NUREG/CR-0061
LA-7260
c.3

Preparation of Working Calibration and Test Materials: Plutonium Oxide

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545

NUREG/CR-0061
LA-7260
RS

Preparation of Working Calibration and Test Materials: Plutonium Oxide

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

*Hanford Engineering Development Laboratory, Westinghouse Hanford Company,
P.O. Box 1970, Richland, WA 99352.

Manuscript submitted: April 1978
Date published: August 1978

Prepared for
Office of Standards Development
US Nuclear Regulatory Commission
Washington, DC 20555

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

FOREWORD

This report provides guidance for preparing plutonium oxide working calibration and test materials. These materials are used to calibrate and to maintain quality control surveillance of chemical methods of analysis for plutonium content and isotopic distribution measurements. Similar reports have been issued for plutonium nitrate solution (LA-NUREG-6384, NUREG-0118), uranium nitrate solution (NUREG-0253), and mixed oxide (LA-7322, NUREG/CR-0139). Reports are also planned for other plutonium and uranium materials.

CONTENTS

PREPARATION OF WORKING CALIBRATION AND TEST MATERIALS: PLUTONIUM OXIDE

by

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

ABSTRACT

Procedures are presented for preparing plutonium oxide with assigned values of plutonium content and isotopic distribution. This material is used to calibrate and maintain quality control surveillance of chemical methods for the analysis of nuclear, fuel-cycle plutonium oxide. Detailed statistical treatments are included that give a reliability measure of the prepared material for application to nuclear material accountability and safeguards.

1. INTRODUCTION

Plutonium oxide is a major product-type material in the nuclear fuel cycle. Accurate and precise determinations of the content and isotopic abundance of plutonium in plutonium oxide are essential to accountability and safeguards. Well-characterized materials must be used, therefore, for the calibration and quality control surveillance of the analysis methods. This report is one of a series,[*, 1-3] prepared at the request of the Office of Standards Development of the Nuclear Regulatory Commission, that describes the preparation of materials defined as working calibration and test materials (WCTM) to be used to calibrate uranium and plutonium content and isotopic methods of analysis. Discussed are the chemical preparative procedures designed to produce stable plutonium oxide WCTMs, the establishment of their plutonium content and isotopic distribution values, and their packaging.

2. GENERAL CONSIDERATIONS GOVERNING THE PREPARATION OF A SOLID URANIUM OR PLUTONIUM WCTM

A WCTM must be prepared so that the values of uranium or plutonium content and the 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, in turn, related to a PRCTM. Table I lists the calibration and test materials (CTM) 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 (Refs. 1-3).

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.	New Brunswick Laboratory SRCTMs. International Atomic Energy Agency (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 reliability, are RCTM (first PRCTM, then SRCTM) and WCTM. Other important characteristics of a WCTM are stability, chemical similarity to a process material, and reliability of the assigned content and isotopic values consistent with the reliabilities required of the analysis methods to which it pertains. To some degree, these characteristics are interrelated. A process material such as low-temperature calcined plutonium oxide sorbs moisture and other atmospheric components; therefore, it would be a reliable WCTM for only short periods of use. Because stability and reliability are paramount characteristics of a WCTM, chemical similarity to a process material may have to be compromised.

An ideal WCTM for plutonium content purposes would be an RCTM with its certified values of plutonium content, if its chemical composition, including metal and nonmetal impurities, matched that of the process material and if it were available in large quantities at reasonable cost. Neither of these provisions is met by currently available RCTMs. The National Bureau of Standards (NBS) provides six plutonium RCTMs, designated by NBS as standard reference materials (SRM),[4] shown in Table II. The first three, two plutonium metals and plutonium sulfate, are certified for plutonium content with SRM 945 having least reliability because it is intended as a matrix material for preparing impurity reference materials. The last three SRMs listed are certified only for isotopic distribution. Although the three SRMs certified for plutonium content can be converted to the chemical form of a WCTM, such as plutonium oxide, they are highly pure and the impurities in the produced WCTM rarely would match that of a

TABLE II

NBS PLUTONIUM STANDARD REFERENCE MATERIALS

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

[a] Element weight.

plant material. More importantly, their low supply (as reflected by high cost) limits their use to the calibration of the methods used to characterize WCTMs.

The range of the isotopic distribution values of the three SRMs (946, 947, and 948) certified for isotopic distribution covers most plutonium materials currently encountered in the nuclear fuel cycle. Their limited supply (and high cost) does not deter their use as isotopic distribution WCTMs because the technique of thermal ionization mass spectrometry, used world-wide, requires 1 μg or less of plutonium per analysis. Many laboratories find it practical to use separate WCTMs for content and isotopic distribution measurements, with SRMs 946, 947, and 948 serving the latter purpose. We subscribe to this practice. When this is not done, an independent isotopic distribution analysis of the WCTM by a second laboratory is recommended.

For reasons discussed above, a WCTM for plutonium content use should, at this time, be prepared using a starting material other than an RCTM. Several modes of chemical analysis apply to establish the plutonium content, depending on the starting material and the preparation process. In general, two plutonium content measurements that agree are required. One measurement can have a calculated value when the WCTM is prepared by using a weighed quantity of a characterized starting material under complete recovery conditions. This computed value is termed the *makeup* value. When the value is not computed, the plutonium content of the WCTM shall be established by one laboratory using two different analytical methods or by two laboratories using the same or different methods.

As stated previously, WCTMs must be prepared so that their uranium and plutonium content and isotopic distribution values are related directly to PRCTMs or to SRCTMs (which, in turn, are related to PRCTMs). This requirement is achieved by using PRCTMs (or PRCTM-related SRCTMs) to calibrate the methods used to analyze starting materials and WCTMs. These calibrations shall be concurrent with the analysis of the starting material or WCTM; and the number of replicate measurements of the RCTM and of the starting material or WCTM shall be equal. The RCTM for content characterization normally is a solution prepared on a weight basis using weights traceable to NBS mass references. Its chemical composition shall simulate that of the starting material or WCTM with respect to uranium or plutonium content and impurity element concentrations. Adding impurity elements to an RCTM solution can affect its stability adversely. A recommended alternative is to add an impurity solution aliquot to each individually delivered RCTM aliquot at the time of the analysis.

Important considerations governing the selection of methods used to determine uranium and plutonium contents of starting materials and WCTMs are high precision capability and freedom from impurity effects. The first is important because the required number of replicate measurements lessens as the method precision improves. Freedom from impurity effects minimizes inaccuracy. When two methods are used for the characterization, their impurity effects should be different to decrease inaccuracy that can be caused by less-than-detected impurities and by slight differences in the impurity element composition of the RCTM and that of a starting material or WCTM.

A major operation in a WCTM preparation is statistical treatment of the characterization analysis results. The statistical treatments vary depending on the starting material's reliability and the characterization analysis options. Section 5 discusses the statistical treatments as they apply to the plutonium oxide WCTM and the Appendix presents calculations for typical examples.

3. PLUTONIUM OXIDE WCTM PREPARATION

Two preparations are described. One uses plutonium metal and the other uses plant-produced plutonium oxide as a starting material. Plutonium metal is dissolved in hydrochloric acid, a solution of impurities is added, the mixture is evaporated, and the residue is calcined at 900°C to constant weight. The operations are simple, designed for complete recovery so that a makeup value is calculable when characterized plutonium metal is used. Plant plutonium oxide, often low-fired at ~500°C, is calcined to constant weight at 900°C. A calcining temperature of 900°C produces plutonium oxide that does not readily sorb atmospheric moisture and, important to WCTM usage, any sorbed moisture is evolved by reheating. The produced plutonium oxide is sieved and ground to promote homogeneous distribution of plutonium and impurities so that subsamples are representative. General aspects of these two preparations are summarized in Table III and Fig. 1. Included are the various options that apply to establish the plutonium content value as discussed in Sec. 2.

In the preparation in which the starting material is plutonium metal, plutonium chloride is calcined to plutonium oxide. Most plant plutonium oxide is produced by calcining plutonium oxalate. However, plutonium oxalate is not a stoichiometric compound and a makeup value is not calculable for plutonium oxide produced from it. Many plutonium salts, including chloride, nitrate, sulfate, fluoride, and oxalate, calcine to plutonium oxide.[5,6] Its appearance and some properties, such as particle size and acid dissolution rate, differ for the various salts, and as a function of calcining temperature. For use as a WCTM for plutonium content (and isotopic measurements), plutonium oxide produced at 900°C from the metal or any of its salts is considered to apply to plant plutonium oxide.

The preparation of a plutonium oxide WCTM by direct calcination of plutonium metal or a compound is not recommended. It is most unlikely that the impurity contents would match closely those of a plant plutonium oxide. Also, blending a pure plutonium oxide with metal and nonmetal impurities is not recommended. It is difficult to attain complete recovery, which is necessary to calculate a makeup value, and a large effort is required to attain homogeneity.

The preparations are written in a style intended for use by experienced analysts. All chemicals shall be at least American Chemical Society (ACS) reagent grade. Water shall be distilled or

TABLE III

PREPARATION OF PLUTONIUM OXIDE WCTM CHARACTERIZED FOR PLUTONIUM CONTENT

Starting Material	Starting Material Characterization	WCTM Preparation	WCTM Characterization
≥99.95% pure Pu metal	Two methods or one method and calculated purity based on complete impurity analysis	Dissolution with HCl, addition of impurities, evaporation, and calcination to constant weight at 900°C	Two methods or, if starting material characterized and if prepared under complete recovery conditions, one method and use of makeup value
<99.95% pure Pu metal	Two methods	As above	As above
Plant Pu oxide	Not applicable	Calcine if low-fired material	Two methods

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 at least 4 h, rinsed thoroughly in distilled or deionized water, and dried. All volumetric glassware shall be calibrated according to NBS Circular 602. All weights shall be traceable to NBS certified weights as described in NBS Circular 547, Sec. 1.

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

3.1. Plutonium Metal As Starting Material

This WCTM preparation is written for conditions of complete recovery so that a makeup value is calculable. If a makeup value is not to be used, the starting material and container used for calcination need not be weighed and quantitative recoveries during dissolution, evaporation, and calcination are unnecessary. The preparation is written for 25 g of starting material. Larger amounts can be processed using scaled-up apparatus. It applies to other starting materials using appropriate dissolutions.

Either quartz or platinum is recommended as the container material for the calcination. Both are resistant to hydrochloric acid and maintain constant weight at 900°C. Because a quartz container can chip, it must be handled carefully when a WCTM having a makeup value is prepared. For dissolution of the plutonium metal, a quartz Erlenmeyer flask is recommended. An advantage is that it can serve as the container for the calcination thereby avoiding a transfer of the dissolved plutonium solution.

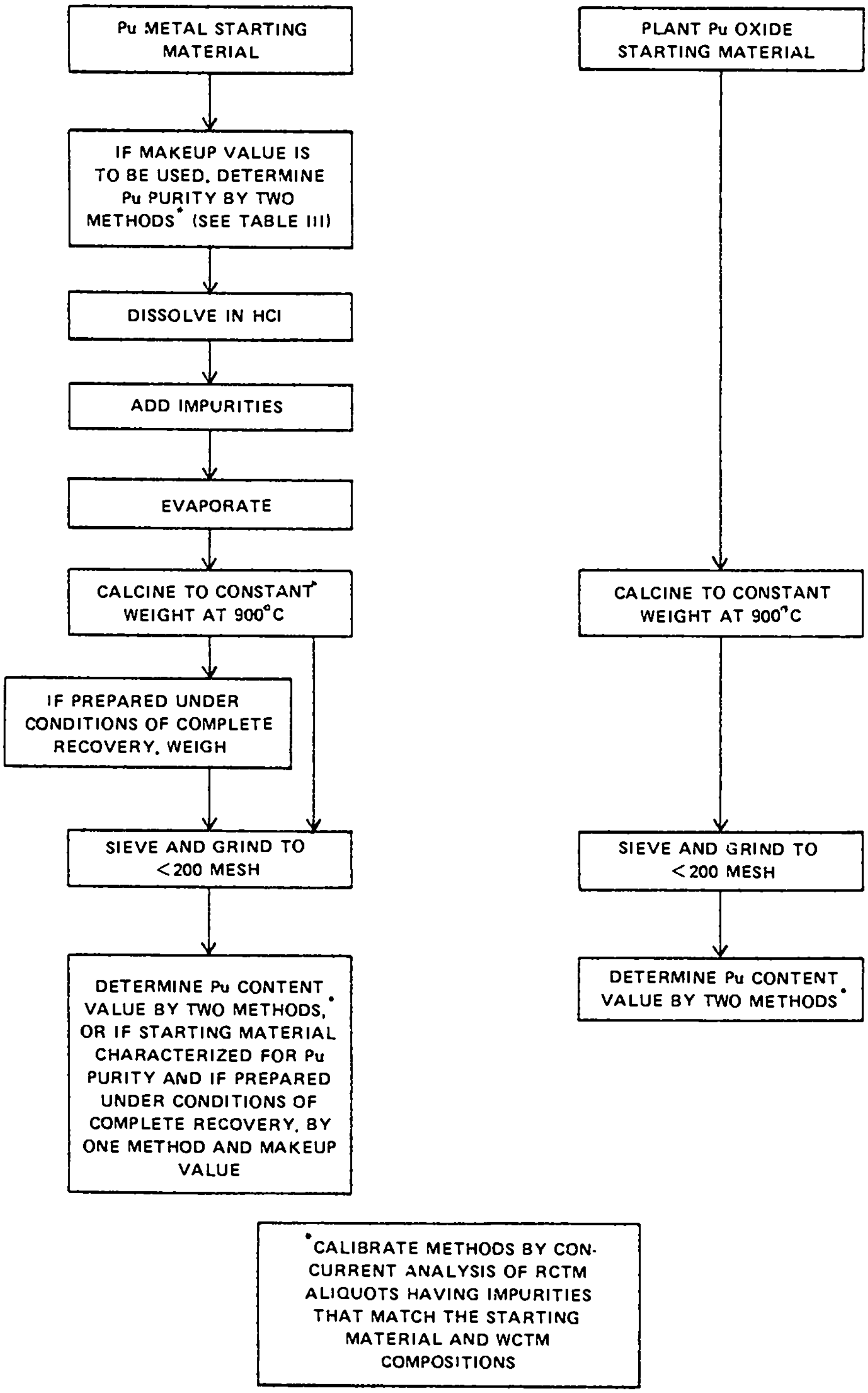

Fig. 1.
General operations of preparing a plutonium oxide WCTM characterized for plutonium content.

a. Reagents

HCl, 6*M*. Use HCl distilled in quartz apparatus so that impurities uncharacteristic of plant plutonium oxide are not introduced.

b. Apparatus

1. Balance, analytical, sensitivity of 0.1 mg.
2. Erlenmeyer flask, quartz, 200-ml, with quartz cover.
3. File, metal.
4. Funnel, Teflon, to fit in Erlenmeyer flask to prevent spattering loss.
5. Furnace, muffle.
6. Hot plate.
7. Ice baths, two, one for cooling the Erlenmeyer flask during dissolution of the plutonium metal, the other for precooling the 6*M* HCl. (If a WCTM is being prepared to have a makeup value, the ice used for cooling the Erlenmeyer flask should be prepared from distilled or deionized water to avoid a weight change caused by deposition of impurities on the flask.)
8. Platinum dish, ~200-ml, with platinum or quartz cover.

c. Procedure

Notes:

i. After the plutonium dissolves, add impurities that match those in plant plutonium oxide. Metals are more important because they tend to affect plutonium analytical methods. Common nonmetals, such as carbon, chloride, fluoride, nitrogen, and sulfur, mostly volatilize at 900°C. Phosphorus, which does not volatilize and which affects most plutonium methods, should be added. The impurities are conveniently added as a hydrochloric acid solution.

ii. In steps 1, 2, and 3, a quartz Erlenmeyer flask is heated to constant weight at 900°C. This is necessary only when a makeup value is to be calculated.

iii. When a platinum dish is used as the calcining container for a WCTM being prepared with a makeup value, heat it and its cover at 900°C to constant weight before transferring the plutonium solution to it (step 10).

iv. All weighings are made at the balance sensitivity of 0.1 mg.

1. Heat the quartz Erlenmeyer flask at 900°C for 16 h.
2. Cool the flask in a desiccator to ambient temperature and weigh.
3. Repeat steps 1 and 2, except decrease the heating period from 16 to 4 h, until consecutive weights agree to within 2 mg. This uncertainty, for 28 g of plutonium oxide prepared from 25 g of plutonium metal starting material, corresponds to a relative uncertainty of about 0.01%. Use the average of the two agreeing weights.
4. Clean the plutonium metal with a new metal file until its entire surface is shiny.
5. Transfer 25 g of the cleaned metal to the tared flask and weigh. Record the temperature and pressure for a buoyancy correction calculation.
6. Place the flask with metal in the ice bath containing ice made from distilled water.
7. Cool 100 ml of 6*M* HCl in the other ice bath for at least 10 min, transfer 50 ml to the flask, and immediately place the funnel in the flask. The plutonium metal must be submerged completely; if not, add more 6*M* HCl.

8. As the reaction subsides, add cooled 6*M* HCl through the funnel to maintain a moderate dissolution rate. The flask may be removed from the ice bath as necessary to maintain dissolution. All 100 ml of cooled 6*M* HCl should be added to provide a final acid normality >2 for 25 g of plutonium metal dissolved.

9. After several hours, inspect the solution for undissolved residue. If present, heat the solution moderately. Complete dissolution is necessary. Otherwise, the calcined plutonium oxide will be heterogeneous.

10. Add the impurity solution followed by 6*M* HCl rinses unless a platinum dish is to be the calcining container. If so, quantitatively transfer the plutonium solution to the platinum dish using 6*M* HCl rinses. Then add the impurity solution to the dish.

11. Slowly evaporate the solution mixture to dryness. To prevent loss by spattering, leave the funnel in the flask or place the cover on the platinum dish along with beaker hooks.

12. If plutonium has deposited on the funnel or cover, as determined by alpha particle counting, rinse off the plutonium with 6*M* HCl into the flask or dish. Again evaporate slowly to dryness.

13. Repeat step 12 as necessary. Cautiously increase heat after the final evaporation until all moisture is evolved; otherwise spattering may occur during calcination.

14. Place the flask with a quartz cover, or the dish with its cover but without the beaker hooks, in an unheated muffle furnace.

15. Gradually increase the temperature, taking about 4 h to reach 125°C to prevent spatter, then increase the temperature to 900°C and heat for 16 h.

16. Remove the cover and inspect it for spattered residue. If present, scrape the residue into the flask or dish.

17. Cool the flask or dish in a desiccator to ambient temperature and weigh.

18. Repeat steps 15, 16, and 17, except decrease the heating period from 16 to 4 h, until consecutive weights agree to within a value that provides an uncertainty in the makeup value consistent with the precision required of the WCTM (see Sec. 4.3). Again, an uncertainty of 2 mg for 28 g of plutonium oxide corresponds to a relative uncertainty of about 0.01%. Use the average of the two agreeing weights.

19. Proceed to Sec. 3.3 for sieving and grinding operations.

3.2. Plant Plutonium Oxide As Starting Material

The batch selected should be typical of the plant process and have been produced from a single lot of plutonium oxalate or other intermediate material. A mixture of several batches may have heterogeneous plutonium content and isotopic distributions. Even if the batch selected had been produced at ≥900°C, it shall be heated to constant weight at 900°C to remove any sorbed water.

a. Apparatus

1. Balance, analytical, sensitivity of 0.1 mg.
2. Container, platinum or quartz, size commensurate with quantity of material to be ignited. The depth of material should not exceed 2 cm.
3. Furnace, muffle.

b. Procedure

Note: All weighings are made at the balance sensitivity of 0.1 mg.

1. Heat a platinum or quartz container at 900°C for 16 h.
2. Cool the container in a desiccator and weigh it.
3. Repeat steps 1 and 2, except decrease the heating period from 16 to 4 h, until consecutive weights agree to within 0.01% of the weight of material to be heated.
4. Transfer the material to the container.
5. Place the container in an unheated muffle furnace.
6. Gradually increase the temperature, taking about 2 h to reach 125°C; then increase the temperature to 900°C and heat for 16 h.
7. Cool the container in a desiccator to ambient temperature and weigh it.
8. Repeat steps 7 and 8 until consecutive weights agree to within 0.01% of the weight of material.
9. Proceed to Sec. 3.3 for sieving and grinding operations.

3.3. Sieving and Grinding Calcined Plutonium Oxide

To enhance homogeneity, the calcined plutonium oxide produced as described in Sec. 3.1 or 3.2 is ground as necessary and sieved through a U.S. standard series 200-mesh screen, and mixed.

a. Apparatus

1. Blender, V-type, or equivalent. Stainless steel shell is recommended. Capacity is commensurate with quantity of plutonium oxide mixed.
2. Mortar and pestle. Boron carbide is recommended.
3. Sieve. U.S. standard 200-mesh. Stainless steel is recommended.

b. Procedure

1. Sieve all the calcined plutonium oxide.
2. Grind the unsieved portion.
3. Resieve the ground portion.
4. Repeat steps 2 and 3 until all the material is sieved.
5. Transfer the sieved material to a blender and mix for at least 2 h.

3.4. Packaging

Soon after its preparation, a prepared WCTM should be distributed into vials to minimize its inadvertent contamination in one container. The quantity per vial is an individual laboratory's decision dependent on the quantity used for analysis. A recommended limit is the quantity required for 10 analyses. Separate packagings of a WCTM characterized for both plutonium content and isotopic distribution measurements is not necessary. Effort is saved by using aliquots from one dissolved portion for both measurements. Packaging of microgram quantities for isotopic distribution measurement is subject to cross-contamination effects.

The type of vial can vary and an inert atmosphere is unnecessary. The 900°C calcined WCTM does not sorb moisture readily. Furthermore, it is characterized and thereafter used for plutonium content measurements on a dried basis after heating. An inexpensive, suitable container is a glass vial with a screw-fit plastic lid. A lead or aluminum foil should be placed in the lid because the usual plastic or cardboard insert will decompose in time and contaminate the WCTM. Packaging in a secondary container that is contamination-free on its outer surface facilitates transfers among laboratory areas.

4. ESTABLISHMENT OF WCTM VALUES

Two criteria, in addition to those presented previously, apply to both characterizing and later using the WCTM for plutonium content measurement. The material is heated to obtain a reproducible dry state. Each dissolved portion is inspected for residue, and, if present, various options apply.

Although 900°C calcining produces plutonium oxide quite stable to moisture sorption, some occurs as a function of relative humidity.[7] For example, 900°C calcined plutonium oxide stored in 85% relative humidity air gained 0.2% weight in two months. Reheating at 110°C for 24 h or 125°C for 7 h restored the original dry weight. Either of these heating conditions or heating at 900°C for 1 h may be used.

The dissolution of 900°C calcined plutonium oxide by acids, including HNO_3 and HF mixtures, at ambient pressure is slow and often incomplete. Pressurized acid reactions at higher temperature, including use of a sealed quartz tube,[8] a sealed reflux tube,[9] and a Teflon-container metal shell,[10] promote complete dissolution. A H_2SO_4 and HNO_3 mixture containing $(NH_4)_2SO_4$ to raise the boiling point has been recommended for dissolving high-fired plutonium oxide.[11] Fusions using molten salts such as sodium bisulfate[12] are also effective.

To establish complete dissolution, each solution is inspected carefully for residue including fine suspension shown by the Tyndall effect. Options that apply if a residue or suspension is present are further dissolution treatment (and reinspection), filtration followed by measurement of the plutonium on the filter, or rejection of this WCTM portion. The filtration shall give complete recovery of the solution and the residue. A recommended filter is a 0.45-μm pore size, acid-resistant plastic membrane, such as Gelman Vinyl Metricel. The plutonium quantity on the filter may be determined nondestructively by gamma counting with a relative standard deviation of $\leq 10\%$. A solution shall not be used for plutonium measurement when the plutonium amount on the filter exceeds 0.1% of that in solution unless this amount is determined by chemical analysis. The plutonium content value is calculated by summing the measured quantities in solution and on the filter.

The above also applies to a WCTM prepared from plutonium oxide being characterized or later used for isotopic distribution measurements.

4.1. Plutonium Content Values

A WCTM prepared using an RCTM as the starting material (not recommended by us for reasons given in Sec. 2), and prepared under conditions designed to give complete recovery, may be characterized for its plutonium content by one method. Statistical tests compare the results to the makeup value. An optional, but less desirable, mode is to characterize the WCTM using two different methods followed by statistical comparisons of the obtained results. This foregoes use of a makeup value which is the justifying reason for using an RCTM as the starting material.

The same options apply to a WCTM prepared using plutonium metal that is not an RCTM, except the plutonium content of the metal must be established by two different methods if a makeup value is computed. When ≥99.95% pure metal 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. There are no options for a WCTM prepared from an uncharacterized starting material, such as plant plutonium oxide. The plutonium content value shall be determined by two different methods followed by appropriate statistical tests of comparison.

As discussed previously, considerations governing the selection of the plutonium methods are high precision capability and freedom from interference effects caused by impurities present in the starting material or WCTM. When two methods are used, their impurity effect behaviors should be as different as is practical.

Each analytical method shall be calibrated at the time a starting material or WCTM is analyzed, using an equal number of aliquots of an RCTM that simulates the WCTM in plutonium and impurity element contents. A suggested practice to attain simulation of impurity elements is to add them as a solution to the delivered aliquots of the RCTM. The results for the starting material or WCTM are computed relative to the concurrent results obtained for the RCTM.

The above requires knowing the impurity contents of a starting material and WCTM. Because metal ions rather than nonmetal ions usually interfere with plutonium methods, techniques that provide a multielemental metal analysis generally are used. Applicable techniques include emission spectrography, spark source mass spectrometry, and x-ray fluorescence.

Methods recommended for analyzing plutonium oxide for accountability purposes are based on controlled potential coulometry and amperometry.[12] These and other electrometric methods are described by Rodden[13] and in an ASTM standard.[14]

4.2. Plutonium Isotopic Distribution Values

The analytical method, thermal ionization mass spectrometry following chemical separation of plutonium, shall be calibrated at the time a WCTM is analyzed using aliquots of an RCTM with an isotopic distribution closest to that of the WCTM. This requirement holds even for an isotopic distribution WCTM prepared from an RCTM because the WCTM may have become contaminated during preparation. As for the assay method calibration, the number of RCTM aliquots analyzed shall equal that of the WCTM. Because the accuracy of the mass spectrometric measurement is affected almost solely by impurity elements having isotopes in the plutonium range, the low-mass impurity elements present in the WCTM may be omitted. Both the WCTM and RCTM aliquots shall undergo the same chemical treatments, just before mass spectrometry measurements, 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[15] or nitric acid[13] media also separate most impurity elements that can affect measurement precision by causing unstable plutonium emission. Low levels of ^{238}Pu, <0.1%, can be determined more accurately by alpha spectrometry.

4.3. Criteria Governing Number of Replicate Analyses

The number of equal aliquots of a starting material or WCTM and of the concurrently analyzed RCTM is selected to produce a desired limit of error (LE)* for the value of the plutonium content or isotopic distribution assigned to the WCTM. This LE is a function of the precision required for the plutonium content 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) to which an LE and relative limit of error (RLE) can be assigned. The LE can be further distributed among the plant materials in an MBA.

The LE to be associated with the plutonium content or isotopic distribution of a WCTM is selected, on an arbitrary basis, to be ≤1/3 of the LE associated with the plant material. As shown later, this selection provides for attaining satisfactory measurement precisions without an unreasonable number of replicate analyses. Using this relationship, the number of replicate analyses of the WCTM and RCTM is calculated as follows.

The RLE associated with the plutonium content or isotopic distribution of the WCTM is

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

in which M is the measured average plutonium content or isotopic distribution

$$\mathrm{LE} = 2\ \mathrm{S_M} \tag{2}$$

$$\mathrm{LE} = 2\ \mathrm{S_1}/\sqrt{\mathrm{n}} \ , \tag{3}$$

in which S_M is the standard deviation of the mean, S_1 is the standard deviation for a single measurement of the analytical method in use in the laboratory preparing the WCTM, and n is the number of replicate aliquots analyzed concurrently for both the WCTM and RCTM.

Combining Eqs. (1) and (3) gives

$$\mathrm{RLE} = 100\ (2\ \mathrm{S_1})/\mathrm{M}\sqrt{\mathrm{n}} \quad , \tag{4}$$

and solving for n,

$$\mathrm{n} = 4\ (100\ \mathrm{S_1/M})^2/\mathrm{RLE}^2 \tag{5}$$

because 100 S_1/M is defined as the relative standard deviation in a percentage for a single measurement (RSD_1).

$$\mathrm{n} = 4\ \mathrm{RSD}_1^2/\mathrm{RLE}^2 \quad . \tag{6}$$

An example will demonstrate how n decreases with improving measurement precision.

Assume that the assigned RLE for the plutonium content of the plutonium oxide in an MBA is 0.45%. The RLE of the plutonium content of the WCTM is ≤(1/3) (0.45%) = ≤0.15%. Two

---

*The LE of an estimator T is defined[16] as twice the standard deviation of T. The relative limit of error (RLE), expressed as a percentage, is 100 LE/T.

methods having predicted RSD$_I$ values of 0.1 and 0.3% are available to establish the plutonium content of the WCTM. The computed values of n are

for RSD$_I$ = 0.1%

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

for RSD$_I$ = 0.3%

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

The advantage of using a more precise method is apparent. One restriction to the number of analyses, again arrived at arbitrarily, is setting the minimum at n = 5. For this example, the plutonium content of the WCTM could be established by analyzing five replicate aliquots each of the WCTM and concurrently analyzed RCTM by the method having a precision of 0.1% RSD$_I$ contrasted to 16 replicate aliquots each by the less precise method.

5. STATISTICAL TESTS AND ASSIGNMENTS OF VALUES TO WCTMs

Statistical tests are given in Secs. 5.2 and 5.3 to compute the assigned value and associated uncertainty for the plutonium content of WCTMs and in Sec. 5.4 for plutonium isotopic distribution. These tests cover the two modes of characterization, one based on two different methods of analysis and the other based on a makeup value and one analysis method.

5.1. Terminology

Three major symbols used are

Symbol	Definition
n	Number of replicate aliquots of the WCTM and the concurrently processed RCTM analyzed by a method for plutonium content or isotopic distribution.
M	Mean (arithmetic average) of n results.
S	Standard deviation for a single result, computed by the standard formula

$$S = \left(\frac{\sum\left(X_i - M\right)^2}{n - 1}\right)^{\frac{1}{2}} ,$$

in which X_i is an individual result, M is the mean, 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	RCTM	one
2	WCTM	one
3	RCTM	two
4	WCTM	two

Therefore, M_2 is the mean plutonium content or isotopic distribution value for a WCTM obtained using method one and S_3 is the computed standard deviation of the results for an RCTM obtained using method two.

In the subsequent sections, many of the statistical tests are reported by Natrella.[17]

5.2. Tests for Two Methods of Analysis

Examples of the tests presented in this section are in Sec. A of the Appendix.

5.2.1. Test of Precisions

This test compares the precision of the results obtained by the same method for the WCTM and the RCTM.

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 RCTM are different.

5. Do the same test for Method 2 for

$F = S_3^2/S_4^2$,

$F\,(1 - \alpha/2,\ n_3 - 1,\ n_4 - 1)$, and

$F\,(1 - \alpha/2,\ n_4 - 1,\ n_3 - 1)$.

This test is somewhat sensitive to normality. An assessment for nonnormality is available[18] that, however, has poor leverage for small populations. A possible chemical cause for a precision difference is a different impurity composition of a WCTM and RCTM, especially impurities that catalytically affect measurement methods for plutonium. Another cause can be the presence of small quantities of hydrolyzed plutonium in one or more analyzed aliquots caused by an insufficient acid concentration at some point in the chemical treatment.

When a significant difference is obtained for one or both methods, the source should be established and, if possible, the methods modified. The WCTM and RCTM then should be reanalyzed. If a significant difference again is obtained, the WCTM shall be rejected.

5.2.2. Calculation of WCTM Mean Value Relative to RCTM

The plutonium content value assigned to the WCTM, related directly to the concurrently analyzed RCTM, is calculated by

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

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

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 defined previously; and R is the plutonium content value of the RCTM, assumed to have insignificant error and, therefore, a constant for statistical calculations.

5.2.3. Test of Equality 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.[19]

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

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

$$V_4 \approx \bar{X}_4^2 \left(\frac{s_3^2}{n_3 M_3^2} \right) + \left(\frac{s_4^2}{n_4 M_4^2} \right) ;$$

$$f_4 \approx \frac{V_4^2}{\left(\bar{X}_4^2 s_3^2 / n_3 M_3^2 \right)^2 / \left(n_3 - 1 \right) + \left(\bar{X}_4^2 s_4^2 / n_4 M_4^2 \right)^2 / \left(n_4 - 1 \right)} .$$

The variance of $(\bar{X}_2 - \bar{X}_4)$ is $(V_2 + V_4)$, for which the associated degrees of freedom are given by[19]

$$f \approx \frac{\left(V_2 + V_4 \right)^2}{\left(V_2^2 / f_2 \right) + \left(V_4^2 / f_4 \right)} .$$

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

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

with f degrees of freedom rounded to the nearest integer. Find, in a t table, $t\,(1 - \alpha/2, f)$. If $T > t\,(1 - \alpha/2, f)$, conclude that the population means differ significantly.

If the population means differ significantly, no value is assignable to the WCTM. Investigate causes including effects of impurities on the two methods. Repeat one or both sets of analyses, as appropriate. If no cause can be established, reject the WCTM.

5.2.4. 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 ≤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 the two means $\bar{X}_2$ and $\bar{X}_4$ by

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

in which

$$W_2 = \frac{\left(1 / V_2 \right)}{\left(1 / V_2 \right) + \left(1 / V_4 \right)} \quad \text{and}$$

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

in which V_2 and V_4 are the variances associated with $\overline{X}_2$ and $\overline{X}_4$ (see Sec. 5.2.3).

Calculate the standard deviation S_A associated with A by the approximation[20]

$$S_A \approx \left[\frac{1}{W}\left\{1 + \frac{4}{f_2} w_2\left(1 - w_2\right) + \frac{4}{f_4} w_4\left(1 - w_4\right)\right\}\right]^{\frac{1}{2}} ,$$

in which

$$W = (1/V_2) + (1/V_4) \quad .$$

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

$$f_A = \frac{1}{\left(w_2^2/f_2\right)+\left(w_4^2/f_4\right)} ,$$

in which f_2 and f_4 are the degrees of freedom associated with V_2 and V_4 (see Sec. 5.2.3).

Calculate the LE and RLE by

$$LE = 2\ S_A \text{ and}$$

$$RLE = 100\ LE/A \quad .$$

Establish whether the LE or RLE meets the requirement of $\leq 1/3$ 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 analysis.

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

$$CI = A \pm S_A\ t(1 - \alpha/2, f_A) \quad .$$

5.3. Tests for Makeup Value and One Method of Analysis

5.3.1. Makeup Value Calculation

This calculation applies to a preparation in which a quartz flask is used both for dissolution of the starting material and for calcination to plutonium oxide. A different calculation applies when separate containers are used for the dissolution and the calcination.[3]

Calculate the makeup value of the WCTM by

$$M = \frac{F\ b\left(W_2 - W_1\right)}{W_3 - W_1} ,$$

in which M = gram plutonium per gram of WCTM; F = fractional plutonium content of starting material; b = air buoyancy correction factor for starting material calculated using physical constants, assumed to have insignificant error and therefore a constant for statistical calculations; W_2 = grams of quartz flask plus starting material; W_1 = grams of quartz flask; and W_3 = grams of quartz flask plus calcined plutonium oxide WCTM.

The air buoyancy correction factor for plutonium metal is 0.99992 using brass weights at sea level. In the above relationship, no air buoyancy correction factor is included for the plutonium oxide weight (denominator). None is needed when the WCTM is used at the laboratory where it is prepared.

The approximate precision, expressed as the variance associated with M, derived by propagation of error is

$$V_M = \frac{b^2}{\left(W_3 - W_1\right)^2} \left\{ \left(W_2 - W_1\right)^2 V_F + F^2 \left[V_{W_2} + \left(\frac{W_2 - W_1}{W_3 - W_1} - 1 \right)^2 V_{W_1} + \left(\frac{W_2 - W_1}{W_3 - W_1} \right)^2 V_{W_3} \right] \right\} ,$$

in which an individual V is the estimated variance associated with the subscripted variable.

The approximate standard deviation is

$$S_M = (V_M)^{1/2} \quad .$$

The degrees of freedom associated with S_M can be approximated by Satterthwaite's formula, as follows.

Using the substitute notation

$$V_M = \left(C_1 V_{W_1}\right) + \left(C_2 V_{W_2}\right) + \left(C_3 V_{W_3}\right) + \left(C_F V_F\right) ,$$

in which

$$C_1 = \frac{b^2 F^2 \left(W_2 - W_3\right)^2}{\left(W_3 - W_1\right)^3}$$

$$C_2 = \frac{b^2 \; F^2}{\left(W_3 - W_1\right)^2}$$

$$C_3 = \frac{b^2 F^2 \left(W_2 - W_1\right)^2}{\left(W_3 - W_1\right)^3}$$

$$C_F = \frac{b^2F^2\left(W_2 - W_1\right)^2}{\left(W_3 - W_1\right)^2} \quad .$$

The approximate degrees of freedom are

$$f_M \approx \frac{\left(V_M\right)^2}{\left(C_1 V_{W_1}\right)^2 / f_1 + \left(C_2 V_{W_2}\right)^2 / f_2 + \left(C_3 V_{W_3}\right)^2 / f_3 + \left(C_F V_F\right)^2 / f_F} \quad ,$$

in which f_1, f_2, f_3, and f_F are the degrees of freedom associated with V_{W_1}, V_{W_2}, V_{W_3}, and V_F, respectively.

Calculate an approximate 95% confidence interval for the makeup value by

$$CI = M \pm S_M \, t \, (1 - \alpha/2, f_M) \quad .$$

Calculate the LE and RLE by

$$LE = 2\, S_M \text{ and}$$

$$RLE = 100\, LE/M \quad .$$

5.3.2. Calculation of Mean Value Based on Results of One Method of Analysis

This calculation is essentially identical to that presented in Sec. 5.2.1.

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

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

3. Find, in an F table,

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

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

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

4. If

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

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

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

As discussed in Sec. 5.2.1, the source of the difference should be established and, if possible, the method modified. Then the WCTM and RCTM should be reanalyzed. If a significant difference again is obtained, the WCTM shall be rejected.

5. Calculate the mean value of the WCTM by

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

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

5.3.3. 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 $\overline{X}_2$, by

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

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

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

$$t = \frac{\left|\bar{X}_2 - M\right|}{\sqrt{V_M + V_2}}\ ,$$

with $f_2 + f_m$ degrees of freedom, rounded to the nearest integer.

Find, in a t table, $t\,(1 - \alpha/2,\ f_2 + f_m)$. If $T > t\,(1 - \alpha/2,\ f_2 + f_m)$, conclude that the population means estimated by M and $\overline{X}_2$ are different.

If the population means estimated by M and $\overline{X}_2$ 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 RCTM 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. 5.2 apply.

5.3.4. Assignment of WCTM Value

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

Calculate the LE and RLE associated with M by

$$LE = 2\ S_M \text{ and}$$

$$RLE = 100\ LE/M \quad .$$

Establish whether the LE or RLE meets the requirement of $\leq 1/3$ 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_M, 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. 5.2. If this alternate approach is not feasible, the WCTM must be rejected.

5.4. Tests Applied to Isotopic Distribution WCTMs

As discussed in Sec. 2, plutonium isotopic distribution usually is determined by one method—thermal ionization mass spectrometry. Thus the statistical treatment given in Sec. 5.3 normally will apply to establishing the isotopic distribution of a WCTM. Should a second laboratory also analyze the WCTM, the statistical treatment given in Sec. 5.2 applies. For most nuclear fuel materials, the isotope of interest for accountability and safeguards measurement purposes is ^{239}Pu. For WCTMs prepared to have an assigned ^{239}Pu abundance, the statistical tests are applied solely to this isotope. When the purpose of the WCTM is other isotopes, the statistical tests should be appropriately applied.

5.5. Correction of Plutonium Content and Isotopic Distribution Values for Radioactive Decay

The plutonium content and isotopic distribution values of RCTMs, WCTMs, and starting materials are corrected for radioactive decay of the various plutonium isotopes. The decays are

Parent	Daughter	Parent Half-Life (yr)	Daughter Formation Rate from Monoisotopic Parent (µg/g per yr)
^{238}Pu	^{234}U	87.8	7860
^{239}Pu	^{235}U	24 390	28
^{240}Pu	^{236}U	6540	106
^{241}Pu	^{241}Am	14.7	46 060
^{242}Pu	^{238}U	387 000	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 an NBS SRM 949 metal.

Pu Isotope	Fractional Atom Abundance	x	Daughter Formation Rate	=	Daughter Formed in First Year (μg/g)
238	0.00003		7860		0.2
239	0.97617		28		27.7
240	0.02324		106		2.5
241	0.00054		46060		24.9
242	0.00002		1.8		0.01
					Total 55.4

The correction increases as the relative quantities of the shorter lived isotopes ^{241}Pu and ^{238}Pu increase. The formation is not constant with time because the relative amounts of the parent isotopes are changing. Reference 21 details the exact calculations and includes a FORTRAN IV program for the computations.

ACKNOWLEDGMENTS

E. G. Selleck, W. B. Brown, and S. P. Turel, US Nuclear Regulatory Commission, provided guidelines and general reviews. Technical reviews and improvements were provided by M. H. Campbell and J. L. Jaech, Exxon Nuclear Company; C. D. Bingham, Department of Energy, New Brunswick Laboratory; and S. F. Marsh, Los Alamos Scientific Laboratory.

REFERENCES

1. S. S. Yamamura, F. W. Spraktes, J. M. Baldwin, R. L. Hand, R. P. Lash, and J. P. Clark, "Preparation of Working Calibration and Test Materials-Uranyl Nitrate Solution," Allied Chemical Corporation Idaho Chemical Programs report NUREG-0253 (May 1977).

2. J. E. Rein, S. F. Marsh, G. C. Swanson, G. R. Waterbury, G. L. Tietjen, and R. K. Zeigler, "Preparation of Working Calibration and Test Materials: Plutonium Nitrate Solution," Los Alamos Scientific Laboratory report LA-NUREG-6348 (January 1977).

3. J. E. Rein, G. L. Tietjen, R. K. Zeigler, and G. R. Waterbury, "Preparation of Working Calibration and Test Materials: Mixed Oxide," Los Alamos Scientific Laboratory report LA-7322 (NUREG/CR-0139). In preparation.

4. "Catalog of NBS Standard Reference Materials," Office of Standard Reference Materials, National Bureau of Standards Special Publication 260 (June 1975).

5. C. F. Metz and G. R. Waterbury, *The Transuranium Actinide Elements*, Treatise on Analytical Chemistry, Part II, Vol. 9, I. M. Kolthoff and P. J. Elving, Eds. (Interscience, New York, 1962).

6. G. R. Waterbury, R. M. Douglass, and C. F. Metz, "Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate, and Oxalate," Anal. Chem. **33**, 1018-1023 (1961).

7. G. R. Waterbury, Compiler, "Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle, Program Status Report June 1972 to June 1973," Los Alamos Scientific Laboratory report LA-5347-SR (August 1973).

8. 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).

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

10. 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).

11. L. M. Angeletti, W. J. Bartscher, and M. J. Maurice, "Controlled Potential Coulometric Determination of Plutonium and Uranium Using a Mercury Pool Electrode," Z. Anal. Chem. **246**, 297 (1969).

12. R. G. Gutmacher, F. Stephens, K. Ernst, J. E. Harrar, J. Magistad, S. P. Turel, and T. E. Shea, "Methods for the Accountability of Plutonium Oxide," US Nuclear Regulatory Commission report, in press.

13. C. J. Rodden, Ed., "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle-Second Edition," US Atomic Energy Commission report TID-7029 (2nd Ed.) (1972).

14. ANSI/ASTM C697-77, "Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear Grade Plutonium Dioxide Powders and Pellets," American Society for Testing and Materials (1977).

15. 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).

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

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

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

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

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

21. 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 (November 1976).

APPENDIX

STATISTICAL TEST EXAMPLES

A. TESTS FOR TWO METHODS OF ANALYSIS

A plutonium-content WCTM is prepared for calibrating and for maintaining quality control surveillance of plant process plutonium oxide. The RLE assigned to the material is 0.25%. The WCTM is prepared using plant plutonium oxide as outlined in Sec. 3.2 and applicable later sections. The two analytical methods used to establish the plutonium content of the WCTM are potentiometry and amperometry, termed Methods 1 and 2, respectively.

1. Estimated Number of Replicate Analyses of the WCTM and Concurrently Analyzed RCTM (Sec. 4.3)

Required RLE of WCTM is

≤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

$\mathrm{RSD}_{i_1} = 0.04\%$ and

$\mathrm{RSD}_{i_2} = 0.06\%$.

Estimated number of replicate analyses is

$n \approx 4\ (\mathrm{RSD}_i)^2/(\mathrm{RLE})^2$

$n_1 \approx 4\ (0.04)^2/(0.083)^2 \approx 0.93$

$n_2 \approx 4\ (0.06)^2/(0.083)^2 \approx 2.09$.

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

2. Analysis Data

The RCTM is prepared using NBS SRM 949 plutonium metal. Impurity elements are added to aliquots of the RCTM to simulate the composition of the WCTM. The calculated amount of plutonium (R) in each RCTM aliquot is 0.10000 g. The WCTM aliquots are heated at 110°C for 24 h before weighing and dissolution. The weight of each WCTM aliquot is 0.11040 g. The solutions are filtered and the amount of plutonium on each filter, determined by gamma counting, is not significantly different from background and is considered as zero. The results for the solutions, in units of gram plutonium, are

Method 1		**Method 2**	
RCTM	**WCTM**	**RCTM**	**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

3. Calculated Means and Standard Deviation (Sec. 5.1)

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

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

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

The values are

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

4. Test of Precisions (Sec. 5.2.1)

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

Method 1

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

$$F\ (1 - \alpha/2\ ,\ n_1 - 1\ ,\ n_2 - 1)\ \text{or}\ F\ (.975\ ,\ 4\ ,\ 4) = 9.6$$

$$1/F\ (1 - \alpha/2\ ,\ n_2 - 1\ ,\ n_1 - 1)\ \text{or}\ 1/F\ (.975\ ,\ 4\ ,\ 4) = \frac{1}{9.6} = 0.104\ .$$

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

Method 2

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

$$F\ (1 - \alpha/2\ ,\ n_3 - 1\ ,\ n_4 - 1)\ \text{or}\ F\ (.975\ ,\ 4\ ,\ 4) = 9.6$$

$$1/F\ (1 - \alpha/2\ ,\ n_4 - 1\ ,\ n_3 - 1)\ \text{or}\ 1/F\ (.975\ ,\ 4\ ,\ 4) = \frac{1}{9.6} = 0.104\ .$$

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

5. Calculation of WCTM Mean Value Relative to RCTM (Sec. 5.2.2)

Calculate the two WCTM means

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

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

The $\overline{X}_2$ and $\overline{X}_4$ values are grams of plutonium in the 0.11040-g aliquots of the WCTM. The calculated values of gram plutonium per gram of WCTM are 0.87865 and 0.87817, respectively.

6. Tests of Equality of Means (Sec. 5.2.3)

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

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

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

$$\approx 9.20047 \text{ x } 10^{-10}$$

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

$$\approx \frac{\left(9.20047 \text{ x } 10^{-10}\right)^2}{\dfrac{\left[(0.097003)^2(0.000045)^2/5(0.10010)^2\right]^2}{4} + \dfrac{\left[(0.097003)^2(0.000052)^2/5(0.09710)^2\right]^2}{4}}$$

$$\approx 7.8$$

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

$$\approx (0.096951)^2 \left(\frac{(0.000045)^2}{5(0.10002)^2} + \frac{(0.000079)^2}{5(0.09697)^2} \right)$$

$$\approx 1.628238 \text{ x } 10^{-9}$$

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

$$\approx \frac{\left(1.628238 \text{ x } 10^{-9}\right)^2}{\dfrac{\left[(0.096951)^2(0.000045)^2/5(0.10002)^2\right]^2}{4} + \dfrac{\left[(0.096951)^2(0.000079)^2/5(0.09697)^2\right]^2}{4}} .$$

$$\approx 6.2 .$$

Compute the t statistic

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

with f degrees of freedom in which

$$t = \frac{|0.097003 - 0.096951|}{\sqrt{9.20047 \times 10^{-10} + 1.628238 \times 10^{-9}}}$$

$$= 1.03$$

$$f \approx \frac{\left(V_2 + V_4\right)^2}{\left(V_2^2 / f_2\right) + \left(V_4^2 / f_4\right)}$$

$$\approx \frac{\left(9.20047 \times 10^{-10} + 1.628238 \times 10^{-9}\right)^2}{\left(9.20047 \times 10^{-10}\right)^2 / 7.8 + \left(1.628238 \times 10^{-9}\right)^2 / 6.2}$$

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

Find, in a t table, t $(1 - \alpha/2,f)$ = t (0.975, 12) = 2.179. Because $t = 1.03 < t\,(1 - \alpha/2,f) = 2.179$, conclude that the two means are not different.

7. Assignment of WCTM Value (Sec. 5.3.4)

Calculate the assigned value A.

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

$$W_2 = \frac{1/V_2}{1/V_2 + 1/V_4} = \frac{1/9.20047 \times 10^{-10}}{1/9.20047 \times 10^{-10} + 1/1.628238 \times 10^{-9}}$$

$$= 0.63895$$

$$W_4 = \frac{1/V_4}{\left(1/V_2 + 1/V_4\right)} = \frac{1/1.628238 \times 10^{-9}}{1/9.20047 \times 10^{-10} + 1/1.628238 \times 10^{-9}}$$

$$= 0.36105$$

$$A = (0.63895)\ (0.097003) + (0.36105)\ (0.96950)$$

$$= 0.096984 \quad .$$

As given in Sec. 5 above, this value is in terms of gram of plutonium per 0.11040 g of the WCTM. The calculated value of gram of plutonium per gram of WCTM is 0.87848.

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

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

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

$$W = \left(\frac{1}{9.20047 \times 10^{-10}} \right) + \left(\frac{1}{1.628238 \times 10^{-9}} \right)$$

$$= 1701061824 \quad .$$

$$S_A \approx \left[\frac{1}{1701061824} \left\{ 1 + \frac{4}{7.8} (0.63895) \ (1 - 0.63895) \right. \right.$$

$$\left. \left. + \frac{4}{6.2} (0.36105) \ (1 - 0.36105) \right\} \right]^{\frac{1}{2}}$$

$$\approx 0.000027293 \quad .$$

In terms of gram of plutonium per gram of WCTM,

$$S_A \approx 0.000027293/0.11040 \approx 0.00024722$$

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

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

$\approx$ 13.63 or 14 rounded to the nearest integer.

Calculate the LE and RLE.

In terms of gram of plutonium per gram of WCTM

$$LE = 2 \ S_A$$

$$= 2 \ (0.00024722)$$

$$= 0.00049444$$

$$\begin{aligned} RLE &= 100\ LE/A \\ &= (100)\ (0.00049444)/(0.87848) \\ &= 0.056\%. \end{aligned}$$

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

From (1), required RLE = 0.083%. Hence, RLE of 0.056% for the WCTM meets the requirement.

Calculate the 95% confidence interval for the assigned value in terms of gram of plutonium per gram of WCTM.

$$CI = A \pm S_A\ t\ (1 - \alpha/2, f_A)$$

$$t\ (1 - \alpha/2, f_A) = t\ (0.05,\ 14) = 2.145$$

$$\begin{aligned} CI &= 0.87848 \pm (0.00024722)\ (2.145) \\ &= 0.87795 \text{ to } 0.87901. \end{aligned}$$

B. TESTS FOR MAKEUP VALUE AND ONE METHOD OF ANALYSIS

A plutonium content WCTM is prepared for calibrating and for maintaining quality control surveillance of plant process plutonium oxide. The RLE assigned to the material is 0.50%. The WCTM is prepared using a high-purity plutonium metal described in Sec. 3.1 and applicable later sections. The plutonium content of the metal was established by a potentiometric titration and by subtracting the total measured impurities from 100% with agreeing results. The method of analysis used to establish the plutonium content of the WCTM is potentiometry.

1. Estimated Number of Replicate Analyses of the WCTM and Concurrently Analyzed RCTM (Sec. 4.3)

Required RLE of WCTM is

$\leq 1/3$ of RLE of plant process stream

$\leq 1/3\ (0.50\%) = 0.167\%.$

Estimated precision, as RSD_I, of method is 0.04%.
Estimated number of replicate analyses is

$$n \approx 4\ (RSD_I)^2/(RLE)^2$$

$$n \approx 4\ (0.04)^2/(0.167)^2 \approx 0.23.$$

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

2. Analysis Data

The RCTM is prepared using NBS 949 metal. Impurity elements are added to aliquots of the RCTM to simulate the compositon of the WCTM. The calculated amount of plutonium (R) in each RCTM aliquot is 0.12000 g. The WCTM aliquots are heated at 110°C for 24 h before weighing and dissolution. The weight of each WCTM aliquot is 0.13760 g. The solutions are filtered and the amount of plutonium on each filter, determined by gamma counting, is not significantly different from background and is considered as zero. The results, in units of gram plutonium, are

RCTM	WCTM
0.11993	0.12055
0.11990	0.12052
0.11985	0.12048
0.11982	0.12058
0.11988	0.12053

3. Calculated Mean and Standard Deviation Based on the Method Results (Sec. 5.3.2)

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

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

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

The values are

RCTM

$M_1 = 0.119876$

$S_1 = 0.000043$

WCTM

$M_2 = 0.120532$

$S_2 = 0.000037$.

4. Test of Precision (Sec. 5.2.1)

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

$F = S_1^2/S_2^2 = (0.00043)^2/(0.000037)^2 = 1.35$

$F\ (1 - \alpha/2,\ n_1 - 1,\ n^2 - 1)$ 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 $1.35 > 0.104$, the precisions are not different.

5. Calculation of WCTM Mean Relative to RCTM (Sec. 5.2.2)

Calculate the WCTM mean.

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

$= 0.120532\ (0.12000/0.119876)$

$= 0.12066$.

The $\overline{X}_2$ value is gram of plutonium in the 0.13760-g aliquots of the WCTM. The calculated value of gram plutonium per gram of WCTM is 0.87689.

6. Makeup Value (Sec. 5.3.1)

The makeup data are

Component	Symbol	Value	S	V	f
Fraction Pu content of starting material	F	0.9997	0.0004	1.6 E-7	6
Air buoyancy correction	b	0.99992	zero	zero	-
Weight of quartz flask plus starting material, g	W_2	50.2798	0.002	4E-6	1
Weight of quartz flask, g	W_1	10.3785	0.002	4E-6	1
Weight of quartz flask plus calcined plutonium oxide WCTM	W_3	55.8266	0.002	4E-6	1

The degrees of freedom, f, of 6 associated with F is based on characterization of the plutonium content of the starting material using two methods, each with four replicate analyses. Each of the three weights, W_1, W_2, and W_3, is the average of duplicates, giving one degree of freedom for each.

The WCTM is to be used solely at the laboratory where prepared; therefore, an air buoyancy correction to its weight is not required.

Calculate the makeup value M, associated standard deviation S_M, and associated degrees of freedom f_M.

$$M = \frac{F\ b\ (W_2 - W_1)}{W_3 - W_1}$$

$$= \frac{(0.9997)\ (0.99992)\ (50.2798 - 10.3785)}{55.8266 - 10.3785}$$

$$= 0.87762\ .$$

This value is in units of gram plutonium per gram of WCTM. The calculated value per 0.13760-g aliquot is 0.12076 g of plutonium.

$$V_M \approx \frac{b^2}{(W_3 - W_1)^2} \left\{ (W_2 - W_1)^2\ V_F + F^2 \left[V_{W_2} + \left(\frac{W_2 - W_1}{W_3 - W_1} - 1 \right)^2 V_{W_1} + \left(\frac{W_2 - W_1}{W_3 - W_1} \right)^2 V_{W_3} \right] \right\}$$

$$\approx \frac{(0.99992)^2}{(55.8266 - 10.3785)^2} \left\{ (50.2798 - 10.3785)^2\ (1.6\ E\text{-}7) + (0.9997)^2 \left[(4\ E\text{-}6) + \left(\frac{50.2798 - 10.3785}{55.8266 - 10.3785} - 1 \right)^2 \left(4\ E\text{-}6\right) + \left(\frac{50.2798 - 10.3785}{55.8266 - 10.3785} \right)^2 \left(4\ E\text{-}6\right) \right] \right\}$$

$$\approx 1.267640\ E\text{-}7\ .$$

$$S_M = (V_M)^{\frac{1}{2}}$$

$$\approx (1.267640\ E\text{-}7)^{\frac{1}{2}}$$

$$\approx 3.564\ E\text{-}4\ .$$

This value is in units of gram plutonium per gram of WCTM. The corresponding value for a 0.13760-g aliquot is 4.90 E-5 g of plutonium.

$$f_M \approx \frac{\left(V_M\right)^2}{\left(C_1\ V_{W_1}\right)^2 / f_1 + \left(C_2\ V_{W_2}\right)^2 / f_2 + \left(C_3\ V_{W_3}\right)^2 / f_3 + \left(C_F\ V_F\right)^2 / f_F}$$

$$C_1 = \frac{b^2F^2\left(\frac{W_2 - W_1}{W_3 - W_1} - 1\right)^2}{\left(W_3 - W_1\right)^2}$$

$$= \frac{(0.99992)^2\ (0.9997)^2\ \left(\frac{50.2798\ -\ 10.3785}{55.8266\ -\ 10.3785} - 1\right)^2}{(55.8266\ -\ 10.3785)^2}$$

$$= 7.2060\ \text{E-6} \quad .$$

$$C_2 = \frac{b^2\ F^2}{(W_3 - W_1)^2} = \frac{(0.99992)^2\ (0.9997)}{(55.8266\ -\ 10.3785)^2} = 4.8377\ \text{E-4} \quad .$$

$$C_3 = \frac{b^2\ F^2\left(W_2 - W_1\right)^2}{\left(W_3 - W_1\right)^4} = \frac{(0.99992)^2\ (0.9997)^2\ (50.2798\ -\ 10.3785)^2}{(55.8266\ -\ 10.3785)^4}$$

$$= 3.7289\ \text{E-4} \quad .$$

$$C_F = \frac{b^2\ F^2\left(W_2 - W_1\right)^2}{\left(W_3 - W_1\right)^2} = \frac{(0.99992)^2\ (0.9997)^2\ (50.2798\ -\ 10.3285)^2}{(55.8266\ -\ 10.3785)^2}$$

$$= 0.7702 \quad .$$

$$f_M \approx \frac{(1.267640\ \text{E-7})^2}{\frac{[(7.2060\ \text{E-6})\ (4\ \text{E-6})]^2}{1} + \frac{[(4.8377\ \text{E-4})\ (4\ \text{E-6})]^2}{1} + \frac{[(3.7289\ \text{E-4})\ (4\ \text{E-6})]^2}{1} + \frac{[(0.7702)\ (1.6\ \text{E-7})]^2}{6}}$$

$$\approx 6.3 \text{ or } 6 \quad .$$

Calculate an approximate 95% confidence interval for the makeup value.

$$CI = M \pm S_M\ t\ (1 - \alpha/2, f_M)$$

$$= 0.87762 \pm (3.5604\ \text{E-4})\ (2.477)$$

$$= 0.87673 \text{ to } 0.87850 \quad .$$

This interval is in units of gram plutonium per gram of WCTM. The corresponding interval for a 0.13760-g aliquot is 0.12063 to 0.12088 g of plutonium.

7. Test of Makeup Value and Analysis-Based Mean (Sec. 5.3.3)

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

$$V_2 \approx \bar{X}_2^2 \left(\frac{s_1^2}{n_1 M_1^2} + \frac{s_2^2}{n_2 M_2^2} \right)$$

$$\approx (0.12066)^2 \left(\frac{(0.000043)^2}{5(0.119876)^2} + \frac{(0.000037)^2}{5(0.120532)^2} \right)$$

$$\approx 6.4903 \times 10^{-10} \quad .$$

$$f_2 \approx \frac{V_2^2}{\left(\bar{X}_2^2 s_1^2 / n_1 M_1^2\right)^2 \Big/ \left(n_1 - 1\right) + \left(\bar{X}_2^2 s_2^2 / n_2 M_2^2\right)^2 \Big/ \left(n_2 - 1\right)}$$

$$\approx \frac{\left(6.4903 \times 10^{-10}\right)^2}{\dfrac{\left(\dfrac{(0.12066)^2 \; (0.000043)^2}{5(0.119876)^2}\right)^2}{4} + \dfrac{\left(\dfrac{(0.12066)^2 \; (0.000037)^2}{5(0.120532)^2}\right)^2}{4}}$$

$$\approx 7.8 \text{ or } 8 \quad .$$

Compute the t statistic.

$$t = \frac{\left|\bar{X}_2 - M\right|}{\sqrt{s_M^2 + V_2}}$$

$$= \frac{\left| 0.12066 - 0.12076 \right|}{\sqrt{(4.90 \times 10^{-5})^2 + 6.4903 \times 10^{-10}}}$$

$$= 1.81 \quad .$$

Find, in a t table, $t(1 - \alpha/2, f_2 + f_m) = t(0.975, 14) = 2.145$. Because $t = 1.81 < t(1 - \alpha/2, f_2 + f_m) = 2.145$, conclude that the makeup value and the determined mean are not different.

8. Assignment of WCTM Value (Sec. 5.3.4)

The makeup value 0.12076 is assigned. This value is in units of gram plutonium per 0.13760-g aliquot.

The makeup value, in units of gram plutonium per gram of WCTM, is 0.87762.

Calculate the LE and RLE.

$$\begin{aligned} \text{LE} &= 2\ S_M \\ &= 2\ (0.0003560) \\ &= 0.000712 \end{aligned}$$

$$\begin{aligned} \text{RLE} &= 100\ \text{LE/M} \\ &= (100)\ 0.000712/0.87762 \\ &= 0.081\% \quad . \end{aligned}$$

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 requirement.

C. TESTS FOR PLUTONIUM ISOTOPIC DISTRIBUTION

A WCTM, prepared from plant plutonium oxide, 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 RCTM (Sec. 4.3)

Required RLE of WCTM is

$\leq 1/3$ of RLE of plant process stream

$\leq 1/3\ (0.40\%) = 0.133\%$.

The estimated precision, as RSD_t, of the measurement is 0.03%.

Estimated number of replicate analyses is

$$n \approx 4\ (\text{RSD}_t)^2/\text{RLE}^2$$

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

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

The RCTM is NBS SRM 946. The certified value (R) of the ^{239}Pu isotopic abundance, corrected for radioactive decay of the various plutonium isotopes to the day analyzed (Sec. 5.5), is 83.539 at.%. The results obtained by both laboratories are tabulated in Table A-I.

2. Calculated Means and Standard Deviations (Sec. 5.1)

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

$$M = \Sigma X/n$$

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

TABLE A-I

TABULATION OF ISOTOPIC DISTRIBUTION RESULTS

		Pu Isotopic Abundance (at.%)				
Laboratory	**Material**	**238**	**239**	**240**	**241**	**242**
Producing	RCTM	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	RCTM	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	RCTM	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.

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

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

3. **Test of Precision (Sec. 5.2.1)**

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

$F = S_1^2/S_2^2 = 0.015^2/0.022^2 = 0.46$

$F\ (1 - \alpha/2,\ n_1 - 1,\ n_2 - 1)$ 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 Mean Value Relative to RCTM (Sec. 5.2.2)**

Calculate the two WCTM means.

$\overline{X}_2 = M_2(R/M_1) = 83.904$

$(83.539/83.509) = 83.934$

$\overline{X}_4 = M_4(R/M_3) = 83.920$

$(83.539/83.559) = 83.900$.

5. Test of Equality of Means (Sec. 5.2.3)

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

$$V_2 \approx \bar{X}_2^2 \left(\frac{s_1^2}{n_1 M_1^2} + \frac{s_2^2}{n_2 M_2^2} \right)$$

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

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

$$f_2 \approx \frac{V_2^2}{\left(\bar{X}_2^2 s_1^2 \big/ n_1 M_1^2\right)^2 \big/ \left(n_1 - 1\right) + \left(\bar{X}_2^2 s_2^2 \big/ n_2 M_2^2\right)^2 \big/ \left(n_2 - 1\right)}$$

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

$$\approx 7.1 \quad .$$

$$V_4 \approx \bar{X}_4^2 \left(\frac{s_3^2}{n_3 M_3^2} + \frac{s_4^2}{n_4 M_4^2} \right)$$

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

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

$$f_4 \approx \frac{V_4^2}{\left(\bar{X}_4^2 s_3^2 \big/ n_3 M_3^2\right)^2 \big/ \left(n_3 - 1\right) + \left(\bar{X}_4^2 s_4^2 \big/ n_4 M_4^2\right)^2 \big/ \left(n_4 - 1\right)}$$

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

$$\approx 8.0 \quad .$$

Compute the t statistic,

$$t = \frac{|\bar{x}_2 - \bar{x}_4|}{\sqrt{v_2 + v_4}}$$

with f degrees of freedom in which

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

$$= 2.52 \quad .$$

$$f \approx \frac{\left(v_2 + v_4\right)^2}{v_2^2 / f_2 + v_4^2 / f_4}$$

$$f \approx \frac{\left(1.4233 \times 10^{-4} + 4.0154 \times 10^{-5}\right)^2}{\left(1.4233 \times 10^{-4}\right)^2 / 7.1 + \left(4.0154 \times 10^{-5}\right)^2 / 8.0}$$

$\approx$ 10.9 or 11 rounded to the 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.

☆U.S. GOVERNMENT PRINTING OFFICE: 1978—777-089/140

Available from
US Nuclear Regulatory Commission
Washington, DC 20555

Available from
National Technical Information Service
Springfield, VA 22161

Microfiche	$ 3.00	126-150	7.25	251-275	10.75	376-400	13.00	501-525	15.25
001-025	4.00	151-175	8.00	276-300	11.00	401-425	13.25	526-550	15.50
026-050	4.50	176-200	9.00	301-325	11.75	426-450	14.00	551-575	16.25
051-075	5.25	201-225	9.25	326-350	12.00	451-475	14.50	576-600	16.50
076-100	6.00	226-250	9.50	351-375	12.50	476-500	15.00	601-up	--[1]
101-125	6.50								

[1]. Add $2.50 for each additional 100-page increment from 601 pages up.