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INVESTIGATION INTO THE DISSOLUTION AND
DIRECT ASSAY OF HIGH-FIRED PLUTONIUM DIOXIDE

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Quality Engineering and Control
Standards Laboratory
CHEMISTRY STANDARDS GROUP

SUBJECT DESCRIPTORS

Plutonium Dioxide
High-Fired Plutonium Dioxide
Direct Analytical Assay
Solubility
Ceric Sulfate
Coulometric Titration

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INVESTIGATION INTO THE DISSOLUTION AND DIRECT ASSAY OF HIGH-FIRED PLUTONIUM DIOXIDE

James K. Patterson

Abstract. A fusion-melt and dissolution assay method has been developed and tested for the quantitative analysis of high-fired plutonium dioxide. The method employs fusion of the plutonium dioxide at temperatures greater than the melting point of an eutectic mixture of potassium pyrosulfate plus sodium peroxide. The resultant melt is then titrated directly by either controlled potential coulometry or a gravimetric titration, using standardized ceric sulfate as the titrant. It has been concluded from these investigations that by using the techniques described, high-fired plutonium dioxide (stoichiometric) can be quantitatively dissolved and assayed to a degree heretofore beyond the state-of-the-art, while showing direct traceability to the Federal standards. After fusion, the dissolution and direct assay is applicable to existing routine analytical procedures. The method was designed so as to minimize physical handling, simplify the chemical operations, and maximize the personal safety of the analyst at an appreciable cost savings per analysis.

INTRODUCTION

Plutonium chemists have been interested in the measurement of high-fired plutonium dioxide ($\text{PuO}_{2.00}$) because the high-fired state provides the only known stoichiometric ratio of plutonium to oxygen (1).¹ The two major difficulties which were previously encountered are: (a) a practical, economic, and safe method for the quantitative dissolution of the oxide, and (b) indirect assay techniques following such dissolution, if any. Fusion methods have shown the greatest potential for the dissolution of high-fired plutonium dioxide because wet methods have not provided quantitative results. Historically, fusion results have been complex, time-consuming, and at best sporadic for

quantitative dissolution. W. F. Muehlberg exhibited the ability to fuse and dissolve refractory and other difficult fusible materials, such as ferosilicones and chrome ore with sodium peroxide over a free flame (2). G. W. C. Milner *et al.*, have shown capability for fusion and dissolution of high-fired refractory materials containing plutonium [including plutonium oxide plus uranium oxide ($\text{PuO}_2 - \text{UO}_2$), plutonium oxide plus thorium oxide ($\text{PuO}_2 - \text{ThO}_2$), and as plutonium carbides coated with pyrolytic graphite] with ammonium hydrogen sulfate (3, 4). Work at Rocky Flats using potassium pyrosulfate ($\text{K}_2\text{SO}_4 \cdot \text{SO}_3$) as the fusion reagent (including the use of a free flame) has been negative, or at best highly variable. Fusion reagents (fluxes) have been classified as acidic, basic, oxidizing, or reducing (5). A sample composed of a substance with acidic properties is decomposed by fusion with a basic flux and vice versa. Potassium pyrosulfate is a strong basic flux and sodium peroxide is a strong oxidizing flux. Therefore, a judicious blend of the two has proved to produce a counterpoise whereby the sodium peroxide oxidizes, or disintegrates, the refractory components. Then the potassium pyrosulfate converts the now available plutonium into the readily soluble plutonium sulfate through metathesis.

EXPERIMENTAL

Method:

The method developed during the study was based on the theory of complete fusion using an eutectic mixture of potassium pyrosulfate plus sodium peroxide (9 to 1 ratio). It was eventually designed so as to minimize physical handling, simplify the plutonium chemical operations, and maximize the personal safety of the analyst. The method therefore employs a common fusion-dissolution vessel and flame fusion in a safety glove box. The cooled fusion melt was dissolved in a mineral acid matrix

¹ Numbers in parentheses relate to references at end of text.

and analyzed directly. Titration standardization techniques, employing as a test material known stoichiometric $\text{PuO}_{2.00}$ (lattice parameters 5.396 angstroms), were used to prove the method's reliability (6). The standard techniques included:

1. Ceric sulfate assay by the following four steps—
 - (a) dissolution of the plutonium (Pu) sample,
 - (b) dilution to a specific volume with a matrix common to both standardization and assay [1N HNO_3 plus 1N H_2SO_4 (nitric plus sulfuric acid)],
 - (c) reduction of the plutonium to the Pu(III) valence state with titanous chloride, and
 - (d) gravimetric titrations of the Pu(III) to Pu(IV) with cerium(IV) (about 0.026 N in 4N H_2SO_4) with the Ce(IV) being the mass standardized [equivalent Ce(IV) per gram titrant as titre] transfer vehicle from the Federal National Bureau of Standards (NBS) arsenous oxide (NBS SRM 83c), plutonium metal (NBS SRM 949d), and plutonium sulfate tetrahydrate (NBS SRM 944) to the assay of the stoichiometric plutonium dioxide.
2. Controlled potential coulometry traceable to the Federal standard plutonium sulfate tetrahydrate (NBS SRM 944) via Federal electrical standards.

Safety Precautions:

This assay presupposes expertise on the part of the analyst for plutonium safety, criticality, and chemistry. It should be emphasized that plutonium dioxide is more hazardous to health than metal because of its small particle size. The fusion mixture is extremely hazardous and sodium peroxide, which reacts violently (explosive) when brought into contact with organics or easily oxidizable materials, must be handled with care.

In addition to the equipment and reagents normal to the chemical assay of plutonium, the following special equipment and reagents are required.

Equipment and Reagents:

Flame Fusion Glove Box

A stainless-steel glove box was modified to permit high temperature melting using an open gas-air flame. The glove box has safety features designed to prevent an explosion or an uncontrolled fire.

Quartz Fusion Flask

The specially designed and locally fabricated fusion flask was a wide-mouthed quartz flask [approximate volume of 60 millilitres (ml)] fitted with a vented quartz cap. The flask was designed to provide a minimum surface area for the fusion melt while preventing loss from spatter and volatilization.

Meker Blast Burner

The fusion flame was produced by a natural gas-air mixture of approximately 55 percent fuel to 45 percent air as registered by rotometers located in the individual supply, prior to passing through a mixing valve in line with the burner.

Platinum-Calomel Redox Electrode

The platinum indicator electrode coupled with the calomel reference electrode indicated the large change in potential of the Ce(IV)—Ce(III) redox couple at the equivalence point in the ceric sulfate assay method.

Digital Voltmeter

A six-place DVM was used to display the change in potential of the Ce(IV)—Ce(III) redox couple as detected by the calomel-platinum redox electrode. The DVM was also used to display the integrated electrolysis current resulting from the transformation of the Pu(III)—Pu(IV) redox during the controlled potential coulometric titration.

Controlled Potential Coulometer

A high-precision controlled potential coulometer was used to compare the plutonium assay to

Electrical National Standards. The coulometer was calibrated absolutely, in coulombs per volt, by integrating the current resulting from a known constant voltage over a certified precision resistor (7).

Anhydrous Potassium Sulfate

An Americal Chemical Society (ACS) analytical reagent grade (ARG) $K_2SO_4 \cdot SO_3$ was used.

Sodium Peroxide

An ACS analytical reagent grade (ARG) Na_2O_2 was used.

Titanous Chloride

A 20 percent solution (standardized) ($TiCl_3$) from LaMotte Chemical was used.

Mineral Acid Matrix

A mixture of ARG mineral acids equivalent to 1N HNO_3 (nitric) plus 1 N H_2SO_4 (sulfuric) was used.

Ceric Sulfate Titrant

An ARG $Ce(HSO_4)_4$ in 4N H_2SO_4 was used.

Sulfamic Acid Crystals

An ARG $NH_2 - SO_3H$ was used.

Preparation of Stoichiometric Plutonium Dioxide:

The stoichiometric high-fired plutonium dioxide used to test the fusion and dissolution was prepared as follows: Double electrorefined plutonium metal was converted to plutonium hydride (PuH_2) and the resulting hydride was converted to plutonium dioxide, as described by R. P. Degrazio (6). The resultant plutonium dioxide was fired for 90 hours

in a muffle furnace controlled at 850 °C. This stoichiometric high-fired plutonium dioxide was redundantly sampled, fused, and analyzed by two independent assay methods.

Sample and Flux Preparation:

Determination was made that before a sample can be satisfactorily fused, it must first be reduced to an extremely fine state of subdivision (small particle size), usually by mechanical grinding, and then intimately mixed with the flux. The high-fired plutonium dioxide used for this study was homogeneous and the particle size [in micrometres (μm)], ranged from 16.74 percent less than 0.3 to 0.06 percent greater than 13.2 with 95 percent being less than 3.3 as determined by a Quantimeter® 720-particle size analyzer] was such that mechanical grinding was not necessary (6).

The integrity of the gravimetric aliquots used for the assay measurement of a highly hygroscopic (plutonium dioxide) sample must be maintained. This was done by heating the sample for a minimum of one hour in a muffle furnace controlled at 300 °C, transferring the hot aliquot (approximately 0.2 grams) directly into the flux, and immediately mixing them.

Fusion in Quartz:

The fusion was performed in a fused-quartz flask. The advantages of fused quartz are: (a) it is transparent and therefore the fusion process is visible to, and thus controllable by, the analyst; [NOTE: Repeated or prolonged fusions resulted in some devitrification of the bottom of the flask but this did not seriously obscure the fusion process from the analyst.] (b) fused quartz has a sufficiently high melting point and is nonvolatile below its softening point of 1700 °C; (c) at the fusion temperature (800 to 900 °C), the quartz is insignificantly attacked by the alkaline properties of the fusion melt; (d) it is easily shaped into a container which can be used both for fusion and partial dissolution thus minimizing sample transfer; and (e) it has a low coefficient of expansion (5×10^{-7}). The analyst must be cognizant of the brittleness of fused quartz and its susceptibility to mechanical shock.

Preparation of Flux:

Each fusion flux was prepared by combining 5.4 grams of anhydrous potassium sulfate ($K_2SO_4 \cdot SO_3$) with 0.6 grams of sodium peroxide (Na_2O_2) in a screw-cap plastic vial. The flux was mixed by gentle agitation and transferred into a clean dry fusion flask. A tare weight was obtained (± 0.01 milligrams) using a semi-micro analytical balance which was certified by the Rocky Flats Physical Metrology Laboratory (PML). The fusion flask was transferred into the glove box containing the plutonium dioxide sample. Approximately 0.2 grams of the sample was quickly transferred from the muffle furnace into the fusion flask and mixed with the flux. The fusion flask was transferred back into the glove box containing the semi-micro balance and gross weighed. The fusion flask containing the sample plus flux was transferred to the flame-fusion glove box and the mixture was fused.

General Fusion Criteria:

The major problem in the fusion and dissolution of high-fired plutonium dioxide was found by this investigator, and by others, to be the discipline by which the fusion process was accomplished. The modified glove box, which permitted a free flame rather than electric heating, showed greater promise for success than other parametric considerations. Difficulty in obtaining a choice mixture of fusion salts also posed a major problem. The latter problem was solved by trial and error over a discrete range of mixtures after $K_2SO_4 \cdot SO_3$ and Na_2O_2 were selected following an extensive literature search (2, 3, 4, 5). This range was evaluated to: (a) optimize the oxidizing and disintegrating properties of the Na_2O_2 on refractories, while minimizing the explosive characteristics resulting from locally high concentrations between the oxidant and easily oxidizable materials; and (b) optimize the availability of the plutonium for metathesis with the $K_2SO_4 \cdot SO_3$, thereby converting the insoluble plutonium dioxide into a readily soluble plutonium sulfate; a 9 to 1 ratio of $K_2SO_4 \cdot SO_3$ to Na_2O_2 proved to be the mixture which optimized the fusion. The perennial difficulty encountered in the fusion of refractories such as plutonium dioxide was solved by using careful techniques during the flame fusion, with astute

observations of the melt, followed by immediate corrective action by the analyst. Details for specific, as well as general, directions and guidance to perform a successful fusion are discussed later.

Discussion of Unsuccessful Fusions:

During the experimental period, several failures were encountered. Some were immediately evident and others became apparent during the dissolution steps.

Typical of those immediately evident were the ones with excessive frothing. Apparently, the flask and fusion mixture have poor heat-transfer characteristics. Occasionally, the initial frothing produced large bubbles in the insipient fusion melt and separated it into two layers. This allowed the top layer to cool below the melt temperature (200 to 300 °C), leaving the bottom layer deficient in flux material and mobility. Superheating the bottom layer beyond the transition point of solid to liquid did not remedy the problem. Lack of mobility, heat transfer, and intimate contact between the plutonium dioxide and flux prevented metathesis and the plutonium dioxide was not fused. Therefore, this effort was terminated as a failure.

Other failures which became evident during the dissolution steps were those retaining a mound of solid matrix during the insipient fusion stage; the liquid portion began to flow around this mound. Thus it was determined that the heat transfer was not adequate to cause the mound to melt and therefore, as the temperature was increased, that portion of the plutonium dioxide trapped in the mound was only partially available for fusion. As metathesis progressed in the available portion, the amber color changed to a dark red. This melt was not uniform in color and it was noticeably viscous. The elapsed time for this semifusion was in excess of 20 minutes.

Discussion of Successful Fusions:

While the fusion of high-fired plutonium dioxide is chemical in nature, a successful fusion requires astute observation, careful techniques, and discipline by the analyst. Intimate contact between the finely divided plutonium dioxide and flux

is the key to a successful fusion. A smooth transition from the solid mixture to the molten insipient fusion requires mobility as well as heat. The mobility enables the heat transfer to be more uniform and the particles of plutonium dioxide slowly reform to the sulfate and classic fused dissolution occurs. The requirement of continued agitation and swirling by a rotary motion removes and erodes portions of the plutonium dioxide particles and exposes a further particulate surface to the fusion matrix.

This was dramatically evidenced by the successful fusion of samples as great as one gram of plutonium dioxide in 6 grams of flux and the failure to fuse samples as small as two-tenths of one gram in 6 grams of flux. Thus, the success or failure of a fusion is determined during this initial portion of the fusion where the solid mixture must make a smooth transition into the molten insipient fusion.

Successful Fusion:

A successful fusion requires that the temperature of the mixture be slowly increased to the insipient fusion by passing the flask through the periphery of the free flame with continued agitation and swirling by a rotary motion. Minute local explosions have been noted frequently during this portion of the fusion. It is postulated that this phenomenon results from the rapid oxidation of the mixture by the sodium peroxide in granular form. The next observation was appreciable frothing of the melt. The corrective action here was to reduce the heat and prolong the time for this portion of the fusion by moving the flask farther from the flame. Vigorous agitation and swirling by a rotary motion with a gradually increased temperature produced a dark amber liquid. A series of small bubbles were also observed at the interface between the flask and the liquid. As the temperature was increased, metathesis was also evidenced by a color change from dark amber to the translucent pink characteristic of molten plutonium sulfate. The lapsed time for this successful fusion was less than 10 minutes.

Partial Dissolution of Fusion:

The fusion melt was thermally cooled to ambient temperature and the fusion flask containing the

soluble plutonium sulfate was transferred into a glove box for dissolution of the cooled fusion melt. The fusion flask was placed on a hot plate controlled at low heat and 25 ml of matrix ($1\text{N HNO}_3 + 1\text{N H}_2\text{SO}_4$) were added. Continued heating and occasional swirling broke up the melt and produced partial dissolution, as refluxing rinsed down the inside of the flask. The fused sample was now ready for quantitative transfer in preparation for the assay titrations described in detail later.

The volume must be increased to 150 ml or more with the matrix before a fusion melt from 6 grams of flux will completely dissolve. The general titrations are attached as proceduralized appendices (A and B) at the end of text.

Assay by Ceric Sulfate Titration:

To check the volatility of the plutonium at the fusion temperature, as well as to confirm the plutonium recovery, one issue weight (nominally 1.0 gram) of NBS 944 was divided into two aliquots. One aliquot was dissolved in the matrix ($1\text{N HNO}_3 + 1\text{N H}_2\text{SO}_4$). The other was fused with 6 grams of flux and dissolved in the matrix. Both aliquots were titrated as noted in Appendix A. Page 9. The observed assay values were 0.4749 grams per gram (g/g) Pu and 0.4751 g/g Pu, respectively. This compares favorably with the NBS certified value of 0.4750 ± 0.0005 g/g Pu.

The results of the experiment showed the assay of the fused plutonium dioxide was common to the standardization of the Ce(IV) titrant. Therefore, any variation between the theoretical and measured assay using this titration method must be due to incomplete fusion and dissolution of the stoichiometric plutonium dioxide ($\text{PuO}_{2.00}$).

The $\text{PuO}_{2.00}$ assay of 0.88197 g/g Pu was calculated from an atomic weight of 15.9994 for oxygen and 239.12 for plutonium; the plutonium atomic weight was calculated as the weighted mean of the isotopic abundance (given in weight percent) (8, 9, 10, 11).

The contents of a fusion flask was quantitatively transferred into a 400-ml graduated tall-form beaker containing a Teflon® coated stirring bar.

The transfer was performed with a stream of the matrix from a 500-ml polyethylene wash bottle. The volume of the matrix in the 400-ml beaker was increased to 200 ml. The beaker was placed on a magnetic stirrer and the dissolution of the melt was completed with the Teflon® coated magnetic stirring bar rotating at medium speed. The ceric sulfate titrimetric assay, proceduralized as Appendix A, was followed from the appropriate step, (Titration for Standardization; through the net gram of titrant). Example calculations are also included in Appendix A, Page 9.

The observed mean assay from 15 determinations, using this ceric sulfate titration (see Table I) of 0.8818 ± 0.0003 g/g Pu was within statistical agreement with the 0.88197 g/g Pu for $\text{PuO}_{2.00}$.

Assay by Controlled

Potential Coulometry Titration:

Prior to the assay of the stoichiometric plutonium dioxide, the then current controlled potential coulometric titration standardization and comparison qualification method (using NBS SRM 944 and perchloric acid as the supporting electrolyte) was tested for interference from the fusion, subsequent dissolution with the mineral acid matrix, and then direct titration assay.

One issue weight (nominally 1.0 gram) of NBS-944 was divided into two aliquots. One aliquot was dissolved with the matrix ($1\text{N HNO}_3 + 1\text{N H}_2\text{SO}_4$), quantitatively transferred into a pre-tared 200-ml glass stoppered volumetric flask, brought to a final volume of approximately 190 ml, and assayed as described later. The other aliquot was subjected to the fusion process described earlier; as though it were a sample of plutonium dioxide, and quantitatively transferred into a pre-tared 200-ml glass stoppered volumetric flask. The transfer was performed with a stream of matrix from a 500-ml polyethylene wash bottle after partial dissolution, as described earlier. The volume of the 200-ml volumetric flask was adjusted to approximately 190 ml with the matrix, and dissolution was completed with a hot plate controlled at low heat and manually swirling in a rotary manner. The sample was thermally cooled to ambient temperature.

Mass fractions of both aliquots were titrated using 1M HNO_3 in the isolated Vycor® salt bridges and

TABLE I. Ceric Titrimetric Assay of Stoichiometric Plutonium Dioxide. [Plutonium dioxide ($\text{PuO}_{2.00}$), using titanous chloride (TiCl_3) as reductant.]

Sample Weight (grams)	Titration Net (grams)	*Assay (gram per gram plutonium)
0.16853	25.85241	0.88202
0.14523	22.28514	0.88229
0.13891	21.29890	0.88161
0.15459	23.72426	0.88240
0.14946	22.91490	0.88155
0.23921	36.71585	0.88272
0.22294	34.18743	0.88172
0.21167	32.49292	0.88264
0.20329	31.20115	0.88248
0.23191	35.55019	0.88140
0.36693	56.23008	0.88113
0.28216	43.23342	0.88100
0.24895	38.16065	0.88136
0.19213	29.46441	0.88177
0.35021	53.69008	0.88149

*Corrected for iron and uranium content.

Assay Summary:

N (number of observations)	= 15
$\bar{X}$ (arithmetic mean)	= 0.88184
S (standard deviation of sample)	= 0.00055

95 Percent Confidence Interval:

$$0.88184 \pm 2.145 \left(\frac{0.00055}{\sqrt{15}} \right) \\ \pm 0.0003 \text{ grams per gram plutonium}$$

1M HClO_4 plus $0.02\text{M NH}_2 - \text{SO}_3\text{H}$ (sulfamic acid) as the supporting electrolyte. Compared to the NBS-944 certified 0.4750 ± 0.0005 g/g Pu, the respective observed mean assay of 0.4604 g/g Pu ($0.4654, 0.4621, 0.4537$) and 0.4511 g/g Pu ($0.4536, 0.4573, 0.4425$) were biased low. This investigator attributed the obvious low bias to an interference with the supporting electrolyte.

TABLE II. Titrimetric Assay of Stoichiometric Plutonium Dioxide by Controlled Potential Coulometry.

Plutonium Dioxide Sample Weight (grams)	Final Solution Weight (grams)	Aliquot Weight (grams)	Digital Voltmeter (volts)	Background (volts)	* Assay (grams per gram plutonium)
0.18612	188.8308	1.83834	1.767	0.038	0.88099
		1.89927	1.827	.038	.88232
		2.31344	2.202	.024	.88187
		2.12696	2.039	.038	.88123
		1.95097	1.875	.038	.88199
		2.44798	2.341	.036	.88199
		2.19848	2.104	.035	.88154
		1.92021	1.837	.028	.88245
		1.95380	1.877	.038	.88167
		1.92248	1.840	.030	.88190
0.13931	208.2201	1.96946	1.297	.038	.88215
		2.03903	1.343	.039	.88250
		1.71448	1.135	.039	.88215
		1.89910	1.248	.034	.88213
		2.06271	1.355	0.036	0.88241

*Corrected for iron and uranium content.

Assay Summary:

N (number of observations) = 15
 $\bar{X}$ (arithmetic mean) = 0.88195
 S (standard deviation of sample) = 0.00044
 95 Percent Confidence Interval:

$$0.88195 \pm 2.145 \left(\frac{0.00044}{\sqrt{15}} \right)$$

±0.0002 grams per gram
plutonium

Mass fractions of the fused aliquot were again titrated using 0.5N H_2SO_4 in the high porosity Vycor® salt bridges and 0.5M H_2SO_4 plus 0.02M $NH_2 - SO_3H$ as the supporting electrolyte. The respective Pu(III)–Pu(IV) redox potentials used [versus the saturated calomel electrode (SCE)] were 0.310-volt reduction and the recorded 0.670-volt oxidation (12, 13). The observed mean assay (see Table II) of 0.4750 is also the NBS certified value.

Appendix B, Page 17, is the proceduralized controlled potential coulometric titration which has

been amended to reflect the use of either perchloric or sulfuric acid as the supporting electrolyte. As modified, the procedure was used for the direct assay of the dissolved fusion melt.

The observed mean assay from 15 determinations, using this amended controlled potential coulometric titration of 0.8820 ± 0.0002 g/g Pu, was within statistical agreement with the 0.88197 g/g $PuO_{2.00}$ (calculated) (see Table II).

Mass fractions of the $PuO_{2.00}$ were fused and assayed. Detailed narratives describing the standardization and assay methods used to confirm the

free-flame fusion, dissolution, and subsequent direct titration of stoichiometric high-fired plutonium dioxide (thus furnishing traceability of measurements to the Federal standards) appear as Appendix A (ceric sulfate titration), Page 9, and Appendix B (controlled potential coulometric titration).

CONCLUSIONS

1. By using the techniques described, high-fired plutonium dioxide can be quantitatively dissolved and assayed to a degree heretofore beyond the *state-of-the-art*, while showing direct traceability to the Federal standards.
2. After fusion, the dissolution and direct assay of high-fired plutonium dioxide is applicable to existing routine analytical procedures.
3. The method minimizes physical handling, simplifies the chemical operations, and maximizes the personal safety of the analyst.
4. The method provides an appreciable cost savings, at no sacrifice of quality, per analysis.
5. The method is simple to use and can be easily taught to an analyst familiar with plutonium chemistry, criticality, and safety requirements.

REFERENCES

1. G. R. Waterbury, M. Douglass, and C. F. Metz. "Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate, and Oxalate." *Journal of Analytical Chemistry* 33:1018-1023. July 1961.
2. W. F. Muehlber. "An Explosion Method for Peroxide Fusions." *Industrial and Engineering Chemistry* 17:690. 1925.
3. G. W. C. Milner, D. Crossley, I. C. Jones, and G. Phillips. "The Rapid Dissolution of Plutonium Dioxide by a Sodium Peroxide Sinter, Followed by Determination of the Plutonium Content by Differential Spectrophotometry." *Analyst* 90:232. 1965.
4. G. W. C. Milner, A. J. Wood, G. Weldrick, and G. Phillips. "The Determination of Plutonium in Refractory Materials by Electrometric Methods after Dissolution by Fusion with Ammonium Hydrogen Sulfate." *Analysis* 92:239-246. April 1967.
5. I. M. Kolthoff and E. B. Sandell. *Textbook of Quantitative Inorganic Analysis*. The McMillan Company, New York. 1938.
6. R. P. Degrazio. *A Prototype Hydriding Apparatus (Application for Plutonium Recovery)*. RFP-2340. Rocky Flats Division, Dow Chemical U.S.A., Golden, Colorado. March 17, 1975.
7. M. T. Kelly, H. C. Jones, and D. J. Fisher. "Electronic Controlled Potential Coulometric Titrator." *Analytical Chemistry* 31:488-491, 956. April 1959.
8. G. Friedlander, J. W. Kennedy, and J. M. Miller. *Nuclear and Radiochemistry*. Second Edition. John Wiley and Sons, Inc., New York 1966.
9. C. J. Rodden, Editor. *Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle*. Second Edition. Office of Information Services, U. S. Atomic Energy Commission, Washington, D. C. 1972.
10. J. C. Barton. "The Use of Atomic Weights in Uranium Measurement." Pages 382-403. *Analytical Chemistry, In Nuclear Reactor Technology. October 12-14, 1960*. USAEC Report TID-7606. Gatlinburg, Tennessee. January 1961.
11. L. A. König, J. H. E. Mattauch, and A. H. Wapstra. "1961 Nuclide Mass Table." *Nuclear Physics* 31:18-42. 1962.
12. W. D. Schultz. "Extensive Review of Methods and Variations." U. S. Atomic Energy Report, ORNL-2921. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 1960; *Analytical Chemistry* 35:922. 1963; *Talanta* 10:833. 1963.
13. F. A. Scott and R. M. Pekema. *Analysis for Plutonium by Controlled Potential Coulometry*. Paper No. 914. Second International Conference on the Peaceful Uses of Atomic Energy. Volume 28. Geneva, Switzerland. 1958.

APPENDIX A.

**Procedure for the Standardization and Transfer of
Ceric Sulfate to the Direct Assay of Plutonium Metal and Plutonium Salts.**

An assay method was designed to transfer values of certified reference materials [National Bureau of Standards, Standard Reference Materials (NBS SRM)] to the titre of cerium(IV) and thence to the assay of plutonium metal and salts. The method was a modification of that described by J. Corpel and F. Regnaud.^{A-1}

The method employs reduction of the test material with titanium(III) solution in the presence of sulfamic acid and titration with Ce(IV) solution. The titanous chloride (TiCl_3) has the following advantages over the metal reductors: (1) It is capable of rapid and precise reduction of the test material [Pu(IV) to Pu(III)] in a nitric acid media by using a slight excess of titanium(III) ions; (2) The excess of Ti(III) is easily detected, it is spontaneously destroyed by reacting with nitrate ions using air as an auxiliary oxidant and in a 1N HNO_3 matrix, this reaction is complete in 5 minutes time; (3) The method uses a matrix of nitric acid and sulfuric acid; and (4) It is tolerant of moderate chloride concentrations.

The method as described by Corpel and Regnaud was modified to use gravimetric measurement, rather than volumetric, of the Ce(IV) titrant and a potentiometric detection and display for the Ce(IV)–Ce(III) redox equivalence points.

Any material that reacts with ceric sulfate (other than plutonium) and is present must be removed or measured by some other means so the plutonium assay can be corrected accordingly. Corrections for iron and uranium, the most common for plutonium assay, were included in the calculations.

The assay method used to determine Ce(IV) titre and assay plutonium materials consists of the following four steps: (1) dissolution of the plutonium sample, (2) dilution to a specific volume with

a common matrix (1N HNO_3 + 1N H_2SO_4), (3) reduction of the plutonium to Pu(III) with Ti(III), and (4) gravimetric titration of the Pu(III) to Pu(IV) with Ce(IV) ($\sim 0.025\text{N}$ in 4N H_2SO_4). The titre of the Ce(IV) being the transfer vehicle from Federal standards to the plutonium assay. The Ce(IV) titre was mass standardized with arsenous oxide (NBS SRM 83c), plutonium metal (NBS SRM 949d), and plutonium sulfate tetrahydrate (NBS SRM 944). The equivalence point for the Ce(IV)–Ce(III) couple was detected potentiometrically with a bright platinum-wire coil indicator electrode coupled with a saturated calomel reference electrode (SCE). The large change in potential at the equivalence point (Figure 1-A) as detected by the platinum indicator electrode was *read out* in millivolts on a 6-place digital voltmeter.

PREPARATION OF THE CERIC SULFATE TITRANT

A primary solution of ceric sulfate ($\sim 0.2\text{N}$ in 4N H_2SO_4) was prepared by *CAUTIOUSLY* (with thorough stirring) adding two full bottles (18 pounds) of ARG sulfuric acid to 36 litres of distilled water in a 50-litre carboy. Two 5-pound bottles of ARG ceric sulfate [$\text{Ce}(\text{HSO}_4)_4$] were added to the hot acid solution with agitation. The mixture was purged with air for 3 hours with intermittent agitation of the carboy in a rotary manner. The mixture was aged for about 6 months and siphoned through a fine-fritted glass filter funnel into two 20-litre glass jugs. About 40 litres of an intermediate solution ($\sim 0.05\text{N}$ in $\sim 4\text{N}$ H_2SO_4) was prepared from this primary solution and aged for about one month in a glass carboy. Slightly less than 4 litres of this intermediate solution was siphoned off into an 8-litre polyethylene jug. The siphon tip was kept at least 2 inches from the bottom of the carboy and care was exercised not to disturb any sediment which might be present. The solution in the polyethylene jug was diluted in a 1 to 1 ratio with

^{A-1}J. Corpel and F. Regnaud. "Cerimetry in Nitric Acid Media Applications to the Determination of Iron, Uranium, and Plutonium." *Analytical Chemistry Acta* (RFP Trans-146) 27:36. 1962.

4N H_2SO_4 , thoroughly mixed and transferred into 4 glass, 2-litre screw cap bottles. This Ce(IV) titrant ($\sim 0.026\text{N}$ in 4N H_2SO_4), after filtration and two subsequent careful transfers, had no detectable particulates, therefore was stable in excess of 40 weeks.^{A-2}

STANDARDIZATION OF THE CERIUM(IV) TITRANT

A portion of this titrant (No. 1) was standardized with arsenous oxide (NBS SRM 83c), plutonium metal (NBS SRM 949d), and plutonium sulfate tetrahydrate (NBS SRM 944). The special techniques required for NBS SRM 83c are described later. The standardization procedure using plutonium SRM's was identical for metal and sulfate tetrahydrate after dissolution of the respective species.

Dissolution of Plutonium (NBS SRM 949d):

The NBS certified metal weight was recorded from the ampoule. One issue-unit (nominally 0.5 grams) was quantitatively transferred into a 400-millilitre (ml) tall form graduated beaker containing a Teflon® coated magnetic stirring bar and dissolved with 5 ml of 9N HCl (hydrochloric). After 15 minutes, the inside of the beaker was rinsed down with a stream of the matrix ($1\text{N HNO}_3 + 1\text{N H}_2\text{SO}_4$) from a 500-ml polyethylene wash bottle. The beaker was placed on a magnetic stirrer and the calomel-platinum electrode couple was inserted into the beaker. [NOTE: The saturated calomel electrode (SCE) was previously charged with a fresh saturated potassium chloride (KCl) solution. The asbestos wick was also determined to be open.] This assembly was placed near the front of the titration box with the graduations on the beaker facing out. The sample was now ready for titration as described under the section: *Titration for Standardization*.

^{A-2}O. A. Ohweiler, J. O. Meditsch, and C. M. S. Piatnicki. "A Critical Study of the Standardization of Cerium(IV) Solutions with Arsenic Trioxide." *Analytical Chemistry Acta* 63:341-349. 1973.

Dissolution of Plutonium Sulfate Tetrahydrate (NBS SRM 944):

A vial containing one issue unit (nominally 1.0 gram) of NBS-944 was weighed on a semi-micro analytical balance, previously certified by the Physical Metrology Laboratory (PML). The contents of the vial were *dumped* into a clean 400-ml tall form graduated beaker containing a Teflon® coated magnetic stirring bar. The vial was again weighed and the difference was calculated as the weight of NBS-944 in the beaker. The beaker was placed on a hot plate controlled at medium heat and the mineral acid matrix was added to the 200-ml mark on the beaker. After 20 minutes, the beaker was transferred to a magnetic stirrer controlled at medium speed. After dissolution was complete (10 minutes), the solution was cooled to ambient temperature and the calomel-platinum electrode couple was inserted into the beaker. The sample was now ready for titration as described under the next section.

Arsenous oxide (As_2O_3) (NBS SRM 83c) was used in the standardization with the following modifications: (1) Nitric acid interferes with this titration; (2) The As_2O_3 must be prepared by initial dissolution with caustic; (3) Osmic acid (0.01M OsO_4 in $7.2\text{N H}_2\text{SO}_4$) is required to catalyze the reaction between cerium(IV) ions and arsenic(III) ions in 2M sulfuric acid;^{A-3} and (4) The As_2O_3 must be dried for a minimum of one hour at 110°C and stored in a vacuum dessicator charged with fresh magnesium perchlorate [$\text{Mg}(\text{ClO}_4)_2$], prior to sampling. The sample preparation and titration procedure used for the plutonium (NBS SRM 949d and 944) were amended to reflect these differences.

A specially designed and locally fabricated quartz-weighing dish was used to allow for weighing the As_2O_3 with a full-micro balance. These weighing dishes were cleaned, heated to 600°C , and stored in a vacuum dessicator charged with fresh $\text{Mg}(\text{ClO}_4)_2$ prior to adding the aliquot of As_2O_3 .

An aliquot of the prepared As_2O_3 was placed into a prepared quartz-weighing dish. The sample was

^{A-3}Ibid.

weighed on a full-micro analytical balance and *dumped* into a 400-ml graduated tall form beaker containing a Teflon® coated magnetic stirring bar. The quartz-weighing dish was again weighed and the difference was calculated as the weight of NBS 83c in the beaker. Then 15 ml of 2N NaOH (sodium hydroxide) was added to the sample by rinsing down the inside of the 400-ml beaker, thereby scavenging any particles of As_2O_3 adhering to the glass. After allowing 15 minutes for complete dissolution of the As_2O_3 , 25 ml of a 20 percent H_2SO_4 solution was added to the sample by again rinsing down the inside of the 400-ml beaker. Distilled water was added to bring the volume in the 400-ml beaker to the 200-ml mark. The 100 micro-litres of the osmic acid solution was added and the As_2O_3 sample was titrated to the potentiometric Ce(IV)–Ce(III) redox equivalence point.

Titration for Standardization:

The matrix volume was adjusted to 200 ml and the magnetic stirrer was set to rotate at medium speed. Sulfamic acid crystals (0.5 grams) were added to the beaker. If crystals adhered to the electrodes or the inside of the beaker, they were rinsed down with a stream of distilled water from a 500-ml polyethylene wash bottle. The digital voltmeter (DVM) was switched from standby to record. After 5 minutes, the sulfamic acid crystals were dissolved and the DVM reading had stabilized. The magnitude of this reading was not important; the large change in potential at the Ce(IV)–Ce(III) equivalence point, as detected by the platinum-indicator electrode and displayed on the DVM, represented the titration end point (Figure 1-A). Nitrite ions titrate the Ce(IV) and therefore must be destroyed. The sulfamic acid destroys the nitrite ions and prevents their re-forming during the titration by a reaction of the type: $\text{HNO}_2 + \text{NH}_2 - \text{SO}_3\text{H} \rightarrow \text{H}_2\text{SO}_4 + \text{N}_2 + \text{H}_2\text{O}$.

The titanous chloride (TiCl_3) solution was added dropwise to the beaker, forming a slight excess of Ti(III) ions. The excess was indicated by three things: (1) The DVM registered a lower reading, usually 98 to 100 millivolts (mv); (2) The color

FIGURE 1-A. Cerium(IV)–Cerium(III) Equivalence Data.

of the solution became a dark purple; and (3) Excessive outgassing of the solution occurred. The electrodes and inside of the beaker were again rinsed down with distilled water. After 5 minutes the nitrate oxidized the excess Ti(III) ions and the DVM reading had stabilized.

An aliquot of the titrant was transferred into a weight buret. The weight buret was a 125-ml polyethylene wash bottle fitted with a $\frac{1}{8}$ -inch polyethylene delivery tube drawn down to a fine tip (one drop = 0.02 ml). The weight buret was gross weighed on a 150-gram capacity semi-micro analytical balance (PML certified). The weight buret was covered with a plastic bonnet. This bonnet was prepared by cutting a small hole near the bottom of a small polyethylene bag, inserting the bag over the weight buret, and bringing the delivery tube out through the hole. The bonnet was used to confine the plutonium contamination to the small protruding delivery tip of the weight

buret. The Ce(IV) titrant was added to the beaker as a small stream to near the equivalence point, and then *dropwise*.

A graph of ml Ce(IV) as the abscissa and potential (mV) as the ordinate (Figure 1-A) depicts the equivalence point for the Ce(IV)–Ce(III) redox couple. The graph shows an initial slight increase in potential with the addition of a large volume of Ce(IV) titrant. Near the equivalence point, the potential shows a drastic increase and at the equivalence point 0.02 ml of the titrant produces an increase of 200 millivolts (mV) or more. If the equivalence point is exceeded, the potential again changes slightly for the addition of a large volume of titrant.

After each titration the bonnet was removed from the weight buret and left in the titration box. The weight buret was placed on a *cold* workbench and the delivery tube was decontaminated. Extra care was exercised not to loose the integrity of the tare weight for calculating the net grams of Ce(IV) titrant used in the titration. The delivery tip was decontaminated with a tissue moistened with 9N HCl (hydrochloric) followed by a dry tissue and then checked with an alpha monitor. The weight buret was again weighed on the semi-micro balance and the weight of the Ce(IV) titrant calculated as the difference between the two weighings.

In actual practice, the titre is converted to a factor which is dependent upon the equivalent weight of the sample material being measured. In the case of plutonium, the equivalent weight is the atomic weight calculated as the weighed mean of the isotopic abundance (given in weight percent).^{A-4, A-5} Example calculations should clarify this point.

Example 1 –

Using arsenous oxide (As_2O_3) (NBS 83c), the assigned purity = 0.9999 grams per gram.

^{A-4}C. J. Rodden, Editor. *Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle*. Second Edition. Office of Information Services, U. S. Atomic Energy Commission, Washington, D.C. 1972.

^{A-5}J. C. Barton. "The Use of Atomic Weights in Uranium Measurement." Pages 382-403. *Analytical Chemistry, In Nuclear Reactor Technology*. October 12-14, 1960. USAEC Report TID-7606. Gatlinburg, Tennessee. January 1961.

$\text{As}_2\text{O}_3 = 197.9982$ and $\text{As(II)} \rightarrow \text{As(IV)}$, but with 2 As the equivalent weight of $\text{As}_2\text{O}_3 = 197.8422 \div 4 = 49.46055$

Using 0.86029 grams (NBS 83c) and 72.8463 grams of titrant:

$$\frac{(0.9999) (0.86029 \text{ grams})}{49.46055} = 173.92 \times 10^{-5} \text{ grams per equivalent (g/eq)}$$

$$\frac{173.92 \times 10^{-5} \text{ g/eq}}{72.8463 \text{ grams}} = 238.7 \times 10^{-7}$$

Result = 238.7×10^{-7} equivalent Ce(IV) per gram titrant.

Example 2 –

Using plutonium metal (NBS-949d), the assigned purity = 0.9999 grams per gram plutonium, and atomic weight = 239.08 from the certificate.

Atomic Weight = Equivalent Weight because
Pu(III) . . . Pu(IV) for N = 1
(N = number of observations)

NOTE: The NBS-949d parent material has been physically prepared to make the plutonium-241 isotope abundance so low [approximately 23 parts per million (ppm) on 9-1-72 and increasing at 28 ppm per year] that beta decay to its daughter americium-241 affects the purity value insignificantly for as long as three years.

Using 0.54208 grams (NBS-949d) and 95.1978 grams of titrant:

$$\frac{(0.9999) (0.54208 \text{ grams})}{239.08} = 226.71 \times 10^{-5} \text{ grams per equivalent (g/eq)}$$

$$\frac{226.71 \times 10^{-5} \text{ g/eq}}{95.1978 \text{ grams}} = 238.1 \times 10^{-7}$$

Result = 238.1×10^{-7} equivalent Ce(IV) per gram titrant.

Table I-A summarizes the titre determinations for the 16 titrations (standardizations); 5 from NBS 83c, 6 from NBS 949d, and 5 from NBS 944. An analysis of variance test performed on the three samples ($F_{\text{calculated}} = 1.00$, $F_{\text{tabular}} = 3.81$ at the 5 percent level of significance) showed no significant mean differences. Hartley's test for homogeneity of variances was performed to ensure that the NBS-944 sample did not contain high variability. These statistical results indicate that the experimental method developed for assay is sufficiently precise and accurate for transferring values of NBS SRM's to the titre of Ce(IV) and thence to the assay of plutonium metal and salts.

A fresh batch of titrant (No. 2) was prepared from the intermediate [$\sim 0.05N$ Ce(IV)] solution and standardized for titration of the stoichiometric plutonium dioxide. The standardization was done with 7 samples of plutonium metal (NBS SRM 949d) and 8 samples of plutonium sulfate tetrahydrate (NBS SRM 944). These 15 titrations were done alternately with 15 stoichiometric plutonium dioxide titrations. This was done to make the assay analysis titrations more representative of the standardization titrations. Table II-A summarizes the standardization data. A pooled t-test on the samples of 7 from NBS 949d and 8 from NBS 944 ($t_{\text{calculated}} = 1.04$; $t_{\text{tabular}} = 2.16$ at the 5

TABLE I-A. Standardization of the No. 1 Cerium(IV) Titrant [Equivalent Cerium(IV) per gram titrant] for Transfer from the Federal Standards.

Plutonium Dioxide Sample Weight (grams)	Titrant Net (grams)	Cerium(IV) Titrant [equivalent Ce(IV)] gram titrant ($\times 10^{-7}$)	NBS SRM Data	
0.086029	72.8463	238.7	NBS 83c Certified Assay	= 0.9999 grams per gram plutonium (g/g Pu)
0.079666	67.6055	238.2		
0.077206	65.4732	238.4	Equivalent Weight Arsenic (As) in arsenous oxide (AsO_3)	
0.074935	63.4971	238.6	As(II) $\rightarrow$ As(IV) + 2 electrons (e)	
0.079264	67.1566	238.6	and (2 e) (2 As)	= Net of 4
			$197.8422 \div 4$	= 49.46055
0.54208	95.1978	238.1	NBS 949d Certified Assay	= 0.9999 g/g Pu
0.50196	87.9762	238.6	Equivalent Weight	= Atomic Weight (see reference)
0.51367	90.0296	238.6		= 239.08
0.52761	92.4333	238.7		
0.54660	95.7641	238.7		
0.58059	101.6383	238.9		
1.06050	88.4395	238.2	NBS 944 Certified Assay	= 0.4750 g/g Pu
1.05113	87.8385	237.8	Equivalent Weight	= Atomic Weight (see reference)
1.06101	88.6193	237.9		= 239.08
1.03856	86.2981	239.1		
1.06456	88.6995	238.5		

NOTE: Federal Standards: National Bureau of Standards (NBS), Standard Reference Material (SRM) 83c, 949d, and 944.
Reference: J. C. Barton. "The Use of Atomic Weights in Uranium Measurements." Pages 382-403. *Analytical Chemistry in Nuclear Technology*. October 12-14, 1960. USAEC Report TID-7606. Gatlinburg, Tennessee. January 1961.

percent level of significance) showed no significant mean differences. The two samples were then combined to give the Ce(IV) titre results as follows:

$$\begin{aligned} N \text{ (number of observations)} &= 15 \\ \bar{X} \text{ (arithmetic mean)} &= 240.47 \times 10^{-7} \\ S \text{ (standard deviation of sample)} &= 0.27 \times 10^{-7} \\ \text{95 Percent Confidence Interval:} \end{aligned}$$

$$(240.5 \pm 0.1) \times 10^{-7} \left[\frac{\text{equivalent Ce(IV)}}{\text{gram titrant}} \right]$$

The assay calculations for the ceric sulfate titration method are detailed in the following text.

Examples of Assay Calculations for the Ceric Sulfate Titration Method:

1. Plutonium (Pu) atomic weight from isotopic abundance in weight percent (wt %)

$$\text{Atomic Weight} = \frac{100}{\frac{\text{wt \% Isotope A}}{\text{nuclide Mass A}} + \dots + \frac{\text{wt \% Isotope N}}{\text{nuclide Mass N}}}$$

TABLE II-A. Standardization of the No. 2 Cerium(IV) Titrant [Equivalent Cerium(IV) per gram titrant] Used to Assay the Stoichiometric Plutonium Dioxide.

Plutonium Dioxide Sample Weight (grams)	Titrant Net (grams)	Cerium(IV) Titrant [equivalent Ce(IV)] gram titrant ($\times 10^{-7}$)	NBS SRM Data	
0.53755	93.3216	240.9	NBS 949d Certified Assay	= 0.9999 grams per gram plutonium (g/g Pu)
0.52863	91.8524	240.7	Equivalent Weight	= Atomic Weight (see reference)
0.53039	92.3162	240.3		= 239.08
0.53640	93.4382	240.1		
0.53720	93.3293	240.7		
0.53925	93.6038	240.9		
0.52493	91.3632	240.3		
1.05270	86.9504	240.5	NBS 944 Certified Assay	= 0.4750 g/g Pu
1.06064	87.6525	240.4	Equivalent Weight	= Atomic Weight (see reference)
1.04464	86.3053	240.5		= 239.08
1.05295	86.9968	240.5		
1.04128	86.0039	240.5		
0.47264	39.13748	239.9		
0.63733	52.65595	240.4		
0.42193	34.84798	240.6		

NOTE: Federal Standards: National Bureau of Standards (NBS), Standard Reference Material (SRM) 83c, 949d, and 944. Reference: J. C. Barton. "The Use of Atomic Weights in Uranium Measurements." Pages 382-403. *Analytical Chemistry in Nuclear Technology*. October 12-14, 1960. USAEC Report TID-7606. Gatlinburg, Tennessee. January 1961.

Data Source: Mass Spectroscopy Analysis for Plutonium Isotopes 239, 240, 241, and 242; Alpha Spectroscopy for ^{238}Pu

(N = 6 calculated $\bar{X}$ wt % of each isotope)

Plutonium isotopic weight percent –

$$\begin{aligned} 238 &= \frac{0.018}{238.049520} = 0.000077 & 240 &= \frac{5.8898}{240.053974} = 0.024535 \\ 239 &= \frac{93.7443}{239.052161} = 0.392150 & 241 &= \frac{0.328}{241.056711} = 0.001361 \\ & & 242 &= \frac{0.0193}{242.058710} = 0.000080 \\ & & \text{Total} &= 0.418203 \end{aligned}$$

$$\text{Equivalent Weight Plutonium} = \frac{100}{0.418203} = 239.12$$

$$2. \quad \text{Grams per Gram (g/g) Plutonium} = \frac{[\text{titre of Ce(IV)}] (\text{net gram titrant}) (\text{equivalent weight Pu})}{\text{net gram sample}}$$

$$\text{g/g Pu} = \frac{(240.5 \times 10^{-7}) (25.85241) (239.12)}{0.16853} = 0.88218$$

3. Iron (Fe) Corr, and Uranium (U) Corr as the gram per gram (g/g) Fe or U expressed as g/g Pu –

$$\text{g/g Fe or U as g/g Pu} = \left[\left(\frac{\text{ppm Fe}}{1 \times 10^6} \right) \left(\frac{\text{Eq wt Pu}}{\text{Eq wt Fe}} \right) + \left(\frac{\text{Eq wt Pu}}{\text{Eq wt U}} \right) \left(\frac{\text{ppm U}}{1 \times 10^6} \right) \right]$$

Where: Equivalent Weight Plutonium = 239.12

Equivalent Weight Iron = 55.847

Equivalent Weight Uranium = 238.03

By 6 analyses of Fe by atomic absorbtion and U by ultraviolet fluorescence:

$\bar{X}$ Fe = 28 ppm; $\bar{X}$ U = 38 ppm (parts per million)

$$\begin{aligned} \text{Fe Corr} + \text{U Corr} &= \left[\left(\frac{239.12}{55.847} \right) \left(\frac{28 \text{ ppm}}{1 \times 10^6} \right) + \left(\frac{239.12}{238.03} \right) \left(\frac{38 \text{ ppm}}{1 \times 10^6} \right) \right] \\ &= 12 \times 10^{-5} + 4 \times 10^{-5} = 16 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} 4. \quad \text{Assay} &= [\text{g/g Pu} - (\text{Fe Corr} + \text{U Corr})] = 0.88218 - 0.00016 \\ &= 0.88202 \text{ g/g Pu} \end{aligned}$$

RFP-2402

APPENDIX B.

**Procedure for the Standardization and Comparison
Qualification of Controlled Potential Coulometry Using Plutonium Sulfate Tetrahydrate.**

The accuracy of this controlled potential coulometric measurement of plutonium was ascertained by measurement of National Bureau of Standards, Standard Reference Material (NBS SRM 944) (plutonium sulfate tetrahydrate) as follows: NBS SRM 944 is the Federal chemical standard for assay of plutonium. The salt has been certified by NBS after preparation by New Brunswick Laboratory (NBL), New Jersey, from low plutonium-241 (^{241}Pu) parent material to insure the validity of the certified value assigned over a long period of time due to minimum beta decay effects of the ^{241}Pu isotope. The SRM salt was assigned a Pu assay value of 0.4750 ± 0.0005 grams per gram (g/g) by NBS from measurements conducted redundantly at Los Alamos Scientific Laboratory, Los Alamos, New Mexico (LASL) and NBL, using an atomic weight of 239.076 obtained from isotopic mass measurements made at NBL and NBS.

**Preparation of the NBS 944
(Plutonium Sulfate Tetrahydrate):**

One issue unit (nominally 1.0 g) of NBS-944 standard $[\text{Pu}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}]$ salt was transferred into a calibrated, clean, and tared 50-millilitre (ml) glass stoppered volumetric flask. The contained plutonium was calculated using the NBS certified purity and net weight of NBS-944 in the flask. The standard was dissolved by adding 15 ml of 1M HNO_3 (nitric acid) and heating gently (30°C) overnight. Then 2 ml of concentrated nitric acid and 3 ml of concentrated hydrochloric (HCl) acid were added. The standard was heated for approximately one hour with low heat ($\sim 60^\circ\text{C}$), mixed by swirling in a rotary manner, cooled to ambient temperature, and brought to below the calibrated volume with a dilute nitric acid ($\sim 0.05\text{M}$). The standard was again brought to ambient temperature and to the calibrated volume with the dilute nitric acid mixture. The standard was weighed and a g Pu/g solution was

calculated. The standard was thoroughly mixed by vigorous agitation and swirling. After removal of the 500-microlitre aliquots, the standard was re-weighed and a contained g Pu was calculated.

Preparation of Aliquots of NBS-944 for Titration:

Approximately 500-microlitre aliquots of the standard were transferred into each of five clean and tared 70-ml weighing bottles fitted with ground glass caps. The weight of each aliquot was determined.^{B-1}

**Preparation of the Controlled
Potential Coulometer and Titration:**

The controlled potential coulometer was calibrated electrically, using the procedure described by Kelly *et al.*^{B-2} The calibration was performed as described later and calculated as the ratio of coulombs per volt, by integrating the current resulting from a known constant voltage over a certified precision resistor. The certification of the resistor was performed by the Rocky Flats Physical Metrology Laboratory (PML) using electrical standards traceable to NBS. The value of the calibration resistor was chosen to simulate that of the titration cell during an assay measurement. The calibration factor (f) for the

^{B-1} All weighings were performed using a PML certified semi-micro analytical balance and controlled by measurement of PML certified check weights. The check weights were selected to conform to the tare and gross weights encountered in this work. As an added check, to simulate weighing the aliquots by substitution, a PML calibrated 500-milligram weight was added to the weighing bottles and a weight recovery calculated just prior to the addition of each aliquot.

^{B-2} M. T. Kelly, H. C. Jones, and D. J. Fisher. "Electronic Controlled Potential Coulometric Titrator." *Analytical Chemistry* 31:488-491, 1956. April 1959.

TABLE I-B. Calibration Factor for the Coulometric Titration of Stoichiometric Plutonium Dioxide.

Battery (E) (volts)	Resistance (R) (ohms)	Time (seconds)	Digital Voltmeter (volts)	Time (t) (seconds per volt, calculated)
1.3458	500.8	1464.7	10.5651	138.6357
1.3458	500.8	1378.2	9.9345	138.7287
1.3458	500.8	912.9	6.5856	138.6206
1.3458	500.8	1303.1	9.3992	138.6395
1.3458	500.8	1652.1	11.9097	138.7189
1.3458	500.8	1030.0	7.4318	138.5936
1.3458	500.8	729.7	5.2635	138.6340
1.3458	500.8	1385.0	9.9908	138.6275
1.3458	500.8	1317.8	9.5026	138.6778
1.3458	500.8	1466.7	10.5766	138.6741
1.3458	500.8	1110.1	8.0029	138.7122

$$\Sigma = 1525.2626$$

$$\text{(arithmetic mean)} \quad \bar{X} = 138.6602$$

$$f = \text{milligrams per volt} = \frac{(1000) (E) (t) (\text{equivalent weight})}{(F) (1.0000) (R)}$$

$$= \frac{(1000) (1.3458) (138.6602) (239.12)}{(96490) (1) (500.8)}$$

$$= 0.923425$$

assay of the stoichiometric plutonium dioxide (see Table I-B) was calculated using the following formula:

$$f = \text{milligrams per volt}$$

$$= \frac{(1000) (E) (\text{equivalent weight})}{(F) (1.0000) (R)}$$

Where:

1000 = conversion from grams to milligrams

E = electromotive force of the mercury battery in volts (from the calibration)

t = time as seconds per volt (from the electrical calibration)

Equivalent Weight = molecular weight (from the NBS certificate) expressed in grams of the element measured per number of electron changes

F = one faraday in coulomb equivalence ($96,490.0 \pm 2.4$ coulombs); also 6.0238×10^{23} electrons. Coulombs equal ampere-seconds and the equivalence is unity.

1.0000 = one volt

R = certified resistance of the
precision resistor

Example: Using E, t, R as the observed mean of
11 measurements (see Table I-B) —

$$f = \text{milligrams per volt}$$

$$= \frac{(1000) (1.3458) (138.6602) (239.12)}{(69490) (1) (500.8)}$$

$$= 0.923425$$

The plutonium (NBS 944) coulometric assay was made using the calibrated high-precision controlled potential coulometer as follows:

1. The supporting electrolyte was 1M perchloric acid.
2. The Vycor® salt bridge electrolyte was 1M nitric acid.
3. The reference electrode was saturated calomel electrode (SCE).
4. The working and isolated electrodes were platinum-gauze and 16-gauge wire coil, respectively.
5. The titration mode used was the Pu(III) per Pu(IV) oxidation couple ($n = 1$) with the reduction at 0.535 volts and the oxidation at 0.895 volts versus the SCE.^{B-3 B-4}
6. The ratio of the integrated current versus standard high-precision resistors was displayed as a voltage using a 6-place digital voltmeter (DVM).

A 25-ml aliquot of the titration electrolyte was deoxygenated with argon, preelectrolyzed for the reagent blank, transferred into a weighing bottle containing a mass-measured aliquot of the NBS-944 standard and coulometrically titrated as before. The DVM readings for blank and standard titration were recorded when the integration current had decreased to 20-microamperes during the oxidation cycle. After titration of each of the 5 weighed aliquots, the weighing bottles were cleaned and dried. The standard (50-ml volumetric) was weighed and a g Pu/g solution was calculated. Five more aliquots were transferred, the standard was reweighed, a contained g Pu calculated, and the titration process was repeated. A total of fifteen titrations were made.

The 15 titrations were extended over a consecutive 3-day period with 5 titrations made per day. No precalculations were performed. Therefore, these 15 determinations represent unbiased measurements simulating actual comparison conditions as nearly as possible.

The grams plutonium per grams standard for each aliquot was calculated as follows:

$$\frac{\text{grams plutonium per}}{\text{grams sample}} = \frac{(f) \times (\text{DVM}) \times (\text{FW})}{(\text{SW}) \times (\text{A}) \times (1000)}$$

Where: f = calibration factor in milligrams per volt
 DVM = corrected readout (digital voltmeter)
 FW = final net weight of diluted sample in grams (g)
 SW = sample weight in grams
 A = aliquot weight taken from the FW above
 1000 = conversion factor for converting milligrams (mg)

Table II-B summarizes the 15 assay determinations of NBS SRM 944. An analysis of variance test performed on the three samples (F -calculated = 0.25; F -tabular = 3.89 at the 5 percent level of significance) showed no significant mean differences between assay taken over 3 days. This result indicates there is no electronic drift over a 3-day period.

^{B-3}W. D. Schultz. "Extensive Review of Methods and Variations." U. S. Atomic Energy Report, ORNL-2921. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 1960; *Analytical Chemistry* 35:922. 1963; *Talanta* 10:833. 1963.

^{B-4}F. A. Scott and R. M. Pekema. *Analysis for Plutonium by Controlled Potential Coulometry*. Paper No. 914. Second International Conference on the Peaceful Use of Atomic Energy. Volume 28. Geneva, Switzerland. 1958.

TABLE II-B. First Measured Assay of National Bureau of Standards, Standard Reference Material-944 Dissolved in Nitric Acid and Titrated by Controlled Potential Coulometry.

Digital Voltmeter Correction (volts)	Aliquot Weight (grams)	Assay (grams per gram plutonium)
5.4266	0.55503	0.4747
5.5264	.56367	.4760
5.5348	.56765	.4734
5.7913	.59132	.4755
5.3586	.54788	.4749
5.8371	.59688	.4748
5.7885	.59133	.4753
5.8503	.59900	.4742
5.5823	.56999	.4755
5.7439	.58655	.4755
5.6976	.58234	.4750
5.7564	.58807	.4752
5.8761	.60051	.4750
5.8560	.59767	.4757
5.5367	0.56570	0.4751

NOTE: National Bureau of Standards-944
Certified Assay = 0.4750 ± 0.0005
grams per gram plutonium.
Supporting electrolyte was 1M HClO_4
plus 0.02M $\text{NH}_2 - \text{SO}_3\text{H}$ (perchloric
plus sulfamic acid).

Assay Summary:

N (number of observations) = 15
 $\bar{X}$ (arithmetic mean) = 0.47505
S (standard deviation of sample) = 0.000637

95 Percent Confidence Interval:

$$0.4751 \pm 2.145 \left(\frac{0.000637}{\sqrt{15}} \right)$$

± 0.0004 grams per gram
plutonium

The 3 samples were then combined and a t-test performed (t-calculated = 0.32; t-tabular = 2.15 at the 5 percent level of significance) which showed the experimental assay did not differ significantly from the known certified value of

0.4750. The assays derived from controlled-potential coulometry are traceable to the NBS plutonium standard and therefore can be used to transfer standard values to assign plutonium purity values.

While the standardization described above is valid for the assay of plutonium sulfate tetrahydrate (NBS SRM 944) and plutonium metal (NBS SRM 949d), the measurement of a fused plutonium dioxide sample dissolved in the mineral acid matrix, (as described in the body of this report, Page 6) was found to be chemically incompatible for the coulometric measurement. Sulfuric acid is required as the supporting electrolyte rather than the perchloric acid used during the original standardization. To fully support and check the calibration results reported above, the procedure was amended as follows.

A fusion flux was prepared by combining 5.4 g of $\text{K}_2\text{SO}_4 \cdot \text{SO}_3$ and 0.6 g of Na_2O_2 in a plastic screw-cap vial. The flux was mixed and transferred into a clean dry quartz-fusion flask. A tare weight was obtained using a semi-micro analytical balance certified by the Rocky Flats Physical Metrology Laboratory. An aliquot of NBS-944 was mixed with the fusion flux with gentle agitation and a gross weight obtained using the semi-micro analytical balance. The fusion flask containing the sample plus flux was transferred into the flame-fusion glove box and the mixture was fused. The fusion flask containing the cool melt was transferred into a glove box and the melt was partially dissolved with a matrix of 1N HNO_3 + 1N H_2SO_4 , then quantitatively transferred into a tared 200-ml glass stoppered volumetric flask using the mineral acid matrix. The final volume of matrix was adjusted to approximately 190 ml and the dissolution of the sample was completed with a hot plate controlled at low heat, manually swirling in a rotary manner, and thermally cooling to ambient temperature. The coulometric measurement of 5 titrations was made using the following modifications:

1. The salt bridge electrolyte was 0.5M H_2SO_4 .
2. The supporting electrolyte was 0.5M H_2SO_4 + 0.02M $\text{NH}_2 - \text{SO}_3\text{H}$.

TABLE III-B. Second Measured Assay of Fused National Bureau of Standards, Standard Reference Material-944 by Controlled Potential Coulometry.

Digital Voltmeter Correction (volts)	Aliquot Weight (grams)	Assay (grams per gram plutonium)
2.811	1.92475	0.4750
2.692	1.84285	0.4751
2.736	1.87395	0.4749
2.845	1.94750	0.4751
2.962	2.02792	0.4751

NOTE: National Bureau of Standards-944
 Certified Assay = 0.4750 ± 0.0005
 grams per gram plutonium.
 Supporting electrolyte was $0.5M H_2SO_4$
 plus $0.02M NH_2 - SO_3H$ (sulfuric plus
 sulfamic acid).

Assay Summary:

N (number of observations) = 5

$\bar{X}$ (arithmetic mean) = 0.47504

S (standard deviation of sample) = 0.000089

95 Percent Confidence Interval:

$$0.47504 \pm 2.776 \left(\frac{0.000089}{\sqrt{5}} \right)$$

± 0.0001 grams per gram
plutonium

3. The titration mode was the Pu(III)–Pu(IV) oxidation couple ($n = 1$) with the reduction at 0.310 volts and the recorded oxidation at 0.670 volts versus the SCE.

4. A new calibration factor was calculated with E, t, and R as the observed mean value for eleven measurements (see Table I-B).

The results are summarized in Table III-B and again indicate the mean assay is in statistical agreement with the certified value.

This modification of the standardization procedure provides for the free flame fusion, dissolution, and subsequent direct assay of high-fired plutonium dioxide showing traceability directly to the Federal standards using the controlled potential coulometer as the transfer media.