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Preparation of Working Calibration
and Test Materials for Intra- and
Interlaboratory Surveillance of
Nuclear Materials Measurement Methods —
Plutonium Nitrate Solution

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by

G. C. Swanson
J. E. Rein
S. F. Marsh
G. R. Waterbury



los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544



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CONTENTS

1. INTRODUCTION	1
2. PLUTONIUM SOURCE MATERIALS	2
2.1. NBS Plutonium Certified Reference Materials	2
2.1.1. CRM 944, Plutonium Sulfate Tetrahydrate	2
2.1.2. CRM 949, Plutonium Metal	3
2.1.3. CRM 945, Plutonium Metal	3
2.1.4. CRMs 946, 947, and 948, Plutonium Sulfate Tetrahydrate	3
2.2. Other Plutonium Metal	3
2.3. Plant Plutonium Nitrate Solution	3
3. PREPARATION OF WORKING CTM SOLUTIONS	4
3.1. Preparation of Plutonium Nitrate Solution	4
3.1.1. Source Material Treatment	4
3.1.2. Dissolution of Plutonium Metal and Conversion to Plutonium Nitrate by HBr Method	4
3.1.3. Dissolution of Plutonium Metal and Conversion to Plutonium Nitrate by HCl Method	5
3.1.4. Dissolution of Plutonium Sulfate in Nitric Acid	5
3.1.5. Stabilization of Plant Plutonium Nitrate Solution	6
3.2. Impurities Addition, Aging, Filtration, and Final Dilution of Plutonium Nitrate Solutions	6
3.2.1. Impurities Addition	6
3.2.2. Solution Aging	6
3.2.3. Filtration	6
3.2.4. Final Dilution of Plutonium Nitrate Solution	7
4. PACKAGING OF WORKING CTMS	7
4.1. Materials	7
4.2. Packaging of Total Vial Contents	7
4.3. Packaging for Short-term Solution Storage (up to 3 months)	8
4.4. Packaging for Long-term Solution Storage (3 months to 2 yr)	8
4.5. Packaging of Isotopic Working CTM Solution	9
5. CHARACTERIZATION AND OVERCHECK ANALYSIS OF WORKING CTMS	9
5.1. Determination of Plutonium Content in Filtration Residue	9
5.2. Characterization of Working Assay CTM Solutions Prepared from Plant Nitrate	10
5.3. Overcheck Analysis of Working Assay CTM Solutions Prepared from NBS Materials or other Plutonium Metals	10
5.4. Characterization or Verification of Isotopic Abundance Solutions	10

6. ASSIGNMENT OF REFERENCE VALUES	11
6.1. Comparison of Makeup and Overcheck Values	11
6.1.1. Calculation of Makeup Assay Value	11
6.1.2. Test of Difference Between Makeup and Overcheck Values of Working Assay and Isotopic CTMs	11
6.2. Comparison of Results from Two Analytical Methods	12
6.3. Assigned Value and Standard Deviation for Assay Value	13
6.3.1. Assignment Based on Overcheck and Makeup Agreement	13
6.3.2. Assignment Based on Analyses Agreement	13
6.4. Assigned Value and Standard Deviation for Isotopic Value	13
6.4.1. Uncontaminated Working CTMs Prepared from NBS CRM 946, 947, or 948	13
6.4.2. Isotopic Values Based on Six or More Analyses	13
6.5. Statistical Tests Indicate Disagreement	14
6.5.1. Makeup and Overcheck Values	14
6.5.2. Disagreement of Makeup and Assay by Two Analytical Methods	14
6.6 Correction for ²⁴¹ Pu Decay	14
ACKNOWLEDGMENTS	14
REFERENCES	14

**PREPARATION OF WORKING CALIBRATION AND TEST
MATERIALS FOR INTRA- AND INTERLABORATORY
SURVEILLANCE OF NUCLEAR MATERIALS
MEASUREMENT METHODS--PLUTONIUM NITRATE SOLUTION**

by

G. C. Swanson, J. E. Rein,
S. F. Marsh, and G. R. Waterbury

ABSTRACT

Methods for preparation of working plutonium nitrate calibration and test material (CTM) solutions similar to typical nuclear fuel cycle solutions are described. These working CTM solutions are to be used in calibrating and providing quality control surveillance of analytical methods for measurement of plutonium assay and isotopic abundances. Source materials are prepared from NBS plutonium certified reference materials, highly pure plutonium metal, or plutonium nitrate obtained from a plant inventory. Some solutions are prepared for assay measurement only, some for isotopic abundance measurement only, and others for both purposes. Procedures are described for their packaging and storing as evaporated slurry, solution for short-term storage, and solution for long-term storage. Analytical overcheck and characterization procedures are suggested, and statistical tests to assess the reliability of the working CTM solutions are given.

1. INTRODUCTION

This report outlines methods for preparing working plutonium nitrate calibration and test solutions similar to nitrate solutions in the nuclear fuel cycle. These working solutions are to be used in calibration and quality control surveillance of analytical methods recommended for assay and isotopic

measurements,¹ to minimize intralaboratory variance and interlaboratory differences.

To meet the requirements of a working calibration and test material (CTM)*, the assigned values of plutonium assay and isotopic abundances must be referenced to primary or certified reference materials. In this guide, the primary reference materials are National Bureau of Standards (NBS) Certified Reference Materials (CRMs)**.

*There is a recent international agreement to delete "standard" when referring to "material standards" and to substitute "calibration and test materials" (CTM). Therefore, working standards are now called working calibration and test materials.

**The nomenclature for NBS materials is being changed to eliminate "standard." The NBS Standard Reference Materials (SRM) will be renamed "Certified Reference Materials" (CRM), probably by the time this report is issued.

Plutonium nitrate solution has a long history of instability. The preparation procedures presented here include provisions for long-term storage stability. Factors that have been controlled include acid and plutonium concentration, plutonium oxidation state, and packaging.

The selection of the plutonium source material and the method of preparation of the working CTM solution must produce a solution that simulates the material processed in a plant. The plutonium nitrate solutions may be prepared using NBS CRM plutonium metal or sulfate salt, highly pure plutonium metal from other sources, or plutonium nitrate solution drawn from a plant inventory. Each material has advantages and disadvantages for this purpose. The cost of NBS materials precludes their use in large quantities, and the isotopic compositions of NBS assay CRMs are atypical of nuclear fuel cycle materials. Plutonium metals with isotopic abundances typical of nuclear fuel cycle material can be fabricated, but often they are not readily available. Working CTM solutions prepared from plant material require extensive characterization.

All solutions are prepared on a weight (grams of plutonium per gram of solution) basis, to be consistent with recommended analysis methods.¹ Two methods that start with either NBS CRM metal or other plutonium metal are presented for preparation of working CTM solutions; each method is customized for different storage conditions. A third method using the NBS plutonium sulfate tetrahydrate assay CRM as the source material produces solutions with limited plutonium concentration levels and application restricted to calibration of selected analysis methods. The fourth method converts plant plutonium nitrate solution to a stable plutonium (IV) nitrate solution suitable for characterization and long-term storage. The prepared solutions are packaged either as evaporated slurry for total-content analysis or as solutions for concentration analysis. Different sealed glass containers are used for short- and long-term storage.

The assay values of the working CTMs can be based on agreement of the makeup value with overcheck analysis results from one selected method, or on agreeing results from two different analytical methods. All analytical methods must be calibrated with NBS plutonium CRMs.

National Bureau of Standards isotopic plutonium CRMs may be used as source materials to prepare working CTM solutions restricted to calibration and quality control surveillance of plutonium isotopic measurements. The solutions prepared for assay measurements also may be characterized for isotopic

measurement. For both types, verification by a thermal ionization mass spectrometric method calibrated with NBS isotopic uranium and plutonium CRMs is required.

Examples are presented to demonstrate the use of analytical methods for overcheck or characterization and methods for statistical evaluation of experimental data for assigning assay and isotopic values to working CTMs.

2. PLUTONIUM SOURCE MATERIALS

An ideal source material for preparation of working plutonium nitrate CTM solutions would be an inexpensive, readily available, highly pure, well-characterized metal with isotope abundances like those of the nuclear fuel cycle material processed in a facility. There is no readily available supply of materials that meet these criteria completely, and most laboratories will necessarily use the source materials described below. Before selecting a source material and the analytical methods to use for its characterization, one must consider the source material cost, the preparation time, the characterization cost, the effect of possible bias owing to use of plant nitrate material, and the degree to which the solution will simulate the nuclear fuel cycle material.

2.1. NBS Plutonium Certified Reference Materials²

The NBS provides two plutonium metals and one plutonium sulfate salt that are certified for plutonium content (Table I). These materials are readily available, highly pure, and well characterized but their cost essentially limits their use to method calibrations. Also, none is certified for isotopic abundance, so separate solutions must be prepared for this purpose. The three NBS CRMs for plutonium isotopic abundance also are listed in Table I.

2.1.1. CRM 944, Plutonium Sulfate Tetrahydrate. This stoichiometric material is suitable for preparation of low-concentration working assay CTM solutions. Direct dissolution in HNO_3 produces a stable plutonium (IV) nitrate solution. The recommended maximum plutonium concentration is $<0.1 \text{ M}$ in $\leq 8 \text{ M HNO}_3$.³ Sulfate at a molar concentration twice that of the plutonium is not likely to be typical of nuclear fuel cycle material and it can interfere with analyses. Possible interference mechanisms include competitive complexing of Pu^{4+} , prevention of

TABLE I
NBS PLUTONIUM CERTIFIED REFERENCE MATERIALS

<u>NBS CRM</u>	<u>Type</u>	<u>Amount (g)</u>	<u>Certified For</u>	<u>Value</u>	<u>Comments</u>	<u>Cost^a</u>
944	Plutonium sulfate tetrahydrate	0.5	Pu content	47.50% Pu	~6% ²⁴⁰ Pu	\$ 345
945	Plutonium metal	5	Impurities, Pu content	99.9% Pu	~6% ²⁴⁰ Pu	\$ 101
949	Plutonium metal	0.5	Pu content	99.99% Pu	~3% ²⁴⁰ Pu	\$ 312
946	Plutonium sulfate tetrahydrate	0.25	Isotopic abundance	~12% ²⁴⁰ Pu	~4% ²⁴¹ Pu	\$1315
947	Plutonium sulfate tetrahydrate	0.25	Isotopic abundance	~18% ²⁴⁰ Pu	~4.5% ²⁴¹ Pu	\$1315
948	Plutonium sulfate tetrahydrate	0.25	Isotopic abundance	~ 8% ²⁴⁰ Pu	~0.5% ²⁴¹ Pu	\$ 598

^aJanuary 1974, dollars per gram of plutonium.

quantitative oxidation to Pu⁶⁺, shifting of the Pu³⁺/Pu⁴⁺ redox potential, and precipitation of cations that form insoluble sulfate salts. The isotopic abundances (~6% ²⁴⁰Pu) of this material are not typical of power industry plutonium.

2.1.2. CRM 949, Plutonium Metal. This well-characterized material is widely used to calibrate assay methods used to establish working CTM solution values. The cost precludes its use in large quantities, so high-concentration or large-volume standards cannot be prepared. Its very low extraneous element content makes it an excellent base for preparing simulated nuclear fuel cycle materials simply by adding desired elements to the dissolved metal before adjustment to the final concentration. Such solutions are very useful for establishing interference effects in assay methods. The low ²⁴⁰Pu and ²⁴¹Pu contents of this metal make it atypical of nuclear fuel cycle material, but provide a low americium level, if desired.

2.1.3. CRM 945, Plutonium Metal. This material's major intended use was as a matrix for preparation of emission spectrochemical impurity standards, so it was characterized mainly for impurity metal content. It has been recharacterized recently for plutonium content. Although the 99.9 ± 0.1% uncertainty limits on the plutonium content are larger than those of the CRM 949 metal, the lower cost may permit its use in preparing working CTM solutions. Its ²⁴⁰Pu isotopic abundance is like that of CRM 944 plutonium sulfate, and its suitability for working isotopic CTM solutions is subject to the same considerations.

2.1.4. CRMs 946, 947, and 948, Plutonium Sulfate Tetrahydrate. These materials, expensive and not certified for plutonium content, are restricted to preparation of plutonium nitrate solutions for

plutonium isotopic measurements. The material whose ²⁴⁰Pu and ²⁴¹Pu levels are closest to a plant's nuclear fuel cycle material should be used.

2.2. Other Plutonium Metal

Highly pure plutonium metal with isotope abundances like those of nuclear fuel cycle materials, available in certain AEC contractor laboratories*, is a very desirable starting material for preparation of working CTM solutions. Unfortunately, such material is not readily available. Ideally, the metal should be >99.9% pure, and it should be characterized for metallic and nonmetallic impurities to provide a metal assay by difference so that the prepared plutonium nitrate solution need be verified using only one analytical method (see Sec. 5). An advantage of using specially fabricated metal as the source material is that the working CTM solution can serve for both assay and isotopic measurements.

2.3. Plant Plutonium Nitrate Solution

This material has unique representativeness and low cost; however, to be used as a working CTM solution, it requires extensive characterization. Also, it may introduce bias in assay measurements because of impurity interferences that are difficult to resolve completely. For example, dissolved organic material

*An incomplete list of possible plutonium metal sources includes Atlantic Richfield Hanford Co., Hanford, WA; Los Alamos Scientific Laboratory, Los Alamos, NM; Mound Laboratory of Monsanto Research Corporation, Miamisburg, OH; Rocky Flats Division of Dow Chemical, USA, Golden, CO; and Savannah River Plant of E. I. duPont de Nemours; & Co., Aiken, SC.

may be present and extremely difficult to remove or measure. The characterization for assay is made (see Sec. 5) using at least two analysis methods subject to different impurity interferences.

3. PREPARATION OF WORKING CTM SOLUTIONS

Two methods for preparing plutonium nitrate working solutions using plutonium metal are described. One produces a plutonium (IV) nitrate solution; the other, a solution containing appreciable plutonium (VI). In sealed containers, plutonium nitrate solution that contains only Pu^{4+} is not subject to pressure generation caused by formation of gases from radiolytic reactions with Pu^{6+} and Pu^{3+} .⁴ The solution containing Pu^{6+} is evaporated to a slurry and stored for only short periods. Plutonium sulfate is directly dissolved in nitric acid to produce a solution suitable for long-term storage. Plant nitrate solution is treated to produce a solution suitable for long-term storage.

All the methods produce plutonium nitrate solutions on a weight (g plutonium/g solution) basis, to avoid volume errors and be consistent with recommended analysis methods.¹ The solutions also can be prepared on a volume (g plutonium/ml) basis, but dilutions to volume and aliquoting should be done at the same measured temperature with appropriately calibrated glassware.⁵

3.1. Preparation of Plutonium Nitrate Solution

The four methods differ primarily in initial treatment of the plutonium materials and conversion to nitrate. Subsequent procedures for impurities addition, aging, filtration, and final dilution are the same, with a few noted exceptions, for all plutonium material sources (see Sec. 3.2.). Therefore, only the initial treatments and conversion to nitrates are described separately.

3.1.1. Source Material Treatment. The NBS plutonium metal and plutonium sulfate are used as received. Other plutonium metal should be cleaned to a bright, shiny surface by filing with a new file just before weighing, (Sec. 2.1.1.4.G, Ref. 6). The amount of plutonium required is determined by the concentration and anticipated use of the solution to be prepared. Plant plutonium nitrate solution is subject to special pretreatment described in Sec. 3.1.5.

Plutonium metal or plutonium sulfate is weighed by difference before dissolution. A container plus the plutonium material is weighed (ω_2). After transfer of the plutonium material, the empty container is

weighed (ω_1). Treatment of the data for assigning plutonium concentration values is presented in Sec. 6.

3.1.2. Dissolution of Plutonium Metal and Conversion to Plutonium Nitrate by HBr Method.⁷ The HBr method produces a solution containing Pu^{4+} suitable for long-term storage in sealed containers.

A. Reagents.

1. HBr, 3 M, AR grade.
2. 0.05 M HF-9 M HBr mixture. Add 0.2 ml of 27 M AR grade HF to 99.8 ml of 9 M AR grade HBr.
3. HNO_3 , 15.7 M, 12M, and 3M, AR grade.
4. NaOH, 6 M.

B. Apparatus.

1. Beaker, tall-form, 250-ml.
2. Bromine fume scrubber and steam jacket, consisting of a gas washing bottle filled with 6 M NaOH connected to a fume collector made by attaching a side arm to the cut-off top of a plastic dropping bottle. (Fig. 1). The steam jacket is a covered beaker partially filled with water. The cover is a sheet of plastic topped by a section of round plastic or fiberboard carton trimmed to fit the volumetric flask neck closely to ensure that steam heats the entire length of the flask.

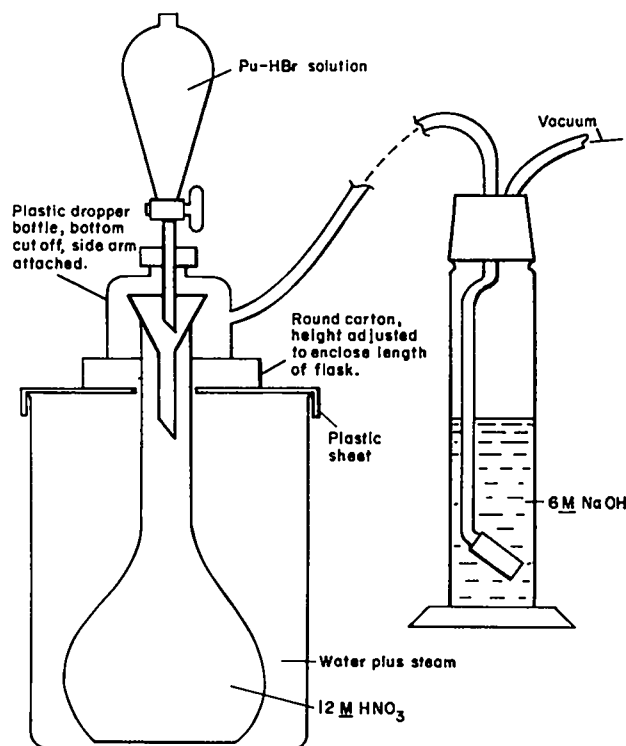


Fig. 1.
Bromine fume scrubber and steam jacket.

3. Flask, volumetric, volume equal to twice that of the plutonium nitrate solution to be prepared.
4. Hot plate.
5. Separatory funnel, 60-ml, with Teflon stop-cock.
6. Watch glass, to cover beaker.

C. Procedure.

1. Add equal volumes of the 0.05 M HF-9 M HBr mixture and water to a 100-ml tall-form beaker to a depth sufficient to cover the plutonium metal to be added in the next step.
2. Transfer the weighed plutonium metal; then cover the beaker immediately with a watch glass to prevent loss by spray. (Cool the beaker with an ice bath to control the reaction rate for large quantities of plutonium metal.)
3. Add 0.05 M HF-9 M HBr mixture at a rate that maintains a rapid, yet controlled, dissolution. The total volume of 0.05 M HF-9 M HBr mixture added should be 1.5 to 2.0 ml/g of plutonium.
4. When dissolution is complete, rinse the watch glass and beaker walls with 3 M HBr.
5. Add to the volumetric flask an amount of 12 M HNO₃ equal to three times the volume of the 0.05 M HF-9 M HBr mixture.
6. Assemble the volumetric flask, separatory funnel, and bromine fume scrubber as shown in Fig. 1.
7. Add the Pu-HBr solution to the separatory funnel with rinsings of 3 M HBr.
8. Heat the water in the steam jacket (beaker) just to boiling; then add the Pu-HBr solution from the separatory funnel to the volumetric flask at a rate of ~1 drop/10 s. (The HNO₃ oxidizes Br⁻ to Br₂ and Pu³⁺ to Pu⁴⁺ as the steam heats the entire volumetric flask to ensure volatilization of Br₂. Too rapid addition of the Pu-HBr may cause bumping and subsequent plutonium loss).
9. Rinse the separatory funnel sequentially with minimal volumes of 3 M HBr, 3 M HNO₃, and 12 M HNO₃. Transfer each rinse slowly to the volumetric flask.
10. Continue the steam heating for ~48 h to completely remove the bromine.
11. Adjust the HNO₃ concentration to 8 M with 15.7 M HNO₃ assuming an equimolar consumption of HNO₃ by the 9 M HBr.
12. Proceed to Sec. 3.2.

3.1.3. *Dissolution of Plutonium Metal and Conversion to Plutonium Nitrate by HCl Method.* NOTE: The HCl method produces a solution containing substantial amounts of Pu⁶⁺ which is packaged as an evaporated slurry (Sec. 4.2).

A. Reagents.

1. HCl, 12 M and 6 M, AR grade.
2. HNO₃, 15.7 M and 8 M, AR grade.

B. Apparatus.

1. Beaker, tall-form, 150-ml, with cover.
2. Steam bath.
3. Watch glass, ribbed, to fit beaker.

C. Procedure.

1. Add enough 6 M HCl to the tall-form beaker to cover the plutonium metal to be added in the next step.
2. Transfer the weighed plutonium metal and cover the beaker to prevent loss by spray. Cool the beaker with an ice bath to control the reaction rate for large quantities of plutonium metal.
3. Add 12 M HCl to maintain a rapid, yet controlled, dissolution. The final volume of 12 M HCl added should be greater than 2 ml HCl/g of plutonium.
4. When dissolution is complete, rinse the watch glass and beaker walls with 6 M HCl.
5. Add 1 ml of 15.7 M HNO₃ to the covered beaker and heat on a steam bath for 30 min to oxidize Pu³⁺ to Pu⁴⁺.
6. Add a volume of 15.7 M HNO₃ equal to the volume of HCl present, cover with a ribbed watch glass, and evaporate to a moist residue. Do not remove the residue from heat, because water will condense on the cooled deliquescent salts and cause hydrolysis.
7. Add 20 ml of 15.7 M HNO₃ and evaporate to a moist residue.
8. Repeat step 7.
9. Resolubilize the salts in a minimal volume of 8 M HNO₃.
10. Proceed to Sec. 3.2.

3.1.4. *Dissolution of Plutonium Sulfate in Nitric Acid.*

Preparation of <0.1 M plutonium nitrate standard is accomplished conveniently by dissolving Pu(SO₄)₂·4H₂O in warm 8 M HNO₃. This procedure is used to prepare working assay or isotopic CTM solutions.

A. Reagent.

HNO₃ 8M, AR grade.

B. Apparatus.

1. Beaker, tall-form, with cover.
2. Hot plate.

C. Procedure.

1. Transfer the weighed Pu(SO₄)₂·4H₂O to the beaker.
2. Add a minimal volume of 8 M HNO₃ to effect dissolution. Warm the acid to <50°C on the hot plate to speed dissolution.
3. Proceed to Sec. 3.2.

3.1.5. Stabilization of Plant Plutonium Nitrate Solution. Plant plutonium nitrate solutions are adjusted to 8 M in HNO₃ and treated to ensure dissociation of plutonium polymers.¹ In treatment and subsequent procedures, the plutonium becomes diluted. Therefore, the source material should be selected or be concentrated by low-temperature evaporation to contain 1.5 times more plutonium than usual to produce a working CTM solution that typifies the plant plutonium nitrate streams. It is recommended that at least a 6-month supply of working CTM solution be prepared to compensate for the expense of characterization. The starting material must be a single-phase, homogeneous solution according to the criteria established in Ref. 1.

A. Reagents.

1. HF, 27 M, AR grade.
2. HNO₃, 15.7 M and 2 M, AR grade.

B. Apparatus.

1. Beakers, with covers, size appropriate for the volume of working CTM to be prepared.
2. Magnetic mixer.
3. Magnetic stirring bar, Teflon-coated.

C. Procedure.

1. Add the plant plutonium nitrate solution to a beaker whose capacity is at least four times that of the solution.
2. Adjust the acid concentration to 8 M by adding 15.7 M HNO₃ or 2 M HNO₃. Do not dilute plutonium solutions with water, as hydrolysis may occur.⁸
3. Add enough 27 M HF to produce a solution that is 0.05 M in HF.
4. Insert the magnetic stirring bar, cover the beaker, and magnetically stir at least 2 h.
5. Remove the stirring bar, rinse it with 8 M HNO₃, and proceed to Sec. 3.2.

3.2. Impurities Addition, Aging, Filtration, and Final Dilution of Plutonium Nitrate Solutions

3.2.1. Impurities Addition. The solutions prepared from plutonium metal or plutonium sulfate require addition of impurities, typically metal ions, to simulate nuclear fuel cycle materials. Because the specific impurities and their concentrations vary, only general directions for addition of impurities are given.

Prepare an impurity mixture in 8 M HNO₃ using at least AR grade metals or nitrate salts at concen-

trations such that a small (1- or 2-ml) volume of impurity solution contains the appropriate amount of each impurity for the total weight of plutonium. Add the appropriate volume of impurity solution to the plutonium nitrate solution from Sec. 3.1.2, 3.1.3., or 3.1.4. and swirl the solution to homogenize it.

3.2.2. Solution Aging. All plutonium nitrate solutions, except those prepared by dissolution of plutonium metal in HCl are aged to provide time for radiolytically generated H₂O₂ to reduce any Pu⁶⁺ to Pu⁴⁺. Two weeks is enough to ensure that >99% of the plutonium is Pu⁴⁺ (Ref. 7). Because reduction of Pu⁶⁺ by H₂O₂ produces gas, the solution is vented to the atmosphere while aging. The volumetric flask is covered with an inverted beaker to decrease evaporation. Aging also allows time for precipitate formation, and any precipitates are removed by filtration after the aging.

3.2.3. Filtration. Filter the plutonium nitrate solution through a plastic membrane filter into a tared volumetric flask whose capacity is twice the volume of the final working CTM solution, to allow thorough mixing by swirling. Any residue is analyzed for plutonium (Sec. 5.1), and the assay value is corrected or the solution is subjected to assay analysis by two analytical methods.

A. Reagent.

HNO₃, 8 M, AR grade.

B. Apparatus.

1. Filter adaptor, custom made, to allow direct filtration into the volumetric flask. (Fig. 2.)
2. Filter support plus chimney, Millipore No. XX10-025-00, or equivalent.
3. Filters, plastic membrane, 0.45- μ m pore size, Millipore Mitex, or equivalent.
4. Flask, volumetric, with ground glass stopper.

C. Procedure.

1. Weigh a clean, dry, volumetric flask with stopper (ω_3).
2. Insert the filter holder into the adaptor and mount it on the flask.
3. Mount the filter and chimney on the holder and apply suction.
4. Transfer the plutonium nitrate solution slowly to the chimney and rinse the plutonium nitrate container and chimney walls three times with 8 M HNO₃ to ensure quantitative transfer.
5. Remove the filter and analyze for plutonium content (see Sec. 5.1).

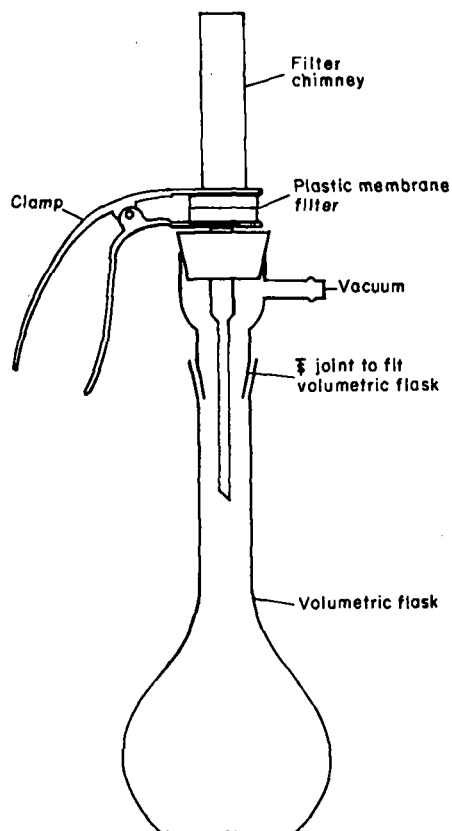


Fig. 2.
Filtration apparatus.

6. Remove the filter adaptor and filter, washing the delivery tube with 8 M HNO₃.
7. Adjust the filtrate to final concentration (see next section).

3.2.4. *Final Dilution of Plutonium Nitrate Solution.* The final plutonium concentration is adjusted to that of plant materials, and the nitric acid concentration may be adjusted to 6 to 12 M, to ensure Pu⁴⁺ stability. Use 2 M HNO₃ to dilute, or 12 to 15.7 M HNO₃ to concentrate, the acid. Dilution with less than 2M HNO₃ may cause plutonium hydrolysis.⁸ When the concentrations have been adjusted, weigh the stoppered flask (ω_4) and swirl the contents to homogenize it.

4. PACKAGING OF WORKING CTMS

Three modes of packaging working CTM solutions provide plutonium reference values of total content per vial (g plutonium/vial), solution concentration (g

plutonium/g solution), or both. A working CTM calibrated for total content is packaged as an evaporated slurry in glass vials with polyethylene stoppers. A working CTM calibrated for concentration is packaged in a 25-ml volumetric flask with a polyethylene stopper for short-term storage (to 3 months), or in a flame-sealed glass ampoule for long-term storage (3 months to 2 yr). Also described is the packaging of the working CTM solutions prepared for isotopic abundance measurements only.

4.1. Materials.

4.1.1. Ampoule, 2-mm wall thickness, 30-mm o.d. at base, 13-mm o.d. at neck, with 50-mm body length for each 10 ml of solution to be stored and 130-mm neck length for ease in sealing, made of borosilicate glass, (Fig. 3).

4.1.2. Bottle, wash, polyethylene, 30-ml.

4.1.3. Funnel, glass, drawn-out 6-mm stem (Fig. 3), with 1-mm delivery tip. A ring of plastic tubing is placed above the tip to act as a spacer to prevent the tip from touching the ampoule neck. The funnel stem should be treated on the outside with a nonwetting agent, Dryfilm, or equivalent.

4.1.4. Flask, volumetric, 25-ml, polyethylene-cone, screw-cap seal, Corning No. 5650, or equivalent.

4.1.5. Holder, polyethylene, made from a 60-ml polyethylene bottle (Fig. 4).

4.1.6. Hot plate.

4.1.7. Lamp, heat, controlled from variable voltage source.

4.1.8. Vial, specimen, "3-dram," polyethylene stopper, Fisher No. 3-339C or equivalent.

4.2. Packaging of Total Vial Contents.

4.2.1. Clean, dry, and label enough 3-dram vials for the individual standards to be packaged.

4.2.2. Transfer 10 to 20 ml of the working CTM solution to a 30-ml wash bottle and weigh.

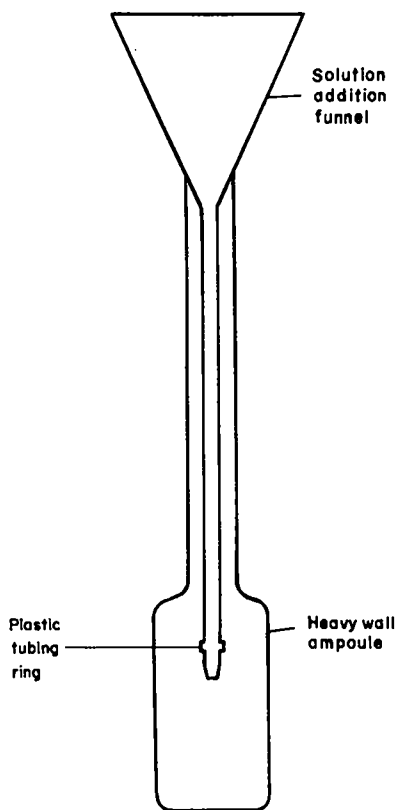


Fig. 3.
Ampoule plus funnel.

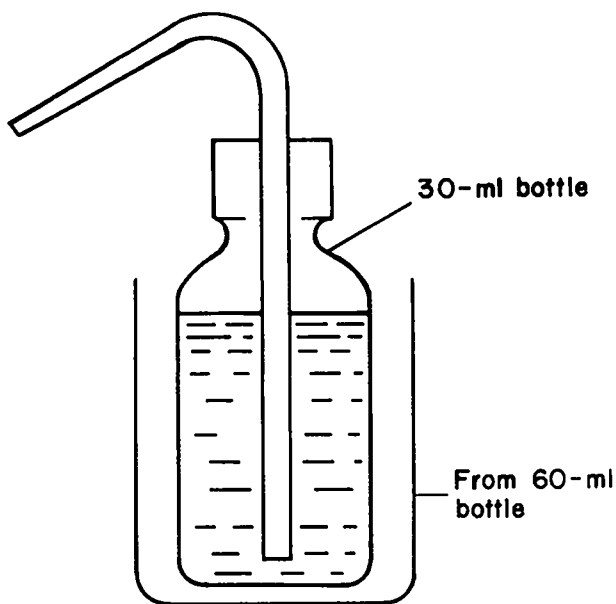


Fig. 4.
Polyethylene wash bottle and holder.

4.2.3. Using forceps, place the wash bottle in the holder and deliver the desired amount of plutonium directly to the bottom of a vial. Release the pressure on the delivery bottle carefully so that no solution is left in the delivery tip.

4.2.4. Using forceps, return the wash bottle to the balance, weigh it, and record the vial number and the delivered solution weight.

4.2.5. Repeat steps 4.2.2 through 4.2.4 until the desired number of vials has been packaged.

4.2.6. Slowly evaporate the solution using a hot plate and heat lamp, until a slurry is obtained. Do not evaporate to dryness; plutonium nitrate salt is hygroscopic and sorbed water may cause hydrolysis and formation of a plutonium species that is difficult to solubilize.

4.2.7. After the slurry cools, stopper each vial and store it upright.

4.2.8. For analysis, wash the entire contents from a vial using 8 M HNO₃.

4.3. Packaging for Short-Term Solution Storage (up to 3 months).

4.3.1. Weigh a clean, dry, 25-ml volumetric flask with its screw cap.

4.3.2. Deliver ≤ 15 ml of the working CTM solution directly to the flask, and cap the flask.

4.3.3. Weigh the flask and contents, and record the flask number and delivered weight.

4.3.4. Transfer the flask to a plastic bag and seal the bag to provide secondary containment of plutonium and keep the flask dust free.

4.3.5. Reweigh the flask and contents just before use, correct the concentration for any evaporative weight loss, and shake the flask vigorously before opening. As these flasks are not designed for pressure containment, do not store these solutions longer than 3 months.

4.4. Packaging for Long-Term Solution Storage (3 months to 2 yr).

4.4.1. Clean, dry, and label enough ampoules for the individual working CTM solutions to be packaged.

Store the ampoules so as to prevent contamination on the exterior or in the neck until they are flame sealed.

4.4.2. Insert the funnel into the ampoule neck, being careful to keep the funnel tip from touching the ampoule neck.

4.4.3. Transfer the desired amount of solution into the ampoule.

4.4.4. If an ampoule cannot be immediately flame sealed, place a rubber stopper in its neck.

4.4.5. Within 1 h of filling, flame seal the ampoule neck ~70 mm above the body, using an oxygen-gas flame. Complete the seal in <1 min to avoid warming the solution, and anneal the seal in an air and gas flame. (Because the ampoule is sealed, the concentration cannot change and ampoule weight data are not required. Test the seal by inverting each ampoule for 24 h on a filter paper and examining for leakage. Discard any leaky ampoules.)

4.4.6. Store each ampoule upright in a sealed plastic bag.

4.4.7. To open an ampoule, place it in a suitable plutonium containment box, shake it vigorously, let the solution drain from the tip, make a deep, 5- to 10-mm-long scratch with a new file surface on the neck ~20 mm below the seal, and touch either end of the scratch with a white-hot glass or quartz rod so that the neck cracks evenly. Tap lightly with the rod to remove the tip cleanly. If the solution has been stored longer than 1 yr, freeze it in a dry ice and ethanol bath before opening the ampoule. Weight aliquots of the solution should be prepared before evaporative concentration changes occur.

4.5. Packaging of Isotopic Working CTM Solution.

Solutions prepared for isotopic analysis only need not be protected from minor evaporative concentration changes. Flasks with an outer-fitting ground glass stopper are recommended, because use of inner stoppers may cause isotopic contamination. Preferably, the solution should be distributed to a series of containers so that accidental contamination will not force rejection of the entire solution. Aliquots should be removed only with new, disposable droppers to prevent cross contamination.

5. CHARACTERIZATION AND OVERCHECK ANALYSIS OF WORKING CTMS

Working CTMs for assay measurements which were prepared using NBS materials or other highly pure plutonium metal shall be verified by overcheck analysis using one analytical method. Those prepared using plant plutonium nitrate shall be characterized by analyses using at least two analytical methods. Working CTM solutions for isotopic abundance measurements shall be verified or characterized by overcheck analysis using thermal ionization mass spectrometry. The verification or characterization samples are drawn randomly from the evaporated slurries or solutions packaged as discussed in Sec. 4.

Major considerations in selection of the analytical methods should be minimal interference from impurity elements and precision as good as or better than the analytical methods being monitored. All methods used for assay overchecks shall be calibrated with NBS CRM 949 (plutonium metal) or 944 (plutonium sulfate). Calibration of the mass spectrometer used for isotopic abundance overchecks is described in Sec. 5.4.

5.1. Determination of Plutonium Content in Filtration Residue.

As stipulated in Sec. 3.2.3, all working CTMs prepared for assay measurements shall be filtered to remove any residue. The residue from filtration of plant nitrates being prepared as CTMs is discarded without analysis. Any residue from other preparations shall be analyzed for its total plutonium content, preferably by a procedure that gives complete dissolution followed by a determination such that the uncertainty of the overall measurement is <20% relative standard deviation. Typical dissolution treatments are fusions with various fluxes and acid reactions including use of the sealed tube technique.⁹ Applicable measurement techniques include alpha counting,¹⁰ isotope dilution mass spectrometry,⁶ and spectrophotometry.¹¹

When the quantity of plutonium measured in the residue is <0.1% of the total computed plutonium in the solution, the residue may be discarded and the final results may be corrected as described in Sec. 6.1.1. If the plutonium measured in the residue is >0.1% of the total computed quantity in the solution, the residue is still discarded but the solution shall be subjected to overcheck analysis per Sec. 5.2. for working assay CTMs prepared from plant plutonium nitrate.

5.2. Characterization of Working Assay CTM Solutions Prepared from Plant Nitrate

As described in Sec. 6.5.1.A, this section also shall apply to materials prepared from NBS CRMs and other plutonium metal if the overcheck analysis disagrees with the makeup value or the residue is $>0.1\%$ of the total plutonium content.

The working CTM solution, if its impurity content is unknown, shall first be characterized for metal impurity content, usually by an emission spectrographic analysis¹ to guide selection of the two analytical methods to be used for overcheck analyses. The methods should give maximum freedom from interference, as well as a knowledge of the quantitative effects of any interfering impurities. Preferably, the two analytical methods should be subject to different impurity effects. As previously stated, both methods shall be calibrated with NBS CRM 949 or 944. The precision of each method, propagated from all systematic and random sources, shall be $\leq 0.10\%$ relative standard deviation for the mean of n replicate analyses.

At least four aliquots of the working CTM material shall be analyzed using each method. If an outlier rejection test is applied and a result is rejected, additional analyses shall be done to provide at least four accepted results for each method.

Statistical treatment of the data for calculation of the plutonium concentration value is presented in Sec. 6.2.

5.3. Overcheck Analysis of Working Assay CTM Solutions Prepared from NBS Materials or Other Plutonium Metals

The impurity element contents of these starting materials usually are low and known. If they are not known, measure the impurities by emission spectrographic analysis¹ so that the total impurity element contents, both those added during preparation and those in the starting materials, can be obtained. The analytical method to be used for the overcheck analysis shall be selected to give maximum freedom from interference, and, in case of interference, a knowledge of the bias so that the results can be corrected. The method shall be calibrated with NBS CRM 949 or 944.

At least three aliquots shall be analyzed so that the relative standard deviation of the mean, propagated from all systematic and random sources, is $\leq 0.10\%$. An outlier rejection test shall not be applied to only

three results. Statistical tests to evaluate agreement of the overcheck analysis results with the calculated makeup value are presented in Sec. 6.1.2.

5.4. Characterization or Verification of Isotopic Abundance Solutions

The same analytical technique, thermal ionization mass spectrometry, shall be used to characterize working isotopic abundance CTM solutions prepared from materials other than NBS plutonium isotopic reference materials and to overcheck solutions prepared from the NBS plutonium isotopic reference material (CRM 946, 947, or 948). The two measurements differ only in the number of aliquots analyzed, at least six being required for the solutions not prepared from the NBS plutonium isotopic reference materials and at least three required for solutions prepared from them. An acceptable alternate method for measurement of the ^{238}Pu isotopic abundance is alpha pulse height spectrometry.¹²

Table II lists the expected standard deviation for a single determination by thermal ionization mass spectrometry for 0.01 to 100% isotopic abundance. If the calculated standard deviation for a single determination of the characterization or overcheck analyses exceeds the tabulated values by a factor of 2 or more, the number of aliquots analyzed shall be increased so that the standard deviation of the mean is < 2 times the standard deviation of the mean that would be obtained for $n = 6$ and $n = 3$, as appropriate, using Table II values.

Electron multiplier detectors shall be calibrated for mass discrimination factors using the NBS U-500 isotopic CRM.¹ When a working CTM solution is analyzed, an NBS plutonium isotopic CRM (946, 947, or 948), closest in isotopic composition to the working CTM solution, also shall be processed at a rate of one

TABLE II
STANDARD DEVIATION^a FOR PLUTONIUM
ISOTOPIC COMPOSITION BY THERMAL IONIZATION
MASS SPECTROMETRY

Isotopic Abundance, (wt%)	Standard Deviation ^b
0.01	0.0005
0.05	0.002
0.1	0.003
0.5	0.01
1.0	0.02
2.0 to 100	0.03

^aRandom error component for an analysis of one filament loading with at least 4.5 complete scans.

^bAbsolute units.

CRM per three samples. Any significant bias corrections shall be applied to the analytical results.

All plutonium samples, aliquots of both the working CTM and the NBS isotopic CRM, shall undergo chemical treatment before mass spectrometric analysis, to remove americium and uranium that interfere at masses 241 and 238. This chemical treatment usually involves ion exchange separation in hydrochloric¹² or nitric acid media.⁶

6. ASSIGNMENT OF REFERENCE VALUES

Statistical tests are provided to compare overcheck results from one analytical method with the makeup values for assay and isotopic working CTMs prepared from NBS CRMs or other plutonium metal, and to compare results obtained by two analytical methods for characterization of working assay CTMs whose starting material makeup value is not available. When overcheck values confirm makeup values, the makeup value is assigned with the standard deviation calculated from the overcheck data. When the results from the two analytical methods agree, the assigned value and standard deviation are statistically computed from the pooled analysis data.

6.1. Comparison of Makeup and Overcheck Values

6.1.1. *Calculation of Makeup Assay Value.* The makeup assay value is calculated using

$$\hat{\mu} = \frac{F(\omega_2 - \omega_1) - y}{(\omega_4 - \omega_3)} \quad (1)$$

where

$\hat{\mu}$ = makeup assay, grams of plutonium per gram of solution.

F = weight fraction of plutonium in starting material.

$\omega_1, \omega_2, \omega_3,$ and ω_4 are appropriate weights defined in Sec. 3.

y = grams of plutonium in filtered residue, described in Sec. 5.1.

Example 1. A working assay CTM solution is synthesized from NBS CRM 945 metal with the following values.

$$F = 0.999.$$

$$\omega_2 = 7.2639 \text{ g.}$$

$$\omega_1 = 2.1321 \text{ g.}$$

$$\omega_3 = 33.5791 \text{ g.}$$

$$\omega_4 = 87.2179 \text{ g.}$$

$$y = 0.0000 \text{ g (no residue present).}$$

The solution has a makeup assay value:

$$\hat{\mu} = 0.09558 \text{ g plutonium/g solution.}$$

6.1.2. *Test of Difference Between Makeup and Overcheck Values of Working Assay and Isotopic CTMs.* This is a test of the hypothesis that there is no difference between the makeup and overcheck values.

$$t = \frac{|\hat{\mu} - \bar{x}|}{\hat{\sigma} / \sqrt{n}} \quad (2)$$

where

t = calculated statistic.

$\hat{\mu}$ = makeup assay value (see Example 1) or appropriate NBS certified isotopic abundance value corrected for ²⁴¹Pu decay to time of analysis.

\bar{x} = the mean of n overcheck analysis results for the assay value or the mean of n overcheck analysis results for the appropriate isotope abundance.

$\hat{\sigma}$ = "best" estimate of the standard deviation of the assay analytical method based on m analyses, or "best" estimate of the standard deviation of the isotope abundance based on m analyses in which the result is the average value for 4.5 scans of a filament loading in the mass spectrometer.

Note that the "best" estimate of σ is that based on past experimental, preferably long-term, experience with the method. It is not the standard deviation of the results associated with \bar{x} .

The computed t value is compared to tabulated values for degrees of freedom = m-1. The hypothesis of no difference is accepted when the computed t value is less than the tabulated value at the 0.05 significance level.

A probable difficulty in the ²³⁸Pu isotopic abundance analysis is high bias caused by natural uranium contamination in the filament material. A laboratory should correct for such bias before the t test computation.

Example 2. For the working assay CTM in Example 1, three overcheck analysis results of an amperometric titration were 0.09549, 0.09556, and 0.09554 g plutonium/g solution. Also, $\hat{\sigma} = 0.06$ relative percent equivalent to an absolute value of 0.000057, based on $m = 10$.

$$t = \frac{|0.09558 - 0.09553|}{0.000057/\sqrt{3}}$$

$$= 1.52$$

The tabulated value of t at the 0.05 significance level for nine degrees of freedom is 2.26; therefore, the overcheck is accepted as confirming the makeup value.

Example 3. If for the working assay CTM in Example 1 the three overcheck analysis results of an amperometric titration were 0.09570, 0.09565, and 0.09562 g plutonium/g solution, with the same values for $\hat{\sigma} = 0.000057$ absolute based on $m = 10$,

$$t = \frac{|0.09558 - 0.09566|}{0.000057/\sqrt{3}}$$

$$= 2.43$$

The tabulated value at the 0.05 significance level for nine degrees of freedom is again 2.26; therefore, the overcheck does not confirm makeup (see Sec. 6.5.1).

Example 4. A working isotopic CTM prepared from NBS CRM 946 had a ^{239}Pu isotopic abundance of 83.360% after correction for ^{241}Pu decay. Three analysis results of thermal ionization mass spectrometry for ^{239}Pu abundance were 83.370, 83.365, and 83.375%. Also, $\hat{\sigma} = 0.010\%$ absolute based on $m = 50$.

$$t = \frac{|83.360 - 83.370|}{0.010/\sqrt{3}}$$

$$= 1.73$$

The tabulated value at the 0.05 significance level for 49 degrees of freedom is 2.01; therefore, the overcheck confirms the NBS value and isotopic contamination is not indicated. For complete

acceptance of the NBS values, the t values computed for ^{240}Pu , ^{241}Pu , and ^{242}Pu should also indicate agreement.

6.2. Comparison of Results from Two Analytical Methods

This test applies to results obtained by using two analytical methods for working assay CTMs prepared from plant plutonium nitrate. It also applies to two sets of overcheck results for different methods for working assay CTMs prepared from NBS CRMs or plutonium metal when the first set of overcheck results did not confirm that makeup value or residue was $>0.1\%$ of total plutonium.

The t test is:

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_p \sqrt{1/n_1 + 1/n_2}} \quad (3)$$

where

t = calculated statistic.*

\bar{x}_1 = the mean of n_1 results from method 1.

\bar{x}_2 = the mean of n_2 results from method 2.

s_p = pooled standard deviation for the two sets of results.

$$s_p = \sqrt{\frac{s_1^2 (n_1 - 1) + s_2^2 (n_2 - 1)}{n_1 + n_2 - 2}}$$

The computed t value is compared to tabulated values for degrees of freedom = $n_1 + n_2 - 2$. The hypothesis of no difference is accepted when the computed t value is less than the tabulated value at the 0.05 significance level.

When the computed t value exceeds the tabulated value, the two overcheck characterizations disagree. Probable causes and possible actions to be taken are discussed in Sec. 6.5.2.

Example 5. The working CTM discussed in Example 3 was characterized by a second method.

*For the test to have maximum effectiveness, n_1 should equal n_2 . If n_1 differs significantly from n_2 , the " t " test becomes less valid.

Plutonium, g/g Solution, by Amperometric Titration	Plutonium, g/g Solution, by Controlled Potential Coulometric Titration
0.09570	0.09580
0.09565	0.09574
0.09562	0.09560
	0.09565

$$\bar{x}_1 = 0.09566 \text{ g plutonium/g solution}$$

$$s_1 = 0.00004$$

$$n_1 = 3$$

$$\bar{x}_2 = 0.09570 \text{ g plutonium/g solution}$$

$$s_2 = 0.00009$$

$$n_2 = 4$$

$$s_p = \sqrt{\frac{(0.00004)^2 \cdot 2 + (0.00009)^2 \cdot 3}{5}}$$

$$s_p = 0.000074$$

$$t = \frac{|0.09566 - 0.09570|}{(0.000074) \sqrt{1/3 + 1/4}}$$

$$= 0.71$$

The tabulated value at the 0.05 significance level for five degrees of freedom ($df = n_1 + n_2 - 2$) is 2.57. These values, therefore, agree and the assigned value is calculated as in Sec. 6.3.2.

6.3. Assigned Value and Standard Deviation for Assay Value

6.3.1. Assignment Based on Overcheck and Makeup Agreement. When the overcheck results confirm the makeup data, the makeup value is assigned with the standard deviation used in the test [Eq. (2)]. The number of determinations (n) used to test agreement is also reported. For the data from Example 2, the assigned value and standard deviation for a single determination are:

$$\hat{\mu} = 0.09558 \text{ g plutonium/g solution.}$$

$$\hat{\sigma} = 0.000057, n = 3.$$

6.3.2. Assignment Based on Analyses Agreement. If the results from the two analytical methods agree, the assigned value is calculated using

$$\bar{x} = \bar{x}_1 w_1 + \bar{x}_2 w_2$$

where

$$w_1 = \frac{n_1/s_1^2}{n_1/s_1^2 + n_2/s_2^2}$$

$$w_2 = \frac{n_2/s_2^2}{n_1/s_1^2 + n_2/s_2^2}$$

for the data from Example 5.

$$w_1 = 0.79 \quad w_2 = 0.21$$

$$\bar{x} = (0.09566)(0.79) + (0.09570)(0.21)$$

$$\bar{x} = 0.09567$$

The weighted standard deviation of the mean is calculated using

$$s_{\bar{x}} = \sqrt{\frac{1}{n_1/s_1^2 + n_2/s_2^2}}$$

$$s_{\bar{x}} = 0.00002$$

The total number of determinations upon which \bar{x} is based also should be listed. Thus, the assigned value and standard deviation are

$$x = 0.09567 \text{ g plutonium/g solution}$$

$$s_{\bar{x}} = 0.00002, n = 7.$$

6.4. Assigned Value and Standard Deviation for Isotopic Value

6.4.1. Uncontaminated Working CTMs Prepared from NBS CRM 946, 947, or 948. The assigned value for each isotope is the corrected NBS value. The standard deviation for each isotope is $\hat{\sigma}$, and the number of determinations of \bar{x} also is listed.

For the ^{239}Pu abundance data from Example 4,

$$^{239}\text{Pu} = 83.360\%$$

$$\hat{\sigma} = 0.010, n = 3.$$

6.4.2. Isotopic Values Based on Six or More Analyses. The assigned value is the average of the data for each isotopic abundance, and the standard deviation is s (the calculated standard deviation of a single determination for the six values) or $\hat{\sigma}$ (the best estimate of the standard deviation of a single measurement of the isotope abundance in which an analysis result is the average value for at least 4.5 scans of a

filament loading in the mass spectrometer). Both standard deviations are calculated, and the larger value is assigned. The number of determinations upon which \bar{x} is based also is listed.

Example 6. For six isotopic abundance measurements of ^{240}Pu in a working CTM, the mean value is 12.975% with $s = 0.017$ and $\sigma = 0.010$.

The assigned value and standard deviation are:

$$\begin{aligned} {}^{240}\text{Pu} &= 12.975\% \\ s &= 0.017, n = 6. \end{aligned}$$

6.5. Statistical Tests Indicate Disagreement

6.5.1. Makeup and Overcheck Values

A. Disagreement of Assay Values. When the makeup and overcheck assay values disagree (Sec. 6.1.2), the working CTM is assayed using a second analytical method subject to different interferences (Sec. 5.2), or it is discarded and a new reference material is prepared. Data from a second analytical method are tested against makeup value using Eq. (2), and if agreement is indicated, the first overcheck data are discarded and the makeup and second analytical method data are used to assign a reference value and standard deviation per Sec. 6.3.1. If the second analytical method results disagree with makeup, they are tested against the first analytical method results using Eq. (3). If the two methods agree, the assigned value and standard deviation limits are computed as in Sec. 6.3.2. Disagreement of the makeup and two analytical method results is discussed in Sec. 6.5.2.

B. Disagreement of Isotopic Values. When the NBS values and the analytical isotopic abundances disagree (Sec. 6.1.2), isotopic contamination of the plutonium is indicated. In this case, the working CTM is reanalyzed to meet the criteria of six or more analyses established in Sec. 5.4.

6.5.2. Disagreement of Makeup and Assay by Two Analytical Methods. When the two analytical results for a working CTM prepared from plant nitrate or the two results and the makeup value for other working CTMs disagree (Sec. 6.5.1), the discrepancy is caused by an error in one or both analytical methods or

the makeup value. Possible sources of error include improper calibration of one or both methods, uncorrected interference effects for one or both methods, loss of material in analysis or synthesis, or miscalculation of data. A recheck of the data may disclose the cause; if it is correctable, the corrections should be applied and the results should be retested statistically. If the cause is unresolved but one method is more suspect than the other, a third method may be used, its results should replace that of the suspect method, and the statistical test should be reapplied. If neither method is suspect, all data are to be discarded. In this case, one can recharacterize using the same methods again or using other methods. Ultimately, if the problem remains unresolved, the prepared working CTM shall be discarded.

6.6 Correction for ^{241}Pu Decay

Plutonium nitrate CTM assigned reference values should be corrected for ^{241}Pu decay on a regular basis. A CTM with a 1% isotopic abundance of ^{241}Pu decreases in total plutonium content at a rate of ~ 40 ppm per month. The corrections should be made at such intervals that the assigned assay value changes by $< 0.05\%$. The recommended half-life for ^{241}Pu is 14.7 y.

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