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EXAMINATION OF FAST REACTOR FUELS

Final Technical Report

April - June 1968

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Patent Group (Brookhaven)

By. *Belkin*

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EXAMINATION OF FAST REACTOR FUELS

— Final Technical Report —

April - June 1968

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THE UNITED STATES ATOMIC ENERGY COMMISSION

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ABSTRACT

In order to determine the capabilities of the Babcock & Wilcox analytical laboratory to characterize FFTF fuels, sintered $\text{UO}_2\text{-PuO}_2$ pellets were obtained from the Pacific Northwest Laboratory (PNL). This characterization required the development and standardization of several analytical methods. Results were obtained for the following measurements:

Assay for uranium and plutonium.

Isotopic assay.

Gas evolution.

Density.

Homogeneity and solid solution.

Development work was also performed, but no results were obtained because of the lack of time to develop completely the methods for measuring the (1) oxygen-to-metal (O/M) ratio, (2) halogen content (chloride and fluoride), and (3) water evolution.

This project was performed under Phase I of the Los Alamos Scientific Laboratory (LASL) program entitled Examination of Fast Reactor Fuels. It was supported by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3968 and covers the period from April 17, 1968, to June 30, 1968.

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1. INTRODUCTION

This report is concerned with the analytical development work and experimental results obtained in the characterization of sintered UO_2 - PuO_2 pellets. The work was performed under Phase I of the Los Alamos Scientific Laboratory (LASL) program entitled Examination of Fast Reactor Fuels. Phase I of the program was designed "to evaluate the present capabilities of potential fuel producers for making the analytical measurements of FFTF fuel necessary to assure the uniformly high-quality fuel required by the LMFBR/FFTF Program."¹

The pellet material analyzed was from a single batch of sintered UO_2 - PuO_2 pellets, produced by the Pacific Northwest Laboratory (PNL). The batch of pellets was divided among the different laboratories involved in this program. It was realized that the material was not a well-characterized standard material, but it was felt that it would serve to indicate the capabilities of the laboratories to make the measurements required for FFTF fuels.

Development work was performed in the Babcock & Wilcox analytical laboratory, and experimental results on the characterization of the pellets were obtained for the following measurements:

- Assay for uranium and plutonium.
- Isotopic assay.
- Gas evolution.
- Density.
- Homogeneity and solid solution.

Development work was also performed, but no results were obtained because of lack of time to develop completely the methods for measuring the (1) oxygen-to-metal (O/M) ratio, (2) halogen content (chloride and fluoride), and (3) water evolution.

The Examination of Fast Reactor Fuels program was supported by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3968. This report covers the period from April 17, 1968, to June 30, 1968.

2. SUMMARY

2.1. Assay for Uranium and Plutonium

The FFTF pellets were analyzed for plutonium and uranium by controlled-potential coulometry. Standardization of the method was performed primarily by electrical means, using chemical standardization for confirmation. Before analysis of the FFTF pellets, chemical standards of known concentrations of uranium and plutonium were prepared and analyzed both on individual and mixed bases. It was concluded that plutonium and uranium can be analyzed in the presence of each other with about the same accuracy as when they are analyzed separately.

Dissolution of the FFTF pellets was accomplished using an acid solution of 13 M nitric acid and 0.01 M hydrofluoric acid. The samples were refluxed using this acid mixture until the pellets were completely dissolved. The analyses of the resulting solutions for plutonium and uranium were performed using standard analytical laboratory procedures. The actual composition of the analyzed pellets was approximately 75% UO_2 -25% PuO_2 and not the 80% UO_2 -20% PuO_2 composition that was mentioned in the description of Phase I.¹

2.2. Isotopic Assay

The FFTF pellets were analyzed for the isotopic composition of plutonium by thermal-ionization mass spectrometry. A method to analyze 3 to 5 μg samples of plutonium was developed. Standardization of the method and instrument was performed using NBS Reference Material No. 948.

In order to remove the interferences of uranium and americium-241 from the sample prior to analysis, a separation procedure was developed. The procedure is an anion exchange separation using Dowex 1-X2, 200-400 mesh, resin. It is based on the differences in the formation of anionic nitrate complexes of the elements.

2.3. Oxygen-to-Metal (O/M) Ratio

The Fisher 10-560-100 TGA System has been adapted for use in the determination of oxygen-to-metal ratios in uranium, plutonium, and mixed uranium and plutonium oxides. The instrument has been installed in a glove box and is in operating condition.

Preliminary development concerned the elimination of severe oscillations or noise in the recorded weight tracing. Qualitative experiments indicated that a precision of 0.005 O/M units or less should be obtainable. Experiments are planned to develop a procedure capable of routinely yielding this precision.

2.4. Gas Evolution

Because of unforeseen difficulties, standardization of the apparatus was not achieved in the available time. However, the data obtained indicated that the FFTF pellets had a gas release of less than 0.040 cc/g, which was corrected to STP when the sample was analyzed at 1600 C and under reduced pressure.

2.5. Halogen Content (Chloride and Fluoride)

The method investigated for the analysis of chloride and fluoride in a nuclear fuel was one employing specific ion electrodes after pyrohydrolysis. In this method the sample is heated in a tube furnace to a temperature of 1000 C in a stream of moist oxygen. The chloride and fluoride in the sample are volatilized and collected as hydrochloric and hydrofluoric acid. Following the halogen separation from the sample, the activities of the chloride and fluoride ions are measured using specific ion electrodes. Several experiments were performed using sodium fluoride as a standard source of fluoride. In all cases, the amount of fluoride found was less than that taken. More development work on the method is required before the chloride and fluoride content of the FFTF pellets can be determined.

2.6. Density

The density of the pellets was determined using the mercury displacement method. It was determined on each of four FFTF pellets and

averaged 10.88 g/cc. A measure of precision for this procedure was obtained using stainless steel pellets.

A geometrical density was also determined on the same four pellets and averaged 10.76 g/cc.

2.7. Water Evolution

A method for the determination of moisture content ranging from 5 ppm to 5×10^5 ppm in solid samples has been developed using a commercial CEC Solids Moisture Analyzer, type 26-321 AMA. The instrument was adapted for glove box use so that plutonium and other highly toxic materials could be analyzed. Results of analyses performed on sodium citrate, 12.25% H₂O by weight, gave a relative accuracy and precision of 0.65% and 0.39%, respectively. Analyses of UO₂ pellets known to contain less than 50 ppm H₂O yielded a result of 35.4 ± 4.3 ppm (95% confidence limits) with a relative standard deviation of 4.21%.

2.8. Homogeneity and Solid Solution

From visual examination of polished sections and alpha autoradiographs, it appeared that solid solution was achieved and that the pellets were homogeneous.

3. ANALYTICAL MEASUREMENTS

3.1. Assay for Uranium and Plutonium

3.1.1. Introduction

The accurate and precise measurement of uranium and plutonium in a mixed nuclear fuel is of great importance. The primary method used in the Babcock & Wilcox analytical laboratory for these determinations and for the analyses of uranium and plutonium in the FFTF pellets was controlled-potential coulometric titration. The actual methods used for uranium and plutonium analyses may be found in Appendix B as Analytical Methods No. U-1 and No. Pu-2. The apparatus used is easily adapted to glove box operation because only the electrolysis cell is required in the glove box while the coulometer and support equipment are located outside the box. Another distinct advantage of this method over other methods is that a separation of uranium and plutonium is not required before analysis. The design² of the controlled-potential coulometric titrator is based on the control of the electrode potential and the determination of the electrolysis current by integration. The potential of the electrode at which the reaction of interest occurs is continuously controlled with respect to the reference electrode, and a portion of the electrolysis current is integrated; the integral is read out as voltage by means of a potentiometer. The quantity of substance oxidized or reduced is calculated from the voltage by means of Faraday's law of electrolysis—the quantity of electricity flowing through a voltaic cell is proportional to the number of equivalents of a chemical substance that are involved in the chemical oxidation-reduction reaction.

3.1.2. Preliminary Development and Standardization

In order to standardize the controlled-potential coulometer for uranium and plutonium analyses, both chemical and electrical³ means were employed. Chemical standards of known concentrations of uranium

and plutonium were prepared and analyzed on an individual basis. It has been found that, on a routine basis, electrical standardization is easier to perform and gives more reproducible results than chemical standardization. However, before relying on the electrical method as the primary means of standardization, it was decided that the relative accuracy of this method should be investigated using chemical standard No. 950a- U_3O_8 . Plutonium chemical standards were prepared on a weight basis from NBS plutonium metal standard No. 949b. Uranium analyses were performed in a 0.5M H_2SO_4 electrolyte, and plutonium analyses were performed in a 1M HClO_4 electrolyte. The results of the analyses of uranium and plutonium are shown in Tables 3-1 and 3-2. These results are within the experimental precision previously found for the analyses of uranium and plutonium. Therefore, it was concluded that electrical standardization could be used as the primary means of standardization of the coulometric titrators.

In order to determine the expected relative accuracy in the determination of uranium and plutonium in the same sample (without prior separation of uranium and plutonium), mixed standards were prepared to contain a nominal plutonium-to-total metal ($\text{Pu}/\text{U} + \text{Pu}$) concentration of 25%. All analyses were performed on a weight basis. Uranium titrations were conducted in a 0.5M H_2SO_4 electrolyte, and plutonium titrations were performed in a 1.0M HClO_4 electrolyte. The results obtained using the electrical standardization method as compared to the absolute amounts present are shown in Table 3-3. It can be concluded that plutonium and uranium can be analyzed in the presence of each other with about the same accuracy as when they are analyzed separately.

In the dissolution of sintered PuO_2 , appreciable amounts of plutonium(VI) may be formed.⁴ It was therefore necessary to investigate another electrolyte because plutonium(VI) is not reduced quantitatively in the 1M perchloric acid electrolyte; however it has been reported that the reduction of plutonium(VI) is quantitative in 0.5M H_2SO_4 .⁵ This reduction was confirmed in our laboratory and, therefore, the 0.5M H_2SO_4 electrolyte was chosen for use in the analysis of samples which might contain plutonium(VI). A mixed standard ($\text{Pu}/\text{Pu} + \text{U} = 20.3\%$) was analysed for plutonium in the 0.5M H_2SO_4 electrolyte in order to determine the

accuracy to be expected using this electrolyte. The average relative accuracy (0.92%) and the precision obtained were adequate, but not as good as those found for plutonium analyses in the 1.0M HClO_4 electrolyte. However, it was concluded that the 0.5M H_2SO_4 electrolyte should be used in order to obtain quantitative reduction of any plutonium(VI) that might be present. It was also thought that precision and accuracy could be increased in this electrolyte because previous work had indicated that they could possibly equal those obtained using the 1.0M HClO_4 electrolyte. Table 3-4 gives the data obtained on relative precision for uranium and plutonium when analyzed from separate and mixed standards.

Before the actual analysis of the FFTF pellets, some development work was done to determine a satisfactory means for dissolving sintered UO_2/PuO_2 . Pellets containing 20% plutonium, made from coprecipitated oxides and sintered at 1650 C, were used as the samples in the dissolution study. Several combinations of nitric acid and hydrofluoric acid were tried as dissolvers. A solution of 13M nitric acid and 0.05M hydrofluoric acid was found to be the best mixture for dissolution. A 1 gram sample which was previously ground to a fine powder was dissolved in 4 hours with refluxing. A white precipitate was left in the flask but was easily removed by filtration. However, it was concluded that the residue was not from the sample, since the analysis of the solution showed a Pu/Pu + U ratio of 20%. The material is believed to result from the attack of the hydrofluoric acid on the coils of the condenser. It was decided that a lower concentration of hydrofluoric acid might decrease the attack on the condenser's coils without appreciably increasing the dissolution time. A solution of 13M nitric acid and 0.01M hydrofluoric acid accomplished dissolution as rapidly as a 13M nitric acid and 0.05M hydrofluoric acid solution. Therefore, it was decided to try this acid mixture in dissolving the FFTF pellet samples. A piece of pellet that was left from the homogeneity experiments was dissolved in the 13M nitric-0.01M hydrofluoric acid solution in approximately 4 hours and no white precipitate was seen in the flask. In order to determine the dissolution rate for a whole pellet, a practice pellet was ground to a fine powder in a stainless steel grinder that had a tungsten carbide-tipped blade and then dissolved in 15 ml of acid solution. Complete dissolution was achieved in 2 hours; however, a spot test of the solution indicated

the definite presence of iron. The results of a coulometric analysis indicated that a few percent of iron were present. Since it is fairly difficult to obtain precision when applying the iron correction coulometrically, it was decided that a different means of dissolution should be tried—a whole pellet was dissolved without grinding. The pellet took 9 hours to dissolve in 15 ml of the acid solution. A spot test for iron showed that only trace amounts were present. It was decided that the iron could be neglected, since it was in such minute amounts and no means were available to accurately determine it. To speed up the dissolution, a whole pellet was ground into a coarse powder in a porcelain mortar; the whole pellet ground in this manner dissolved in 15 ml of the acid solution in 4 hours.

The five pellets that were used for the actual analyses for uranium and plutonium were dissolved as follows:

1. Two pellets were each dissolved in 15 ml of acid solution for 9 hours under reflux conditions.
2. Three pellets were each respectively ground to a coarse powder in a porcelain mortar and dissolved in 15 ml of the acid solution for 4 hours under reflux conditions.

The detailed procedure used for dissolution may be found in Appendix B as Analytical Method No. Sp-7.

3. 1. 3. Results and Discussion

Five randomly selected FFTF pellets were dissolved for analysis. The analyses of the resulting solutions for plutonium and uranium were performed in accordance with standard laboratory analytical procedures. Four analyses were performed for uranium and plutonium on each solution, and all were done on a weight basis. The results of the analyses are given in Table 3-5. The relative precision obtained is given in Table 3-6. A mixed standard was analyzed at the beginning of the analyses; one was also analyzed at the end of the forty analyses. Both results were found to be accurate within experimental limits. Electrical standardization was done at the beginning of each day's work. This procedure is typical of the normal routine that is practiced. It should be mentioned that the actual composition of the pellets was found to be

approximately 75% UO_2 -25% PuO_2 and not the 80% UO_2 -20% PuO_2 pellet composition that was mentioned in the description of Phase I.¹

The analyses of the FFTF pellets for uranium and plutonium proceeded without difficulty and in accordance with standard routine analytical laboratory procedures. Standardization was accomplished primarily by electrical means, using chemical standardization for confirmation. The results obtained using the controlled potential coulometric titration method demonstrated that good precision and accuracy may be achieved using this method.

Table 3-1. Relative Accuracy of the Controlled-Potential Coulometric Analysis of Uranium Using Electrical Standardization

<u>Titration No.</u>	<u>Electrical factor, mg U/mV readout</u>	<u>Uranium taken, mg</u>	<u>Uranium found, mg</u>	<u>Relative error, %</u>
1	20.50	12.73	12.72	0.08
		6.500	6.508	0.12
		6.641	6.658	0.26
		6.553	6.593	0.61
		Average		0.27
2	20.12	6.550	6.589	0.60
		6.526	6.562	0.55
		6.532	6.567	0.54
		6.556	6.581	0.38
		Average		0.52

Table 3-2. Relative Accuracy of the Controlled-Potential
Coulometric Analysis of Plutonium Using
Electrical Standardization

<u>Titration No.</u>	<u>Electrical factor, mg Pu/mV readout</u>	<u>Plutonium taken, mg</u>	<u>Plutonium found, mg</u>	<u>Relative error, %</u>
3	10.65	10.76	10.80	0.37
		10.55	10.65	0.95
		10.64	10.56	0.75
		10.81	10.74	0.65
		12.02	12.12	0.83
		Average		0.71
4	9.991	10.72	10.74	0.19
		10.67	10.74	0.66
		13.48	13.61	0.96
		10.60	10.69	0.85
Average		0.65		

Table 3-3. Relative Accuracy of the Controlled-Potential
Coulometric Analysis of a Mixed Plutonium
and Uranium System

[Pu/U+Pu = 24.2%] Using Electrical Standardization

<u>Titrator No.</u>	<u>Electrical factor, mg U/mV readout</u>	<u>Metal taken, mg</u>	<u>Metal found, mg</u>	<u>Relative error, %</u>
<u>A. Uranium Analysis</u>				
1	20.50	9.392	9.415	0.24
		9.373	9.361	0.13
		9.209	9.263	0.59
		9.224	9.307	<u>0.90</u>
Average				0.47
2	20.12	9.230	9.304	0.80
		9.254	9.344	0.97
		9.241	9.319	0.84
		9.251	9.304	<u>0.57</u>
Average				0.80
<u>B. Plutonium Analysis</u>				
3	10.65	3.006	3.008	0.07
		2.987	3.005	0.60
		2.984	3.008	0.80
		2.987	3.015	<u>0.94</u>
Average				0.60
4	9.991	2.958	2.951	0.24
		2.952	2.960	0.41
		2.951	2.964	0.44
		2.958	2.973	<u>0.51</u>
Average				0.40

Table 3-4. Relative Precision Obtained on Uranium, Plutonium and Mixed Standards

<u>Titration No.</u>	<u>Metal concentration, mg/g solution</u>	<u>Relative standard deviation, %</u>
<u>A. Uranium Standard</u>		
1	11.83 11.85 11.87 11.91	
Average	$11.87 \pm 0.06^{(a)}$	0.291
2	11.91 11.90 11.90 11.89	
Average	$11.90 \pm 0.01^{(a)}$	0.0686
Average of No. 1 & 2	$11.88 \pm 0.02^{(a)}$	0.251
<u>B. Plutonium Standard</u>		
3	10.20 10.25 10.08 10.09 10.25	
Average	$10.17 \pm 0.10^{(a)}$	0.826
4	10.18 10.23 10.26 10.25	
Average	$10.23 \pm 0.06^{(a)}$	0.348
Average of No. 3 & 4	$10.20 \pm 0.05^{(a)}$	0.683
<u>C. Mixed Standard - Uranium</u>		
1	8.647 8.615 8.676 8.704	
Average	$8.661 \pm 0.004^{(a)}$	0.441

^(a) 95% confidence limits.

Table 3-4. (Cont'd)

<u>Titration No.</u>	<u>Metal concentration, mg/g solution</u>	<u>Relative standard deviation, %</u>
2	8.695 8.710 8.699 8.676	
Average	$8.695 \pm 0.023^{(a)}$	0.163
Average of No. 1 & 2	$8.678 \pm 0.027^{(a)}$	0.377
D. Mixed Standard - Plutonium (24.2 wt %) in Perchloric Acid Electrolyte		
3	2.760 2.775 2.781 2.783	
Average	$2.775 \pm 0.017^{(a)}$	0.375
4	2.752 2.766 2.770 2.772	
Average	$2.765 \pm 0.014^{(a)}$	0.326
Average of No. 3 & 4	$2.770 \pm 0.009^{(a)}$	0.375
E. Mixed Standard - Plutonium (20.3 wt %) in Sulfuric Acid Electrolyte		
3	2.530 2.522 2.506	
Average	$2.519 \pm 0.030^{(a)}$	0.484
4	2.478 2.470 2.483	
Average	$2.477 \pm 0.016^{(a)}$	0.265
5	2.492 2.554 2.471 2.481	
Average	$2.500 \pm 0.059^{(a)}$	1.49
Average of No. 3, 4, 5	$2.499 \pm 0.020^{(a)}$	1.14

(a) 95% confidence limits.

Table 3-5. Results of Analyses of FFTF Pellets for
Both Uranium and Plutonium

<u>Metal determined</u>	<u>Weight of sample used, g</u>	<u>Weight of diluted sample, g</u>	<u>Aliquot size, g</u>	<u>Metal concentration, g/g of pellet</u>
<u>A. Pellet No. 1</u>				
Uranium	1.4159	56.7439	0.2350 0.2320 0.2316 0.2355	0.6637 0.6673 0.6665 0.6653
			Average	0.6657
Plutonium	1.4159	56.7439	1.1412 1.1435 1.1459 1.1458	0.2181 0.2197 0.2202 0.2202
			Average	0.2196
<u>B. Pellet No. 2</u>				
Uranium	1.4989	57.8557	0.2416 0.2371 0.2429 0.2392	0.6670 0.6654 0.6631 0.6678
			Average	0.6658
Plutonium	1.4989	57.8557	1.1700 1.1676 1.1733 1.1747	0.2180 0.2201 0.2190 0.2215
			Average	0.2197
<u>C. Pellet No. 3</u>				
Uranium	1.4746	57.4473	0.2359 0.2326 0.2363 0.2459	0.6653 0.6667 0.6686 0.6665
			Average	0.6668
Plutonium	1.4746	57.4473	1.1467 1.1543 1.1637 1.1646	0.2199 0.2213 0.2201 0.2203
			Average	0.2204

Table 3-5. (Cont'd)

<u>Metal determined</u>	<u>Weight of sample used, g</u>	<u>Weight of diluted sample, g</u>	<u>Aliquot size, g</u>	<u>Metal concentration, g/g of pellet</u>
<u>D. Pellet No. 4</u>				
Uranium	1.3595	57.0449	0.2398	0.6646
			0.2381	0.6674
			0.2406	0.6657
			0.2392	0.6650
			Average	0.6657
Plutonium	1.3595	57.0449	1.1561	0.2178
			1.1573	0.2209
			1.1539	0.2208
			1.1611	0.2200
			Average	0.2199
<u>E. Pellet No. 5</u>				
Uranium	1.4203	57.6461	0.2277	0.6624
			0.2307	0.6591
			0.2215	0.6644
			0.2430	0.6625
			Average	0.6621
Plutonium	1.4203	57.6461	1.1532	0.2178
			1.1575	0.2182
			1.1514	0.2204
			1.1572	0.2186
			Average	0.2188

Table 3-6. Relative Precision Obtained on Uranium and Plutonium Analyses Performed on FFTF Pellets

Pellet No.	Metal ion determined	Amount of metal ion found (95% confidence limits), g/g of pellet	Relative standard deviation, %
1	U	0.6657 ± 0.0025	0.236
	Pu	0.2196 ± 0.0016	0.454
2	U	0.6658 ± 0.0033	0.311
	Pu	0.2197 ± 0.0024	0.683
3	U	0.6668 ± 0.0028	0.267
	Pu	0.2204 ± 0.0010	0.282
4	U	0.6657 ± 0.0020	0.186
	Pu	0.2199 ± 0.0023	0.655
5	U	0.6621 ± 0.0035	0.332
	Pu	0.2188 ± 0.0018	0.526

3.2. Isotopic Assay

3.2.1. Introduction

The accurate and precise measurement of the isotopic composition of plutonium is important from the reactor physics standpoint of having a known fissile content ($^{239}\text{Pu} + ^{241}\text{Pu}$) in the nuclear fuel. The method used in the Babcock & Wilcox analytical laboratory for the determination of the isotopic composition was thermal-ionization mass spectrometry. The instrument employed was a triple-filament thermal-ionization mass spectrometer. It is a 12-in. radius, 60° magnet sector, single-focusing instrument. The method used is described in Appendix B as Analytical Method No. Pu-4.

3.2.2. Preliminary Development and Standardization

In order to determine the isotopic composition of the plutonium by thermal-ionization mass spectrometry, it was necessary to prepare the pellet material in a suitable form. The first problem was to dissolve the material. It was found that the same method used for the plutonium and uranium assay could be used. This method is described in detail in Appendix B as Analytical Method No. Sp-7.

Since the decay of ^{241}Pu to ^{241}Am proceeds with a rather short half-life, it was decided that the ^{241}Am would be an interference in the determination of the ^{241}Pu and, therefore, should be separated from the plutonium. Development work was begun on a separation method. It was decided that the method would be more widely applicable to other problems if it also included the separation of uranium(VI) from plutonium(IV). An anion exchange separation, based on the differences in the formation of anionic nitrate complexes of the different elements, was chosen because it appeared to be the easiest and quickest method to develop. Dowex 1-X4 resin is generally used for this separation, but it was felt that Dowex 1-X2 would be as good and might offer even better kinetic characteristics. Experiments were performed on identical columns of Dowex 1-X4, 200-400 mesh, NO_3^- form resin and Dowex 1-X2, 200-400 mesh, NO_3^- form resin using a ^{235}U tracer to determine the elution characteristics of each resin. It was found that the capacity of the Dowex 1-X2 was less than Dowex 1-X4. The Dowex 1-X2, however, gave sharper elution curves with complete removal of the uranium while the elution curves of the uranium on the Dowex 1-X4 column tailed badly at approximately the same flow rates. As a result of these experiments, Dowex 1-X2 was chosen as the resin to be used.

It has been reported that 7.2M nitric acid gave the maximum distribution coefficient for plutonium.⁶ The uranium was retained at this acidity, but the americium was eluted. The uranium was then eluted with 3M nitric acid while the plutonium was still retained. The plutonium was eluted with 0.6M nitric acid; this acidity was the lowest that could be used without polymerization of the plutonium.⁷

After the parameters above were chosen, the amount of eluent needed to elute each element was determined. One-half milliliter fractions of the eluate were counted in order to determine the elution curve for the americium. The resulting curve is shown in Figure 3-1.

The amount of eluent needed to elute the uranium was determined semi-quantitatively from separations on practice material by estimating the amount of uranium in the plutonium during the mass spectrometric determination of the isotopic composition of the plutonium.

Figure 3-1. Elution Curve for ^{241}Am From a 200-400 Mesh Dowex 1-X2 NO_3^- Form Column Using 7.2 M Nitric Acid as the Eluent. (Column, 0.5×7.0 cm; flowrate, ~ 0.2 ml/min; sample solution volume, 0.5 ml; sample size, 3.5mg; total metal, $\sim 80\%$ U, 20% Pu.)

Hence, practice was received on analysis of isotopic composition as well as determination of the amount of eluent needed to elute the uranium. The results are shown in Table 3-7.

The amount of eluent needed to elute the plutonium was determined qualitatively during the practice runs by knowing the approximate amount of plutonium in the initial sample, and by estimating the amount of plutonium present in the mass spectrometric sample from the strength of its signal in the mass spectrometer.

No effort was made to ensure that this separation was quantitative; therefore, no quantitative control of the oxidation state of the elements was performed. Since the purpose of this method was to prepare samples for mass spectrometric analysis, it was felt that a complete quantitative separation was not required. A detailed description of this separation procedure is given in Appendix B as Analytical Method No. Sep. -4.

An open-faced filament loading box was constructed and positioned so that the filaments, after the sample was placed on them, could be directly loaded into the instrument. Several practice runs were performed on separated plutonium samples. As previously mentioned, these analyses not only gave information about the separation procedures, but also provided practice in the determination of the isotopic composition of plutonium. From these practice analyses and using the National Bureau of Standards method as a guide,⁸ conditions were chosen for the isotopic analysis of plutonium.

Several standards were prepared from the National Bureau of Standards' Reference Material No. 948. The preparation consisted of dissolving the material and separating the ^{241}Am from the plutonium. These standards were used to optimize the procedure for the isotopic analysis of the plutonium. The final method used is given in Appendix B as Analytical Method No. Pu-4.

3.2.3. Results and Discussion

A sample was taken from each of three solutions of the pellets dissolved for the plutonium and uranium assay. Each sample was subjected to the separation described in Appendix B as Analytical Method No. Sep. -4. Three aliquots of each separated plutonium solution

were taken for isotopic analysis. In order to determine the correction factors for each ratio measured ($^{239}\text{Pu}/^{240}\text{Pu}$, $^{241}\text{Pu}/^{240}\text{Pu}$, and $^{242}\text{Pu}/^{240}\text{Pu}$) during the analysis of the samples, four standards were analyzed. These standards, prepared from NBS Reference Material No. 948, were analyzed in the following order:

1. Two before the actual analyses of the samples.
2. One in the middle of the analyses.
3. One after the analyses were completed.

The following correction factors were obtained and used in the calculation of the results:

$^{239}\text{Pu}/^{240}\text{Pu}$	0.99805
$^{241}\text{Pu}/^{240}\text{Pu}$	0.99751
$^{242}\text{Pu}/^{240}\text{Pu}$	0.98308

The results obtained on the samples using the method and instrument described in Appendix B as Analytical Method No. Pu-4 are given in Table 3-8.

Table 3-7. Contamination of Plutonium Samples With Uranium as a Function of Separation Conditions

Sample size		Eluents, HNO_3			Uranium in plutonium fraction, %
Volume, ml	Total metal (80% U-20% Pu), mg	7.2 M, ml	3.0 M, ml	0.6 M, ml	
1.0	7.06	4.2	11.0	17.6	3.0
0.5	3.53	4.4	17.6	17.6	>0.1
0.5	3.53	4.4	26.4	17.6	<0.1 ^(a)
0.5	3.53	4.4	35.2	17.6	<0.1 ^(a)

(a) No distinguishable difference.

Table 3-8. Isotopic Composition of Plutonium in the FFTF Pellets

Pellet No.	Isotopic composition, wt %								No. of individual ratios used in the calculation of the isotopic composition		
	²³⁹ Pu	Standard deviation	²⁴⁰ Pu	Standard deviation	²⁴¹ Pu	Standard deviation	²⁴² Pu	Standard deviation	²³⁹ / ²⁴⁰	²⁴¹ / ²⁴⁰	²⁴² / ²⁴⁰
1	86.868	0.017	11.537	0.017	1.461	0.005	0.134	--	11	12	1
	86.860	0.009	11.553	0.009	1.459	0.002	0.128	0.0003	12	11	12
	86.841	0.005	11.570	0.004	1.458	0.002	0.130	0.002	10	11	12
Average	86.856		11.553		1.459		0.131				
2	86.896	0.003	11.527	0.003	1.451	0.001	0.125	0.001	10	12	12
	86.861	0.014	11.559	0.014	1.452	0.005	0.128	0.001	13	10	10
	86.839	0.015	11.586	0.015	1.449	0.003	0.125	0.002	11	15	12
Average	86.865		11.557		1.451		0.126				
3	86.860	0.011	11.558	0.011	1.450	0.003	0.132	0.001	12	12	12
	86.832	0.008	11.584	0.008	1.453	0.003	0.130	0.002	12	10	12
	86.854	0.021	11.555	0.021	1.457	0.005	0.134	0.004	12	10	14
Average	86.849		11.566		1.453		0.132				

3.3. Oxygen-to-Metal (O/M) Ratio

3.3.1. Introduction

The mixed oxides of plutonium and uranium are being widely investigated and characterized for use as fuels. Many important properties, such as melting point, thermal conductivity, ceramic strength, and chemical reactivity are functions of the stoichiometry or oxygen-to-metal (O/M) ratio of the mixed oxide. Consequently, the determination of O/M ratios is one of the most important analyses necessary in characterizing these or any nuclear fuels.

While O/M ratios have been performed routinely on uranium, plutonium, and mixed uranium and plutonium oxides at this laboratory on a gravimetric basis, the method is long, difficult, and not very sensitive. On the basis of published reports,⁹⁻¹² it was decided that the micro-thermogravimetric method was the most suitable technique in O/M analyses because it gives excellent sensitivity and a precision of 0.005 O/M units.^{9,12}

The procedure to be followed is given by W. L. Lyon:⁹ The sample is dried in argon at 110 C, oxidized in air at 700 C, and then reduced at 700 C under a 94% helium, 6% hydrogen atmosphere. The apparatus used in this laboratory was the Fisher 10-560-100 TGA system with minor modifications for use in a glove box.

3.3.2. Preliminary Development and Standardization

The main problem encountered in the development of the Fisher TGA system for O/M analysis was elimination of the severe oscillations or noise in the recorded weight tracing. The oscillations were found to be caused by three things: electrostatic charge in the hangdown tube and wire, aerodynamic effects of the heated gas in the hangdown tube, and radiant heating of the balance chamber situated directly above the furnace.

Elimination of the electrostatic effects was accomplished by changing from a Nichrome hangdown wire to a quartz filament. Also the rigidity of the quartz filament was helpful in attaching it to the balance. Antistatic silicone spray was not suitable, since it could not be used at temperatures above 600 C. In removing the static charge from the

hangdown tube, wiping the outside with a damp cloth or paper towel before it was positioned in the furnace proved adequate.

The solution to the problem of aerodynamic forces acting inside the hangdown tube was given in the Cahn literature¹³ provided with the TGA system. As suggested, changing to a hangdown tube of 16 mm ID or less reduced the noise in recording the weight to a value of less than 1 μ g. In this case, the original hangdown tube of 18 mm ID was replaced with one of 15 mm ID.

The last source of noise was one that was noticeable only when the unit was operating at temperatures in excess of 600 C for ≥ 1.5 hr. When operating at these elevated temperatures for extended periods of time, the furnace casing became hot to the touch and the heat rose to the floor of the balance chamber. This heat caused noise as a result of the effects of different heat sources within the chamber. A noise level as great as 50 μ g was noted when inert samples were held at 850 C for >1.5 hr. To overcome this effect, a piece of 1/2-inch asbestos was cut and mounted ~ 3 inches below the floor of the balance chamber to serve as a heat shield. In this position, the hangdown tube can be removed and replaced normally without removing the heat shield. With this modification, an inert sample was heated to 1000 C and held there for several hours with a noise level of less than 2 μ g. At 800 C for a comparable length of time, there was no noticeable noise in the weight tracing.

The system has also been checked under dynamic gas flows of 0.05 - 0.20 ℓ/min with no significant increase in noise levels.

Preliminary work at this stage of development has shown good response and sensitivity for UO_2 samples. However, no quantitative work on these samples has been completed.

Because of the time required to ready the TGA system for use, development of the method above could not be completed in time to determine O/M ratios on the FFTF pellets. Upon completion of the development phase of the method, analyses of the FFTF pellets for O/M ratios can be performed.

Future experiments will be performed on UO_2 and mixed UO_2/PuO_2 using a sample size of 17 - 19 mg and operating at gas flow

rates of 0.20 l/min. Using these parameters, it has been found that weight changes can be determined to $\pm 1 \mu\text{g}$.

3.4. Gas Evolution

3.4.1. Introduction

The cladding integrity and coolant channel must be maintained because of mechanical and thermal design considerations. Gas pressure buildup within the cladding occurs because of fission gas generation and sorbed gas release. If sufficient pressure is generated, the cladding may swell or rupture. Fission gas generation may be calculated from fuel burnup data. However, sorbed gas released from the fuel is variable and must be measured. Generally, the allowable release is specified below certain limits. The volume of gas evolved on heating the fuel specimen can be calculated by measuring the increase in pressure within a closed system that contains this sample. The detailed procedure for this measurement is given in Appendix B as Analytical Method No. G-1.

3.4.2. Preliminary Development and Standardization

The apparatus for measuring gas evolution was operated initially with calcium carbonate. The amount of CO_2 released when the sample was heated to 1600 C was determined by measuring the pressure increase within the closed system. The initial pressure within the system was on the order of 0.02 to 0.15 mm Hg absolute. Four determinations were made on Fisher Certified Reagent CaCO_3 , the results of which are listed in Table 3-9. It appears that the apparatus has a bias since the gas release measured in each case was about 40% of that theoretically available from complete decomposition of the specimen.

3.4.3. Results and Discussion

The gas release measurements for CaCO_3 indicate there is a bias in the system and/or the procedure for determining gas evolution. At this time the cause of this bias is not known, but it could be caused by the following:

1. In the case of the CaCO_3 experiment, the deviation between actual and theoretical gas release could result from incomplete

decomposition of the CaCO_3 . This is believed to be unlikely. The sample was heated about 800 C above its decomposition temperature, and a small amount of the sample was used and the measurement was made at a reduced pressure, less than one-tenth of an atmosphere of pressure.

2. The bias could be caused by adsorption of some of the released gas within the system.

3. The non-ideal character of the released gases would also affect the measurement.

While a reproducible bias was indicated for the decomposition of CaCO_3 , it has not been established that this bias can be applied to the indicated gas release from pellets. There was insufficient time during the contract period to explore this problem in detail, so it was decided to measure the gas release of the FFTF pellets by means of the existing system and procedure. Four determinations were made on the FFTF pellets and the sample size for each determination was four pellets. The values obtained on the pellet samples (Table 3-10) appeared realistic and were fairly reproducible; however, it is felt that the values are low, based on the results of the CaCO_3 experiments. The correction factor indicated from the measurement of CaCO_3 decomposition was not applied to the data given in Table 3-10.

Table 3-9. Gas Evolution of CaCO_3

Run No.	Weight sample, g	Gas release		Ratio of actual versus theoretical
		Actual cc at STP	Theoretical cc at STP	
1	0.0157	1.37	3.52	0.39
2	0.0100	0.97	2.24	0.43
3	0.0102	0.99	2.28	0.43
4	0.0094	0.84	2.11	0.40

Table 3-10. Gas Evolution of FFTF Pellets

<u>Run No.</u>	<u>Pellet No.</u>	<u>Total sample weight, g</u>	<u>Gas released, cc/g at STP</u>
1	7, 8, 9, 10	5.8340	0.017
2	53, 54, 55, 56	5.5663	0.010
3	57, 58, 59, 60	5.5905	0.015
4	61, 62, 63, 64	5.9022	0.016

3.5. Halogen Content (Chloride and Fluoride)

3.5.1. Introduction

The halogen content of a nuclear fuel is an important consideration. Chemical reactions of chloride on stainless steel, and fluoride on Zircaloy and aluminum may result in corrosion, embrittlement and ultimate failure^{14,15} of these cladding materials unless chloride and fluoride concentrations are maintained at low levels. (A level of 25 ppm¹⁶ for each has been specified for FFTF fuel.) It is important to know the fluoride content of a nuclear fuel, because during recycle, fluoride is generally added as a catalyst to promote dissolution and it may appear in the final product. In addition, an α, n reaction on fluorine may lead to handling problems during recycle.

The pyrohydrolytic method¹⁷⁻¹⁹ was chosen to separate chloride and fluoride from a nuclear fuel sample. The sample is pyrohydrolyzed at 1000 C in a stream of moist oxygen. The chloride and fluoride present in the sample are volatilized, and they react with the moist oxygen stream to form HCl and HF. Following pyrohydrolysis of a sample and collection of the HCl and HF, the activities of the chloride and fluoride ions are measured using specific ion electrodes.

The method is easily adapted to glove box operation. The tube furnace, specific ion electrodes, and analytical balance for weighing samples are all located inside the box. The furnace controller, specific ion meter, oxygen manifold, and other auxiliary equipment are located external to the box.

3.5.2. Preliminary Development and Standardization

To check the equipment and method, experiments were carried out with known amounts of sodium fluoride. It was found that too much sodium fluoride would cause breakage of the quartz tubes through the attack of hydrofluoric acid liberated on the quartz. The use of sample sizes of less than 25 mg of sodium fluoride eliminated this problem.

Several additional quantitative experiments were carried out using sodium fluoride as a standard. The results are shown in Table 3-11. It can be seen that, in all cases, the fluoride found was less than that taken. More work is needed to determine whether the fluoride is not being quantitatively removed from the sodium fluoride or if it is being lost in the system. Since more experimental work is needed on this method, no results could be reported for the FFTF pellets in time to meet the schedule.

Table 3-11. Quantitative Experiments to Determine the Recovery of Fluoride From the Pyrohydrolytic Separation of Sodium Fluoride

Experiment No.	Pyrohydrolytic conditions					Time of separation, min	Fluoride taken, ppm	Fluoride found, ppm
	Furnace temp, C	Moist O ₂ flow rate, l/min	Flux used	Condenser used	Collecting medium			
1	1000	5	No	No	H ₂ O	60	100	0
2	1000	5	Tungstate	No	H ₂ O	60	100	20
3	1000	5	Tungstate	No	H ₂ O	150	100	21
4	1000	5	Tungstate	Yes	H ₂ O	60	50	15
5	1000	5	Tungstate	Yes	H ₂ O	60	50	21
6	1000	5	Tungstate	Yes	H ₂ O	120	50	16
7	1000	5	U ₃ O ₈	Yes	0.001N KC ₂ H ₃ O ₂ 0.001N HC ₂ H ₃ O ₂	60	100	21
8 ^(a)	1000	5	Tungstate	Yes	H ₂ O	60	100	14

(a) A platinum combustion boat was used to contain the sample instead of the high-fired clay combustion boat used in all other experiments.

3.6. Density

3.6.1. Introduction

Knowledge and control of the density of the fuel in a nuclear reactor is important because it affects the fissile loading per unit volume of the core. The density of a specimen can be determined in various ways. For this program it was specified that the density be determined by the mercury displacement technique. In this method the sample weight is obtained directly, and the sample volume is determined by measuring the amount of mercury displaced by the sample when it is put in a pycnometer. The detailed procedure used in the density determination is given in Appendix B as Analytical Method No. D-3.

3.6.2. Preliminary Development and Standardization

Using the mercury displacement method, numerous density determinations were made on three stainless steel pellets which had the approximate dimensions of the FFTF pellets. The results of these determinations are listed in Table 3-12.

3.6.3. Results and Discussion

Two mercury displacement densities and one geometric density were made on each of the four FFTF pellets, the results of which are listed in Table 3-13.

Since the initial reporting of the FFTF pellet density in the letter progress report, data analysis has indicated that only the initial mercury displacement density of a pellet is valid. It is suspected that after one determination is made, the pellet pore structure may be altered by intrusion of mercury into the open pores. Hence, subsequent mercury displacement measurements would be in error.

Table 3-12, which shows the results for density determinations of three stainless steel pellets, is given only to show the precision that is possible under present operating conditions. This precision cannot be applied to the data obtained for the FFTF pellets, since only one determination can be made on each pellet. Because there is only one value it is statistically impossible to determine a precision. (There is no average and $n-1$ is zero.) However, if the four pellets are

considered as representative of the pellet batch, a precision number can be calculated. Using the density values given in Table 3-13, a relative standard deviation of 1.10% is obtained. This is larger than the deviation for the stainless steel pellets, as would be expected, since a smaller number of determinations are considered and different mixed-oxide pellets are used. In contrast, the same pellet can be used for the stainless steel pellet density determinations.

In making the measurement it is essential that excess mercury is not present on the pycnometer, since a volume of mercury equivalent to a 1-millimeter diameter sphere would result in an error of approximately 3% in the volume determination of a sample having the approximate volume of a typical fast reactor fuel pellet. A second source of error is the sample weight. At present, the relative humidity within the glove box is on the order of 55%; therefore, the humidity is sufficiently high to cause some weight gain by moisture adsorption. Some moisture will be removed during the mercury-filling sequence of the determination, the result of which is that the error introduced by moisture is variable and not known.

Under the current expansion of the laboratory facilities, more glove box space will become available for making the density determination. A vacuum desiccator will be installed to remove moisture from the pellet and to aid in ensuring that the pycnometer assembly is dry. Space will also be available for cleaning solutions to assure removal of any excess mercury from the pycnometer assembly. These procedures should increase the precision of the density measurement.

Table 3-12. Relative Precision Obtained on Stainless Steel Pellets

Sample	Density, g/cc	Relative standard deviation, %
Pellet 1	7.84	
	7.84	
	7.84	
	7.87	
	7.86	
	7.93	
	7.78	
	7.71	
Average	$7.83 \pm 0.06^{(a)}$	0.89
Pellet 2	7.86	
	7.81	
	7.76	
	7.87	
	7.74	
	7.80	
	7.80	
Average	$7.81 \pm 0.06^{(a)}$	0.90
Pellet 3	7.81	
	7.94	
	7.87	
	7.74	
	7.75	
	7.86	
	7.89	
	7.87	
	7.86	
Average	$7.84 \pm 0.04^{(a)}$	0.76

^(a) 95% confidence level.

Table 3-13. Density of FFTF Pellets

Pellet No.	Evacuation pressure, μ Hg ^(a)	Atmospheric pressure, mm Hg ^(b)	Density, g/cc	
			Mercury displacement	Geometrical
2	50	746.5	10.73	10.70
3	50	746.5	10.96	10.81
5	50	747.5	10.99	10.84
6	50	747.5	10.82	10.68
Average			10.88	10.76

(a) Measured with McLeod gage.

(b) Measured with Texas Instrument Fused Quartz Pressure Gage Model 142. This pressure is absolute box pressure.

Conditions of the test:

Box temperature 25 C.

Box relative humidity 50%.

Mercury temperature 25 C.

3.7. Water Evolution

3.7.1. Introduction

The analysis of sorbed moisture content is one of the many analytical determinations which must be made in characterizing a nuclear fuel for use in reactors. Specifications for FFTF fuel pellets require that water evolution be less than 30 ppm.²⁰ Since pellet weights are ~1.5 gm, such analyses necessitated a method capable of microgram determinations of sorbed water in the sample. The possibility of using large samples (i.e., a large number of pellets) was avoided because this technique would mask differences in moisture content from pellet to pellet. In view of these requirements, the Consolidated Electrodynamics Corporation Solids Moisture Analyzer, type 26-321 AMA, which is capable of operating at temperatures from ambient to 1000 C, handling sample sizes from 10 mg to 10 g, and having a sensitivity of 0.1 μ g, was selected for use in the moisture analysis of the FFTF pellets.

The principle of operation is basically one of electrolysis. The sample is heated in the oven in a flow of dry nitrogen, which serves as a carrier gas. The moisture driven from the sample is swept from the oven into the moisture analysis cell by the carrier gas. The cell consists of two electrodes maintained at a fixed potential and connected by a thin film of P_2O_5 , a nonconductor. The moisture is absorbed from the carrier gas by the P_2O_5 , converting it to $P_2O_5 \cdot H_2O$, a conductor that serves as the electrolyte for the electrolysis process. As the absorbed moisture is electrolyzed, the current used is integrated until it reaches a change equal to the number of coulombs necessary to electrolyze 0.1 μ g of water. At this point the integrator is discharged and a pulse is generated to drive a scaler, reading in tenths of a microgram. The process then repeats itself and continues until all the absorbed moisture is electrolyzed and the P_2O_5 film is again rendered nonconducting.²¹

3.7.2. Preliminary Development and Standardization

The instrument was easily modified for glove box use. The oven assembly and analysis cell mounted on the top of the electronics chassis were disconnected, and the electrical leads from the electronics to the cell and oven were lengthened to 10 feet. Thus, only the cell and oven are placed in the glove box, leaving the electronics outside to facilitate electrical repairs.

Before installation in the glove box, a check was performed on the accuracy and precision to be expected during use of this instrument, using hydrated sodium citrate as a standard. The accuracy of the analysis was based on the following reaction and calculations:

$$\text{Mol wt } Na_3C_6H_5O_7 \cdot 2H_2O = 294.11$$

$$H_2O = 18.015$$

$$\frac{2 \times 18.015}{294.11} \times 100 = 12.25\% \text{ (wt \% of } H_2O \text{)}$$

In order to minimize the effect of atmospheric moisture introduced while placing the sample in the oven, and also any sorbed

moisture on the sample, the sample pan, containing a weighed amount of sodium citrate, was placed in the oven at ambient temperature.

The analysis was allowed to run until the counting rate of the scaler dropped to the background rate. (The background counting rate is a function of the moisture content in the carrier gas and is nearly independent of oven temperature. The background rate was determined prior to the sample analysis by placing only the sample pan in the oven at 150 C and checking the counting rate of the scaler with a stop watch until a constant rate was obtained.) At this point the scaler was reset to zero and the oven temperature raised to 150 C. The time required for the counting rate to decrease to the background rate was noted and the analyzer was then turned off. The net moisture content was obtained by subtracting the total background (the background rate multiplied by the analysis time) from the scaler's readout.

Five analyses were performed on sodium citrate. An average weight percent of 12.33 ± 0.06 (95% confidence limits) was found. The relative standard deviation was 0.39% and the relative accuracy was 0.65%. All values were higher than the theoretical water of hydration content, 12.25%, indicating that not all the sorbed moisture was removed from the sample during the blank determination.

A similar check was performed on low-moisture-content samples in order to determine the relative precision that could be expected for samples such as the FFTF pellets. Since no standards were available, uranium dioxide pellets of ~1.4 g each and containing less than 50 ppm water were chosen for this check. Since the moisture content of these pellets is mostly sorbed water rather than water of hydration, the previously described method was not suitable. Instead, a blank was determined by inserting only the sample pan into the oven, raising the temperature to 150 C, and allowing the counting rate to decrease to the background level. Four blanks were run, giving an average of $16.2 \pm 3.3 \mu\text{g}$ (95% confidence limits). The average blank and the total background were subtracted from the gross readout for each pellet. The analyses of the pellets were performed at 150 C and required ~30 minutes per analysis. These pellets were analyzed, yielding an average moisture content of $35.4 \pm 4.3 \text{ ppm}$ (95% confidence limits). The relative standard deviation was 4.21%.

Several problems occurred during installation of the instrument in the glove box:

1. During the installation the quartz oven assembly was broken. Since quartz is quite brittle and in operation the oven assembly is under pressure of the flowing carrier gas, great care must be taken to prevent breakage while handling with gloves.

2. While replacing the broken oven assembly with a new one, considerable difficulty was encountered in reconnecting the gas inlet and outlet tubes. The tubing is tight-fitting, thin-walled, 1/8-inch Teflon, quite ready to collapse when bent. The collapse of the tubing provided a restriction, causing condensation of moisture before it could reach the analysis cell, and reduction of carrier gas flow rate. As a result, analysis of standards gave low moisture contents and very long analysis times.

3. The carrier gas drying tube supplied with the instrument did not operate efficiently when the instrument was used on a laboratory-supply nitrogen line. (Apparently the tube was not capable of reducing fluctuations in the carrier gas moisture content to a constant value.) Consequently, considerable drifting in background was encountered.

All of these factors made analysis of low-moisture-content samples, such as the FFTF pellets, impossible in the instrument's present condition.

Modifications have been undertaken to replace the present oven assembly with one of more sturdy construction, to change the Teflon tubing to Teflon-lined rubber tubing, and to replace the single drying tube with three larger ones, positioned in series with each other. On completion of the above modifications, analyses for water evolution of FFTF pellets and other low-moisture-content samples can be performed.

3.8. Homogeneity and Solid Solution

3.8.1. Introduction

Safety considerations in fast reactors require minimum plutonium agglomerations within the fuel material. The plutonium distribution may be investigated by observing the degree of solid solution

and homogeneity. This distribution was investigated by microscopic examination and alpha autoradiographs of polished pellet sections. A detailed description of the procedure used is given in Appendix B as Analytical Method H-2.

3.8.2. Preliminary Development and Standardization

The methods used for performance of these examinations were developed under an existing AEC project prior to this work.⁴

3.8.3. Results and Discussion

As shown in Figures 3-2 through 3-5, the pellet examined had two phases, the mixed oxide matrix and a pore phase. By visual examination, the mixed oxide matrix appeared uniform, with no third phase material evident in either unetched or etched specimens; therefore, it was assumed that solid solution was achieved. Three types of pores were present in the pellet: massive pores of irregular shape, intergranular pores, and grain-boundary pores.

Homogeneity of the pellet, with respect to plutonium-rich areas, was investigated by visual examination of alpha autoradiographs of a polished pellet section. Parts a, b, and c of Figure 3-6 are photographs in which the alpha autoradiograph (the cellulose nitrate emulsion) was used as a negative; thus a plutonium-rich area would appear as a white spot.

Two problems arose in evaluating the alpha autoradiographs; namely the effect of thickness variations and other defects inherent in the aluminum foil used in this process, and defects in the cellulose nitrate emulsion. Thickness variations in the foil caused the ripple effect that can be observed in the alpha autoradiographs. Defects in the emulsion, such as a bubble, would show up as a dark area, and dust on the emulsion would show up as a light area. Both of these defects had the described light effect when the alpha autoradiograph was used as a negative. The reverse shading would occur if the radiograph were used as a positive.

Figures 3-6a and 3-6b are photographs of two different alpha autoradiographs of the same pellet, in which the aluminum foil was oriented with respect to the pellet by a difference of 90 degrees. In order to determine which light areas were due to plutonium-rich

areas and which light areas were artifacts, the two alpha autoradiographs were superimposed in the same photograph (double exposure), yielding Figure 3-6c. This helped to mask out the ripple effect. If a light spot showed up in all three photographs, it would have indicated a plutonium-rich area. Since the magnification of these figures was 14.4X, a light spot of approximately 1 mm in diameter will represent a 70-micron diameter plutonium-rich area within the pellet. In Figures 3-6a, 3-6b, and 3-6c the same light area could not be detected in all the photographs, visually indicating the absence of plutonium-rich areas of ~70 microns diameter or greater.

In parts a and b of Figure 3-7, the different alpha autoradiographs were used as a positive in producing the photomicrograph, and thus the light areas now indicated plutonium-deficient areas. The mirror image of the area shown in the polished specimen (Figure 3-8) is shown in the alpha autoradiographs in Figure 3-7. The light area noted in the lower left side of parts a and b of Figure 3-7 (foil at 0 and 90 degrees) is shown as a large pore in Figure 3-8. This pore was measured to be approximately 0.030 inch deep; thus the alpha particles from material in the bottom of the pore had to travel a greater distance than alphas being emitted from the surface of the mount. This distance was approximately 1/50 the total distance traveled by plutonium alpha particles in air. It appeared that the alpha particles emitted from the bottom of the pore were attenuated to such a degree that they could not penetrate the aluminum foil placed between the sample and the cellulose nitrate film used to make the alpha autoradiograph. It was found, however, that a pore approximately 0.010 inch deep would not show up on the alpha autoradiograph.

From the photomicrographs and alpha autoradiographs it appeared that a homogeneous solid solution was achieved. It is realized that this evaluation of homogeneity and degree of solid solution is on a visual basis only, and that X-ray analysis and usual homogeneity standards are to supplement the findings. An X-ray unit for both diffraction and emission analysis of plutonium-bearing samples is presently being set up.

Figure 3-2. FFTF Pellet No. 4, Unetched

250×

1 cm = 40 microns

Figure 3-3. FFTF Pellet No. 4, Etched

250×

1 cm = 40 microns

Figure 3-4. FFTF Pellet No. 4, Unetched

400x

1 cm = 25 microns

Figure 3-5. FFTF Pellet No. 4, Etched

400x

1 cm = 25 microns

Figure 3-6. Alpha Autoradiographs of FFTF Pellet No. 6
(14.4× original magnification, 1 cm = 810 microns)

(a)

(b)

(c)

Note: Reproduction processes resulted in a 16% reduction of each part of the figure.

Figure 3-7. Alpha Autoradiographs of FFTF Pellet No. 6
(100X, 1 cm = 100 microns)

(a)

(b)

Figure 3-8. FFTF Pellet No. 6 — Unetched Mirror Image
of Figures 3-7a and 3-7b

100X

1 cm = 100 microns

APPENDIX A
Storage and Handling Procedures

The pellets were received on May 14, 1968, and were immediately removed from the shipping container in a glove box which contained no liquids. They were then put in numbered 2-ml plastic vials and placed in a rack. The temperature and relative humidity of the glove box were recorded every day at the same time to ensure that no large changes in conditions took place. The temperature range in the glove box was 21 to 26 C and the range of the relative humidity was from 41 to 66%.

Although the shipping containers were adequate, one pellet was found to be chipped. It is felt that, for material of this type, a better shipping container is needed. The pellets should be individually packed and sealed in order to avoid direct contact with each other and the atmosphere. In this way, a pellet could remain sealed with respect to the atmosphere and no direct handling of it would take place until the actual analysis was performed.

APPENDIX B
Analytical Methods

The following pages are standard analytical procedures developed by B&W for the examination of fast reactor fuels.

Babcock & Wilcox

Research and Development Division
Nuclear Development Center

P.O. Box 1260 Lynchburg, Va. 24505

Method No. U-1

Revision No. 1

Date June, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Controlled-Potential Coulometric Determination of Uranium

Written by: R. C. Hochel/E. A. Banks/D. H. Schmitt

Revised by: R. H. Dodd - 6/68

Approved by: D. H. Schmitt - 6/68

1. SCOPE AND PRINCIPLE

This method is applicable to the determination of milligram quantities of uranium in aqueous solution. Generally, quantities of uranium of 1-10 milligrams in a volume of 3 milliliters or less¹ are taken for analysis. The procedure is electrolytic and is performed in 0.5 M H₂SO₄ containing 0.02 M sulfamic acid electrolyte using a mercury cathode. Two electrolyses are carried out. The first is a pre-reduction at +0.085 volts vs. the saturated calomel electrode (SCE) and is used to eliminate the interference of small amounts of iron(III) and other oxidants strong enough to oxidize mercury. The mercury(I) ions formed are reduced to metallic mercury during this reduction. Pre-reduction also eliminates interference from the more electropositive ions. This electrolysis is then followed by a reduction of U(VI) to U(IV) at -0.325 volts vs. the SCE. Integration of the current consumed during the reduction of the uranium provides an accurate measurement of the quantity of uranium present by means of Faraday's Law of electrolysis.

Nitrate and chloride do not interfere when their concentrations are less than 0.15 M and 0.1 M, respectively in the sample. However, both cause a positive bias at higher concentrations. Large amounts of phosphate do not interfere with the electrolysis, but do require that the titration vessel be cleaned thoroughly between samples in order to remove the precipitate that results from the reaction of uranium(IV) and phosphoric acid.² Interference from nitrite is eliminated by the sulfamic acid in the electrolyte. Plutonium does not present an interference.

This procedure is the property of Babcock & Wilcox and is intended for internal use. It is subject to change without notice, and the Company cannot assume liability for its completeness or accuracy.

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However, copper(II) presents a definite interference because it is reduced at the same potential as uranium.

2. APPARATUS

- 2.1 Electronic controlled-potential coulometric titrator
- 2.2 Rubicon potentiometer
- 2.3 Electrolysis apparatus (see Figure 1)
 - 2.3.1 Pyrex titration cell, 1.45" ID x 1.62" OD x 2" height
 - 2.3.2 Vycor tubes, 5-1/2" long (top of tube is Vycor 7913, bottom is Vycor 7930)
 - 2.3.3 Platinum wire, 16 gauge
 - 2.3.4 Reference electrode, Calomel 2-5/8" long, fiber junction, pin plug Coleman #3-590
 - 2.3.5 Teflon cap and support for cell and electrode
 - 2.3.6 Stirring apparatus (1800 rpm constant speed motor)
- 2.4 Stopwatch
- 2.5 Volumetric glassware
- 2.6 Argon gas and regulator
- 2.7 Dummy load consisting of precision battery and resistor

3. REAGENTS

- 3.1 Triply distilled mercury
- 3.2 0.5 M sulfuric acid containing 0.02 M sulfamic acid
- 3.3 Concentrated nitric acid
- 3.4 Argon gas
- 3.5 Uranium oxide chemical standard No. 950a - U_3O_8 available from National Bureau of Standards.

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4. PREPARATION OF STANDARDS

Standardization may be accomplished by electrical and/or chemical means. Electrical standardization has been found to be more dependable and easier to perform than chemical standardization on a routine basis. However, results obtained by these two methods should be in good agreement with each other. It is recommended that electrical standardization be used on a routine basis and that chemical means should be employed periodically as an alternate method in order to simulate actual conditions of analysis.

4.1 Electrical Standardization

Electrical standardization is performed using a "dummy load" in place of the chemical titration cell normally used for analysis. The "dummy load" consists of a precision battery and resistor. The electrical standardization factor is determined by measuring the time required for a certain potential change to occur using both the "dummy load" and the instrument in its normal titration mode. The actual number of coulombs per volt may then be calculated. Also, a conversion factor to be used in converting the actual readout for a chemical sample to the quantity of substance oxidized or reduced can be calculated from the equivalent weight of the substance and Faraday's constant.

4.1.1 Procedure for Electrical Standardization in Reduce/Negative Mode

4.1.1.1 Connect the counter (isolated) electrode lead (red) to one end of a 100-ohm precision resistor that is calibrated to +0.05%.

4.1.1.2 Connect the controlled electrode lead (black) to the other end of the resistor.

4.1.1.3 Connect a 4- μ f non-electrolytic capacitor across the resistor.

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4.1.1.4 Connect the positive terminal of a 1.345-volt mercury battery to the counter (isolated) electrode lead (red).

4.1.1.5 Connect the reference lead (white) to the negative terminal of the mercury battery.

4.1.1.6 Turn the REDUCE/OXIDIZE switch to the REDUCE position.

4.1.1.7 Turn the CURRENT RANGE switch to the 100 ma range.

4.1.1.8 Throw the CONT. POT. SUPPLY switch (located on the rear of the chassis) to the OFF position.

4.1.1.9 Throw the TITRATE switch to the RESET position and then to the TITRATE position.

4.1.1.10 With the readout device, measure the potential across the 100-ohm resistor.

4.1.1.11 Calculate the current (I) through the resistor as follows:

Let E = potential across the resistor, volt,

R = resistance of the resistor, ohms,

then Current Through the Resistor, amp = $I = \frac{E}{R}$.

4.1.1.12 Connect the readout device to the readout leads from the instrument. Turn the READOUT switch to the X1 position.

4.1.1.13 Throw the TITRATE switch to the RESET position and then to the TITRATE position.

4.1.1.14 With the timer, measure the time required for the readout to change from 0.010 volt to 0.110 volt.

4.1.1.15 Calculate the electrical factor (F) of the instrument as follows:

Let I = current through the resistor, amp,

V = readout change = 0.100 volt, and

T = time required for readout to change 0.100 volt, second.

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Then the Electrical Factor, coulombs/volt of readout = $F = \frac{IT}{V}$

4.1.1.16 Measure the potential across the resistor again at the end of the timing procedure. If it has changed from the initial value, the average of the two readings should be used in calculating the current.

4.1.2 Procedure for Electrical Standardization in Oxidize/Positive Mode

For calibration in the OXIDIZE position, repeat the above procedure by turning the REDUCE/OXIDIZE switch to OXIDIZE and reversing the polarity of the mercury battery.

4.2 Chemical Standardization

4.2.1 Heat some NBS U_3O_8 at $850^\circ C$ for 1 hour in air to insure the stoichiometry of the U_3O_8 . Repeat to constant weight.

4.2.2 Transfer approximately 0.75 gram to a previously tared 50 ml volumetric flask. (Weigh accurately on a 4-place analytical balance.)

4.2.3 Determine actual quantity of uranium present ($0.8480 \times$ weight of U_3O_8 taken).

4.2.4 Add a small volume of concentrated HNO_3 to the volumetric flask and heat slightly, if necessary, to dissolve the U_3O_8 .

4.2.5 Dilute the $UO_2(NO_3)_2$ solution to volume using distilled H_2O . Weigh the flask and determine the actual weight of the contents. The actual concentration may then be determined on a volume basis (mg U/ml) or a weight basis (mg U/g solution).

4.2.6 Divide the contents of the 50 ml volumetric flask into smaller portions to minimize evaporation effects and thus maintain a good primary standard. This may be done by removing 10 ml aliquots of the original dilution and transferring

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them to previously tared 10 ml volumetric flasks. The flasks are stored until needed. When a standard is required, the flask is weighed and an actual concentration of uranium is determined. In this way, corrections for evaporation are eliminated. Another means for minimizing evaporation is to store the prepared standards in a refrigerator.

5. PROCEDURE

In order to obtain the best results, Sections 5.1 and 5.3 must be carried out in the sequence as given and also on a daily basis.

5.1 Set-up of Readout Device

5.1.1 Connect readout leads from coulometric titrator to Rubicon potentiometer.

5.1.2 With potentiometer switch OFF and SC and EMF buttons up, turn knurled knob of potentiometer until pointer coincides with scale zero.

5.1.3 Turn potentiometer switch ON and adjust zero line of ground glass scale to hairline of spot by pressing down on scale and sliding it in proper direction.

5.1.4 With potentiometer ON, depress SC button and adjust rheostat for zero deflection of pointerlite.

5.2 Calibration of Coulometric Titrator (Indiana Instrument and Chemical Corporation, Automatic Controlled Potential Coulometric Titrator, ORNL Model Q-2005-X50)

5.2.1 With titrator ON, in REDUCE/NEGATIVE MODE, in RESET, and on SPAN CAL positions, turn potentiometer ON and adjust the POTENTIAL SPAN ADJUST to give a readout of 1 volt.

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5.3 Integrator Bias Adjustment

The integrator bias is adjusted in the mode in which actual measurements are made. (REDUCE/NEGATIVE FOR URANIUM, OXIDIZE/POSITIVE FOR PLUTONIUM)

5.3.1 Turn TITRATE switch to RESET position.

5.3.2 Disconnect cell leads from the instrument.

5.3.3 Turn REDUCE/OXIDIZE switch to the REDUCE position.

5.3.4 Turn POLARITY switch to NEG position.

5.3.5 Turn READOUT switch to INTEGRAL-X100 position; the readout should be less than 0.001 volt. Check actual potentiometer reading.

5.3.6 Turn TITRATE switch to TITRATE position and start stopwatch.

5.3.7 Observe readout after 5 minutes. If it has changed more than 0.001 volt, adjust the integrator BIAS using the knob at the right of the titrator and repeat steps 5.3.2 through 5.3.6.

5.3.8 Repeat the above procedure until the readout changes less than 0.001 volt in 5 minutes.

5.3.9 After BIAS adjustment has been made, turn TITRATE switch to RESET and READOUT switch to X1.

5.4 Coulometric Analysis of Uranium Samples

5.4.1 Add 10 ml of 0.5 M H_2SO_4 containing 0.02 M sulfamic acid to the titration cell.

5.4.2 Add the sample containing 1-10 mg uranium in a volume of 3 ml or less.*

*For total uranium analysis, the uranium in the sample must be completely in the +6 oxidation state. If it is not in this state, it should be quantitatively oxidized to the +6 level with a non-interfering oxidizing agent such as nitric acid before the analysis is carried out.

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5.4.3 Position titration cell and electrodes; turn on argon gas supply and allow gas to purge titration cell at a rate of 200 cc/min; start stirring motor. Allow gas to purge titration cell for 3 minutes before beginning titration.

5.4.4 Perform a reduction at +0.085 volts vs. SCE until cell current has decreased to 50 μ amp. END POINT switch should remain on MAN during this operation.

5.4.5 Reset the titrator, adjust settings to REDUCE/NEGATIVE, turn control potential dial to -0.325 volts, turn TITRATE switch to TITRATE, and after current begins to flow, move END POINT switch to AUTO and allow reduction to continue until current has decreased to 50 μ amp. The titration will then be ended automatically and the readout voltage should be recorded.

6. CALCULATION OF RESULTS

Let F = electrical factor, coulombs/volt (see paragraph 4.1.1.15)

M = formula weight of the substance reacted, g/mole

n = number of Faradays (1 Faraday = 96,487 coulombs)

Then conversion factor = $\frac{FM}{n \ 96,487}$

Example:

Let F = 40.00 coulombs/volt

M = 238.0 g U/mole (It should be remembered that this value will change as the isotopic composition of the uranium changes.)

n = 2 Faradays

$$\begin{aligned}\text{Conversion factor} &= \frac{(40.00)(238.0)}{(2)(96,487)} = 0.04933 \text{ g/volt} \\ &= 0.04933 \text{ mg/mv} \left(20.27 \frac{\text{mv}}{\text{mg}}\right)\end{aligned}$$

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For an actual sample analysis, the readout in millivolts is multiplied (or divided) by the conversion factor to obtain weight of U reacted.

Example:

Let conversion factor = 20.27 mv/mg

Let sample readout = 30.00 mv

Let aliquot volume = 0.2000 ml

Then concentration of U = $\frac{30.00 \text{ mv}}{(20.27 \text{ mv/mg})(0.2000 \text{ ml})} = 7.400 \text{ mg/ml}$

7. PRECISION AND ACCURACY

7.1 Precision

The average relative standard deviation (R.S.D.) for 81 analyses for total U in $\text{U}(\text{NO}_3)_4$ solutions was 0.66%, and for 9 analyses of uranium in uranyl nitrate solution was 0.26%. For a series of "knowns" containing only U, the RSD for 8 analyses was 0.25%. For a series of "knowns" containing 24.2 w/o Pu and 75.8 w/o U the RSD for 8 uranium analyses was 0.38%. The RSD for 10 weight analyses of UO_2 sol was 0.39%. It appears from the above that the precision may be dependent on the type of sample analyzed.

7.2 Accuracy

The average relative error of known weight standard containing only U was 0.40% for 8 samples. The average relative error for a known weight standard containing 24.2 w/o Pu and 75.8 w/o U was 0.64% for the 8 uranium samples.

8. OPERATING SUGGESTIONS

The following suggestions are intended to serve as a guide toward more efficient operation of the coulometric titrators.

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8.1 Coulometer

8.1.1 Leave power on at all times.

8.1.2 Never operate instrument in TITRATE position unless chemical cell or dummy load is connected. (An exception to this is when BIAS adjustment is being made.)

8.1.3 Calibrate on a daily basis prior to performing any actual analysis.

8.1.4 Adjust bias on a daily basis following calibration. Perform this adjustment in the mode in which analyses will be done.

8.1.5 Electrically standardize each instrument at least once per week.

8.1.6 Chemically standardize each instrument at least once per week.

8.2 Potentiometer

8.2.1 Adjust standard cell frequently during each day's operation.

8.2.2 Leave pointerlite off except when measurements are actually being made.

8.3 Titration Cell

8.3.1 At the beginning of each day perform the following: empty contents of Vycor tubes and replace with fresh electrolyte, remove stopper from Calomel cell and add saturated KCl to cell if required (stopper should always be removed, even though KCl is not required, to equalize pressure), clean around stirring rod and Teflon cap if required.

8.3.2 The stirring rod must be constructed properly and positioned correctly in the titration cell since stirring has been found to be an important parameter in obtaining a good titration.

8.4 Shutdown Procedure (At the end of each day's operation, the following should be performed)

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- 8.4.1 Turn instrument to RESET
- 8.4.2 Turn OFF potentiometers
- 8.4.3 Turn OFF all stirring motors
- 8.4.4 Turn OFF gas supply at tank
- 8.4.5 Raise gas inlet tube above level of liquid in titration cell.
- 8.4.6 Replace old sample with fresh electrolyte.

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FIGURE 1. COULOMETRIC TITRATION VESSEL

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REFERENCES

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Babcock & Wilcox

Research and Development Division

Nuclear Development Center

P.O. Box 1260 Lynchburg, Va. 24505

Method No. Pu-2

Revision No. 1

Date June, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Controlled-Potential Coulometric Determination of Plutonium

Written by: R. H. Dodd

Revised by: R. H. Dodd - 6/68

Approved by: D. H. Schmitt - 6/68

1. SCOPE AND PRINCIPLE

This method is applicable to the determination of milligram quantities of plutonium in aqueous solution. Generally, quantities of plutonium of about 5 milligrams in a volume of 3 milliliters or less¹ are taken for analysis when the utmost precision is desired. Titration of smaller samples is possible but results will be less precise. Titration of 1 milligram or less should be corrected by running a reagent blank and deducting the reading for the blank from the results for the sample when plutonium is titrated. Small amounts of nitrate (less than 1 M HNO_3) and iron and large amounts of uranium do not present serious interferences in this method.² Sulfate does present an interference¹ in the 1 M HClO_4 electrolyte and if present in other than trace amounts, it is best to titrate in 0.5 M H_2SO_4 to avoid the interference. Also, organic material causes immediate fouling of the control electrode resulting in low cell current, long titration times and erratic results. For a determination of plutonium two electrolyses are performed. First a quantitative reduction of plutonium to Pu(III) is performed, followed by a quantitative oxidation of Pu(III) to Pu(IV). Integration of the current consumed in the oxidation electrolysis provides an accurate measurement of the quantity of plutonium present by means of Faraday's Law of electrolysis. Samples containing Pu(III) and Pu(IV) are electrolytically reduced at +0.555 volts vs. the SCE and subsequently oxidized at +0.895 volts vs. the SCE. (A platinum gauze

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electrode is used as the working (control) electrode.) The supporting electrolyte used in this case is 1.0 M perchloric acid containing 0.02 M sulfamic acid; the latter to destroy traces of nitrite which would present an interference in the method. Pu(VI) is not quantitatively reduced to Pu(III) in the perchloric acid electrolyte. Samples containing or thought to contain Pu(VI) are analyzed in a 0.5 M sulfuric acid electrolyte containing 0.02 M sulfamic acid. Reduction of Pu(VI) and Pu(IV) is performed at +0.310 volts vs. the SCE followed by an oxidation of Pu(III) to Pu(IV) at +0.700 volts vs. SCE.³ It should be noted that iron is reduced and oxidized at these potentials using the sulfuric acid electrolyte and therefore presents an interference if the Pu:Fe weight ratio is 40:1 or less. For the analysis of plutonium in samples containing Pu(VI) and interfering amounts of iron a secondary titration is performed, as is discussed in paragraph 5.6.

2. APPARATUS

- 2.1 Electronic controlled-potential coulometric titrator
- 2.2 Rubicon potentiometer
- 2.3 Electrolysis apparatus (see Figure 1):
 - 2.3.1 Pyrex titration cell, 1.45" ID x 1.62" OD x 2" height
 - 2.3.2 Vycor tubes, 5-1/2" long (top of tube is Vycor 7913, bottom is Vycor 7930)
 - 2.3.3 Platinum gauze, 45 mesh
 - 2.3.4 Platinum wire, 16 gauge
 - 2.3.5 Reference electrode, Calomel 2-5/8" long, fiber junction, pin plug Coleman #3-590
 - 2.3.6 Teflon cap and support for cell and electrodes
 - 2.3.7 Stirring apparatus (1800 rpm constant speed motor)

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- 2.4 Stopwatch
- 2.5 Volumetric glassware
- 2.6 Argon gas and regulator
- 2.7 Dummy load consisting of precision battery and resistor

3. REAGENTS

- 3.1 1.0 M perchloric acid containing 0.02 M sulfamic acid
- 3.2 1.0 M nitric acid
- 3.3 Concentrated nitric acid
- 3.4 0.5 M sulfuric acid containing 0.02 M sulfamic acid
- 3.5 Argon gas
- 3.6 Plutonium metal standard -- available from National Bureau of Standards (#949b)

4. PREPARATION OF STANDARDS

Standardization may be accomplished by electrical and chemical means. Electrical standardization has been found to be more dependable and easier to perform on a routine basis than chemical standardization. However, results obtained by these two methods should be in good agreement with each other. It is recommended that electrical standardization be used on a routine basis and that chemical means should be employed periodically as an alternate method in order to simulate actual conditions of analysis.

4.1 Electrical Standardization

A complete discussion of electrical standardization may be found in Analytical Method No. U-1, Controlled Potential Coulometric Determination of Uranium, paragraph 4.1. It should be noted in the calculation of electrical factor for plutonium that plutonium undergoes a one electron change in oxidation of Pu(III)

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to Pu(IV) as compared to a two electron change for reduction of U(VI) to U(IV) and therefore this difference should be taken into account.

4.2 Chemical Standardization

4.2.1 Weigh the NBS plutonium metal standard accurately on a four-place analytical balance as a comparison to the NBS weight. The standard contains approximately 500 mg of plutonium.

4.2.2 Transfer the weighed plutonium to a previously tared 50 ml volumetric flask.

4.2.3 Add a small volume of concentrated HCl to the volumetric flask to dissolve the plutonium. The metal dissolves rapidly and forms a deep blue colored solution of PuCl_3 . Since the reaction is quite vigorous, care should be taken to avoid loss of sample.

4.2.4 Dilute the PuCl_3 solution to volume with 1.0 M HNO_3 . The color of the solution will change from blue to light brown as Pu(III) is oxidized to Pu(IV) by the HNO_3 . Weigh the flask and determine the actual weight of the contents. The actual concentration may then be determined on a volume basis (mg Pu/ml) or a weight basis (mg Pu/gm solution).

4.2.5 In order to maintain a good primary standard it has proven worthwhile to subdivide the contents of the 50 ml volumetric flask into smaller portions and therefore evaporation effects are minimized. This may be done by removing 10 ml aliquots of the original dilution and transferring them to previously tared 10 ml volumetric flasks. The flasks are stored until needed. When a standard is needed, the flask is weighed and an actual concentration of plutonium is determined. In this way, corrections for evaporation are eliminated.

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5. PROCEDURE

In order to obtain the best results, Sections 5.1 through 5.3 must be carried out in the sequence as given and also on a daily basis.

5.1 Set-up of Readout Device

5.1.1 Connect readout leads from coulometric titrator to Rubicon potentiometer.

5.1.2 With potentiometer switch OFF and SC and EMF buttons up, turn knurled knob of potentiometer until pointer coincides with scale zero.

5.1.3 Turn potentiometer switch ON and adjust zero line of ground glass scale to hairline of spot by pressing down on scale and sliding it in proper direction.

5.1.4 With potentiometer ON, depress SC button and adjust rheostat for zero deflection of pointerlite.

5.2 Calibration of Coulometric Titrator (Indiana Instrument and Chemical Corporation, Automatic Controlled Potential Coulometric Titrator, ORNL Model Q-2005-X50)

5.2.1 With titrator ON, in OXIDIZE/POSITIVE MODE, in RESET, and on SPAN CAL positions, turn potentiometer ON and adjust the POTENTIAL SPAN ADJUST to give a readout of 1 volt.

5.3 Integrator Bias Adjustment

The integrator bias is adjusted in the mode in which actual measurements are made. (OXIDIZE/POSITIVE for plutonium, REDUCE/NEGATIVE for uranium.)

5.3.1 Turn TITRATE switch to RESET position.

5.3.2 Disconnect cell leads from the instrument.

5.3.3 Turn REDUCE/OXIDIZE switch to the OXIDIZE position.

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5.3.4 Turn POLARITY switch to POS position.

5.3.5 Turn READOUT switch to INTEGRAL-X100 position; the readout should be less than 0.001 volt. Check actual potentiometer reading.

5.3.6 Turn TITRATE switch to TITRATE position and start stopwatch.

5.3.7 Observe readout after 5 minutes. If it has changed more than 0.001 volt, adjust the integrator BIAS using the knob at the right of the titrator and repeat steps 5.3.2 through 5.3.6.

5.3.8 Repeat the above procedure until the readout changes less than 0.001 volt in 5 minutes.

5.3.9 After BIAS adjustment has been made, turn TITRATE switch to RESET and READOUT switch to X1.

5.4 Coulometric Analysis of Plutonium Samples Containing Pu(III) and/or Pu(IV)

5.4.1 Add 10 ml of 1.0 M HClO_4 containing 0.02 M sulfamic acid to the titration cell.

5.4.2 Add the sample containing about 5 mg plutonium in a volume of 3 ml or less.

5.4.3 Position titration cell and electrodes; turn on argon gas supply and allow gas to purge titration cell at a rate of 200 cc/min; start stirring motor.

5.4.4 Perform a reduction at +0.555 volts vs. SCE until current has decreased to about 30 μamp . END POINT switch should remain on MAN during this operation.

5.4.5 Reset the titrator, turn control potential dial to 0, adjust settings to OXIDIZE/POSITIVE, turn TITRATE switch to TITRATE, turn CONTROL POTENTIAL dial to +0.895 volts vs. SCE and after current begins to flow, move END POINT switch to AUTO and allow oxidation to continue until current has decreased to 30 μamp . The titration will then be ended automatically and the readout voltage should be recorded.

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5.5 Coulometric Analysis of Plutonium in Samples Containing Pu(VI) but No Iron

Since Pu(VI) is not reduced quantitatively in HClO_4 electrolyte, a 0.5 M H_2SO_4 electrolyte is used to achieve a complete reduction. Sulfate complexes plutonium more strongly than perchlorate, therefore the reduction/oxidation potentials are lower correspondingly. Since iron is reduced and oxidized in the sulfuric acid medium, it may be necessary to apply corrections for iron (see Paragraph 5.6).

5.5.1 Add 10 ml of 0.5 M H_2SO_4 containing 0.02 M sulfamic acid to the titration cell.

5.5.2 Add sample containing about 5 mg plutonium in a volume of 3 ml or less.

5.5.3 Position titration cell and electrodes; turn on argon gas supply and allow gas to purge titration cell at a rate of 200 cc/min; start stirring motor. It is much more important to remove dissolved oxygen from the sulfuric acid electrolyte than from other electrolytes.

5.5.4 Perform a reduction at +0.310 volts vs. SCE until current has decreased to about 30 μamp . END POINT switch should remain on MAN during this operation.

5.5.5 Reset titrator, turn control potential dial to 0, adjust settings to OXIDIZE/POSITIVE, turn TITRATE switch to TITRATE, turn CONTROL POTENTIAL dial to +0.700 volts vs. SCE and after current begins to flow, move END POINT switch to AUTO and allow oxidation to continue until current has decreased to 30 μamp . The titration will then be ended automatically and the readout voltage should be recorded.

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5.6 Coulometric Analysis of Plutonium in Samples Containing Pu(VI) and Iron

Plutonium and iron are oxidized and reduced at the same potentials in the sulfuric acid electrolyte. Therefore it may be necessary to apply a correction to the titration readout when iron is present in the sample. This correction may be calculated if the concentration of iron in the sample is known. Usually, however, the concentration of iron in the sample is unknown and the correction must be applied in a different manner. Iron and plutonium in the sample are first quantitatively oxidized to Fe(III) and Pu(VI) by fuming the sample with 2 ml of concentrated HClO_4 for 15 minutes or by evaporation to fumes using H_2SO_4 followed by dilution to 0.5 M H_2SO_4 and treatment with excess of AgO to convert Pu(IV) to Pu(VI). The excess AgO is destroyed by warming the solution to 85°C before the titration is performed. The titration is then performed by reducing Pu(VI) and Fe(III) to Pu(III) and Fe(II) followed by an oxidation of Pu(III) and Fe(II) to Pu(IV) and Fe(III). The net reaction is then the difference of the two or Pu(VI) to Pu(IV).

5.6.1 Add sample containing Pu(VI) and Fe to Pyrex titration cell.

5.6.2 If sample contains no sulfate, add 2 ml of concentrated HClO_4 and fume for 15 minutes (take care that solution does not go to dryness).

5.6.3 If sample contains sulfate, evaporate to fumes with H_2SO_4 , dilute to 0.5 M H_2SO_4 and treat with an excess of solid AgO to convert Pu(IV) to Pu(VI). Destroy AgO by warming the sample to 85°C.

5.6.4 Add 10 ml of 0.5 M H_2SO_4 containing 0.02 M sulfamic acid to the sample in the titration cell.

5.6.5 Position titration cell and electrodes; turn on argon supply and allow gas to purge titration cell at a rate of 200 cc/min; start stirring motor.

5.6.6 Perform a reduction at +0.270 volts vs. SCE until current has decreased to 30 μamp . End point switch should be on AUTO during this operation. Record reduction readout.

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5.6.7 Reset titrator, turn control potential dial to 0, adjust settings to OXIDIZE/POSITIVE, turn TITRATE switch to TITRATE, turn CONTROL POTENTIAL dial to 0.700 volts vs. SCE and after current begins to flow, move END POINT switch to AUTO and perform oxidation until current has decreased to 30 μ amp. The readout should be recorded when titration is completed.

5.6.8 The reduction and oxidation reactions are:

- (1) Reduction: $\text{Fe(III)} \rightarrow \text{Fe(II)}$
 $\text{Pu(VI)} \rightarrow \text{Pu(III)}$
(2) Oxidation: $\text{Fe(II)} \rightarrow \text{Fe(III)}$
 $\text{Pu(III)} \rightarrow \text{Pu(IV)}$

By subtracting equations (1) from equations (2) the net reaction of $\text{Pu(VI)} \rightarrow \text{Pu(IV)}$ is obtained. It should be noted that the net reaction is that of a 2 electron change and therefore this change must be considered when calculations are made.

6. CALCULATION OF RESULTS

6.1 Sample calculation for samples as analyzed in Paragraphs 5.4 and 5.5.

6.1.1 Let electrical factor = 10.15 mv/mg (or 0.09852 mg/mv)

6.1.2 Let readout voltage = 50.40 mv

6.1.3 Let aliquot volume = 1.000 ml

6.1.4 Then concentration of Pu = $\frac{50.40 \text{ mv}}{(10.15 \text{ mv/mg})(1.000 \text{ ml})} = 4.966 \text{ mg/ml}$

6.2 Sample calculation for samples as analyzed in Paragraph 5.6.

6.2.1 Let electrical factor = 20.30 mv/mg (or 0.04926 mg/mv)

(Electrical factor is twice that in 6.1.1 since there is a two (2) electron change.)

6.2.2 Let readout voltage from 5.6.1 = 100.5 mv

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6.2.3 Let readout voltage from 5.6.7 = 70.2 mv

6.2.4 Let aliquot volume = 0.2000 ml

6.2.5 Then concentration of Pu = $\frac{(100.5 \text{ mv} - 70.2 \text{ mv})}{(20.30 \text{ mv/mg})(0.2000 \text{ ml})} = 7.463 \text{ mg/ml}$

7. PRECISION AND ACCURACY

7.1 Precision

The RSD for 26 weight analyses for total Pu in an "ampoule" was 0.82%. The average RSD for a series of 38 samples containing Pu(VI) and U resulting from gel addition contact experiments was 1.33% for triplicate analyses on each sample. The RSD for 9 weight analyses of PuO₂ sol was 0.37%. For a series of "knowns" containing only Pu the RSD for 9 analyses was 0.68%. For a series of "knowns" containing 24.2 w/o Pu and 75.8 w/o U, the RSD was 0.38% for 8 analyses. It can be seen from the above results that precision is dependent on the type of sample that is analyzed.

7.2 Accuracy

The average relative error of a known weight standard containing Pu only was 0.68% for 9 samples. The average relative error for a known weight standard containing 24.2 w/o Pu and 75.8 w/o U was 0.50% for 8 samples.

8. OPERATING SUGGESTIONS

The following suggestions are intended to serve as a guide toward more efficient operation of the coulometric titrators.

8.1 Coulometer

8.1.1 Leave power on at all times.

8.1.2 Never operate instrument in TITRATE position unless chemical cell or dummy load is connected. (An exception to this is when BIAS adjustment is being made.)

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8.1.3 Calibrate on a daily basis prior to performing any actual analysis.

8.1.4 Adjust bias on a daily basis following calibration. Perform this adjustment in the mode in which analyses will be done.

8.1.5 Electrically standardize each instrument at least once per week.

8.1.6 Chemically standardize each instrument at least once per week.

8.2 Potentiometer

8.2.1 Adjust standard cell frequently during each day's operation.

8.2.2 Leave pointerlite off except when measurements are actually being made.

8.3 Titration Cell

8.3.1 At the beginning of each day perform the following: empty contents of Vycor tubes and replace with fresh electrolyte, remove stopper from calomel cell and add saturated KCl to cell if required (stopper should always be removed, even though KCl is not required, to equalize pressure), clean around stirring rod and Teflon cap if required.

8.3.2 It is important⁴ to change Vycor tubes when changing from one electrolyte to another; i.e. from H_2SO_4 to $HClO_4$. Therefore, a spare set of Vycor tubes should be stored in the electrolyte not being used in order to be able to switch over to the other electrolyte without having to condition the tubes.

8.3.3 Since organic material is known to foul the control electrode, the electrodes must be periodically removed, boiled in concentrated HNO_3 , and rinsed thoroughly before being reused. It is good practice to have a spare control electrode available for each titration cell. This clean electrode can be substituted when

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the electrode in use becomes fouled. Indications of a fouled electrode are low initial cell currents (<10 mv), long titration times, and poor precision.

8.3.4 The stirring rod must be constructed properly and positioned correctly in the titration cell since stirring has been found to be an important parameter in good titration.

8.4 Shutdown Procedure (At the end of each day's operation, the following should be performed)

- 8.4.1 Turn instrument to RESET
- 8.4.2 Turn OFF potentiometers
- 8.4.3 Turn OFF all stirring motors
- 8.4.4 Turn OFF gas supply at tank
- 8.4.5 Raise gas inlet tube above level of liquid in titration cell
- 8.4.6 Replace old sample with fresh electrolyte

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Figure 1. Coulometric Titration Vessel

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Method No. Sp-7

Revision No. _____

Date June, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Dissolution of Sintered UO_2/PuO_2 Samples

Written by: R. H. Dodd - 6/68

Approved by: D. H. Schmitt - 6/68

1. SCOPE AND PRINCIPLE

This method describes the techniques used in handling and dissolving sintered UO_2/PuO_2 samples in preparation for U and Pu analysis. The dissolution^{1,2,3} is performed by refluxing the sample in a solution of 13 M HNO_3 and 0.01 M HF. The dissolution may also be performed in 13 M HNO_3 and with HF concentrations as high as 0.05 M but these higher concentrations result in the formation of a white precipitate, presumed to be silica which must be separated prior to analysis. There is apparently no silica formed during dissolution in 0.01 M HF.

If the sample to be dissolved is in pellet form, the sample is crushed prior to dissolution in order to increase the surface area and thus to increase the dissolution rate. Care should be taken, however, during the crushing process not to introduce contaminants such as iron from a stainless steel grinder which might present an interference in subsequent analysis. For this reason, a porcelain mortar and pestle is recommended for crushing the sample.

2. APPARATUS

2.1 Analytical balance

2.2 Hot plate

2.3 Reflux condenser (Graham) with 28/15 ball joint, 10" height

2.4 Flat-bottomed boiling flasks, 250 ml with 28/15 socket joint

2.5 Ring stand and clamps

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2.6 Mortar and pestle, porcelain

2.7 Tongs and forceps

2.8 Volumetric glassware

3. REAGENTS

3.1 13 M nitric acid which is also 0.01 M hydrofluoric acid

3.2 1 M nitric acid

4. PREPARATION OF STANDARDS

Not applicable for this method.

5. PROCEDURE

5.1 Transfer the sample of UO_2/PuO_2 to a previously tared flat-bottomed boiling flask; reweigh to determine the actual weight of the sample. If the sample is a pellet, it may be desirable to crush it to increase the rate of dissolution; follow steps 5.1.1 and 5.1.2.

5.1.1 Weigh the uncrushed pellet; transfer to a mortar and pestle and grind until a satisfactory particle size is obtained. Take care to avoid sample loss during the grinding operation.

5.1.2 Perform a quantitative transfer of the crushed sample to a previously tared flat-bottomed boiling flask, reweigh to determine the actual weight of the sample.

5.2 Transfer the flask containing the sample to the refluxing apparatus. Add 15 ml of 13 M HNO_3 , 0.01 M HF (for a 1.0-1.5 gram sample) to the boiling flask; connect the flask to a condenser and reflux until the sample is dissolved. It may be necessary to reflux the sample for several hours in order to obtain complete dissolution.

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5.3. Following the dissolution, allow the solution to cool.

5.4 Quantitatively transfer the solution to a previously tared volumetric flask; dilute to volume using 1 M HNO_3 and reweigh to determine the weight of contents. (Since weight and volume are both known, analytical results may be given on either a weight or volume basis.)

6. CALCULATION OF RESULTS

Not applicable for this method.

7. ACCURACY AND PRECISION

Not applicable for this method.

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Method No. Pu-4

Revision No.

Date July, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Mass Spectrometric Determination of the Isotopic Composition of Plutonium

Written by: J. W. Ewing - 6/68

Approved by: D. H. Schmitt - 7/68

1. SCOPE AND PRINCIPLE

This method is applicable to the determination of the isotopic composition of plutonium using a triple-filament, thermal-ionization mass spectrometer. It is designed for a sample size of 3-5 μ g of plutonium as a deposit produced by evaporating an aqueous plutonium nitrate solution to dryness on the two side filaments. The method is a slightly modified version of the one developed at the National Bureau of Standards.¹ The most significant characteristic of the procedure is the "peak switching" in which isotopic ratios are measured by alternately monitoring the peak heights of the two isotopes involved.

2. INSTRUMENTATION

2.1 Mass Spectrometer

The mass spectrometer is a 12" radius, 60° magnet sector, single focusing instrument. For plutonium analysis, it is used in a triple-filament thermal-ionization mode. The instrument was assembled following the National Bureau of Standards redesign of the Consolidated Electrodynamics Corporation Model 21-703 and uses a tube, source, and collector fabricated by C.E.C. to 21-703 specifications. An electron multiplier is not currently used in the system.

This procedure is the property of Babcock & Wilcox and is intended for internal use. It is subject to change without notice, and the Company cannot assume liability for its completeness or accuracy.

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2.2 Measuring System

The measuring system utilizes an Applied Physics Corporation Model 31 MS Electrometer Amplifier and a strip chart recorder with an "expanded-scale" attachment. This attachment allows greater sensitivity and precision by nulling all but the top increment of the signal. This top increment is then measured using the full width of the chart paper.

2.3 Filament Loading Box

For plutonium analysis, an open-faced box is attached to the source opening of the spectrometer. All sample handling and filament loading is done in this box. This procedure allows safe and efficient sample and filament preparation while minimizing the spread of radioactive contamination.

3. SAMPLE PREPARATION

3.1 Pre-Treatment

This procedure is followed in order to obtain a filament loading solution of approximately 15 μg Pu/ml in 1:19 nitric acid ($\sim 0.8\text{M}$). About 0.25 ml of this solution is used to load the filaments. The usual samples have been previously processed according to the plutonium dioxide dissolution procedure, B&W Analytical Method No. Sp.-7, and the chemical separation procedure, B&W Analytical Method No. Sep.-4. This treatment yields a plutonium nitrate solution in dilute nitric acid which is evaporated to dryness.

The sample is usually received as a dried deposit in the tip of a 5.0 ml conical, glass centrifuge tube in a sealed plastic bag contained in a paper carton.

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The sample size has been specified as 3-5 μg Pu. This size is a compromise between the larger samples, which give larger signals yielding greater precision and the contamination hazard associated with such larger samples.

The dried sample is transferred into the open-faced filament loading box and the bag is unsealed. About 0.25 ml of dilute nitric acid (1:19) is added to the sample. A minimum of four hours is required for sample dissolution. Overnight soaking is preferred.

3.2 Filament Loading

The filaments are made from 0.030" wide x 0.0012" thick rhenium and are neither baked nor treated in any manner. The sample solution is transferred dropwise to the two rhenium side filaments. The sample solution is dried using 1A of alternating current. After all of the sample solution has been transferred to the two filaments and dried, the filament current is increased to 1.2A for a period of 2 minutes. The current is then increased slowly until a black phase has disappeared or until 2A has been reached, at which time the current is reduced to zero.

The filaments are then assembled into a unit using a clean block and jig.

4. PROCEDURE

4.1 Instrument and Filament Preparation

4.1.1 Instrument Venting, Loading, and Pumpdown

The spectrometer is vented with helium, the source flange removed, and the filament assembly placed in position.

The flange is replaced and held in position by the "house vacuum" (508-635 Torr) until the bolts of the flange with the gold "O" ring seal are in place and tightened to the proper torque.

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The "house vacuum" valve is closed and the two valves of the roughing pump are opened. Roughing continues for 10 minutes despite the fact that a base pressure of 2×10^{-3} Torr is achieved within three minutes.

The valves of the roughing pump are then closed and the mercury diffusion pump gate valve is opened. After 3 minutes, the ion pump gate valve is opened. The source ion gauge is degassed for 1 minute.

4.1.2 Filament Outgassing

When the source pressure as indicated on the source ion gauge reached 1×10^{-6} Torr, outgassing of the sample and filaments is begun. The center filament current is set at 5A and the side filaments at 1A. Outgassing continues for 5 minutes at which point the filament currents are turned off. All filament currents remain at zero for a minimum of 10 minutes. Liquid nitrogen is introduced into the source "cold-finger" 3 minutes after the outgassing current is turned off. The ion gauge is outgassed for 1 minute. At the end of the 10 minute dormant period, the pressure in the source region should be less than 5×10^{-7} Torr and should be falling slowly. If this condition does not prevail, the gold "O" ring on the source region flange is probably leaking. Also during the 10 minute dormant period, the main amplifier input is grounded; the amplifier and recorder zero controls adjusted; and the zero readings of the various amplifier ranges noted for possible future reference.

4.1.3 Filament Temperature Adjustment

When the vacuum and measuring systems are ready, the accelerating voltage is turned on (8.5 kV). Date, time, and source pressure data are noted on the chart. Any unusual conditions or procedures pertinent to the particular sample such as sample size, trouble in loading, unusual color of sample during loading, etc. are also noted.

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The center filament current is set at 5A. The magnet current is adjusted so that the Re-187 ion beam falls on the detector. Then, the center filament current is increased until the Re-187 signal is 650 mV.

The side filament currents are set at 1A. A mark is made on the chart at this time as a time reference for future manipulations. Starting at this time, a rigid schedule is used in the control of filament temperatures and the collection of data.

At the 5 minute mark, the center filament is readjusted so that the Re-187 signal is kept at 650 mV. The magnet current is then adjusted to the point where the Pu-239 signal is expected. Only in rare cases will a signal be found at this side filament current setting.

At the 6 minute mark, the side filament currents are increased to 1.5A. A small plutonium signal is usually obtainable at this setting. If uranium contamination is present, care must be taken not to confuse the plutonium signal with the uranium signal which usually predominates at this temperature.

At the 11 minute mark, the center filament current is increased slightly so that the Re-187 signal remains at 650 mV. The Re-187 signal has usually reached equilibrium by this time so that it should not need further adjustment.

At the 12 minute mark, the side filament currents are increased to 1.7A.

At the 18 minute mark, the side filament currents are increased to about 1.8A.

At the 24 minute mark, the side filament currents are increased to about 1.9A.

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The analyst must determine, from experience and the "feel" of the earlier side filament adjustments, the exact amount of side filament current adjustment. If the temperature is increased past a variable critical point, the signal will decay at a very high rate making peak height measurements very difficult with consequent poor precision. On the other hand, if the temperature is held too low, the signal is so small that measurement precision is also poor.

4.2 Ratio Measurement

Measurement of the Pu-239/Pu-240 ratio is begun at the 30 minute mark. However, the analyst must determine the amplifier ranges that will provide the most precise data for each ion beam in time to allow the measurement of the background on either side of each ion beam prior to the 30 minute mark.

The magnet current is changed, using a pre-set switch, each 30 seconds from one ion beam to the other until twelve acceptable ratio measurements have been made. If the instrument response seems inconsistent, the analyst may reject a measurement by marking an X through the minor isotope trace.

The background is again determined immediately after a set of ratio measurements on both sides of each of the ion beams on the range used in the ratio measurement.

A set of Pu-241/Pu-240 ratio measurements and finally a set of Pu-242/Pu-240 ratio measurements are made in similar fashion to the Pu-239/Pu-240 measurements above, including the pertinent baseline measurements before and after each set of ratio measurements.

At the conclusion of the Pu-242/Pu-240 measurements, the Re-187 signal is measured and noted on the chart. The following data are then recorded on the chart:

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Date & Time

Source Region Ion Gauge Reading

Sample Number

Final Filament Current Readings

Any unusual aspects of the preparation or measurement

4.3 Chart Reading

The baseline reading of all but the largest ion beam is determined as that reading of the trace extrapolated between the traces on either side of the ion beam trace that falls directly under the maximum ion beam reading. The baseline reading of the largest ion beam in the spectrum is the minimum baseline reading at some distance from the spectrum.

Ion beam ratios are made by projecting on the chart paper a line between two consecutive major beam traces. A "best fit" straight line is drawn through the minor beam trace. Chart paper readings of each beam reading are then made at the same point.

5. CALCULATION OF RESULTS

5.1 Manual Calculations

The mass spectrometer is usually used in a mode in which the data is in the form of ratios. Considering a four isotope system, each of three would be compared to the fourth isotope yielding three ratios as the output data.

5.1.1 Atom Percent Calculations

In essence, these three ratios can be transformed into an isotopic analysis by a simple normalization process. The units resulting from such a computation are known as atom percent values.

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If A, B, C and D represent the signal strengths of the four isotopes of a 4 isotope element, the mass spectrometer data might be the ratios: $\frac{B}{A}$, $\frac{C}{A}$ and $\frac{D}{A}$.

Atom percent values are calculated as follows:

$$\text{Atom \% of isotope B} = \frac{B/A \times 100}{\frac{A}{A} + \frac{B}{A} + \frac{C}{A} + \frac{D}{A}}$$

$$C = \frac{C/A \times 100}{\frac{A}{A} + \frac{B}{A} + \frac{C}{A} + \frac{D}{A}}$$

$$D = \frac{D/A \times 100}{\frac{A}{A} + \frac{B}{A} + \frac{C}{A} + \frac{D}{A}}$$

$$A = \frac{A/A \times 100}{\frac{A}{A} + \frac{B}{A} + \frac{C}{A} + \frac{D}{A}}$$

If: $B/A = 0.5$

$C/A = 2.0$

$D/A = 3.0$

$$\text{Atom \% isotope A} = \frac{1 \times 100}{1 + .5 + 2 + 3} = \frac{100}{6.5} = 15.38\%$$

$$B = \frac{.5 \times 100}{1 + .5 + 2 + 3} = \frac{50}{6.5} = 7.69\%$$

$$C = \frac{2 \times 100}{1 + .5 + 2 + 3} = \frac{200}{6.5} = 30.77\%$$

$$D = \frac{3 \times 100}{1 + .5 + 2 + 3} = \frac{300}{6.5} = 46.15\%$$

99.99%

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5.1.2 Weight Percent Calculations

To determine the weight percent values for an isotopic analysis, it is necessary to know the atom percent values and the mass of each isotope. If it is desired to calculate weight percent values for the previous hypothetical problem, it will be necessary to assign some isotope mass values:

Isotope A: 100.00 amu

Isotope B: 101.01 amu

Isotope C: 102.03 amu

Isotope D: 104.05 amu

The product of atom percent values and mass values is then calculated for each isotope

$$A \quad 15.38 \times 100.00 = 1,538.00$$

$$B \quad 7.69 \times 101.01 = 776.77$$

$$C \quad 30.77 \times 102.03 = 3,139.46$$

$$D \quad 46.15 \times 104.05 = \frac{4,801.91}{10,256.14}$$

$$A \text{ weight \% isotope A} = \frac{1538.00 \times 100}{1538.00+776.77+3139.46+4801.91} = \frac{153,800.00}{10,256.14} = 15.00\%$$

$$B = \frac{776.77 \times 100}{10256.14} = 7.57\%$$

$$C = \frac{3139.46 \times 100}{10256.14} = 30.61\%$$

$$D = \frac{4801.91 \times 100}{10256.14} = \frac{46.82\%}{100.00\%}$$

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5.2 Computer Processing

All data are written on a form from which cards are punched for computerized data reduction. The computer program is a general purpose isotopic analysis program which provides either isotopic ratios or atom and weight percent values and the standard deviation values of each set of measurements.

5.2.1 Computer Input

The following input data are required:

Sample number

Total number of isotopes

Desired output (ratios or ratios plus atom and
weight percents)

Order of isotopes presented

Mass of each isotope

Number of points for each ratio set

Statistical variance limit for individual data
point rejection

Ratio correction factor composed of:

amplifier calibration factor for ranges
used in each set

"bias" factor determined from deviation
of standards data from certified values.

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5.2.2 Computer Output

The computer provides a great variety of printout data including all input data, baseline data and range correction factors, raw ratio values and much other data. The printout of the results includes for each ratio:

Uncorrected set averages with standard deviation

Correction factors (amplifier + bias)

Corrected set averages with standard deviation

If so requested in the input, the printout also includes for each isotope:

Atom percent values with standard deviation

Weight percent values with standard deviation

5.3 Correction Factors

Background baseline corrections are applied before individual ratio calculations.

Amplifier calibration corrections and bias corrections are combined and applied after the ratio measurements have been averaged.

Data are normally rejected if they fall outside of the range of plus or minus twice the standard deviation of the group.

All ratio measurements are made relative to Pu-240.

Method No. Pu-4

Revision No.

Date July, 1968

REFERENCE

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Technical Note 277, U. S. Government Printing Office, Washington, D. C.,
20402, July 25, 1966, p. 45.

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Method No. Sep-4

Revision No. _____

Date June, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Separation of Uranium(VI), Plutonium(IV) and Americium(III)
by Anion Exchange Chromatography for Mass Spectrometric
Analysis

Written by: D. H. Schmitt - 6/68

Approved by: D. H. Schmitt

1. SCOPE AND PRINCIPLE

This method is applicable to the separation of milligram quantities of uranium(VI), plutonium(IV), and americium(III) in aqueous solution for mass spectrometric analysis. The separation is based on the ion exchange behavior of anionic nitrate complexes of both plutonium(IV) and uranium(VI) from 7.2 M nitric acid. These complexes are sorbed on an anion exchange column from the 7.2 M nitric acid while the americium(III) is not retained. The nitric acid concentration of the eluent is then reduced to 3 M and the uranium(VI), because its nitrate complex has a weaker formation constant than that of plutonium(IV), is eluted while the plutonium(IV) is still held on the column. The plutonium(IV) is removed with 0.6 M nitric acid. This acidity is the minimum that can be used without polymerization occurring.² Although Dowex 1-X4 in the NO_3^- form has been used by several workers,³ it has been found experimentally in the Babcock & Wilcox laboratory that Dowex 1-X2, 200-400 mesh, NO_3^- form gave a sharper elution band for a U-235 tracer and that flow rates (~0.2 ml/min) were comparable to the Dowex 1-X4 in the small columns (0.5 x 3, 0.5 x 4, and 0.5 x 5 cm) used.

Since fluoride is an interference in this separation, it has been found necessary to complex the fluoride present from the dissolver solutions with a 100-fold mole excess of boric acid.

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Column conditions were chosen to obtain good conditions for the separation (i.e., the sample volume was kept as small as possible (<0.5 ml) and the actual capacity of the resin used was kept below 2% of theoretical capacity.)⁴

2. APPARATUS

- 2.1 Glass chromatographic columns 0.5 x 10 cm; 4 x 30 cm
- 2.2 Glass wool
- 2.3 Long-stemmed medicine dropper
- 2.4 Pipettes
- 2.5 5 ml glass conical centrifuge tubes

3. REAGENTS

- 3.1 7.2 M nitric acid
- 3.2 3.0 M nitric acid
- 3.3 1.0 M nitric acid
- 3.4 0.6 M nitric acid
- 3.5 Dowex 1-X2, 200-400 mesh, NO_3^- or Cl^- form
- 3.6 Saturated boric acid solution (~0.8 M)
- 3.7 Concentrated nitric acid
- 3.8 Silver nitrate solution

4. PREPARATION OF ION EXCHANGE RESIN

Since the nitrate form of Dowex 1-X2 is somewhat unstable, it is desirable to store the resin in the chloride form and convert it to the nitrate form in small batches. In order to remove the fines and excess organic material, it is good practice to backwash the resin before converting it to the nitrate form.

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4.1 Procedure for the Preparation of the Dowex 1-X2, 200-400 Mesh Resin

4.1.1 Fill a glass-fritted chromatographic column (4 x 30 cm) about 1/2 full of reagent grade Dowex 1-X2, 200-400 mesh ion exchange resin.

4.1.2 Connect the column to the deionized water and backwash the column with a flow rate that will raise the resin to about 3/4 the height of the column.

4.1.3 Continue backwashing for 2-3 hours or until the water at the top of the column appears free of very fine particles of resin and organic contamination.

4.1.4 Disconnect the deionized water line from the column.

4.1.5 Wash the column with 1.0 M nitric acid at a flow rate of ~1 ml/min.

4.1.6 Check the column eluate periodically by placing a few drops of it in a silver nitrate solution. The formation of a white precipitate indicates the presence of chloride.

4.1.7 Continue washing until no more precipitate is visible when the eluate is checked with the silver nitrate solution. In order to insure that all the chloride is removed, wash the column with an additional 60 ml of 1.0 M nitric acid.

4.1.8 Wash the resin with deionized water until the pH of the eluate is >4.

4.1.9 Remove the resin from the column and allow to air dry. This amount of resin should be sufficient for several separations.

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5. PROCEDURE

5.1 Sample Preparation

5.1.1 Complex the fluoride present with a 100-fold mole excess of boric acid. (Note: Since solid boric acid is quite insoluble, a saturated solution of boric acid (~0.8 M) should be used to complex the fluoride.)

5.1.2 Adjust the nitric acid concentration to ~7.2 M with concentrated nitric acid.

5.1.3 Choose a sample size so that the sample volume does not exceed 0.5 ml and the total amount of metal ion present does not exceed 4.0 mg. A convenient pipettable size should also be chosen.

5.2 Column Preparation

5.2.1 Place a small piece of glass wool in the bottom of a 0.5 x 10 cm column to support the ion exchange resin.

5.2.2 Slurry enough of the ion exchange resin with 7.2 M nitric acid to prepare the number of columns desired.

5.2.3 Pour the slurry into the column with gentle tapping in such a way as to avoid the formation of air bubbles. If an air bubble is trapped in the column, the column should be repacked.

5.2.4 Wash the column with 7.2 M nitric acid until a tightly packed 0.5 x 7 cm column is formed.

5.2.5 Keep the resin wet with the 7.2 M nitric acid until the sample is placed on it. Under no circumstances, allow it to go dry.

5.3 Separation Procedure

5.3.1 Place the sample on top of the resin.

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5.3.2 Elute the americium(III) with one column volume of 7.2 M nitric acid (4.4 ml).

5.3.3 Elute the uranium(VI) with five column volumes of 3.0 M nitric acid (22.0 ml).

5.3.4 Elute the plutonium(IV) with four column volumes of 0.6 M nitric acid (17.6 ml).

5.3.5 Collect each fraction in a clean 30 ml polyethylene bottle. Label each bottle.

5.4 Sample Preparation for Mass Spectrometric Analysis

5.4.1 Place an aliquot of the plutonium fraction containing 3-5 μg of plutonium into a 5 ml glass conical centrifuge tube.

5.4.2 Place the tube under a heat lamp and evaporate the sample.

5.4.3 After evaporation, the sample may be submitted for mass spectrometric analysis. (NOTE: Great care should be taken during the whole procedure to avoid external contamination of the final sample.)

6. CALCULATION OF RESULTS

Not applicable for this method.

7. ACCURACY AND PRECISION

Not applicable for this method.

Method No. Sep-4

Revision No.

Date June, 1968

REFERENCES

1. J. P. Faris and R. F. Buchanan, "Anion Exchange Characteristics of the Elements in Nitric Acid and Nitrate Solutions and Application in Trace Element Analysis," ANL-6811, July 1964, Argonne National Laboratory, Chemistry, Argonne, Ill. 60440.
2. D. B. James, "Anion-Exchange Processing of Plutonium," LA-3499, p. 35, January 20, 1967, Los Alamos Scientific Laboratory of the University of California, Chemistry, Los Alamos, New Mexico.
3. Ibid, p. 40.
4. O. Samuelson, Ion Exchange Separations in Analytical Chemistry, John Wiley & Sons, New York, 1963, pp. 125-137.

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Method No. G-1

Revision No.

Date July, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Procedure for Determination of Gas Evolution

Written by: A. H. Bremser

1. SCOPE AND PRINCIPLE:

The volume of gas evolved from a substance as it is heated can be calculated from measurement of the increase in pressure within a closed system which contains the sample. The procedure used was designed so that at the initiation of the test the fuel is in approximately the same condition as it will be prior to its final enclosure in the clad material - i.e., just before the end cap is welded in place.

2. APPARATUS:

The gas evolution apparatus, as shown in Figures 1, 2, and 3 consists of the sample holder, a gas train which can be evacuated, pressure gages, and a tube furnace for heating the sample. This apparatus was constructed by B&W. The major items available commercially are the sample tube which is a McDaniel 997 high alumina tube (McDaniel Part No. 997 PT 38(COE) 10-1/2 inches long), Hastings Thermocouple Vacuum Gage, Texas Instrument Fused Quartz Gage, Model 142, with 0-100 cm Hg bourdon tube, mechanical vacuum pumps, and the Pyro Micro-optical Pyrometer.

3. PROCEDURE:

3.1 Calibrating optical pyrometer temperature to sample temperature.

3.1.1 Place sample tube in furnace with thermocouple within tube. Have bead of thermocouple in contact with bottom of sample tube.

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3.1.2 Bring furnace up to test temperature, as indicated by thermocouple. Take optical pyrometer reading. This reading is the temperature at which the end of the sample tube must be maintained during the determination of gas release.

3.2 Setting T.I. Gage

3.2.1 Close valve 2, open valve 1 and pump on system until the two thermocouple gages read the same. Adjust zero point of TI gage according to manufacturer's instructions.

3.2.2 Close valve 1. Allow reference side of TI gage to pump down. Obtain pressure of reference side using thermocouple gage. If pressure is greater than the smallest gage division of the TI gage, note pressure and use to correct TI gage pressure.

3.3 Determination of Gas Evolution

3.3.1 Place furnace in its lower position so that sample tube is completely out of furnace. Heat furnace to test temperature.

3.3.2 Weigh sample and place in sample tube.

3.3.3 Close valves 1 and 5, open valves 2, 3, 4, and 6.

3.3.4 Pump down sample tube to approximately 100 microns of mercury.

3.3.5 Close valve 4 and check for leakage by taking pressure readings on TI gage over short time intervals.

3.3.6 Open valve 5 and pump down helium supply line.

3.3.7 Close valve 6. Backfill with helium to atmospheric pressure. Close valve 5.

3.3.8 Open valve 4 momentarily to allow helium to flow into sample tube, then close valve 4.

3.3.9 Insert plunger assembly all the way in and measure l_x (Figure 2) with verniers and record as l_1 .

3.3.10 Measure pressure and record as P_1 .

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3.3.11 Pull plunger out about 4 inches. Measure ℓ_x with verniers and record as ℓ_2 .

3.3.12 Measure pressure and record as P_2 .

3.3.13 Repeat steps 3.3.9 to 3.3.12 two more times. When finished, plunger should be reinserted all the way in. The series of steps from 3.3.9 to 3.3.13 allow the apparent volume of the system at ambient temperature to be calculated.

3.3.14 Open valve 4 and 6 and evacuate system to 100 microns Hg or less.

3.3.15 Close valve 4 and take pressure readings from TI gage every two minutes for ten minutes.

3.3.16 Record both time and pressure in 3.3.15. If the change in pressure is less than 20 microns (using 0-100 cm Hg bourdon tube), bring furnace up over sample tube. (If the leak rate is greater than above, test is terminated and system resealed.)

3.3.17 Take pressure readings every two to five minutes until the rate of pressure change becomes constant. Check temperature periodically during this step.

3.3.18 Using the procedure described in section 3.3.9 to 3.3.13, determine apparent volume at temperature and record.

3.3.19 Remove furnace, allow sample tube to cool and remove sample.

4. CALCULATIONS:

4.1 Determination of Apparent Volume

$$V = \frac{P_2 (\ell_2 - \ell_1) d^2}{(P_1 - P_2) 4\pi}$$

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where: V = volume

P_2 = pressure with plunger out (mm Hg)

P_1 = pressure with plunger in (mm Hg)

d = diameter of plunger (cm)

ℓ_1 & ℓ_2 = plunger location (cm)

4.2 Determination of Average Gas Temperature

4.2.1 Assume a temperature profile along specimen tube and take temperature of rest of system as ambient.

4.2.2 Determine volume of system in each temperature segment and multiply the volume of the segment by the average temperature of the segment.

4.2.3 Add up the Volume-Temperature products and divide summation by the total volume to get the average gas temperature.

4.3 Calculation of Gas Release

$$\frac{P_2 V_2}{P_1 V_1} = \frac{n_2 RT_2}{n_1 RT_1} \quad \text{Eq. 4.3.1}$$

where: subscript 1 is room temperature value

subscript 2 is test temperature value

$$n_2 = n_1 + \Delta n \quad \text{Eq. 4.3.2}$$

where: Δn is moles of gas released

$$\frac{P_2 V_2 T_1}{P_1 V_1 T_2} = \frac{n_2}{n_1} = \frac{n_1 + \Delta n}{n_1} = 1 + \frac{\Delta n}{n_1} \quad \text{Eq. 4.3.3}$$

$$n_1 = \frac{P_1 V_1}{R T_1} \quad \text{Eq. 4.3.4}$$

$$\text{let } V_g = \frac{\Delta n RT}{P} \quad \text{Eq. 4.3.5}$$

where: T = 298°K

R = the gas constant

P = 760 mm Hg

V_g = volume of gas released

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Solve Eq. 4.3.3 for Δn , substitute in Eq. 4.3.4 and Eq. 4.3.5 and solve for V_g . Let $T = T_1$ and $P = 760$.

$$\text{Thus } V_g = \frac{1}{760} \left[\frac{P_2 V_2 T_1}{T_2} - P_1 V_1 \right] \quad \text{Eq. 4.3.6}$$

$$V_{gs} = \frac{V_g}{W_s} \quad \text{Eq. 4.3.7}$$

Where: V_1 = apparent measured volume at room temperature (cc)

P_1 = pressure of the system just before furnace is raised over specimen tube (mm Hg)

T_1 = room temperature ($^{\circ}\text{K}$)

V_2 = apparent measured volume at test temperature (cc)

T_2 = average gas temperature ($^{\circ}\text{K}$)

P_2 = last pressure reading before rate of pressure change becomes constant. This is determined by plotting pressure vs time (mm Hg)

V_g = gas released corrected to 298°K and 760 mm Hg (cc)

W_s = weight of sample (gm)

V_{gs} = gas released corrected to 298°K and 760 mm Hg ($\frac{\text{cc}}{\text{gm}}$)

Figure 1. Sorbed Gas Release Apparatus

Note: Shaded area indicates volume of apparatus during determination.

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Figure 2. Plunger Assembly for Volume Determination
of Sorbed Gas Release Apparatus

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Figure 3. Sample Tube Assembly and Location of Sample in Furnace

Note: All dimensions are in inches.

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Method No. D-3
Revision No. _____
Date July, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Procedure for Density Determination by Mercury Displacement Pycnometry

Written by: A. H. Bremser

1. SCOPE AND PRINCIPLE:

The density is calculated from the ratio of weight to volume of the sample. The weight of the specimen is determined directly and the volume is calculated from the weight of mercury displaced by the specimen in a pycnometer. The volume obtained includes all surface-exposed pores more than approximately 17 microns in diameter.¹ Penetration of surface pores by mercury is determined by the pressure of the system both before and after contacting the specimen with mercury.

2. APPARATUS:

A schematic diagram of the apparatus used in this determination is shown in Figure 1. This apparatus was constructed by B&W except for the sample holder which is a penetrometer assembly obtained from the American Instrument Company. The penetrometer assembly was modified in that the stem was out off just above the graduation marks to facilitate handling. For powders, Aminco assembly 5-7113 is used and for solids (pellets), assembly 5-7112 is used.

3. PROCEDURE:

- 3.1 Place empty sample holder in assembly.
- 3.2 Close valves 4 and 5, open valves 1, 2, and 3.
- 3.3 Evacuate system to 100 microns of Hg. With valves 2 and 3 open, the mercury will be at level A (Figure 1).

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3.4 Close valve 1, then valve 2.

3.5 Slowly open valve 4 until the mercury rises over the sample holder to level B (Figure 1).

3.6 Close valve 4 and valve 3.

3.7 Slowly open valve 1. This will fill the sample holder with mercury.

3.8 Open valves 2 and 3 and remove sample holder.

3.9 Weigh sample holder and record weight as W_{HF} (weight holder filled).

3.10 Empty sample holder and clean off all mercury.

3.11 Weigh sample and place in sample holder. Record sample weight as W_s .

3.12 Place sample holder and sample in apparatus and repeat steps 3.2 through 3.8 above.

3.13 Weigh sample holder and sample after filling with mercury and record weight as W_{HFS} .

3.14 Remove sample and clean sample holder for the next determination.

3.15 Perform calculations as shown in the next section.

4. CALCULATIONS:

$$P_s = \frac{W_s}{V_s}$$

$$V_s = \frac{W_{HF} - (W_{HFS} - W_s)}{P_{Hg}}$$

$$P_s = \left(\frac{W_s (P_{Hg})}{W_{HF} - W_{HFS} + W_s} \right)$$

where: P_s = density of sample (gm/cc)

P_{Hg} = density of mercury (gm/cc)

V_s = volume of sample (cc)

W_s = weight sample (gm)

W_{HF} = weight holder filled with mercury (gm)

W_{HFS} = weight holder with sample filled with mercury (gm)

Method No. D-3

Revision No.

Date July, 1968

REFERENCES

- 1 - Pore Structure Analysis, Bulletin 2300, American Instrument Company, Inc.
December 1960.

Date July, 1968

The diagram illustrates a vacuum manifold system for sample analysis. It features two vertical glass tubes, each partially filled with a stippled substance labeled 'Mercury'. The left tube has two horizontal lines, 'A' and 'B', indicating different levels or sections. The right tube is connected to a 'Sample Holder' at the top, which includes an 'O-Ring' seal. A central manifold connects the two tubes and includes five valves: V1, V2, V3, V4, and V5. Valve V1 is connected to a line labeled 'To McLeod Gage and Vacuum Pump' with an upward arrow. Valve V2 is located at the bottom of the central manifold. Valve V3 is at the very bottom, connecting the two vertical tubes. Valves V4 and V5 are positioned higher up on the left and right sides, respectively. A legend at the bottom left shows a box labeled 'V' followed by the text 'Valve'.

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Method No. H-2

Revision No.

Date July, 1968

STANDARD ANALYTICAL PROCEDURE

TITLE OF METHOD: Procedure for Evaluation of Homogeneity and Solid Solution

Written by: A. H. Bremser

1. SCOPE AND PRINCIPLE:

A visual observation of a sample for plutonium homogeneity and extent of solid solution formation can be made by examination of polished surfaces and alpha autoradiographs of these surfaces. The alpha autoradiograph can be thought of as a replicating technique which shows the radiation damage experienced by the replica due to alpha particles emitted by matter within the surface of the sample.¹

2. APPARATUS: grinder

2 Syntron bowl polishers

6 μ and 1/2 μ diamond paste

Ultrasene

ultrasonic cleaner

microscope

320 & 600 grit silicon carbide paper

3. PROCEDURE:

3.1 Polishing and Microscopic Examination

3.1.1 Mount sample in "Kold Mount" or other suitable room temperature setting epoxy resin.

3.1.2 Grind mounted sample on 320 grit silicon carbide paper, using water as a lubricant, until a flat surface is obtained. If sample is relatively

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smooth and flat this step may be omitted.

3.1.3 Continue grinding on 600 grit silicon carbide paper to obtain smooth surface.

3.1.4 Clean for 5 minutes in water using ultrasonic cleaner.

3.1.5 Polish in Syntron bowl polisher using 6 micron diamond and Ultrasene as a lubricant. Use a minimum setting on vibrator control to maintain a specimen travel around the bowl of 3 to 6 rpm. A load of approximately 1100 grams is placed on the mount. Polish for 1 hour.

3.1.6 Clean in ultrasonic cleaner in water for 10 minutes

3.1.7 Polish on 1/2 micron diamond under the conditions set forth in step 3.1.5.

3.1.8 Wash in ultrasonic cleaner in water for 5 minutes.

3.1.9 Clean in ultrasonic cleaner repeatedly using non-contaminated water until sample becomes smear free (using cotton swab) with regard to radioactive material. (When smear free, the sample may be brought into the hood containing the microscope.)

3.1.10 Visually examine specimen for pores and second phase material under various magnifications. Take photomicrographs of representative areas of the polished specimen.

3.1.11 Etching of the specimen is required to observe the grain structure. Return specimen to the box and etch for 40 to 60 minutes at room temperature using 13 molar HNO_3 and .01 molar HF solution (100 ml 70% HNO_3 ; 0.05 ml 48% HF; 21 ml H_2O). Wash specimen as set forth in step 3.1.9 before bringing sample into the microscope hood. The sample must be examined shortly after etching due to attack by the residual etchant.

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3.2 Alpha Autoradiography

3.2.1 Preparation of the plate¹

3.2.1.1 Dissolve one ounce of non-explosive cellulose nitrate, PARLODION*, in 550 ml of amyl acetate. The solvent is added over a 48 hour period with stirring. Upon the last addition of solvent allow mixture to stand for 24 hours.

3.2.1.2 Place sufficient solution on a clean, dust-free microscope slide to form a coated area of approximately 1 cm in diameter.

3.2.1.3 Allow to dry in a dust-free atmosphere at room temperature for 48 hours.

3.2.1.4 Anneal for 4 hours at 100°C to remove any residual solvent.

3.2.1.5 Store plates until ready for use.

3.2.2 Preparation of Sample

3.2.2.1 Polish specimen as set forth in section 3.1. The alpha autoradiograph is generally made on an unetched specimen.

3.2.3 Exposure and processing of the plate

3.2.3.1 Place smear-free sample in hood. Lay a piece of smooth household aluminum foil over the polished specimen and place the alpha-autoradiographic plate on the foil so that the cellulose nitrate film is in contact with the foil. Place a 100 gram weight on the plate to insure good contact.

3.2.3.2 Expose plate for about 15 minutes.

3.2.3.3 Remove plate from specimen and monitor using an alpha counter.

*
Trade name of Mallinckrodt Chemical Works.

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3.2.3.4 Develop cellulose nitrate film in 6 molar sodium hydroxide at 55°C for 2-1/2 to 4 minutes. Wash in demineralized water and dry in dust-free atmosphere.

3.2.3.5 The plate may be used either as a positive (direct observation using a microscope) or a negative. In the former case, the exposed areas of the plate will appear dark and in the latter as white areas.

Method No. H-2

Revision No.

Date July, 1968

REFERENCES

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Carlson, RV
Central Files (6)
Croft, MW
Dewell, EH
Dodd, RH
Ewing, JW
Ferrell, LJ
Gurley, RN
Hochel, RC
Johnson, CR
Jones, HM

Kerr, JM
Kingsley, RS
Kosiancic, EJ
Library (2)
Lynch, ED
Marsh, SF
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Rosenberger, GG
Schmitt, DH (2)
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