NUREG-0118
LA-NUREG-6348

PREPARATION OF WORKING CALIBRATION AND TEST MATERIALS: PLUTONIUM NITRATE SOLUTION

Los Alamos Scientific Laboratory
of the University of California
for
U. S. Nuclear Regulatory Commission

Available from
National Technical Information Service
Springfield, Virginia 22161
Price: Printed Copy $4.00 ; Microfiche $3.00

NUREG-0118
LA-NUREG-6348
NRC-13

PREPARATION OF WORKING CALIBRATION AND TEST MATERIALS: PLUTONIUM NITRATE SOLUTION

J. E. Rein
S. F. Marsh
G. C. Swanson*
G. R. Waterbury
G. L. Tietjen
R. K. Zeigler

*Hanford Engineering Development Laboratory, Westinghouse Hanford Company

Manuscript Completed: May 1976
Date Published: January 1977

Los Alamos Scientific Laboratory
of the University of California
Los Alamos, New Mexico 87545

Prepared for the U. S. Nuclear Regulatory Commission
Under U. S. Energy Research and Development Administration
Contract W-7405-Eng. 36

FOREWORD

This report provides guidance for preparing plutonium nitrate working calibration and test materials. These materials are used to calibrate and to maintain quality control surveillance of chemical methods of analysis for plutonium assay and isotopic distribution measurements. Similar reports will be issued for other plutonium and uranium materials.

CONTENTS

PREPARATION OF WORKING CALIBRATION AND TEST MATERIALS: PLUTONIUM NITRATE SOLUTION

by

J. E. Rein, S. F. Marsh, G. C. Swanson,
G. R. Waterbury, G. L. Tietjen, and R. K. Zeigler

ABSTRACT

Procedures are presented for preparing plutonium nitrate solutions with assigned values of plutonium concentration and isotopic distribution. These solutions are used to calibrate and maintain quality control surveillance of chemical methods for the analysis of nuclear fuel cycle plutonium nitrate. Detailed statistical treatments are included that establish the reliability of the prepared materials when applied to nuclear material accountability and safeguards.

1. INTRODUCTION

Plutonium nitrate, usually as a solution, is a major material in the nuclear fuel cycle. It is an in-process intermediate in nearly all phases of the plutonium nuclear industry. Accurate and precise measurements of the concentration and isotopic abundance of plutonium in plutonium nitrate are highly important for accountability and safeguards. Therefore, well-characterized materials must be used for the calibration and quality control surveillance of the analysis methods. This report is the first in a series* prepared at the request of the Office of Standards Development of the Nuclear Regulatory Commission and describes the preparation of materials defined as working calibration and test materials (WCTMs) used in the analysis of plutonium nitrate. Discussed are the chemical preparative procedures designed to produce stable plutonium nitrate WCTMs, the establishment of their plutonium and isotopic distribution values, and their packaging.

2. GENERAL CONSIDERATIONS GOVERNING THE PREPARATION OF A SOLUTION WCTM

A WCTM must be prepared so that the values of uranium or plutonium concentration and isotopic distribution assigned to it are related to a primary reference calibration and test material (PRCTM) or to a secondary reference calibration and test material (SRCTM) which is related to a PRCTM. Table I lists the calibration and test materials (CTMs) that, in

---

**The Idaho Chemical Programs Office of the Allied Chemical Corporation and the Los Alamos Scientific Laboratory are preparing reports for uranium-containing and plutonium-containing WCTMs.*

TABLE I

DEFINITIONS OF CALIBRATION AND TEST MATERIALS (CTMs)

Designation	Abbreviation	Definition	Examples
Reference calibration and test material	RCTM	General term for any CTM recognized as a reference material.	
Primary reference calibration and test material	PRCTM	Extremely well-characterized material, certified and distributed by appropriate national or international standards agency.	National Bureau of Standards standard reference materials (NBS SRMs). International Atomic Energy Agency standard (S) materials.
Secondary reference calibration and test material	SRCTM	Typical, less-pure material, well-characterized against a PRCTM, usually by several laboratories.	Proposed New Brunswick Laboratory SRCTMs. International Atomic Energy Agency reference (R) materials.
Working calibration and test material	WCTM	Representative material, well-characterized against an RCTM, used for internal methods calibration or interlaboratory comparison.	International Atomic Energy Agency Intercomparison (I) materials. Safeguards Analytical Laboratory Evaluation (SALE) Program exchange samples.

descending order of credibility, are PRCTMs, SRCTMs, and WCTMs. Other important characteristics of a WCTM are stability, chemical similarity to a process material, and a reliability of the assigned plutonium value consistent with the reliability required of the analysis method. To some degree, these characteristics are interrelated. The chemical composition of a process material may have a short-lived stability and so the reliability will be poor. Because stability and reliability are paramount characteristics of a WCTM, chemical composition similarity may have to be compromised.

An ideal starting material for most solution WCTMs is a PRCTM or SRCTM of high-purity uranium or plutonium metal or compound, with its certified values of uranium or plutonium content and/or isotopic distribution. With such a material, the WCTM is prepared by (a) transferring a weighed portion of the metal or compound to a previously weighed flask, (b) dissolving the metal or compound with an appropriate acid, (c) adding a solution of impurity elements to produce a composition that simulates a nuclear fuel cycle material, (d) adding more acid as necessary to attain a stable uranium or plutonium concentration that also simulates, if feasible, the nuclear fuel cycle material, (e) mixing the solution until it is homogeneous, (f) weighing the solution, and (g) computing the uranium or plutonium concentration using the certified uranium or plutonium values of the starting material, the weight of the starting material, and the weight of the final solution. This computed value is termed the "makeup value." (This term also applies to the computed value when the starting material is other than a PRCTM or SRCTM.)

An erroneous makeup value can be caused by failure to record a proper weight. The makeup value therefore must be verified by analyzing the WCTM for its uranium or plutonium concentration, its isotopic distribution, or both. Another cause for error in the concentration makeup value is incomplete solubility of the uranium or plutonium. During preparation, but before final weighing, the solution must be filtered, the filter and any residue analyzed for uranium or plutonium, and corrective computations applied.

A WCTM may be prepared by using a starting material other than a PRCTM or SRCTM. Two modes of chemical analysis then apply to establish the uranium or plutonium concentration value of the WCTM. First, determine the uranium or plutonium content of the starting material by using two different analytical methods and then verify the makeup value by an analysis of the WCTM by using one method. Second, forego any analysis of the starting material and then determine the uranium or plutonium concentration of the prepared WCTM by using two different methods of analysis.

To determine uranium or plutonium isotopic distribution, the technique of thermal ionization mass spectrometry is used throughout the world. The only significant exception is the use of gas mass spectrometers to analyze the uranium after its conversion to uranium hexafluoride, a capability that exists in uranium gaseous diffusion facilities and in a restricted number of other facilities. When the starting material used to prepare an isotopic distribution WCTM is not a PRCTM or SRCTM, an independent analysis by a second laboratory is recommended.

As previously stated, WCTMs must be prepared so that the values assigned to their uranium or plutonium concentrations and isotopic distributions are related directly to PRCTMs or SRCTMs. This condition is achieved by using PRCTMs (or SRCTMs) to calibrate every method used to analyze starting materials and WCTMs. These calibrations must be done when a starting material or WCTM is analyzed, and the number of replicate measurements of the PRCTM (or SRCTM) and of the starting material or WCTM shall be equal. The PRCTM (or SRCTM) normally is used as a solution, prepared on a weight basis using weights traceable to National Bureau of Standards (NBS) mass references. The chemical composition of the PRCTM (or SRCTM) solution shall simulate that of the starting material or WCTM with respect to uranium or plutonium concentration, uranium or plutonium isotopic distribution, and impurity element concentrations. Rather than prepare the PRCTM (or SRCTM) solution with the impurity elements, thereby endangering its stability, the impurities may be added to the individually delivered aliquots of the solution at the time of the analysis.

Important considerations governing the selection of methods used to determine uranium or plutonium concentrations are high precision capability and freedom from impurity effects. The former is important because the required number of replicate measurements lessens as the method precision improves. Freedom from impurity effects is necessary to minimize inaccuracy. When two methods are used for the characterization, they should have impurity effects as different as possible to minimize any inaccuracy that may be caused by less-than-detected impurities and by the fact that the impurity element composition of the PRCTM (or SRCTM) solution does not match exactly that of a starting material or WCTM.

A major operation in preparing a WCTM is the statistical treatment of the results of the analyses used for its characterization. The statistical treatments vary as a function of the credibility level of the starting material and the modes of chemical analysis used to establish the uranium or plutonium concentrations and isotopic distributions. Section 5.4 discusses the statistical treatments as they apply to the plutonium nitrate WCTM, and subsequent sections present calculations for a series of typical examples.

3. PLUTONIUM NITRATE WCTM PREPARATION

This section describes chemical preparative procedures for plutonium nitrate solution WCTMs (hereafter referred to as WCTM) using starting materials of plutonium sulfate, plutonium metal, or a plant's plutonium nitrate solution.

3.1. Starting Materials

A PRCTM used as the starting material provides highest credibility to a WCTM. The National Bureau of Standards provides six plutonium standard reference materials (SRMs)[1] shown in Table II. The first three SRMs listed are certified for plutonium content, with SRM 945 having least credibility because its intended major purpose is to serve as a matrix material for preparing impurity reference materials. The last three SRMs listed are certified only for isotopic distribution. There is no plutonium SRM certified for both total plutonium content and isotopic distribution.

The quantity of plutonium used to prepare a plutonium concentration WCTM normally is in the 10- to 100-g range. Thus, use of SRM 944 and 949 (and 945 as well) is not economically feasible, but they serve the vital role of providing the basis of calibrations for the analytical methods used to determine the plutonium contents of the starting materials and the prepared WCTMs. With no supply of economic PRCTMs or SRCTMs certified for plutonium content, the commonly used starting material is a plant plutonium nitrate. Special treatments, presented in Sec. 3.2.3., are required to ensure its stability. The plutonium concentration value of a WCTM prepared from a plant plutonium nitrate must be established by analyses

TABLE II

NBS PLUTONIUM STANDARD REFERENCE MATERIALS

NBS SRM	Type	Amount (g)[a]	Certified For	Nominal Value	Comments	Cost ($)[b]
944	Plutonium sulfate tetrahydrate	0.5	Pu content	47.50% Pu	6% ^{240}Pu	168
945	Plutonium metal	5.	Impurities, Pu content	99.95% Pu	6% ^{240}Pu	102
949	Plutonium metal	0.5	Pu content	99.99% Pu	3% ^{240}Pu	316
946	Plutonium sulfate tetrahydrate	0.25	Isotopic abundance	12% ^{240}Pu	4% ^{241}Pu	632
947	Plutonium sulfate tetrahydrate	0.25	Isotopic abundance	18% ^{240}Pu	4.5% ^{241}Pu	632
948	Plutonium sulfate tetrahydrate	0.25	Isotopic abundance	8% ^{240}Pu	0.5% ^{241}Pu	300

---

[a] Element weight.

[b] Dollars per gram of plutonium. NBS Special Publication 260. Supplement 1975 Price List. US Department of Commerce. National Bureau of Standards. Washington. DC 20234.

using two different methods. Another starting material is plutonium metal of relatively high purity; however, there is no commercial supply.* The major disadvantage of using plutonium metal is that it is not soluble in nitric acid to produce the WCTM directly. It therefore is dissolved in other acids, then chemical treatments are made to produce stable plutonium nitrate.

The range of the isotopic distribution values of the three SRMs (946, 947, and 948) cover most plutonium nitrate materials encountered in the nuclear fuel cycle. Their high cost is not a deterrent to their use as isotopic distribution WCTMs because the thermal ionization spectrometric measurement technique requires only about 1 μg of plutonium per determination. Most laboratories find it practical to use separate WCTMs for plutonium concentration and plutonium isotopic distribution measurements, with one or more of SRM 946, 947, and 948 serving the latter purpose. The authors subscribe to this practice.

3.2. Chemical Procedures

As stated in the previous section, the NBS SRMs 946, 947, and 948, certified for isotopic abundance, are the usual starting materials for isotopic distribution WCTMs. They are soluble in nitric acid to produce a plutonium nitrate WCTM directly. The only additional treatment is to add impurities to attain similarity to the plant material. As stated in the preparation procedure (Sec. 3.2.1.c, step 6), filtration (Sec. 3.5) may be omitted during the preparation of the isotopic distribution WCTMs because the NBS SRMs are homogeneous and incomplete solubilization does not affect the isotopic distribution of the soluble fraction. Section 3.2.1 also covers the preparation of plutonium concentration WTCMs using plutonium sulfate as the starting material. For this case, the probable starting material would be NBS SRM 944.

Two procedures are presented for preparing a plutonium concentration WCTM using plutonium metal as the starting material. These procedures involve dissolutions with hydrobromic acid (Sec. 3.2.2.1) and hydrochloric acid (Sec. 3.2.2.2) followed by chemical treatments to effect conversion to plutonium nitrate. The procedure using plant plutonium nitrate is given in Sec. 3.2.3.

Following the dissolution of starting materials and any special treatments to effect conversion to plutonium nitrate, impurities are added (Sec. 3.3), the solution is aged to ensure stability (Sec. 3.4), the solution is filtered (Sec. 3.5), and is diluted to its final state (Sec. 3.6).

General aspects involved in preparing plutonium concentration WTCMs for all the above starting materials are summarized in Table III and Fig. 1. Included is a summary of the various options that apply to establishing the plutonium concentration value of the WCTM based on the general discussion given in Sec. 2.

The subsequent methods are written in a format intended for use by experienced analysts. Apparatus normally found in a well-equipped laboratory is not listed. All reagents for each method are listed, but preparatory instructions are given only for those reagents that require uncommon treatment or where ambiguity may exist. All chemicals shall be at least ACS reagent grade. Water shall be distilled or deionized. Reagents shall be stored in containers that do not affect their quality, including leached impurities and concentration changes caused by transpiration or evaporation. Glassware shall be cleaned by immersion in hot nitric acid for > 4 h, rinsed thoroughly in distilled or deionized water, and dried.

**Possible suppliers include Atlantic Richfield Hanford Company, Richland, WA; Los Alamos Scientific Laboratory, Los Alamos, NM; Mound Laboratories of Monsanto Research Corporation, Miamisburg, OH; Rocky Flats Laboratory, Golden, CO; and Savannah River Plant of E. I. DuPont de Nemours and Company, Aiken, SC.*

TABLE III

PREPARATION OF PLUTONIUM NITRATE WCTMs CHARACTERIZED FOR PLUTONIUM CONCENTRATION

Starting Material	Characterization of Starting Material	Preparation of WCTM	Establishment of Pu Concentration
PRCTM of NBS SRM 944, Pu $(SO_4)_2 \cdot 4H_2O$, plus added impurities[a]	None	Dissolve in HNO_3 (Sec. 3.2.1)	Two assay methods or one assay method and calculated (makeup) value based on starting material and solution weights
PRCTM of NBS SRM (949 or 945) Pu metal plus added impurities[a]	None	HBr method (Sec. 3.2.2.1) or HCl method (Sec. 3.2.2.2)	As above
Pu metal other than NBS SRM, ≥99.95% pure, plus added impurities	Two assay methods or one assay method and calculated purity based on complete impurity analysis	As above	Two assay methods or, if starting material characterized, one assay method and calculated (makeup) value based on starting material and solution weights
Pu metal other than NBS SRM, <99.95% pure, plus added impurities	Two assay methods	As above	As above
Plant plutonium nitrate	Not applicable	Treatment to destroy Pu polymers and to attain oxidation state stability (Sec. 3.2.3)	Two assay methods

---

[a] Seldom used because of high cost.

Unless stated to higher tolerances, all values for measurements (such as volume, weight, and time) are given as integers with an implied uncertainty of 5 rel%. The means of delivery or measurement shall be at the discretion of the analyst. When higher tolerances are called for, the actual limits are given such as 10 ± 0.1 ml, or decimal values are listed. For decimal values, the implied uncertainty is 5 in the subsequent digit. Thus a volume of 10.0 ml is equivalent to 10 ± 0.05 ml. Again, the means of delivery or measurement is at the discretion of the analyst. All volumetric glassware shall be calibrated according to NBS Circular 602

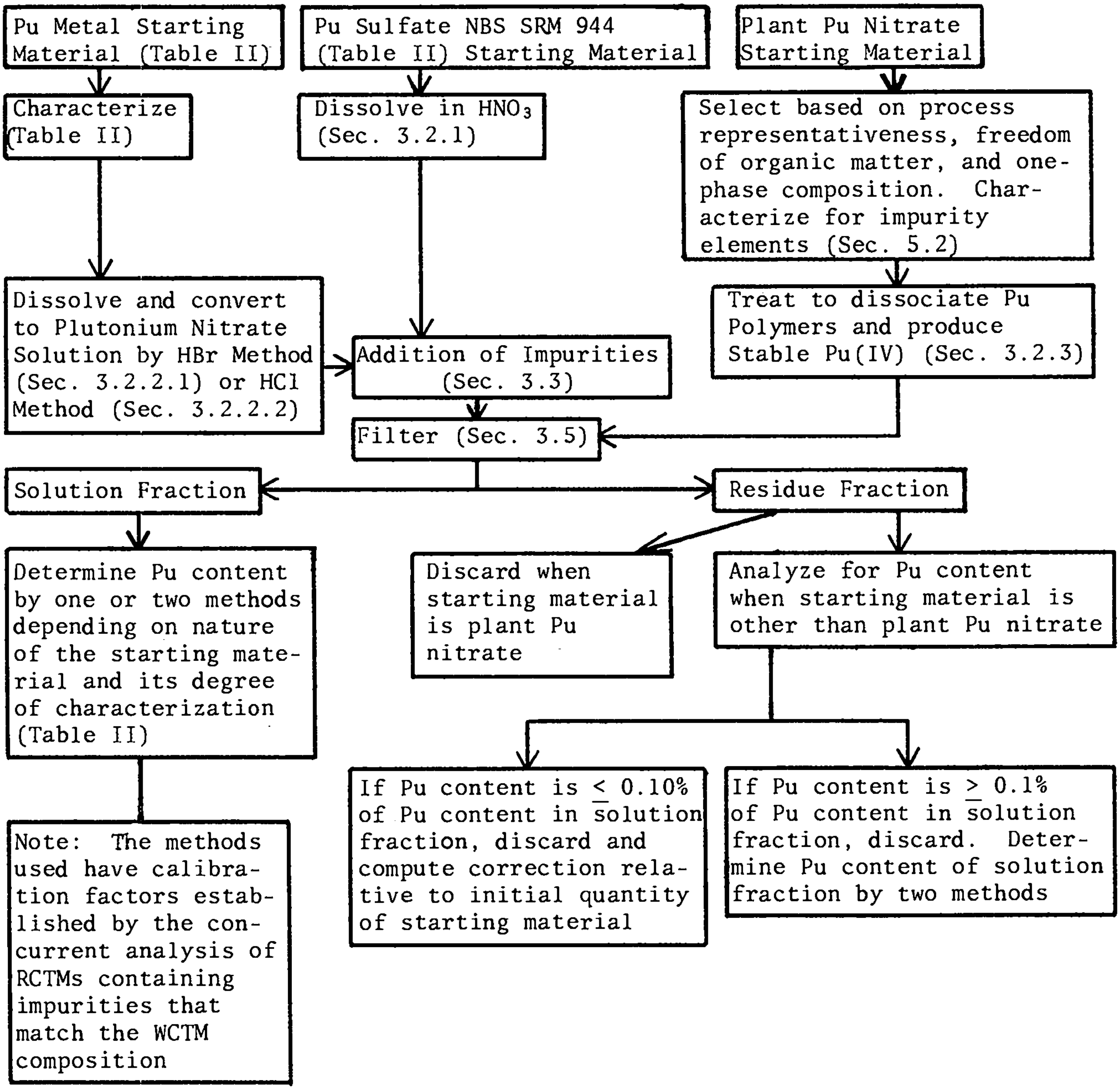

Fig. 1.
General operations involved in preparing a plutonium nitrate concentration WCTM.

and all weights shall be traceable to NBS certified weights as described in NBS Circular 547, Sec. 1.

Health safety rules for handling plutonium metal and solutions must be rigidly followed and adequate protection for the operator must be ensured by use of suitable gloveboxes and protective clothing.

3.2.1. Plutonium Sulfate as Starting Material

This procedure is intended mainly to prepare plutonium concentration or isotopic distribution RCTMs or WCTMs from the appropriate NBS SRMs. Because of the high cost, only small quantities would probably ever be prepared. The quantity of compound as $Pu(SO_4)_2 \cdot 4H_2O$ supplied (Table II) is 0.5 g of the assay SRM 944, and 0.5 g of the three isotopic SRMs (946, 947, and 948). This corresponds to 0.24 and 0.25 g of plutonium, respectively. The recommended maximum concentration of $Pu(SO_4)_2$ in 8M HNO_3 is about 0.05M.[2] The usual working concentration of an isotopic abundance CTM is on the order of 0.004M (1 μg Pu/μl). Packaging can be any of the recommended modes given in Sec. 4.

a. **Reagent**

HNO_3, 8M.

b. **Apparatus**

1. Beaker, tall-form, 250-ml, with unribbed watch glass as cover.
2. Hot plate.

c. **Procedure**

1. Weigh the desired quantity of plutonium sulfate to ±0.0001 g in an appropriate container (W_2). For WCTMs being prepared for isotopic distribution only, the weighing precision in this step and step No. 3 can be about 5 rel%.
2. Transfer the weighed material to a 250-ml tall-form beaker.
3. After transferring the material, weigh the empty container (W_1) to ±0.0001 g. Record the temperature to permit buoyancy correction.
4. Add a quantity of 8M HNO_3 to give the concentration of plutonium desired for the CTM and cover the beaker with a watch glass.
5. Place the beaker on a hot plate set to warm the solution to about 50°C and allow the dissolution to proceed to completion.
6. After dissolution apparently is complete, let the solution stand overnight, then look for trace undissolved material. If any is present, further reaction time including moderate heating may produce further dissolution. If the residue persists and is estimated to be more than 0.5% of the original material, it is suggested that the solution not be used as an RCTM or WCTM if the intended application is assay purposes. (All solutions are filtered before packaging, see Sec. 3.5, and small quantities of residue are tolerable.) As far as is known, the three NBS isotopic SRMs are not heterogeneous relative to isotopic abundance distribution; therefore, incomplete dissolution will not adversely affect the integrity of isotopic abundance CTMs prepared from these materials.
7. Proceed to Sec. 3.3.

3.2.2. Plutonium Metal as Starting Material

Two chemical procedures, one involving dissolution of plutonium metal with hydrobromic acid and the other with hydrochloric acid, are presented. The first procedure produces a stable Pu(IV) nitrate solution suitable for any of the packaging modes given in Sec. 4. The second produces a solution containing plutonium partially in the +6 oxidation state suitable only for packaging as a slurry (Sec. 4.2). The WCTMs produced by the hydrobromic acid procedure are on a weight (g Pu/g solution) basis, which is recommended as most accurate. These WCTMs also can be prepared on a volume (g Pu/ml) basis provided that any subsequent aliquots of the solution are taken after adjusting the temperature of the solution to equal that when the WCTM was prepared. The WCTMs packaged as an evaporated slurry are on the basis of total quantity of plutonium per vial.

NBS SRM plutonium metals are used as received with the weight of the SRM 949 samples provided on each container. The oxide coating on other plutonium metals is removed before weighing.

3.2.2.1. Hydrobromic Acid Procedure[3]

Following the directions will give a solution of 10 g of plutonium in ∿141 ml of 8M HNO_3. This acidity level is considered essential to stability. Dilution with 8M HNO_3 may be used to produce a lower plutonium concentration.

a. Reagents

1. HBr, 3M.
2. 0.05M HF-9M HBr mixture. Add 0.17 ml of 29M HF to 99.8 ml of 9M HBr.
3. HNO_3, 15.7M, 12M, and 3M.
4. NaOH, 6M.

b. Apparatus

1. Bromine fume scrubber and steam jacket. This consists of a 250-ml gas-washing bottle (half filled with 6M NaOH) connected to a fume collector made by attaching a side arm to the cut-off top of a plastic dropping bottle (Fig. 2). The steam jacket is a covered beaker about one-quarter filled with water. The cover is a sheet of polyethylene topped by a section of round polyethylene or fiberboard carton trimmed to fit the volumetric flask neck closely to ensure that steam heats the entire flask length.
2. Flask, volumetric, 200-ml.
3. Funnel, glass or plastic, 55-mm diam, short 25-mm stem, with an unribbed watch glass as a cover.
4. Hot plate.
5. Separatory funnel, 125-ml, with Teflon stopcock adjusted to be leakproof.

c. Procedure

1. Clean the plutonium metal, just before weighing, by filing it with a new metal file to expose a bright, shiny surface.
2. Weigh 10 g of the metal to ±0.0001 g in an appropriate container (W_2).
3. Add 5 ml each of 0.05M HF-9M HBr mixture and water to 125-ml separatory funnel.
4. Transfer the weighed metal to the separatory funnel, then immediately place a 55-mm-diam funnel in the separatory funnel and place a watch glass on top of the glass funnel. This will prevent any loss of solution by fine spray.
5. After transferring the metal, weigh the empty container (W_1) to ±0.0001 g. Record the temperature to permit buoyancy correction.
6. Add 20 ml of 0.05M HF-9M HBr mixture through the glass funnel maintaining a moderate rate of dissolution. Keep the watch glass on the funnel when not adding acid. This volume of acid mixture, for 10 g of plutonium, prevents hydrolysis of plutonium and provides a final solution volume within the capacity of a 200-ml volumetric flask.
7. After the dissolution reaction is apparently complete, let the solution stand overnight, then look for trace undissolved material. If any is present, further reaction time may effect more complete dissolution. (Known causes of residue are inadequate removal of plutonium oxide when cleaning the metal and insoluble impurities in the metal, such as silicon.) If the residue persists and is estimated to be more than 0.5% of the original metal, it is suggested that the solution not be used as an RCTM or WCTM. (All solutions are filtered before packaging, see Sec. 3.5, and small quantities of residue are tolerable.)

8. Quantitatively rinse the glass funnel and watch glass with 5 ml of 3**M** HBr directed from a plastic squeeze bottle, collecting the rinse in the separatory funnel.

9. Transfer 60 ml of 12**M** HNO_3 to a 200-ml volumetric flask.

10. Assemble the apparatus shown in Fig. 2 using the separatory funnel containing the dissolved plutonium solution and the volumetric flask.

11. Heat the water in the steam jacket just to boiling.

12. Transfer the dissolved plutonium solution from the separatory funnel to the volumetric flask at a rate of 1 drop/10 s. (HNO_3 oxidizes Br^- to Br_2 and Pu^{3+} to Pu^{4+} and the Br_2 volatilizes at steam heat.) A faster rate of transfer than 1 drop/10 s may cause too vigorous a reaction and spray loss of solution.

13. Quantitatively rinse the separatory funnel sequentially with three ~ 1-ml volumes of 3**M** HBr and five ~1-ml volumes of 12**M** HNO_3 using plastic squeeze bottles.

14. Continue the steam heat for 48 h or longer to volatilize the Br_2 completely.

15. Add a calculated volume of 15.7**M** HNO_3 to adjust the HNO_3 concentration to 8**M**. Assume equimolar consumption of HNO_3 by HBr. When this procedure has been followed the calculated volume of 15.7M HNO_3 is 38 ml.

16. Proceed to Sec. 3.3.

3.2.2.2. Hydrochloric Acid Procedure

This procedure produces a concentrated plutonium nitrate solution with an approximate concentration of 1 g Pu/g solution. The plutonium oxidation state is mixed +4 and +6. The nitric acid concentration is 8**M**.

a. **Reagents**

1. HCl, 12**M**, and 6**M**.
2. HNO_3, 15.7**M**, 8**M**, and 4**M**.

b. **Apparatus**

1. Beaker, tall-form, 250-ml, with ribbed and unribbed watch glasses as covers.
2. Ice bath, convenient size for above beaker.
3. Steam bath, convenient size for above beaker.

c. **Procedure**

1. Clean the plutonium metal, just before weighing, by filing it with a new metal file to expose a bright, shiny surface.

2. Weigh 10 g of the metal to ±0.0001 g in an appropriate container (W_2).

3. Place a tall-form beaker in an ice bath and transfer the weighed metal to the beaker.

4. Weigh the empty container (W_1) to ±0.0001 g. Record the temperature to permit buoyancy correction.

5. Cool 10 ml of 6**M** HCl in the ice bath for 10 min, transfer it to the beaker, and immediately cover the beaker with an unribbed watch glass.

6. As the dissolution reaction subsides, add 40 ml of 6**M** HCl maintaining a moderate rate of dissolution. Keep the watch glass on the beaker when not adding acid. To maintain a moderate dissolution rate, the beaker may have to be removed from the ice bath.

7. After the dissolution reaction is apparently complete, let the solution stand overnight, then look for trace undissolved material. If any is present, further reaction time including moderate heating may dissolve the residue. (Known causes of residue are inadequate removal of plutonium oxide when cleaning the metal and insoluble impurities in the metal, such as silicon.) If the residue persists and is estimated to be more than 0.5% of the original metal, it is suggested that the solution not be used as an RCTM or WCTM. (All solutions are filtered before packaging, see Sec. 3.5, and small quantities of residue are tolerable.)

8. Rinse the watch glass and beaker walls with 10 ml of 6M HCl directed from a plastic squeeze bottle.

9. Add 1 ml of 15.7M HNO_3, immediately cover the beaker, and after the initial reaction subsides, heat on a steam bath for 30 min. The oxidation of Pu^{3+} to Pu^{4+} is initiated.

10. Place a ribbed watch glass on the beaker and evaporate to a volume of 10 ml.

11. After the solution cools, add 30 ml of 4M HNO_3, then evaporate to a moist residue. Do not remove the moist residue from the heat source because water could condense on the deliquescent plutonium nitrate causing hydrolysis and formation of acid-insoluble hydrous oxide.

12. Add 20 ml of 15.7M HNO_3 and evaporate to a moist residue with the ribbed watch glass covering the beaker.

13. Repeat step No. 12.

14. Add 10 ml of 8M HNO_3 and heat to dissolve the plutonium nitrate.

15. Proceed to Sec. 3.3.

3.2.3. Plant Plutonium Nitrate as Starting Material

A plant plutonium nitrate selected as the starting material for a WCTM shall have measured and representative impurity levels and isotopic abundance values. Measurement techniques for impurities are discussed in Sec. 5.2. Also, the selected material must be single phase and have no heterogeneously distributed organic matter.[4] This procedure provides treatments designed to destroy plutonium polymers. In this procedure and subsequent treatments to produce the WCTM, dilution relative to the plutonium concentration of the plant material occurs. The plant material, therefore, should be selected or should be concentrated by low-temperature evaporation to contain 1.5 times the plutonium concentration of the usual level of the plant stream. An ample supply of the WCTM should be prepared because plutonium concentration is costly to establish, and requires using two different analytical methods. Packaging can be any of the modes given in Sec. 4.

a. Reagents

1. HF, 29M.
2. HNO_3, 15.7M, and 2M.

b. Apparatus

1. Beakers. Appropriate size for the volume of WCTM to be prepared, with unribbed watch glasses as covers.
2. Hot plate.

c. Procedure

1. Transfer a desired volume of the selected plant plutonium nitrate solution to a beaker having a capacity at least four times the volume attained in step 2 below.

2. Adjust the HNO_3 concentration to 8M by adding an amount of 15.7M HNO_3 or 2M HNO_3 calculated based on the HNO_3 concentration of the plant plutonium nitrate solution. Do not use water as a diluent because localized concentrations of low acidity in solution may cause hydrolysis of the plutonium and formation of an insoluble hydrous oxide.[5]

3. Add a calculated volume of 29M HF to produce a solution that is 0.05M in HF.

4. Heat the solution at 80 to 90°C for at least 2 h at a moderate rate so that no solution is sprayed to the beaker walls.

5. Proceed to Sec. 3.4.

3.3. Impurities Addition

The solutions prepared from plutonium metal or plutonium sulfate probably will require added impurities, typically metal ions, to simulate the applicable plant stream. Because the specific impurities and their concentrations vary, only general directions for this operation are given.

Prepare a solution in 8M HNO_3 that contains all the desired impurities at sufficiently high concentrations so that a small (1- or 2-ml) volume of this solution will contain the appropriate amount of each impurity when added to the plutonium nitrate solution obtained by the procedures in Sec. 3.2.1, 3.2.2.1, or 3.2.2.2. The solution of impurities should be prepared using analytical reagent grade (or purer) metals or nitrate salts. After adding the calculated volume of the impurities solution, mix the plutonium nitrate solution thoroughly.

3.4. Aging to Attain Stability

All plutonium nitrate WCTMs prepared for plutonium concentration measurements, except those prepared by dissolving plutonium metal in hydrochloric acid (Sec. 3.2.2.2), are aged to provide time for radiolytically generated H_2O_2 to reduce any produced Pu^{6+} to Pu^{4+}. Two weeks ensures that >99% of the plutonium is Pu (IV).[3] Because the reduction of Pu^{6+} by H_2O_2 produces gas, the solution is open to the atmosphere during the aging period. The volumetric flask or beaker is loosely covered, however, to decrease evaporation. The aging period also provides a reasonable time for precipitate formation, an undesirable effect often occurring in plutonium nitrate solutions.

3.5. Filtration

Every plutonium nitrate WCTM intended for use in plutonium concentration measurements is filtered, even when no precipitate is apparent. The recommended filter is a plastic membrane-type, resistant to 8M HNO_3, with a 0.45-μm pore size. The receiver of the filtered solution is a tared volumetric flask. The filter (with residue) is analyzed for its plutonium content, most conveniently (Sec. 5.1) by gamma counting, and the assay value of the WCTM either is corrected for the measured residual plutonium, or the WCTM is characterized for its plutonium concentration using two different assay methods.

a. **Reagent**

HNO_3, 8M.

b. **Apparatus**

1. Filter adaptor, custom-made, that provides for direct filtration into a volumetric flask (Fig. 3).
2. Filter support plus chimney, Millipore No. XX10-025-00, or equivalent.
3. Filters, plastic membrane, 0.45-μm pore size, Gelman Vinyl Metricel, or equivalent.
4. Flask, volumetric, with ground glass stopper, size dependent on volume of WCTM to be prepared.

c. **Procedure**

1. Weigh a clean, dry, volumetric flask with stopper (W_3) to ±0.002 g.
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 vacuum.
4. Transfer the plutonium nitrate solution slowly to the chimney and quantitatively rinse the plutonium nitrate container and chimney using 8M HNO_3 directed from a plastic squeeze bottle.

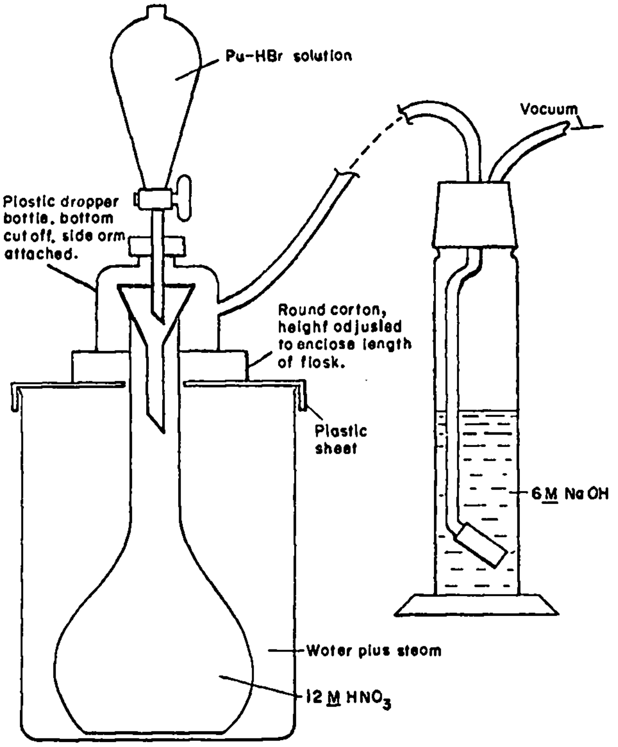

Fig. 2.
Bromine fume scrubber and steam jacket.

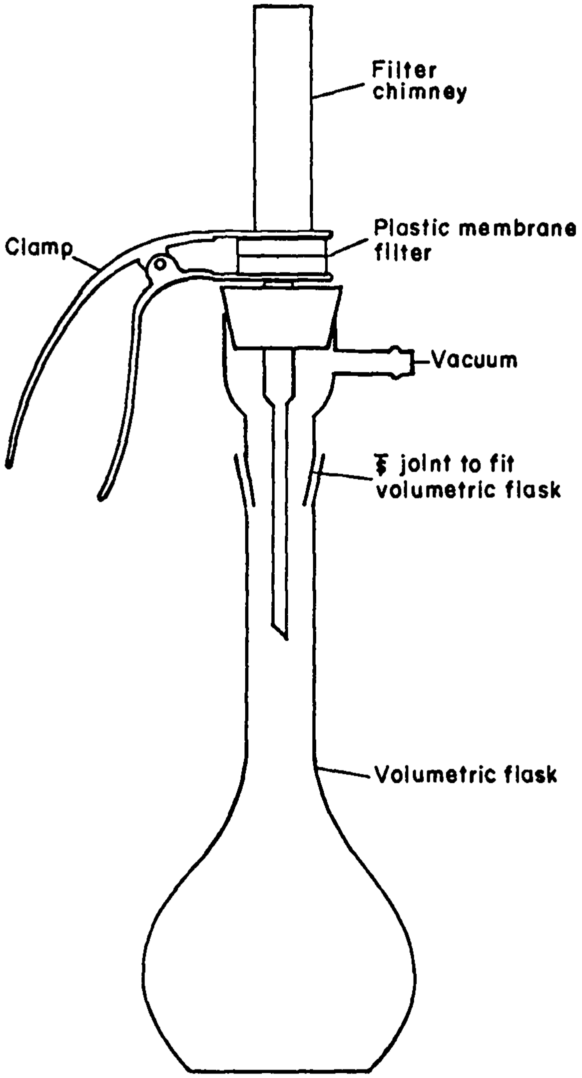

Fig. 3.
Filtration apparatus.

5. Remove the filter chimney and quantitatively rinse the filter with 8M HNO_3 to recover plutonium from solution that diffused to the periphery of the filter.
6. Remove the filter and analyze it for plutonium content according to Sec. 5.1.
7. Remove the filter adaptor and quantitatively rinse the delivery tube with 8M HNO_3 directed from a plastic squeeze bottle.
8. Adjust the filtrate to the desired final concentration according to Sec. 3.6.

3.6. Final Dilution

The plutonium concentration of the WCTM is adjusted to simulate the applicable plant stream, and the HNO_3 concentration is adjusted to 8M to ensure plutonium oxidation state stability as Pu^{4+}. Use 12 to 15.7M HNO_3 to increase acidity or not less than 2M HNO_3 to decrease acidity. Use of water may cause localized formation of plutonium polymer or insoluble hydrous oxide. After completing the adjustment, stopper the flask, and weigh to ±0.002 g

(W_4). With the stopper held tightly in position, invert the flask at least 10 times to attain solution homogeneity. Alternatively, gently lower a 4-cm Teflon-covered magnetic stir bar to the bottom of the flask using an external magnet, stopper the flask, and mix for at least 5 min at a rate that produces a strong vortex. Remove the magnet, do not rinse it, and discard it. Stopper the flask.

4. WCTM PACKAGING

Plutonium nitrate solution or slurry produces gas by alpha radiolysis that can pressurize a sealed container. The degree of pressurization is increased by the presence of Pu^{3+} or Pu^{6+}. Both react with radiolytically generated H_2O_2 to produce Pu^{4+} and additional gas.[6] For this reason, the solutions are treated to produce Pu^{4+} before transferring to containers and sealing. Another factor that affects pressurization is the isotopic distribution of the plutonium.[7] A plutonium nitrate solution having ^{240}Pu and ^{238}Pu isotope abundances of 16.3 and 0.016%, respectively, packaged as outlined in Sec. 4.4, generated 0.53 atm of gas after 20-months storage.[3] Pressure generation rates of solutions with higher ^{238}Pu and ^{240}Pu abundances can be calculated.[7] If excessive pressurization rates are indicated, the solution should be stored only as an evaporated slurry, not in sealed containers.

Three packaging modes of plutonium concentration WCTMs provide (a) a slurry for total plutonium content (grams plutonium per container), (b) a solution for total plutonium content and for plutonium concentration (grams plutonium per gram solution) of short-term (<3-month) storage, and (c) a solution as for (b) but of long-term (≤ 2-year) storage. The slurry container is a glass vial with a polyethylene stopper. The containers for the short- and long-term storage solutions are 25-ml volumetric flasks with polyethylene stoppers and flame-sealed glass ampoules, respectively. Also described is the packaging of WCTMs prepared solely for isotopic distribution measurements.

4.1. Apparatus

1. Ampoule, borosilicate glass, 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 stored solution and 130-mm neck length for ease in sealing (Fig. 4).
2. Bottle, wash, polyethylene, 30-ml.
3. Buret, glass, with long 6-mm-o.d. delivery tube (Fig. 4). Two spacers, cut from polyethylene tubing, are placed on the delivery tube to prevent its direct contact with the ampoule, especially when the buret is withdrawn after solution delivery. The tip of the buret is treated with a nonwetting agent such as Dry-Film (Pierce Chemical Company).
4. File, metal, triangular.
5. Flask, volumetric, 25-ml, screw-cap with polyethylene seal, Corning No. 5650, or equivalent.
6. Forceps, to hold 30-ml wash bottle.
7. Holder, polyethylene, made from a 60-ml polyethylene bottle (Fig. 5).
8. Hot plate.
9. Lamp, heat, 250-W, controlled by variable voltage source.
10. Rubber stoppers, to fit ampoules described in step No. 1.
11. Vial, specimen, "3-dram," polyethylene stopper, Fisher No. 339C, or equivalent.

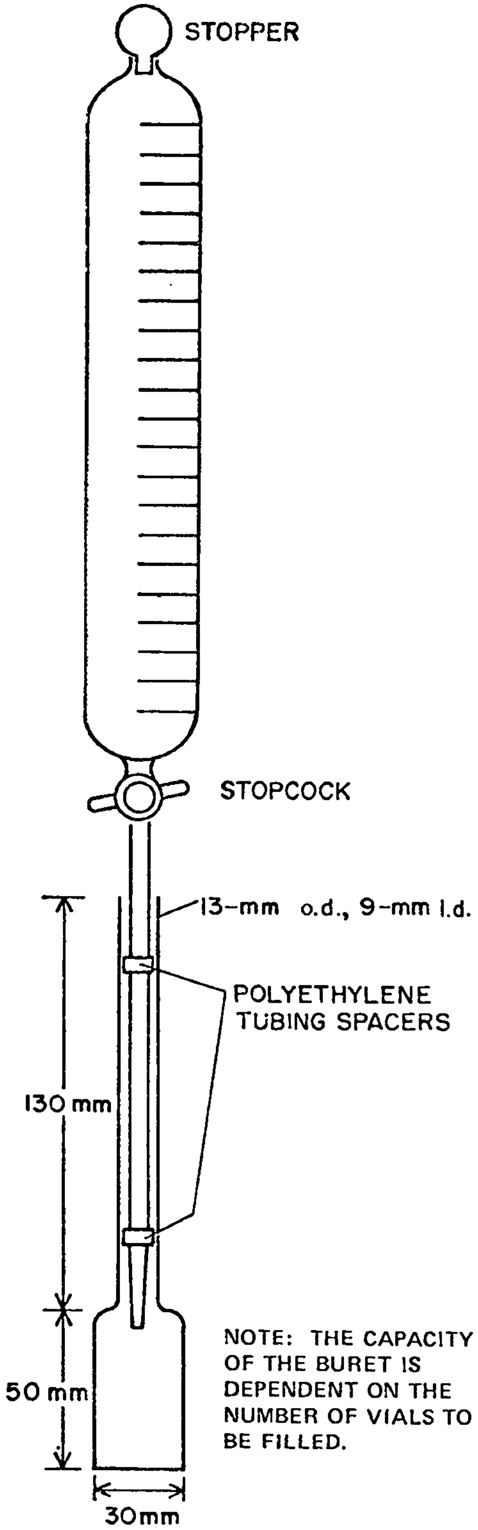

Fig. 4.
Ampoule and buret.

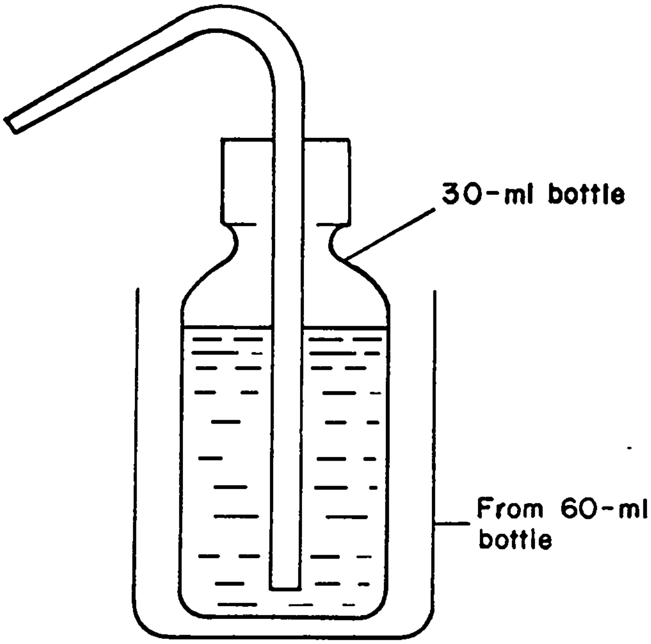

Fig. 5.
Polyethylene wash bottle and holder.

4.2. Slurry for Total Plutonium Content

This packaging mode provides containers with reference values only for the total plutonium content per container. A quantitative transfer of the entire contents of a container is necessary for use.

1. Clean, dry, and label 3-dram vials for the WCTMs to be packaged.
2. Transfer 10 to 20 ml of the WCTM to a 30-ml, polyethylene, wash bottle and weigh to ±0.0001 g.
3. Using forceps, place the wash bottle in the holder and deliver the desired amount of plutonium directly to the bottom of a vial. Forceps, rather than hand squeezing, are used to minimize temperature changes and subsequent weighing errors. Release pressure on the bottle slowly so that solution does not remain in the delivery tip.
4. Using forceps, return the wash bottle to the balance, weigh to ±0.0001 g, and record the vial number and the calculated by-difference solution weight.
5. Repeat steps 3 and 4 for all deliveries.
6. Slowly evaporate the solution to a slurry using a hot plate and heat lamp. Do not evaporate to dryness as denitration will occur. Let some acid remain to prevent water sorption that may cause hydrolysis and formation of insoluble plutonium hydrous oxide.
7. After the slurries attain ambient temperature, stopper the vials and store them in an upright position.
8. For analysis, transfer the entire contents from a vial aided by quantitative rinses of 8M HNO_3 delivered from a plastic squeeze bottle.

4.3. Solution for Total Plutonium Content and/or Plutonium Concentration.

Short-Term (<3-Month) Storage

The 25-ml volumetric flasks used as the containers are not designed for pressure containment; hence, the restriction of not more than 3-month storage. Delivery of solution to the flasks can be made with an appropriate buret or pipet.

1. Weigh a clean, dry, 25-ml volumetric flask with polyethylene stopper.
2. Deliver ≤15 ml of the WCTM to the flask and cap it.
3. Weigh the flask to ±0.0001 g and record the flask number and the calculated delivered weight.
4. Transfer the flask to a plastic bag and seal the bag.

5. Reweigh the flask to ±0.0001 g just before use, shake the flask vigorously before opening, and correct the concentration for any evaporative weight loss.

4.4. Solution for Total Plutonium Content and/or Plutonium Concentration.

Long-Term (≤2-Year) Storage

The containers are flame-sealed, thick-walled glass ampoules designed for ≤10 ml of solution storage. Normally the packaging is for plutonium concentration. If the packaging is to be for total plutonium content per ampoule, the ampoule must be weighed before transfer of the WCTM and again after the transfer. The weighing instructions are not given in the following operational sequence.

1. Clean, dry, and label heavy-wall ampoules for the WCTMs to be packaged.
2. Insert the buret (Fig. 4) into an ampoule, being careful not to let the tip of the buret touch the inside wall of the ampoule.
3. Transfer the desired amount of WCTM to an ampoule, then temporarily seal the ampoule with a rubber stopper.
4. 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, anneal in an air-gas flame, and allow the ampoule to cool.
5. Test the integrity of the seal by inverting the sealed ampoule, smearing the seal with a filter paper, and alpha counting the paper. Reject any leaky ampoules.
6. Store the ampoules upright in a block and seal in a plastic bag to keep dust-free.
7. To open an ampoule, place it in a suitable plutonium containment box, shake it vigorously, and let the solution drain from the tip. Freeze the solution by placing the ampoule in crushed dry ice. Make a deep, 5- to 10-mm-long scratch on the neck ~20 mm below the seal with a new file 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. When the solution is to be used as a plutonium concentration WCTM, transfer aliquots before evaporative concentration changes occur. For use as a total plutonium WCTM, quantitatively transfer the entire contents with 8M HNO_3 rinses.

4.5. Solution for Plutonium Isotopic Distribution

WCTMs prepared only for isotopic analysis need not be protected from minor evaporative concentration changes. The recommended container is a flask with an outer-fitting ground glass stopper because the possibility for inadvertent isotopic contamination is less. Preferably, the solution should be distributed to a series of containers so that accidental contamination will not force rejection of the entire solution. Remove aliquots only with new disposable droppers to prevent cross contamination.

5. ESTABLISHMENT OF WCTM VALUES

Section 2 presents the general considerations governing solution WCTMs and Fig. 1 outlines the options for establishing the plutonium concentration values of the plutonium nitrate WCTMs. A discussion of WCTMs prepared solely for isotopic distribution measurements is presented later.

A WCTM prepared using a PRCTM (or SRCTM) as the starting material shall be analyzed for its plutonium concentration by one method. Statistical tests compare the results to the makeup value (see Sec. 2 for definition). Optionally, but less desirable, analyze the WCTM using two different methods, then statistically compare the two sets of results. This foregoes use of the makeup value which, almost without exception, should be a highly credible value. Essentially the same options apply for a WCTM prepared using plutonium metal as a starting material that is neither a PRCTM nor a SRCTM. However, the plutonium content of the metal must be established by two different methods if a makeup value is computed. When highly pure metal, defined as 99.95+% purity, is used, one of the two methods can be the determination of total metallic and nonmetallic impurities, then computation of the plutonium content by subtracting the sum of the impurities, on a percentage basis, from 100.

**The ampoule sealing and annealing should be done by an experienced glassblower.*

For a WCTM prepared from an uncharacterized starting material, such as plant plutonium nitrate, there is no option. The plutonium concentration shall be determined by two different methods followed by appropriate statistical tests of comparison. As discussed in Sec. 2, every analytical method used shall be calibrated at the time a WCTM is analyzed. This calibration shall be done with aliquots of a PRCTM or SRCTM solution that simulates the WCTM in plutonium concentration and impurity contents (see Sec. 5.2). Also, as discussed in Sec. 6.1, the number of determinations of the WCTM and PRCTM (or SRCTM) shall be equal.

For an isotopic distribution WCTM prepared from a PRCTM (or SRCTM), it still is necessary to verify its integrity by analysis because it may have become contaminated during preparation. For this purpose, aliquots of another solution prepared using the same PRCTM as the starting material shall be analyzed concurrently and in equal number to the WCTM. The impurity elements present in the WCTM may be omitted from the freshly prepared PRCTM since the accuracy of thermal ionization mass spectrometry measurements is affected principally by nonplutonium isotopes of the same mass. Both the WCTM aliquots and the freshly prepared PRCTM aliquots shall undergo the same chemical treatment, just before mass spectrometry measurements are made, to separate americium and uranium because ^{241}Am and ^{238}U are mass interfering isotopes. The usual separation techniques of ion exchange in hydrochloric acid[8] or nitric acid[9] media also separate most impurity elements that can cause unstable plutonium emission to adversely affect the precision of the plutonium isotopic measurement.

In addition to the above topics, this section describes the determination of the plutonium content of the filtered residue obtained during a WCTM preparation and the basic concepts involved in the statistical treatment of data leading to the establishment of the WCTM assigned values.

5.1. Plutonium Content of Filtered Residues

As stipulated in Sec. 3.5, each WCTM prepared for plutonium concentration measurement undergoes a filtration treatment. The filter, with residue, may be discarded without analysis whenever the plutonium concentration value of the WCTM is to be established on the basis of two different analytical methods. This is the usual situation for a WCTM prepared with a plant plutonium nitrate as the starting material.

The method used to determine the plutonium content of the residue shall have a precision of at least 20% relative standard deviation. Either a nondestructive assay or a dissolution followed by a sensitive measurement technique may be used. Applicable nondestructive assay techniques are x-ray fluorescence and gamma counting, the latter requiring a calculation, based on the plutonium isotopic distribution, to convert from counts of a specific isotope to total plutonium. Dissolution treatments include fusions using various fluxes and pressurized acid reactions. Apparatus for the latter includes the sealed quartz tube,[10] the sealed-reflux tube,[11] and the Teflon-container metal shell.[3] High sensitivity measurement techniques include alpha counting,[12] isotope dilution mass spectrometry,[9] and spectrophotometry.[13]

When the measured plutonium content of the residue is $\leq$0.1% of the total plutonium content of the WCTM, the residue (or the dissolved residue) may be discarded and the plutonium content of the WCTM calculated as given in Sec. 6.2 or 6.3. When the residue plutonium content is >0.1% of the WCTM plutonium content, the residue (or the dissolved residue) may again be discarded, but the plutonium content of the WCTM must be established by two different analytical methods.

5.2. Methods for Plutonium Concentration Measurements of Starting Materials and WCTMs

As stated previously (Sec. 2), criteria governing the selection of methods for plutonium concentration determinations are high precision and no or minimum effect by the impurities present in the starting material or WCTM. When two methods are used to establish the plutonium value, their impurity effect behavior should be as different as is practical. Also as stated, aliquots of a PRCTM (or SRCTM) shall be analyzed at the same time and in equal number as the starting material or WCTM. The results for the starting material or WCTM are computed relative to the results obtained for the PRCTM (or SRCTM). The chemical composition of the analyzed PRCTM (or SRCTM) aliquots, therefore, must match that of the starting material or WCTM with regard to plutonium concentration and impurity contents. A recommended practice is to add impurities to the individually delivered aliquots of a freshly prepared PRCTM (or SRCTM) that produce a simulated composition at the time of analysis.

The above requires knowledge of the impurity content of the WCTM or starting material. For a WCTM prepared using a high-purity plutonium material, such as metal and added known quantities of impurities, the impurity content can be based on calculation. When the WCTM is prepared from uncharacterized material, such as plant plutonium nitrate, and for characterizing a starting material, the impurity contents shall be determined by analysis. Because metal ions rather than nonmetal ions mainly interfere with plutonium assay methods, techniques that provide a multielemental metal analysis generally are used. Applicable techniques include emission spectrography, spark source mass spectrometry, neutron activation, and x-ray fluorescence.

The usual methods for determining plutonium concentration are based on electrotitrimetry.

5.3. Plutonium Isotopic Distribution Measurements

It is believed that the discussions of this topic previously presented in Secs. 2, 3.1, and 4.5 have been adequate to require no further comment. The statistical treatment of isotopic distribution results is presented in the next section.

5.4. Criteria Covering Number of Replicate Analyses

The number of equal aliquots of the starting material or WCTM and of the concurrently analyzed PRCTM (or SRCTM) is selected to produce a desired limit of error* (LE) for the value of the plutonium concentration or isotopic distribution assigned to the WCTM. This LE is a function of the precision required for the plutonium concentration measurement or isotopic distribution of the plant material to which the WCTM applies.

From the safeguards standpoint, a plant material is a component in a material balance area (MBA) for which there is a stipulated LE and relative limit of error* (RLE). The LE of a MBA is distributed among the plant materials in that MBA in a manner determined by the individual facility.

The LE to be associated with the plutonium concentration of a WCTM is selected, on an arbitrary basis, to be ≤1/3 of the LE associated with the plant material to which the WCTM applies. (As will be shown, this selection provides for attainment of satisfactory measurement

---

**The LE of an estimator T is defined[14] as twice the standard deviation of T. The RLE, expressed as a percentage, is 100 LE/T.*

precisions without an unreasonable number of replicate analyses.) This relationship now permits a calculation of the number of replicate analyses of the WCTM and the PRCTM (or SRCTM).

The RLE associated with plutonium concentration of the WCTM is

$$\mathrm{RLE} = 100\ \mathrm{LE}/\mathrm{M}\ , \tag{1}$$

in which M is the measured average plutonium concentration

$$\mathrm{LE} = 2S_M$$
$$\mathrm{LE} = 2S_i/\sqrt{n}\ , \tag{2}$$

in which S_i is the standard deviation (for single measurements) of the analytical method and n is the number of replicate aliquots analyzed concurrently for both the WCTM and PRCTM (or SRCTM).

Combining Eqs. (1) and (2) gives

$$\mathrm{RLE} = 100\,(2\,S_i)/\mathrm{M}\sqrt{n}\ , \tag{3}$$

and solving for n,

$$n = 4(100\,S_i/\mathrm{M})^2/(\mathrm{RLE})^2\ , \tag{4}$$

since 100 S_i/M is defined as the relative standard deviation in percent for a single measurement (RSD_i),

$$n = 4(\mathrm{RSD}_i)^2/(\mathrm{RLE})^2\ . \tag{5}$$

Two examples are given to demonstrate how n decreases with improving measurement precision.

Assume that the required RLE for the plutonium concentration of a plant material in an MBA is 0.45%. The RLE of the plutonium concentration of the WCTM then must be $\leq(1/3)(0.45\%) = \leq 0.15\%$. Two methods are available to establish the plutonium concentration of the WCTM, having predicted RSD_i values of 0.1 and 0.3%. The computed values of n are

for $\mathrm{RSD}_i = 0.1\%$

$$n = 4(0.1)^2/(0.15)^2 = 1.78\ ;$$

for $\mathrm{RSD}_i = 0.3\%$

$$n = 4(0.3)^2/(0.15)^2 = 16\ .$$

The advantage of using highly precise methods is apparent. One restriction to the number of analyses, again arrived at in an arbitrary manner, is setting the minimum at n = 5. For the above examples, then, the plutonium concentration of the WCTM would be established by analyzing five replicate aliquots of the WCTM and concurrently analyzed PRCTM (or SRCTM) by the method with a precision of 0.1% RSD_i and 16 replicate aliquots by the less precise method.

The above criteria apply to establishing the isotopic distribution values of WCTMs with the relationships and computations usually applied to the major isotope of ^{239}Pu.

6. STATISTICAL TESTS AND ASSIGNMENT OF VALUES TO WCTMs.

Statistical tests are presented to compute the assigned value and associated uncertainty for the plutonium concentration of WCTMs. These tests cover the two modes of using two different analysis methods and of using the makeup value and one analysis method. Also presented is a discussion of the statistical tests applied to isotopic distribution WCTMs. These tests are preceded by a discussion of the terminology used in them.

6.1 Terminology

The three major symbols used are

Symbol	Definition
n	Number of replicate aliquots of the WCTM (and of the concurrently analyzed PRCTM) analyzed for plutonium concentration or isotopic distribution by one method.
M	Mean (arithmetic average) of n results.
S	Standard deviation for a single result, computed by the standard formula $S = \sqrt{\Sigma(X_i - M)^2/n - 1}$ in which X_i is an individual result, M is the arithmetic average, and n is the number of replicate results. There are n − 1 degrees of freedom associated with S.

To differentiate among the materials analyzed and the analytical methods used, the following subscripts apply.

Subscript	Material	Method
1	PRCTM (or SRCTM)	one
2	WCTM	one
3	PRCTM (or SRCTM)	two
4	WCTM	two

Thus, M_2 is the mean plutonium (concentration or isotopic distribution) value for a WCTM obtained using method one and S_3 is the computed standard deviation of the results for a PRCTM (or SRCTM) obtained using method two.

At the discretion of the analyst, precision data previously obtained for a method of analysis when used under similar conditions may be pooled with present precision data to obtain a computed standard deviation with an associated larger number of degrees of freedom. Before pooling, a statistical F test (Sec. 6.2.1) shall be made to establish that the past precision is not significantly different from the present precision.

In the subsequent sections, many of the statistical tests are reported by Natrella.[15]

6.2. Tests for Two Methods of Analyses

An example of the tests presented in this section is given as the first example in the Appendix.

6.2.1. Tests of Precisions

This test compares the precision of the results obtained by the same method for the WCTM and the PRCTM (or SRCTM).

1. Choose a level of significance α, usually 0.05.
2. Calculate for Method 1,

$$F = S_1^2/S_2^2 \ .$$

3. Find, in an F table,

$$F(1-\alpha/2, n_1-1, n_2-1),$$

the F value from a $1-\alpha/2$ percentile tabulation entered with n_1-1 degrees of freedom for the numerator and n_2-1 degrees of freedom for the denominator, and

$$F(1-\alpha/2, n_2-1, n_1-1) \ .$$

4. If

$$F > F(1-\alpha/2, n_1-1, n_2-1), \text{ or}$$
$$F < 1/F(1-\alpha/2, n_2-1, n_1-1) \ ,$$

conclude that the precisions obtained for the WCTM and PRCTM are different.

5. Do the same test for Method 2, for

$$F = S_3^2/S_4^2 \ ,$$
$$F(1-\alpha/2, n_3-1, n_4-1) \ , \text{ and}$$
$$F(1-\alpha/2, n_4-1, n_3-1) \ .$$

This test is somewhat sensitive to normality, therefore an indicated significant difference may have been caused by some degree of nonnormality. An assessment for nonnormality is available.[16] A significant difference in precisions for only one method may indicate a difference in the impurity compositions of the WCTM and PRCTM. A significant difference in precisions for both methods indicates a larger compositional difference such as organic matter in the WCTM that causes erratic electrode response in an electrometric titrimetric method. When a significant difference is obtained for either one or both methods, the source of the difference should be established and, if possible, modifications made in the methods. Then, new analyses of the WCTM or PRCTM should be obtained and the test repeated. If the difference cannot be resolved, the WCTM should be rejected.

6.2.2. Calculation of WCTM Mean Based on PRCTM

The plutonium concentration or isotopic value assigned to the WCTM shall be based directly on the PRCTM. Because aliquots of both the WCTM and PRCTM are analyzed concurrently by the same method, the value assigned to the WCTM is the mean value computed by

$$\bar{X}_2 = M_2\,(R/M_1)$$
$$\bar{X}_4 = M_4\,(R/M_3)\ ,$$

in which $\bar{X}_2$ and $\bar{X}_4$ are the mean values assigned to the WCTM; M_1, M_2, M_3, and M_4 are the analysis result means as defined previously; and R is the plutonium content of the PRCTM assumed to have insignificant error and therefore a constant for statistical calculations.

6.2.3. Tests of Means

This test compares the WCTM population means obtained using the two different methods.

The approximate precisions, expressed as variances V_i and degrees of freedom f_i associated with $\bar{X}_2$ and $\bar{X}_4$, are derived by propagation of error and by Satterthwaite's formula.[17]

$$V_2 \approx \bar{X}_2^2\left(\frac{S_1^2}{n_1M_1^2} + \frac{S_2^2}{n_2M_2^2}\right) \ ; \qquad f_2 \approx \frac{V_2^2}{\dfrac{\left(\dfrac{\bar{X}_2^2\,S_1^2}{n_1M_1^2}\right)^2}{n_1 - 1} + \dfrac{\left(\dfrac{\bar{X}_2^2\,S_2^2}{n_2M_2^2}\right)^2}{n_2 - 1}} \ .$$

$$V_4 \approx \bar{X}_4^2\left(\frac{S_3^2}{n_3M_3^2} + \frac{S_4^2}{n_4M_4^2}\right) \ ; \qquad f_4 \approx \frac{V_4^2}{\dfrac{\left(\dfrac{\bar{X}_4^2\,S_3^2}{n_3M_3^2}\right)^2}{n_3 - 1} + \dfrac{\left(\dfrac{\bar{X}_4^2\,S_4^2}{n_4M_4^2}\right)^2}{n_4 - 1}}$$

The variance of $(\bar{X}_2 - \bar{X}_4)$ is $(V_2 + V_4)$, for which the associated degrees of freedom are given by[17]

$$f \approx \frac{\left(V_2 + V_4\right)^2}{\dfrac{\left(\dfrac{\bar{X}_2^2\,S_1^2}{n_1M_1^2}\right)^2}{n_1 - 1} + \dfrac{\left(\dfrac{\bar{X}_2^2\,S_2^2}{n_2M_2^2}\right)^2}{n_2 - 1} + \dfrac{\left(\dfrac{\bar{X}_4^2\,S_3^2}{n_3M_3^2}\right)^2}{n_3 - 1} + \dfrac{\left(\dfrac{\bar{X}_4^2\,S_4^2}{n_4M_4^2}\right)^2}{n_4 - 1}}$$

An approximate two-sided t test of the two WCTM means is given by

$$T = \frac{\left| \bar{X}_2 - \bar{X}_4 \right|}{\sqrt{V^2 + V^4}}$$

with f degrees of freedom, rounded to the nearest integer.

Find, in a t table, t (1-α/2, f).

If T > t (1-α/2, f), conclude that the population means differ significantly.

If the population means test significantly different, no value can be assigned to the WCTM. Investigate for the cause, including the effects of impurities on the two methods. Repeat one or both sets of analyses, as appropriate. If no cause can be established, the WCTM must be rejected.

6.2.4. Assignment of WCTM Value

When the WCTM population means are not significantly different, calculate the value to be assigned to the WCTM and establish whether the associated LE meets the requirement of $\leq$1/3 of the LE associated with the plant material to which the WCTM applies.

Calculate the assigned value A as the weighted average of two means $\bar{X}_2$ and $\bar{X}_4$ by

$$A = W_2 \bar{X}_2 + W_4 \bar{X}_4 ,$$

in which

$$W_2 = \frac{(1/V_2)}{(1/V_2) + (1/V_4)}$$

$$W_4 = \frac{(1/V_4)}{(1/V_2) + (1/V_4)}$$

in which V_2 and V_4 are the variances associated with $\bar{X}_2$ and $\bar{X}_4$ (see Sec. 6.2.3).

Calculate the standard deviation S_A associated with A by the approximation[18]

$$S_A \approx \left[\frac{1}{W} \left\{ 1 + \frac{4}{f_2} W_2 (1 - W_2) + \frac{4}{f_4} W_4 (1 - W_4) \right\} \right]^{\frac{1}{2}}$$

in which

$$W = \left(\frac{1}{V_2}\right) + \left(\frac{1}{V_4}\right)$$

The associated degrees of freedom n_A, rounded to the nearest integer, are

$$n_A = \frac{1}{\dfrac{W_2^2}{f_2} + \dfrac{W_4^2}{f_4}} ,$$

in which f_2 and f_4 are the degrees of freedom associated with V_2 and V_4 (see Sec. 6.2.3). Calculate the LE and RLE by

$\mathrm{LE} = 2S_A$ and
$\mathrm{RLE} = 100\ \mathrm{LE}/A$.

Establish whether the LE or RLE meets the requirement of ≤1/3 the LE or RLE associated with the plant material. If it does not, either increase the number of replicate aliquots analyzed or use more precise methods of analyses.

Finally, calculate an approximate 95% confidence interval for the assigned value by

$$\mathrm{CI} = A \pm t\,(1 - \alpha/2, n_A)\cdot(S_A) \ .$$

6.3. Tests for Makeup Value and One Method of Analysis

An example of the tests presented in this section is given as the second example in the Appendix.

6.3.1. Makeup Value Calculation

Calculate the makeup value of the WCTM by

$$A = \frac{[(F)\ (b)\ (W_2 - W_1)] - c}{W_4 - W_3} ,$$

in which A = grams plutonium per gram of solution, F = fractional plutonium content of starting material, b = air buoyancy correction factor for starting material calculated from physical constants, assumed to have insignificant error and therefore a constant for statistical calculations, W_2 = weight in grams of container plus starting material (Secs. 3.2.1 and 3.2.2), W_1 = weight in grams of container (Secs. 3.2.1 and 3.2.2), c = determined grams of plutonium in filtered residue (Sec. 5.1), W_4 = weight in grams of flask plus plutonium nitrate solution (Secs. 4.3 and 4.4), and W_3 = weight in grams of flask (Secs. 4.3 and 4.4).

The air buoyancy correction factor for plutonium metal is 0.99992 at sea level. In the above relationship, no air buoyancy correction factor is shown for the solution weight (denominator). None is needed when the WCTM is used only at the laboratory where it was prepared.

The approximate precision, expressed as the standard deviation associated with A, derived by propagation of error, is

$$S_A \approx \frac{1}{W_4 - W_3} \left[b^2 \left\{ F^2 \left(S_{W_1}^2 + S_{W_2}^2\right) + \left(W_2 - W_1\right)^2 S_F^2 \right\} + S_c^2 + A^2 \left(S_{W_3}^2 + S_{W_4}^2\right) \right]^{\frac{1}{2}} ,$$

in which an individual S is the estimated standard deviation associated with the subscripted variable.

The calculation of the degrees of freedom associated with S_A is a virtual impossibility and no calculation of the confidence interval is possible.

Calculate the LE and RLE by

$LE = 2\,S_A$ and
$RLE = 100\ LE/A$.

6.3.2. Calculation of Mean Value Based on the Results of the One Method of Analysis

This calculation is essentially identical to that presented in Sec. 6.2.1.

1. Choose a level of significance α, usually 0.05.
2. Calculate

$$F = S_1^2/S_2^2 \ .$$

3. Find, in an F table,

$$F\,(1 - \alpha/2, n_1 - 1, n_2 - 1)$$

the F value from a 1-α/2 percentile tabulation entered with $n_1 - 1$ degrees of freedom for the numerator and $n_2 - 1$ degrees of freedom for the denominator, and

$$F\,(1 - \alpha/2, n_2 - 1, n_1 - 1) \ .$$

4. If,

$F > F\,(1 - \alpha/2, n_1 - 1, n_2 - 1)$, or
$F < 1/F\,(1 - \alpha/2, n_2 - 1, n_1 - 1)$,

conclude that the precisions obtained for the WCTM and PRCTM are different.

As discussed in Sec. 6.2.1, the source of the difference should be established and, if possible, the method should be modified. Then, the WCTM or PRCTM should be reanalyzed and the F test repeated. If the difference cannot be resolved, the WCTM should be rejected.

5. Calculate the mean value of the WCTM by

$$\bar{X}_2 = M_2\,(R/M_1) \ ,$$

in which $\bar{X}_2$ is the mean value assigned to the WCTM, M_1 and M_2 are the analysis result means for the PRCTM and WCTM, respectively, and R is the plutonium content of the PRCTM, assumed to have insignificant error and therefore a constant for statistical calculations.

6.3.3. Test of Makeup Value and Analysis-Based Mean

1. Calculate the approximate precision V_2 expressed as a variance, and degrees of freedom f_2 associated with $\bar{X}_2$ by

$$V_2 \approx \bar{X}^2 \left(\frac{S_1^2}{n_1 M_1^2} + \frac{S_2^2}{n_2 M_2^2} \right) \quad ; \qquad f_2 \approx \frac{V_2^2}{\dfrac{\left(\dfrac{\bar{X}_2^2 \, S_1^2}{n_1 M_1^2} \right)^2}{n_1 - 1} + \dfrac{\left(\dfrac{\bar{X}_2^2 \, S_2^2}{n_2 M_2^2} \right)^2}{n_2 - 1}}$$

2. An approximate two-sided t test of the analysis result mean and the makeup value is given by

$$T = \frac{| \bar{X}_2 - A |}{\sqrt{S_A^2 + V_2}}$$

with f_2 degrees of freedom, rounded to the nearest integer. (This t test is on the conservative side because no degrees of freedom associated with S_A are included.)

Find, in a t table,

$$t\,(1 - \alpha/2, f_2) \ .$$

If $T > t\,(1 - \alpha/2, f_2)$, conclude that the population means estimated by A and $\bar{X}_2$ are different.

If the population means estimated by A and $\bar{X}_2$ test significantly different, no value can be assigned to the WCTM. Investigate the cause, including the effects of impurities on the method, the starting material and all factors involved in establishing the makeup value, and possibly the PRCTM that was concurrently analyzed. If the cause appears to be associated with the makeup value, a second method may be used to establish the WCTM value. In this case, the statistical computations given in Sec. 6.2 apply.

6.3.4. Assignment of WCTM Value

When the population means do not show a significant difference based on the t test in the above section, the makeup value A is assigned to the WCTM.

Calculate the LE and RLE associated with A by

$LE = 2S_A$ and
$RLE = 100\ LE/A$.

Establish whether the LE or RLE meets the requirement of ≤1/3 the LE or RLE associated with the plant material. If it does not, and the precision associated with the analysis result is considerably better than S_A, the alternative of using a second method of analysis should be considered. Then the assignment of the mean value and associated precision could be based on the results of the two methods given in Sec. 6.2. If this alternate approach is not feasible, the WCTM must be rejected.

6.4. Tests Applied to Isotopic Distribution WCTMs

As discussed previously in Sec. 2, virtually only one method (thermal ionization mass spectrometry) is used to determine plutonium isotopic distribution. Thus, the statistical treatment given in Sec. 6.3 normally will apply to establish the isotopic distribution of a WCTM.

Should a second laboratory also analyze the WCTM, then the statistical treatment given in Sec. 6.2 applies. For most nuclear fuel materials, the isotope of interest for accountability and safeguards measurements is ^{239}Pu; therefore, most WCTMs will be prepared to have an assigned ^{239}Pu abundance. For such WCTMs, the statistical tests are applied solely to the ^{239}Pu value. When the purpose of the WCTM is other isotopes, the statistical tests should be appropriately applied.

6.5. Correction of Plutonium Concentration and Isotopic Distribution Values for Radioactive Decay

The plutonium concentration and isotopic distribution values of WCTMs, as well as all starting materials, must be corrected for the radioactive decay of the various plutonium isotopes.[19] The decays are

Parent	Daughter	Parent Half-Life (yr)	Daughter Formation Rate from Monoisotopic Parent (ppm per yr)
^{238}Pu	^{234}U	88	7 860
^{239}Pu	^{235}U	24 400	28
^{240}Pu	^{236}U	6 540	106
^{241}Pu	^{241}Am	14.7	46 060
^{242}Pu	^{238}U	38 700	1.8

The correction involves multiplying the daughter formation rate by the fractional atom abundance of each isotope for a material as shown below for a NBS SRM 949 metal.

Pu Isotope	Fractional Atom Abundance	x	Daughter Formation Rate	=	Daughter Formed in First Year (ppm)
238	0.00003		7 860		0.2
239	0.97617		28		27.7
240	0.02324		106		2.5
241	0.00054		46 060		24.9
242	0.00002		1.8		0.01
			Total		55.4

Note that the formation is not a constant with time because the relative amounts of the parent isotopes are changing. This effect is most pronounced for the shorter half-life parents ^{241}Pu and ^{238}Pu. Corrections should be made at intervals to change the assigned values of starting materials at one-half or less of the assigned limit of error (LE).

ACKNOWLEDGMENTS

Valuable consultation was provided by S. S. Yamamura of Allied Chemical Corporation, ID, and F. W. Spraktes of Aerojet Nuclear Corporation, ID. S. P. Turel, W. B. Brown, E. G.

Selleck, and R. Moore of NRC provided valuable guidelines and reviews. Reviews and valuable suggestions were provided by C. D. Zeis, M. W. Hume, and Y. M. Ferris of the Rocky Flats Plant of Rockwell International, P. W. Seabaugh of the Monsanto Mound Laboratory, and L. T. Corbin of the Oak Ridge Nat'l. Laboratory.

REFERENCES

1. "Standard Reference Materials 1973 Catalog," Office of Standard Reference Materials, National Bureau of Standards Special Publication 260 (April 1973).

2. C. E. Pietri, New Brunswick Laboratory, Personal communication, 1974.

3. G. R. Waterbury, Compiler, "Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle, Program Status Report June 1973 to June 1974," Los Alamos Scientific Laboratory report LA-5696-SR (October 1974).

4. R. G. Gutmacher, F. Stephens, K. Ernst, J. E. Harrar, J. Magistad, T. E. Shea, and S. P. Turel, "Accountability Methods for Plutonium Nitrate Solutions," U. S. AEC report WASH-1282 (February 1974).

5. A. Brunstad, "Polymerization and Precipitation of Plutonium (IV) in Nitric Acid," Ind. Eng. Chem. **51**, 38-40 (1959).

6. F. J. Miner and J. R. Seed, "Radiation Chemistry of Plutonium Nitrate Solutions," Chem. Rev. **67**, 299-315 (1967).

7. G. H. Bryan and J. L. Ryan, "Solid Plutonium Nitrate Shipping Forms," Battelle Pacific Northwest Laboratory report BNWL-SA-4830 (1974).

8. J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, "Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials," Los Alamos Scientific Laboratory report LA-4622 (March 1971).

9. C. J. Rodden, Ed., "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle — Second Edition," U. S. AEC report TID-7029 (2nd Ed.)(1972).

10. C. F. Metz and G. R. Waterbury, "Sealed Tube Dissolution Method with Applications to Plutonium-Containing Materials," Los Alamos Scientific Laboratory report LA-3554 (November 1966).

11. J. W. Dahlby, R. R. Geoffrion, and G. R. Waterbury, "The Sealed-Reflux Dissolution System," Los Alamos Scientific Laboratory report LA-5776 (January 1975).

12. F. L. Moore and J. E. Hudgens, "Separation and Determination of Plutonium by Liquid-Liquid Extraction," Anal. Chem. **29**, 1967 (1955).

13. J. W. Dahlby and G. R. Waterbury, "The Spectrophotometric Determination of Plutonium as the Arsenazo I Complex," Los Alamos Scientific Laboratory report LA-3314 (July 1965).

14. American Nuclear Standards Institute, "Limit of Error Concepts and Principles of Calculation in Nuclear Materials Control," ANSI N15.16 - 1974.

15. M. G. Natrella, **Experimental Statistics**, National Bureau of Standards Handbook 91 (U. S. Government Printing Office, Washington, DC, 1962).

16. American Nuclear Standards Institute, "Assessment of the Assumption of Normality (Employing Individual Observed Values)," ANSI N15.15 - 1974.

17. F. E. Satterthwaite, "An Approximate Distribution of Estimates of Variance Components," Biometrics Bull. **2**, 110-114 (1946).

18. P. Meir, "Variance of a Weighted Mean," Biometrics Bull. **9**, 59-73 (1953).

19. S. F. Marsh, W. D. Spall, R. M. Abernathey, and J. E. Rein, "Uranium Daughter Growth Must Not Be Neglected When Adjusting Plutonium Materials for Assay and Isotopic Contents," Los Alamos Scientific Laboratory report LA-6444 (in preparation).

APPENDIX

STATISTICAL TEST EXAMPLES

A. TESTS FOR TWO METHODS OF ANALYSES

A plutonium concentration WCTM is prepared for calibrating and for maintaining quality control surveillance of a plant process stream. The RLE assigned to the stream is 0.25%. The WCTM is prepared using a plant plutonium nitrate as the starting material. See Sec. 3.2.3 and applicable later sections. The two analytical methods used to establish the plutonium concentration are controlled potential coulometry (termed method 1) and amperometric titration (termed method 2).

1. Estimated Number of Replicate Analyses of the WCTM and Concurrently Analyzed PRCTM (Sec. 5.4)

Required RLE of WCTM is

$\leq$ 1/3 of RLE of plant process stream
$\leq 1/3\ (0.25\%) = 0.083\%$.

Estimated precisions, as RSD_i, of the two methods are

$RSD_{i_1} = 0.04\%$ and
$RSD_{i_2} = 0.06\%$.

Estimated number of replicate analyses is

$$n \approx \frac{4\ (RSD_i)^2}{RLE^2}$$

$$n_1 \approx \frac{4\ (0.04)^2}{(0.083)^2} \approx 0.93$$

$$n_2 \approx \frac{4\ (0.06)^2}{(0.083)^2} \approx 2.09$$

Because these numbers are less than the specified minimum of 5, five replicate aliquots, each of the WCTM and of the PRCTM, are analyzed using each method.

The PRCTM is prepared using NBS SRM 949 plutonium metal, and impurity elements are added to the analyzed aliquots to simulate the composition of the WCTM. The calculated plutonium concentration (R) of the PRCTM is 0.10000 g/g.

The obtained results are

RESULTS
(gram Pu per gram solution)

Method 1		Method 2	
PRCTM	WCTM	PRCTM	WCTM
0.10012	0.09702	0.09999	0.09693
0.10005	0.09710	0.10007	0.09710
0.10017	0.09713	0.10003	0.09697
0.10008	0.09709	0.10005	0.09696
0.10010	0.09716	0.09996	0.09689

2. Calculated Means and Standard Deviations (Sec. 6.1)

Calculate the means (M) and associated standard deviations (S) by

$$M = \frac{\Sigma X}{n}$$

$$S = \sqrt{\frac{\Sigma (X_i - M)^2}{n - 1}}$$

The values are

Method 1	M	S
PRCTM	$M_1 = 0.10010$	$S_1 = 0.000045$
WCTM	$M_2 = 0.09710$	$S_2 = 0.000052$
Method 2		
PRCTM	$M_3 = 0.10002$	$S_3 = 0.000045$
WCTM	$M_4 = 0.09697$	$S_4 = 0.000079$

3. F-Tests of Precisions (Sec. 6.2.1)

Calculate the F ratios for both methods and compare to tabulated F values

Method 1

$$F = \frac{S_1^2}{S_2^2} = \frac{(0.000045)^2}{(0.000052)^2} = 0.75$$

$$F\ (1-\alpha/2,\ n_1 - 1,\ n_2 - 1) \text{ or } F\ (0.975,\ 4,\ 4) = 9.6$$

$$1/F\ (1-\alpha/2,\ n_2 - 1,\ n_1 - 1) \text{ or } 1/F\ (0.975,\ 4,\ 4) = \frac{1}{9.6} = 0.104$$

Because $0.75 < 9.6$ and $0.75 > 0.104$, the precisions are not different.

Method 2

$$F = \frac{S_3^2}{S_4^2} = \frac{0.000045^2}{0.000079^2} = 0.32$$

$$F(1-\alpha/2,\ n_1 - 1,\ n_2 - 1) \text{ or } F\ (0.975,\ 4,\ 4) = 9.6$$

$$1/F\ (1-\alpha/2,\ n_2 - 1,\ n_1 - 1) \text{ or } 1/F\ (0.975,\ 4,\ 4) = \frac{1}{9.6} = 0.104$$

Because $0.32 < 9.6$ and $0.32 > 0.104$, the precisions are not different.

4. Calculations of WCTM Means Based on PRCTM (Sec. 6.2.2)

Calculate the two WCTM means.

$$\bar{X}_2 = M_2\ (R/M_1) = 0.09710\ (0.10000/0.10010) = 0.097003$$

$$\bar{X}_4 = M_4\ (R/M_3) = 0.09697\ (0.10000/0.10002) = 0.096950$$

5. Tests of Means (Sec. 6.2.3)

Calculate the approximate variances and degrees of freedom for both means.

$$V_2 \approx \bar{X}_2^2 \left(\frac{S_1^2}{n_1 M_1^2} + \frac{S_2^2}{n_2 M_2^2} \right)$$

$$\approx (0.097003)^2 \left(\frac{0.000045^2}{5(0.10010)^2} + \frac{0.000052^2}{5(0.09710} \right)$$

$$\approx 9.20047 \times 10^{-10}$$

$$F_2 \approx \frac{V_2^2}{\dfrac{\left(\dfrac{\bar{X}_2^2 \; S_1^2}{n_1 M_1^2}\right)^2}{n_1 - 1} + \dfrac{\left(\dfrac{\bar{X}_2^2 \; S_2^2}{n_2 M_2^2}\right)^2}{n_2 - 1}} \; .$$

$$\approx \frac{(9.20047 \times 10^{-10})^2}{\dfrac{\left(\dfrac{(0.097003)^2 \; (0.000045)^2}{5(0.10010)^2}\right)^2}{4} + \dfrac{\left(\dfrac{(0.097003)^2 \; (0.000052)^2}{5(0.09710)^2}\right)^2}{4}}$$

$$\approx 7.8 \; .$$

$$V_4 \approx \bar{X}_4^2 \left(\frac{S_3^2}{n_3 M_3^2} + \frac{S_4^2}{n_4 M_4^2}\right)$$

$$\approx (0.096950)^2 \left(\frac{(0.000045)^2}{5(0.10002)^2} + \frac{(0.000079)^2}{5(0.09697)^2}\right)$$

$$\approx 1.628204 \times 10^{-9} \; .$$

$$f_4 \approx \frac{V_4^2}{\dfrac{\left(\dfrac{\bar{X}_4^2 \; S_3^2}{n_3 M_3^2}\right)^2}{n_3 - 1} + \dfrac{\left(\dfrac{\bar{X}_4^2 \; S_4^2}{n_4 M_4^2}\right)^2}{n_4 - 1}}$$

$$\approx \frac{(1.628204 \times 10^{-9})^2}{\dfrac{\left(\dfrac{(0.096950)^2 \; (0.000045)^2}{5(0.10002)^2}\right)^2}{4} + \dfrac{\left(\dfrac{(0.096950)^2 \; (0.000079)^2}{5(0.09697)^2}\right)^2}{4}}$$

$$\approx 6.2 \; .$$

Compute the T statistic

$$T = \frac{| \bar{X}_2 - \bar{X}_4 |}{\sqrt{V_2 + V_4}}$$

with f degrees of freedom in which

$$T = \frac{|\, 0.097003 - 0.096950 \,|}{\sqrt{9.20047 \times 10^{-10} + 1.628204 \times 10^{-9}}}$$

$$= 1.05$$

$$f \approx \frac{(V_2 + V_4)^2}{\frac{\left(\frac{\bar{X}_2^2\ S_1^2}{n_1 M_1^2}\right)^2}{n_1 - 1} + \frac{\left(\frac{\bar{X}_2^2\ S_2^2}{n_2 M_2^2}\right)^2}{n_2 - 1} + \frac{\left(\frac{\bar{X}_4^2\ S_3^2}{n_3 M_3^2}\right)^2}{n_3 - 1} + \frac{\left(\frac{\bar{X}_4^2\ S_4^2}{n_4 M_4^2}\right)^2}{n_4 - 1}}$$

$$f \approx \frac{(9.20047 \times 10^{-10}}{\frac{\left(\frac{(0.097003)^2\ (0.000045)^2}{5\ (0.10010)^2}\right)^2}{4} + \frac{\left(\frac{(0.097003)^2\ (0.000052)^2}{5\ (0.09710)^2}\right)^2}{4}}$$

$$\frac{+ \quad 1.628204 \times 10^{-9})^2}{+ \frac{\left(\frac{(0.096950)^2\ (0.000045)^2}{5\ (0.10002)^2}\right)^2}{4} + \frac{\left(\frac{(0.096950)^2\ (0.000079)^2}{5\ (0.09697)^2}\right)^2}{4}}$$

$\approx$ 12.1, or 12 rounded to nearest integer .

Find, in a t table,

$t\ (1 - \alpha/2, f) = t\ (0.975, 12) = 2.179$.

Because $T = 1.05 < t\ (1 - \alpha/2, f) = 2.179$, conclude that the two means are not different.

6. Assignment of WCTM Value (Sec. 6.2.4)

Calculate the assigned value A.

$$A = W_2\ \bar{X}_2 + W_4\ \bar{X}_4$$

$$W_2 = \frac{\frac{1}{V_2}}{\left(\frac{1}{V_2} + \frac{1}{V_4}\right)} = \frac{\frac{1}{9.20047 \times 10^{-10}}}{\frac{1}{9.20047 \times 10^{-10}} + \frac{1}{1.628204 \times 10^{-9}}}$$

$$= 0.63895$$

$$W_4 = \frac{\frac{1}{V_4}}{\left(\frac{1}{V_2} + \frac{1}{V_4}\right)} = \frac{\frac{1}{1.628204 \times 10^{-9}}}{\frac{1}{1.920047 \times 10^{-10}} + \frac{1}{1.628204 \times 10^{-9}}}$$

$$= 0.36105$$

$$A = (0.63895)\ (0.097003) + (0.36105)\ (0.096950)$$

$$= 0.096984$$

Calculate the standard deviation S_A, associated with A, with n_A degrees of freedom.

$$S_A \approx \left[\frac{1}{W}\left\{1 + \frac{4}{f_2} W_2\ (1-W_2) + \frac{4}{f_4} W_4\ (1 - W_4)\right\}\right]^{\frac{1}{2}}$$

$$W = \left(\frac{1}{V_2}\right) + \left(\frac{1}{V_4}\right)$$

$$W = \left(\frac{1}{9.20047 \times 10^{-10}}\right) + \left(\frac{1}{1.628204 \times 10^{-9}}\right)$$

$$= 1701074649 \quad .$$

$$S_A \approx \left[\frac{1}{1701074649}\left\{1 + \frac{4}{7.8}(0.63895)\ (1-0.63895) + \frac{4}{6.2}\ (0.36105)\ (1-0.36105)\right\}\right]^{\frac{1}{2}}$$

$$\approx 0.000027293 \quad .$$

$$n_A \approx \frac{1}{\frac{W_2^2}{f_2} + \frac{W_4^2}{f_4}}$$

$$\approx \frac{1}{\frac{(0.63895)^2}{7.8} + \frac{(0.36105)^2}{6.2}}$$

$\approx$ 13.63 or 14 rounded to nearest integer

Calculate the LE and RLE.

$LE = 2\,S_A$

$= 2\ (0.000027293)$

$= 0.00005459$.

$$\begin{aligned} \mathrm{RLE} &= 100\ \mathrm{LE/A} \\ &= (100)\ 0.00005459/0.096984 \\ &= 0.056\% \ . \end{aligned}$$

Establish whether the LE or RLE meets the requirement of ≤ 1/3 the LE or RLE associated with the plant material.

From (a), required RLE = 0.083%.

Hence RLE of WCTM meets the requirement.

Calculate the 95% confidence interval for the assigned value.

$$\begin{aligned} \mathrm{C\,I} &= \mathrm{A} \pm \mathrm{t}\,(1 - \alpha/2, \mathrm{n_A})\,(\mathrm{S_A}) \\ &= \mathrm{t}\ (0.95,\ 1) = 2.145\ . \\ \mathrm{C\ I} &= 0.096984 \pm 2.145\ (0.000027293) \\ &= 0.096925 \text{ to } 0.097042 \text{ gram plutonium per gram of solution.} \end{aligned}$$

B. TESTS FOR MAKEUP VALUE AND ONE METHOD OF ANALYSIS

A plutonium concentration WCTM is prepared for calibrating and for maintaining quality control surveillance of a plant process stream. The RLE assigned to the stream is 0.50%. The WCTM is prepared using a high-purity plutonium metal by the HBr method described in Sec. 3.2.2.1 and applicable later sections. The plutonium content of the metal had been established by two methods, a potentiometric titration and one based on total impurities measurement, which gave agreeing results. The method of analysis used to establish the plutonium concentration of the WCTM is controlled potential coulometry.

1. Estimated Number of Replicate Analyses of the WCTM and Concurrently Analyzed PRCTM (Sec. 5.4)

Required RLE of WCTM is

≤ 1/3 of RLE of plant process stream
≤ 1/3 (0.50%) = 0.167%.

Estimated precision, as $\mathrm{RSD_i}$, of method is 0.04%.

Estimated number of replicate analyses is

$$n \approx 4(\mathrm{RSD_i})^2/\mathrm{RLE}^2$$
$$n \approx 4(0.04)^2/0.167^2 \approx 0.23\ .$$

Because this number is less than the specified minimum of 5, five replicate aliquots each of the WCTM and of the PRCTM are analyzed.

The PRCTM is prepared using NBS SRM 949 plutonium metal, and impurity elements were added to the analyzed aliquots to simulate the composition of the WCTM. The calculated plutonium concentration (R) of the PRCTM is 0.12000 g/g.

The obtained results are

RESULTS
(gram Pu gram solution)

PRCTM	WCTM
0.11993	0.12065
0.11990	0.12062
0.11985	0.12058
0.11982	0.12068
0.11988	0.12063

2. Calculated Mean and Standard Deviation Based on the Method Results (Sec. 6.3.2)

Calculate the means (M) and associated standard deviations (S) by

$$M = \frac{\Sigma X}{n}$$

$$S = \sqrt{\frac{\Sigma (X_i - M)^2}{n - 1}}$$

The values are

PRCTM

$M_1 = 0.119876$
$S_1 = 0.000043$

WCTM

$M_2 = 0.120632$
$S_2 = 0.000037$.

Calculate the F ratio and compare to a tabulated F value.

$F = S_1^2/S_2^2 = (0.000043)^2/(0.000037)^2 = 1.35$
$F(1 - \alpha/2, n_1 - 1, n_2 - 1)$ or $F(0.975, 4, 4) = 9.6$
$1/F(1 - \alpha/2, n_2 - 1, n_1 - 1)$ or $1/F(0.975, 4, 4) = 0.104$.

Because $1.35 < 9.6$ and $1.35 > 0.104$, precisions are not different. Calculate the WCTM mean.

$\bar{X}_2 = M_2 (R/M_1)$
$= 0.120632 (0.12000/0.119876)$
$= 0.12076$.

3. Makeup Value (Sec. 6.3.1)

The makeup data are

Component	Symbol	Value	S
Fraction Pu content of starting material	F	0.9997	0.0004
Air buoyancy correction	b	0.99992	Zero
Weight of container plus starting material, g	W_2	50.2798	0.0005
Weight of container, g	W_1	10.3785	0.0005
Determined plutonium in residue	c	0.005	0.001
Weight of flask plus plutonium nitrate solution, g	W_4	450.623	0.002
Weight of flask, g	W_3	120.387	0.002

The WCTM is to be used solely at the laboratory where prepared, therefore no air buoyancy correction is required for the plutonium nitrate solution weight.

Calculate the makeup value A and associated standard deviation S_A.

$$A = \frac{\left[(F)\ (b)\ (W_2 - W_1)\right] - c}{W_4 - W_3}$$

$$= \frac{\left[(0.9997)\ (0.99992)\ (50.2798 - 10.3785)\right] - 0.005}{450.623 - 120.387}$$

$$= 0.12077 \quad .$$

$$S_A \approx \frac{1}{W_4 - W_3}\left[b^2 \left\{F^2 \left(S^2_{W_1} + S^2_{W_2}\right) + \left(W_2 - W_1\right)^2 S^2_F\right\} + S^2_c + A^2 \left(S^2_{W_3} + S^2_{W_4}\right)\right]^{\frac{1}{2}}$$

$$\approx \frac{1}{450.623 - 120.387}\left[(0.99992)^2 \left\{(0.9997)^2 (0.0005^2 + 0.0005^2) + (50.2798 - 10.3785)^2 (0.0004)^2\right\} + (0.001)^2 + (0.12077)^2 (0.002^2 + 0.002^2)\right]^{\frac{1}{2}}$$

$$\approx 0.00005 \quad .$$

4. T Test of Makeup Value and Analysis-Based Mean (Sec. 6.3.3)

Calculate the approximate variances and degrees of freedom for $\bar{X}_2$.

$$V_2 \approx \bar{X}_2^2 \left(\frac{S_1^2}{n_1 M_1^2} + \frac{S_2^2}{n_2 M_2^2} \right)$$

$$\approx (0.12076)^2 \left(\frac{(0.000043)^2}{5\ (0.119876)^2} + \frac{(0.000037)^2}{5\ (0.120632)^2} \right)$$

$$\approx (6.4966 \times 10^{-10} \quad .$$

$$f_2 \approx \frac{V_2^2}{\dfrac{\left(\dfrac{\bar{X}_2^2\ S_1^2}{n_1 M_1^2}\right)^2}{n_1 - 1} + \dfrac{\left(\dfrac{\bar{X}_2^2\ S_2^2}{n_2 M_2^2}\right)^2}{n_2 - 1}}$$

$$\approx \frac{\left(6.4966 \times 10^{-10}\right)^2}{\dfrac{\left(\dfrac{(0.12076)^2\ (0.000043)^2}{5\ (0.119876)^2}\right)^2}{4} + \dfrac{\left(\dfrac{(0.12076)^2\ (0.000037)^2}{5\ (0.120632)^2}\right)^2}{4}}$$

$$\approx 7.8, \text{ or } 8$$

Compute the T statistic.

$$T = \frac{|\ \bar{X}_2 - A\ |}{\sqrt{S_A^2 + V_2}}$$

$$= \frac{|0.12076 - 0.12077\ |}{\sqrt{(0.00005)^2 + 6.4966 \times 10^{-10}}}$$

$$= 0,18$$

Find, in a t table,

$t\ (1 - \alpha/2,\ f) = t\ (0.975,\ 8) = 2.306$.

Because $T = 0.18 < t\ (1 - \alpha/2, f) = 2.306$, conclude that the makeup value and the determined mean are not different.

5. Assignment of WCTM Value (Sec. 6.3.4)

The makeup value 0.12077 is assigned.

Calculate the LE and RLE.

$$\begin{aligned} LE &= 2\,S_A \\ &= 2(0.00005) \\ &= 0.00010\ . \\ RLE &= 100\ LE/A \\ &= (100)\ 0.00010/0.12077 \\ &= 0.083\%\ . \end{aligned}$$

Establish whether the LE or RLE meets the requirement of ≤1/3 the LE or RLE associated with the plant material.

From (a), required RLE = 0.167%.

Hence, RLE of WCTM meets the requirements.

C. TESTS FOR PLUTONIUM ISOTOPIC DISTRIBUTION

A WCTM, prepared from a plant plutonium nitrate, is to be characterized for plutonium isotopic distribution. This example is presented for the ^{239}Pu value. The RLE assigned to the stream is 0.40%. The WCTM is analyzed by the producing laboratory and an independent laboratory by thermal ionization mass spectrometry.

1. Estimated Number of Replicate Analyses of the WCTM and Concurrently Analyzed PRCTM (Sec. 5.4)

Required RLE of WCTM is

≤ 1/3 of RLE of plant process stream
≤ 1/3 (0.40%) = 0.133% .

The estimated precision, as RSD_i, of the measurement is 0.03%.
Estimated number of replicate analyses is

$$n \approx 4(RSD_i)^2/RLE^2$$
$$n \approx 4(0.03)^2/(0.133)^2 \approx 0.2\ .$$

Because this number is less than the specified minimum of 5, five replicate aliquots each of the WCTM and of the PRCTM are analyzed.

The PRCTM is prepared using NBS SRM 946, and impurity elements are added to the analyzed aliquots before the ion exchange separation) to simulate the composition of the

WCTM. The certified value (R) of the ^{239}Pu isotopic abundance, corrected for radioactive decay of the various plutonium isotopes to the day analyzed (Sec. 6.5), is 83.539 at.%. The obtained results by both laboratories are tabulated in Table A-I.

TABLE A-I

TABULATION OF ISOTOPIC DISTRIBUTION RESULTS

Laboratory	Material	Pu Isotopic Abundance (at.%) 238	 239	 240	 241	 242
Producing	PRCTM	0.256	83.530	12.160	3.474	0.580
		0.257	83.517	12.165	3.480	0.581
		0.257	83.490	12.187	3.486	0.580
		0.256	83.501	12.189	3.474	0.580
		0.258	83.504	12.181	3.478	0.579
Producing	WCTM	0.105	83.914	13.800	1.968	0.213
		0.103	83.897	13.820	1.972	0.208
		0.110	83.884	13.821	1.976	0.209
		0.107	83.937	13.780	1.959	0.217
		0.107	83.889	13.830	1.958	0.215
Independent	PRCTM	0.243	83.551	12.173	3.463	0.570
		0.246	83.550	12.162	3.472	0.570
		0.247	83.568	12.159	3.460	0.566
		0.246	83.571	12.139	3.469	0.575
		0.251	83.553	12.170	3.454	0.572
Independent	WCTM	0.107	83.929	13.788	1.967	0.209
		0.104	83.918	13.800	1.970	0.208
		0.106	83.914	13.794	1.970	0.216
		0.100	83.907	13.806	1.971	0.216
		0.106	83.930	13.784	1.964	0.216
NBS Values	PRCTM	0.247	83.539	12.175	3.464	0.575

Note: All isotopic data results are given. However, this example is calculated only for the ^{239}Pu data.

2. Calculated Means and Standard Deviations (Sec. 6.1)

Calculate the means (M) and associated standard deviations (S) by

$$M = \Sigma X/n$$

$$S = \sqrt{\Sigma(X_i - M)^2/n - 1}\ .$$

The values, for ^{239}Pu atom % abundance, are

	M	S
Producing Laboratory		
PRCTM	$M_1 = 83.509$	$S_1 = 0.015$
WCTM	$M_2 = 83.904$	$S_2 = 0.022$
Independent Laboratory		
PRCTM	$M_3 = 83.559$	$S_3 = 0.010$
WCTM	$M_4 = 83.920$	$S_4 = 0.010$

3. F-Tests of Precision (Sec. 6.2.1)

Calculate the F ratios for both sets of data and compare to tabulated F values.

Producing Laboratory

$F = S_1^2/S_2^2 = 0.015^2/0.22^2 = 0.46$

$F\,(1 - \alpha/2, n_1 - 1, n_2 - 1)$ or $F\,(0.975, 4, 4) = 9.6$

$1/F\,(1 - \alpha/2, n_2 - 1, n_1 - 1)$ or $1/F\,(0.975, 4, 4) = 1/9.6 = 0.104$.

Because $0.46 < 9.6$ and $0.46 > 0.104$, precisions are not different.

Independent Laboratory

$F = S_3^2/S_4^2 = 0.010/0.010 = 1.0$.

Again, because $1.0 < 9.6$ and $1.0 > 0.104$, precisions are not different.

4. Calculation of WCTM Means Based on PRCTM (Sec. 6.2.2)

Calculate the two WCTM means.

$\bar{X}_2 = M_2(R/M_1) = 83.904\,(83.539/83.509) = 83.934$

$\bar{X}_4 = M_4(R/M_3) = 83.920(83.539/83.559) = 83.900$.

5. T Tests of Means (Sec. 6.2.3)

Calculate the approximate variances and degrees of freedom for both means.

$$V_2 \approx \bar{x}_2^2 \left(\frac{S_1^2}{n_1 M_1^2} + \frac{S_2^2}{n_2 M_2^2} \right)$$

$$\approx (83.934)^2 \left(\frac{(0.015)^2}{5(83.509)^2} + \frac{(0.022)^2}{5(83.904)^2} \right)$$

$$\approx 1.4233 \times 10^{-4} \quad .$$

$$f_2 \approx \frac{V_2^2}{\dfrac{\left(\dfrac{\bar{X}_2^2\ S_1^2}{n_1 M_1^2}\right)^2}{n_1 - 1} + \dfrac{\left(\dfrac{\bar{X}_2^2\ S_2^2}{n_2 M_2^2}\right)^2}{n_2 - 1}}$$

$$\approx \frac{\left(1.4233 \times 10^{-4}\right)^2}{\dfrac{\left(\dfrac{(83.934)^2\ (0.015)^2}{5(83.509)^2}\right)^2}{4} + \dfrac{\left(\dfrac{(83.934)^2\ (0.022)^2}{5(83.904)^2}\right)^2}{4}}$$

$$\approx 7.1 \quad .$$

$$V_4 \approx \bar{X}_4^2 \left(\frac{S_3^2}{n_3 M_3^2} + \frac{S_4^2}{n_4 M_4^2}\right)$$

$$\approx (83.900)^2 \left(\frac{(0.010)^2}{5(83.559)^2} + \frac{(0.010)^2}{5(83.920)^2}\right)$$

$$\approx 4.0154 \times 10^{-5} \quad .$$

$$f_4 \approx \frac{V_4^2}{\dfrac{\left(\dfrac{\bar{X}_4^2\ S_3^2}{n_3 M_3^2}\right)^2}{n_3 - 1} + \dfrac{\left(\dfrac{\bar{X}_4^2\ S_4^2}{n_4 M_4^2}\right)^2}{n_4 - 1}}$$

$$\approx \frac{\left(4.0154 \times 10^{-5}\right)^2}{\dfrac{\left(\dfrac{(83.900)^2\ (0.010)^2}{5(83.559)^2}\right)^2}{4} + \dfrac{\left(\dfrac{(83.900)^2\ (0.010)^2}{5(83.920)^2}\right)^2}{4}}$$

$$\approx 8.0$$

Compute the T statistic,

$$T = \frac{|\ \bar{X}_2 - \bar{X}_4\ |}{\sqrt{V_2 + V_4}} \quad ,$$

with f degrees of freedom in which

$$T = \frac{\left| 83.934 - 83.900 \right|}{\sqrt{1.4233 \times 10^{-4} + 4.0154 \times 10^{-5}}}$$

$$= 2.52$$

$$f \approx \frac{\left(V_2 + V_4\right)^2}{\frac{\left(\frac{\bar{X}_2^2 S_1^2}{n_1 M_1^2}\right)^2}{n_1 - 1} + \frac{\left(\frac{\bar{X}_2^2 S_2^2}{n_2 M_2^2}\right)^2}{n_2 - 1} + \frac{\left(\frac{\bar{X}_4^2 S_3^2}{n_3 M_3^2}\right)^2}{n_3 - 1} + \frac{\left(\frac{\bar{X}_4^2 S_4^2}{n_3 M_4^2}\right)^2}{n_4 - 1}}$$

$$f \approx \frac{\left(1.4233 \times 10^{-4} + 4.0154 \times 10^{-5}\right)^2}{\frac{\left(\frac{(83.934)^2 \ (0.015)^2}{5(83.509)^2}\right)^2}{4} + \frac{\left(\frac{(83.934)^2 \ (0.022)^2}{5(83.904)^2}\right)^2}{4} + \frac{\left(\frac{(83.900)^2 \ (0.010)^2}{5(83.559)^2}\right)^2}{4} + \frac{\left(\frac{(83.900)^2 \ (0.010)^2}{5(83.920)^2}\right)^2}{4}}$$

$\approx$ 10.9, or 11 rounded to nearest integer.

Find, in a t table,

$t\,(1 - \alpha/2, f) = t\,(0.975, 11) = 2.201$.

Because $T = 2.52 > t\,(1 - \alpha/2,\ f) = 2.20$, conclude that the two means are different.

6. Assignment of WCTM Value

Because the two means are different, no value can be assigned to the WCTM.

The source of the difference must be established and one or both laboratories should repeat the measurements. Then the statistical tests must be applied to establish whether a value can be assigned. If this is not done, the WCTM must be rejected.