pyridine, C.P.

4.2.2 Benzene, C.P.

4.2.3 Acetone, C.P.

4.3 Procedure

4.3.1 Weigh green fuel rod (∿15 g) and transfer to a 250 ml Erlenmeyer flask.

4.3.2 Add 100–150 ml of pyridine and heat in a water bath at 75°C until the pitch is dissolved. (∿4 hr)

4.3.3 Decant, rinse twice with pyridine, then repeat 4.3.2.

4.3.4 Transfer the pyridine solution and microspheres to a 60-mesh sieve and wash the microspheres with warm pyridine until all pitch is removed and the pyridine remains clear.

4.3.5 Wash the microspheres 3–4 times with 20 ml portions of benzene.

4.3.6 Wash the microspheres 3–4 times with 20 ml portions of acetone.

4.3.7 Transfer the microspheres to a tared weighing bottle and air dry them for 10 min to remove the highly volatile acetone.

4.3.8 Place the weighing bottle containing the microspheres into a vacuum oven for 30 min at 75°C.

4.3.9 Cool; then weigh microspheres.

5. Disposition of Sample

Return the microspheres to the requestor for physical measurements.

6. Data

Analytical data will be reported on data form UCN-2136A for ultimate transcription to MET-CER-DS-2 or MET-CER-DS-3, or others as appropriate. Append analytical data report sheet with data form MET-CER-D-16.

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Procedure No. MET-FCT-OP-66
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OPERATOR PROCEDURE

Title: Determination of Thorium and/or Uranium in a Green (Unfired) Fuel Rod

Prepared by: F. L. Layton

Approved by: D. A. Costanzo

QA Approval: R. J. Beaver

1. Scope

This specification outlines procedures to be followed for the determination of thorium and/or uranium in a green (unfired) fuel rod.

2. Request

Request for control analyses shall be submitted on sample request forms MET-CER-D-16 and UCN-1910. The original investigator shall indicate on form UCN-1910 any special precautions to be taken with the sample (e.g., fertile and/or fissile particles, enrichment, Biso- and/or Triso-coated particles, accountability, deposition of sample, etc.).

3. Sampling

A fuel rod shall be selected at random from a batch of green (unfired) fuel rods.

4. Dissolution of Green Fuel Rod and Separation of Particles

4.1 Equipment

4.1.1 Water bath, controlled at ∿75°C.

4.1.2 U.S. Standard Sieve, 60 mesh.

4.1.3 Erlenmeyer flasks, 250 ml capacity.

4.2 Reagents

4.2.1 Conc. HNO_3

4.2.2 Conc. $HClO_4$

4.2.3 Na_2CO_3, solid

4.2.4 13M HNO_3 – 0.05M HF

4.2.5 1:20 HF

4.2.6 Pyridine

4.2.7 Acetone

4.3 Procedure

4.3.1 Weigh green fuel rod (∿15 g) and transfer it to a 250 ml Erlenmeyer flask.

4.3.2 Add 100 to 150 ml of pyridine and heat in a water bath at 75°C until the pitch is dissolved and the microspheres can be separated from the solution.

4.3.3 Transfer the pyridine solution and microspheres to a 60-mesh sieve and continue to wash the microspheres with warm pyridine until the pitch is removed and the pyridine solution remains clear.

4.3.4 Wash the microspheres twice with acetone, then transfer them to a tared weighing bottle.

4.3.5 Dry microspheres for 30 min at room temperature or 10 min at ∿75°C, then weigh.

5. Sample Solution Preparation

5.1 Biso-coated particles only.

5.1.1 Equipment

5.1.1.1 Muffle furnace

5.1.1.2 Hotplate

5.1.1.3 Platinum dishes, 100 or 150 ml capacity

5.1.2 Reagents

5.1.2.1 13M HNO_3 – 0.05M HF

5.1.3 Procedure

5.1.3.1 Weigh out a sample to contain an estimated 600–800 mg of heavy metal.

5.1.3.2 Transfer to a 150-ml platinum dish and place in a muffle furnace at 100°C. Introduce CO_2 at a flow of 10–20 cm^3/min. Increase furnace temperature, in 200°C increments, up to 900°C. Maintain sample at each temperature increment below 900°C for 30 min and then maintain the sample at 900°C overnight.

5.1.3.3 Transfer ignited sample to a 400-ml beaker. Rinse the platinum dish with a few milliliters of 13M HNO_3 – 0.05M HF. Use a policeman to remove residue from the dish sidewalls.

5.1.3.4 Add ∿50 ml of 13M HNO_3 – 0.05M to the beaker and heat at 80–90°C until sample is in solution.

5.1.3.5 Cool, then transfer to a tared 200-ml volumetric flask.

5.1.3.6 Dilute to volume with distilled water and weigh.

5.2 Triso-coated particles or mixture of Biso- and Triso-coated particles

5.2.1 Equipment

5.2.1.1 Muffle furnace

5.2.1.2 Spex Mixer-Mill No. 8000, available from Spex Industries, Inc., Metuchen, New Jersey

5.2.1.3 Sample container, hardened steel, 55 ml capacity, Spex No. 8001

5.2.1.4 Platinum dishes, 100 or 150 ml capacity

5.2.1.5 Hotplate

5.2.2 Reagents

5.2.2.1 Conc. HNO_3

5.2.2.2 Conc. $NClO_4$

5.2.2.3 Na_2CO_3, solid

5.2.2.4 13M HNO_3 – 0.05M HF

5.2.2.5 1:20 HF

5.2.3 Procedure

5.2.3.1 Weigh out a sample to contain an estimated 600–800 mg of heavy metal.

5.2.3.2 Transfer to a 150-ml platinum dish and place the dish in a muffle furnace at 100°C. Introduce CO_2 at a flow of 10–20 cm^3/min. Increase furnace temperature, in 200°C increments, up to 900°C. Maintain sample at each temperature increment below 900°C for 30 min and finally maintain at 900°C overnight.

5.2.3.3 Transfer ignited sample to a Spex No. 8001 grinding container, add a 0.5-in.-diam steel ball, and grind for 15 min. in a Spex Mixer-Mill.

5.2.3.4 Transfer ground sample back to the 150-ml platinum dish. To effect a quantitative transfer, wipe the grinding container with strips of acetone-moistened filter paper and include the paper with the sample.

5.2.3.5 Char the paper, then ignite at 900°C for 3–4 hr.

5.2.3.6 Transfer to a 400-ml beaker, add 50 ml of 13M HNO_3 – 0.05M HF, cover beaker with a watch glass, and heat at 80–90°C for 7 hr.

5.2.3.7 After cooling, filter through Whatman No. 42 filter paper. Wash residue thoroughly with water. Set the filtrate aside.

5.2.3.8 Place the filter paper and its contents in a 150-ml platinum dish. Char the paper, then ignite at 900°C for 1–2 hr.

5.2.3.9 Fuse the residue with 10–20 g of Na_2CO_3 over a natural gas-air flame until all reaction stops and melt is clear.

5.2.3.10 Dissolve melt in distilled water. If the solution is clear, dilute it to 100 ml and determine its uranium content fluorometrically. Omit Steps 5.2.3.11–5.2.3.15.

5.2.3.11 If the solution is not clear, filter it through Whatman No. 42 paper and wash the precipitate with water until the washings are neutral.

5.2.3.12 Reduce volume of filtrate and washings (Step 5.2.3.11) to <100 ml, cool, then make to a 100-ml volume. Determine uranium fluorometrically.

5.2.3.13 Place filter paper and its contents (Step 5.2.3.11) into a 250-ml beaker and destroy the paper by wet ashing with HNO_3 and $HClO_4$.

5.2.3.14 Add several drops of 1:20 HF and evaporate the solution to near dryness.

5.2.3.15 Cool, add water, then transfer this solution to the filtrate which has been previously set aside. (Step 5.2.3.7)

5.2.3.16 Transfer the solution from Step 5.2.3.7 or 5.2.3.15 to a tared 200-ml volumetric flask, dilute to volume, and weigh.

6. Heavy Metal Measurement

6.1 Thorium

6.1.1 Equipment

6.1.1.1 pH meter, with calomel and glass electrodes.

6.1.1.2 Weight buret, 10-ml and 30-ml capacity.

6.1.1.3 Magnetic stirrer and stirring bars.

6.1.1.4 Syringe microburet, Model SB2, available from Micro-Metric Instrument Co., Cleveland, Ohio.

6.1.1.5 Syringe, 1.00 µl per division, also available from Micro-Metric Instrument Co.

6.1.1.6 Hotplate

6.1.2 Reagents

6.1.2.1 Perchloric acid.

6.1.2.2 Hydroxlyamine hydrochloride, 20 wt/vol %. Dissolve 100 g of $NH_2OH \cdot HCl$ in water and dilute to 500 ml.

6.1.2.3 Glycine-acetic acid buffer, pH = 2.8. Dissolve 15 g of glycine in one liter of water and add sufficient acetic acid (∿300 ml) to bring the pH to 2.8.

6.1.2.4 Ammonium hydroxide, 1:1. Dilute 50 ml of NH_4OH with 50 ml of water.

6.1.2.5 Ammonium hydroxide, 1:4. Dilute 25 ml of NH_4OH with 100 ml of water.

6.1.2.6 Xylenol orange indicator, 0.1 wt/vol %. Dissolve 100 mg of xylenol orange in 100 ml of 70% ethyl alcohol.

6.1.2.7 Disodium ethylenediamine tetracetate, ∿0.1N. Dissolve ∿9.3 g of EDTA in water and dilute to one liter. Standardize this solution against a standard thorium or copper solution.

6.1.3 Procedure

6.1.3.1 Weigh a sample aliquot (solution from Step 5.2.3.16) estimated to contain 35–45 mg of thorium into a 50-ml beaker.

6.1.3.2 Add 10 drops of $HClO_4$ and heat to perchloric fumes.

6.1.3.3 Cool, wash down beaker sides with water.

6.1.3.4 Add 5 ml of a 20 wt/vol % $NH_2OH \cdot HCl$ solution.

6.1.3.5 Add 2 ml of a glycine-acetic acid buffer solution of pH = 2.8.

6.1.3.6 Using a pH meter, adjust the pH to 3.0 with 1:1 or 1:4 NH_4OH. Add 8 drops of 0.1 wt/vol % solution of xylenol orange.

6.1.3.7 Using a weight buret, titrate with the standard EDTA solution until there is a color change from orange to yellow which fades rapidly.

6.1.3.8 Complete the titration by adding the EDTA from a micrometric syringe until the color change to yellow persists for at least 60 sec.

6.1.4 Calculations

$$\text{Th (mg/g sample)} = \frac{(a + vd)FB}{cW}$$

where a = weight of EDTA solution, g

v = volume of EDTA solution added from syringe, ml

d = density of EDTA solution, g/ml

F = chemical factor, mg Th/g EDTA solution, obtained by titrating a series of thorium standards

B = weight of sample solution, g

c = weight of sample aliquot, g

W = sample weight, g.

6.2 Uranium, volumetric method

6.2.1 Equipment

6.2.1.1 Weight buret, 60-ml capacity.

6.2.1.2 Syringe microburet, Model SB2, available from Micro-Metric Instrument Co., Cleveland, Ohio.

6.2.1.3 Syringe, 1.00 µl per division volume displacement, also available from Micro-Metric Instrument Co.

6.2.1.4 Magnetic stirrer and stirring bars.

6.2.1.5 pH meter, equipped with calomel reference and platinum indicator electrodes.

6.2.2 Reagents

6.2.2.1 Ortho-phosphoric acid, 85%

6.2.2.2 1.5 M sulfamic acid. Dissolve 36.4 g NH_2SO_2OH in water and dilute to 250 ml.

6.2.2.3 1 M ferrous sulfate. Cautiously add 25 ml of concentrated H_2SO_4 to 188 ml of water. Add 70 g of $FeSO_4 \cdot 7H_2O$ and stir until dissolved. Cool, then dilute to 250 ml.

6.2.2.4 8 M nitric acid — 0.15 M sulfamic acid — 0.4% ammonium molybdate. Dissolve 4.0 g $(NH_4)_6MO_7O_{24} \cdot 4H_2O$ in 400 ml H_2O, add 500 ml of conc. HNO_3 and mix. Add 100 ml of 1.5 M sulfamic acid and mix.

6.2.2.5 2% potassium dichromate. Dissolve 2 g of $K_2Cr_2O_7$ in water and dilute to 100 ml.

6.2.2.6 Potassium dichromate, standard solution, ∿0.027 N. Dry and weigh ∿2.5 g of potassium dichromate, dissolve in water, and dilute to 2 liters. Standardize the solution against a standard solution of uranium.

6.2.2.7 Vanadyl sulfate dihydrate, solid.

6.2.3 Procedure

6.2.3.1 Weigh and transfer a portion of the sample solution into a 250-ml beaker. (Sample aliquot to contain 15–150 mg U and to be less than 15 ml in volume.)

6.2.3.2 Place a magnetic stirring bar in the solution; place the beaker on a magnetic stirer; stir slowly.

6.2.3.3 Add 5 ml of sulfamic acid solution.

6.2.3.4 Add 40 ml of H_3PO_4 containing 2 drops of 2% $K_2Kr_2O_7$.

6.2.3.5 Add 5 ml of the ferrous sulfate solution directly to the solution.

6.2.3.6 After 30 sec, add 10 ml of the HNO_3-sulfamic acid-molybdate solution.

6.2.3.7 After the dark brown-black color disappears, allow the solution to stand for 3 min.

6.2.3.8 Add 100 ml of water.

6.2.3.9 Add ∿125 mg of vanadyl sulfate dihydrate.

6.2.3.10 Insert the platinum and calomel electrodes. Turn pH meter to "+MV" and "READ" position.

6.2.3.11 Titrate with standard $K_2Cr_2O_7$ solution from a 60-ml weight buret to a reading of ∿500 MV.

6.2.3.12 Continue the titration from a syringe microburet, adding the dichromate in 0.005-ml increments and recording the MV reading after each addition.

6.2.3.13 Continue incremental additions until a large break occurs, then add an additional increment.

6.2.4 Calculations

6.2.4.1 Calculation of titration end-point

Example:

Volume of Titrant Added	Millivolts	Difference (MV)
0.005 ml	510	
0.010	522	12
0.015	536	14
0.020	559	23
0.025	634	75
0.030	651	17

$$\text{end-point (ml)} = 0.020 + \left[\frac{75 - 23}{2(75) - (23+17)}\right] 0.005$$
$$= 0.020 + 0.002$$
$$= 0.022 \text{ ml}$$

6.2.4.2 Calculations of uranium in sample

$$\text{U(mg/g sample)} = \frac{(a + vd)\ FB}{cW}$$

where a = weight of standard $K_2Cr_2O_7$ added, gram

v = volume of standard $K_2Cr_2O_7$ added, ml

d = density of standard $K_2Cr_2O_7$, g/ml

F = chemical factor, mg U/g $K_2Cr_2O_7$ solution, obtained by titrating a series of U standards.

B = weight of sample solution, gram

c = weight of aliquot, gram

W = sample weight, gram

6.3 Uranium, fluorometric method

6.3.1 Equipment

6.3.1.1 Fluorophotometer, ORNL Model Q-1165

6.3.1.2 Fusion device. Adjust to 900°C for the first two burners and 800°C for the third burner when measured by an optical pyrometer. The fusion period should be 2 min.

6.3.1.3 Pelletizer. Adjust to deliver 300 ± 25 mg of NaF-LiF mixture.

6.3.1.4 Platinum dishes. Available from Fisher Scientific Co.

6.3.1.5 Kahn shaker. Available from Fisher Scientific Co.

6.3.1.6 Blendor. Use a 4-qt. capacity P-K Twin Shell Blendor.

6.3.2 Reagents

6.3.2.1 Trioctylophosphine oxide (TOPO) 0.1 M. Dissolve 25 g of TOPO in 600 ml of cyclohexane.

6.3.2.2 Nitric acid ∿1 M. Dilute 64 ml of HNO_3 to 1 liter with water.

6.3.2.3 Flux, NaF 98% – LiF 2%. Thoroughly blend the powdered anhydrous salts in a Twin Shell Powder Blendor.

6.3.2.4 Hydroxylamine solution. Prepare a saturated solution of $NH_2OH \cdot HCl$ in conc. HCl.

6.3.2.5 Potassium fluoride, 3 M.

6.3.2.6 Dodecane

6.3.2.7 Uranium standard. Prepare a 10 μg U/ml solution in 20% HNO_3 from a more concentrated uranium standard solution.

6.3.3 Procedure

6.3.3.1 Pipet a sample estimated to contain from 1 to 5 mg of uranium into a 20 ml screw cap bottle.

6.3.3.2 Add 5 ml of 1 M HNO_3.

6.3.3.3 If the sample contains iron, add 2 drops of hydroxylamine solution. If the sample contains thorium, add 1 ml of KF solution. Add ∿0.5 ml of conc. HNO_3 to adjust for the added dilution.

6.3.3.4 Pipet 2 ml of 0.1 M TOPO into the bottle.

6.3.3.5 Extract the uranium by shaking the sample for 10 min on a Fisher Kahn Shaker.

6.3.3.6 Centrifuge the bottles and then pipet 50–200 μl aliquots onto NaF-LiF pellets. Do triplicate analyses.

6.3.3.7 Dry pellets, first on a hot plate, then under infrared lamps until the organic solvent has evaporated.

6.3.3.8 Fuse the pellets on the fusion apparatus.

6.3.3.9 Measure the fluorescence of each pellet by means of an ORNL Model Q-1165 fluorophotometer.

6.3.3.10 Determine blank by pipetting 200 μl aliquots of 0.1 M TOPO onto NaF-LiF pellets and follow Steps 6–8 of the Procedure 6.3.3.

6.3.3.11 Read from a calibration curve the amount of uranium which corresponds to the reading on the fluorophotometer.

6.3.4 Calibration Curve

A calibration curve is prepared by carrying aliquots of the 10 μg/ml uranium standard through the above procedure. Plot nanograms of uranium on the pellet as the abscissa versus the fluorescence in millivolts as the ordinate on three-cycle long-log graph paper. The calibration points are shown below.

Uranium Standard (μl)	TOPO (ml)	Aliquot (μl)	Instrument Reading (Uranium, ng)
100	2	100	50
100	2	200	100
200	2	200	200
250	2	200	250
300	2	200	300
500	2	200	500

6.3.5 Calculations

$$\Sigma ng\ U = \frac{100AB}{1000}$$

where 100 = volume of sample solution, ml

A = uranium, ng, from calibration curve

B = dilution factor

7. Data

Analytical data will be reported on data form UCN-2136A for ultimate transcription to MET-CER-DS-2, MET-CER-DS-3, or others as appropriate.

Append analytical data report sheet with data from MET-CER-D-16.

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