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**PREPARATION OF WORKING  
CALIBRATION AND TEST MATERIALS:  
URANYL NITRATE SOLUTION**

Allied Chemical Corporation  
for  
U. S. Nuclear Regulatory Commission

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TEST MATERIALS - URANYL NITRATE SOLUTION

by

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ABSTRACT

Reliable working calibration and test materials (WCTMs) are essential to a meaningful analytical measurements quality assurance program. This report describes recommended methods for the preparation of uranyl nitrate solution WCTMs for testing analytical methods, for calibrating methods, and for testing personnel. Uranyl nitrate solution WCTMs can be synthesized from characterized starting materials or prepared from typical plant materials by thorough characterization with reference to primary or secondary reference calibration and test materials (PRCTMs or SRCTMs). Recommended starting materials are described along with detailed procedures for (a) preparing several widely-used types of uranyl nitrate solution WCTMs, (b) packaging the WCTMs, (c) analyzing the WCTMs to establish the reference values or to confirm the synthesis, and (d) statistically evaluating the analytical data to assign reference values and to assess the accuracy of the WCTMs.

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## 1.0 INTRODUCTION

Table I identifies and defines the various types of calibration and test materials (CTMs). WCTMs are the lowest members of a three-tier CTM hierarchy which has a primary reference CTM (PRCTM), such as the National Bureau of Standards, standard reference materials (NBSSRMs), at the top, and a secondary reference CTM (SRCIM), such as those issued through New Brunswick Laboratory (NBL), in the middle. WCTMs are materials derived from reference CTMs (RCTMs) or characterized against RCTMs. They are intended for use in the surveillance of analytical methods, and for the training and testing of personnel. In this capacity, WCTMs serve as the basis for inventory statements, for estimation of method precision and bias, and for the determination of the significance of any material imbalance. WCTMs of uniformly high quality are essential if these functions are to be performed in a uniform and meaningful way. WCTMs ideally should satisfy the following requirements: (a) they should be stable over extended storage; (b) they should closely match the materials routinely analyzed; (c) they should be inexpensive and convenient to use; and (d) they should have assigned values that have an uncertainty consistent with their intended usage. These requirements are not always compatible and it is often necessary to compromise on the final characteristics of a WCTM giving foremost consideration to the required accuracy. In addition, WCTMs must be clearly traceable to RCTMs. The required traceability is established by calibrating the analytical methods used to characterize or verify the WCTM with a RCTM. The chemical calibration should be accomplished under three important constraints. These are:

- a. The RCTM should match the CTM being characterized with respect to chemical composition and the quantity or concentration of the element or nuclide(s) to be determined.
- b. The RCTM and the CTM being characterized should be analyzed identically.
- c. The RCTM and the CTM being characterized should be analyzed concurrently.

For the uranyl nitrate WCTMs discussed in this report, the RCTM is also a nitrate solution. Such a reference solution, synthesized from weighed portions of a RCTM by straightforward dissolution-dilution procedures free of questionable transfers, chemical treatments, etc., retains the integrity of the parent RCTM and does not require confirmation by analysis. Likewise, synthesis of a uranyl nitrate WCTM from weighed portions of a RCTM by straightforward dissolution-dilution procedures free of questionable transfers, chemical treatments, etc. also retains the integrity of the parent RCTM; however, the absence of blunders in the synthesis must be confirmed by analysis using one method.

Uranyl nitrate solution is a necessary WCTM because many of the existing methods for the determination of uranium concentration and isotopic abundance involve measurement on uranyl nitrate solutions. Indeed, many samples, including uranium metal and  $UO_2$  powder and pellets, are usually

TABLE I

DEFINITIONS AND EXAMPLES OF DIFFERENT  
TYPES OF CALIBRATION AND TEST MATERIALS

<u>CTM Type and Abbreviation</u>	<u>Definition</u>	<u>Examples</u>
Calibration and Test Material (CTM)	A general term that is recommended as a substitute for that which previously has been referred to as a standard or standard material.	Any or all of the materials listed below.
Reference Calibration and Test Material (RCTM)	A general term for any PRCTM or SRCTM or these materials as a group.	Any PRCTM or SRCTM or these materials as a group. See examples below.
Primary Reference Calibration and Test Material (PRCTM)	Material characterized, certified, and distributed by a national or international standards body.	Standard Reference Materials of the National Bureau of Standards (NBS SRMs) and Standard Materials of the International Atomic Energy Agency (IAEA) bearing the IAEA classification, S.
Secondary Reference Calibration and Test Material (SRCTM)	A CTM characterized against PRCTMs, usually by several laboratories. Unlike PRCTMs, SRCTMs can be typical impure materials.	Reference Materials available from New Brunswick Laboratory (NBL) or from IAEA. Those from the latter bear the IAEA classification, R.
Working Calibration and Test Material (WCTM)	A CTM derived from RCTMs or characterized against RCTMs, used to monitor measurement methods to calibrate and test methods and equipment, and to train and test personnel.	Process stream materials and any CTM prepared according to this and related reports; Materials prepared and distributed in the Safeguard Analytical Laboratory Evaluation (SALE) Program; IAEA's Inter-comparison exchange samples.

converted to a nitrate solution for analysis. This report\* describes the preparation and packaging of uranyl nitrate solution WCTMs and the establishment of their uranium concentration and isotopic distribution values.

## 2.0 GENERAL CONSIDERATIONS GOVERNING THE PREPARATION OF A URANYL NITRATE SOLUTION WCTM

Uranyl nitrate WCTMs can be prepared in two ways. They can be synthesized from well-characterized starting materials; i.e., RCTMs, using procedures traceable to NBS standards of mass and volume. The integrity of the starting materials is thus transferred to the WCTMs. In this case, "makeup values" are assigned to the WCTM based on the reference value(s) of the starting material and, for concentration WCTMs, the quantity of starting material and the final dilution. The makeup values must be confirmed by analysis. The second method is to convert any plant uranyl nitrate, uranium metal, or uranium oxide to a homogeneous nitrate solution. In the latter case, two modes of chemical analysis may be applied to establishing the uranium concentration value to the WCTM. The first is to determine the uranium content of the starting material using two different analytical methods and then to verify the makeup value by an analysis of the WCTM using one method. The second is to forego any analysis of the starting material and then to determine the uranium concentration of the prepared WCTM using two different methods of analysis.

For the determination of uranium isotopic distribution, thermal ionization mass spectrometry is the only satisfactory method available and analysis by another laboratory is recommended. For  $^{235}\text{U}$  abundance alone, this technique or gas source mass spectrometry can be used. If the CTM is to be characterized only for its  $^{235}\text{U}$  abundance, then these two methods satisfy the requirement of analysis by two methods.

## 3.0 PREPARATION OF URANYL NITRATE SOLUTION WCTMs

As described above, there is a choice between the synthesis and the characterization methods of preparation and a choice of several starting materials. Among the factors that affect the choice are intended WCTM usage (assay, isotopic distribution or assay and isotopic distribution), total quantity of solution and units of partitioned samples to be prepared, characteristics of the anticipated samples, required accuracy, and cost.

### 3.1 Starting Materials

Materials which could be used to prepare uranyl nitrate WCTM are (a) RCTMs (Table II), (b) any properly characterized material, and (c) various uncharacterized materials. PRCTMs are used when highest credibility is

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\* In this program funded by the Office of Standards Development of NRC, the Idaho Chemical Programs Office of Allied Chemical Corporation and the Los Alamos Scientific Laboratory are preparing a series of reports describing the preparation of various essential WCTMs.



TABLE II

## URANIUM REFERENCE MATERIALS

<u>Material</u>	<u>Certification</u>	<u>Qty and Present Cost Per Unit</u>	<u>Remarks</u>
<u>NBS SRMs (PRCTMs)</u>			
950A, Normal U <sub>3</sub> O <sub>8</sub>	99.94 ± 0.02 wt% U <sub>3</sub> O <sub>8</sub>	25 g/\$36	For preparation of assay WCTMs: material is very low in impurities. Before weighing, ignite at 900°C for 1 hour and store in desiccator.
960, Normal Uranium Metal	99.975 ± 0.017 wt% U	26 g/\$58	For preparation of assay WCTMs: Material is very low in impurities. Surface oxide should be removed as described in the certificate.
Series U-0002 through U-970, U <sub>3</sub> O <sub>8</sub>	Isotopic Distribution Only(a)	1 g/\$57-77	Not certified for U concentration, however, materials are quite stoichiometric with proper ignition and quite pure chemically. May be used as received to prepare isotopic WCTMs.
993, Uranium Solutions	U Concentration(a) U Isotopic distribution	15 g/\$136	For preparation of both assay(d) and isotopic distribution WCTMs.
<u>SRCTMs</u>			
Uranium Metal, depleted (~0.2% <sup>235</sup> U) >99.9 wt% U	U Concentration U Isotopic distribution Impurities	~75 g	For preparation of assay WCTMs: Also can be blended with fully-enriched U metal for preparation of WCTM suitable for both assay and isotopic distribution measurement; remove surface oxide film as described in Section 3.1

TABLE II (cont'd)  
URANIUM REFERENCE MATERIALS

<u>Material</u>	<u>Certification</u>	<u>Qty and Present Cost Per Unit</u>	<u>Remarks</u>
Uranium Metal, fully enriched ( $\sim 93.2\%$ $^{235}\text{U}$ ) $>99.9$ wt% U <sup>(b)</sup>	U Concentration U Isotopic distribution Impurities	$\sim 3$ g	For preparing assay WCTM: also can be blended with depleted U metal or SRM 960 normal U metal to produce WCTM suitable for both assay and isotopic distribution; Remove surface oxide film before weighing.
UO <sub>2</sub> powder, low enrichment <sup>(c)</sup>	2.380 wt% $^{235}\text{U}$ 87.73 wt% U	$\sim 100$ g	For preparing WCTM for both assay and $^{235}\text{U}$ abundance; assay value changes when material is exposed to air.

- 
- References: (a) For the reference values, see NBS Special Publication 260-27[1] or certificates supplied.
- (b) Proposed SRCTMs estimated to be available in FY 1976 from NBL.
- (c) The material currently available is a high-fired material characterized and distributed by NBL at the outset of the Safeguard Analytical Laboratory Evaluation (SALE) Program. Another low-fired, low enrichment material is currently being prepared through the SALE Program.
- (d) Material is intended for determining uranium by isotope dilution mass spectrometry.



required. They are also recommended for preparing WCTMs for thermal ionization mass spectrometry, which requires only very small amounts of material. When large quantities of WCTMs are needed, SRCTMs and plant materials should be used. General aspects involved in the preparation of uranyl nitrate WCTMs are summarized in Tables III and IV and Figures 1 and 2.

### 3.1.1 Pretreatment of starting materials

Uranium metal. Obtain a piece of metal slightly heavier than the desired weight. Pickle the metal in 4 to 6 M  $\text{HNO}_3$  for a few minutes to remove surface oxide, then wash the metal with water, then acetone, and air dry.

$\text{U}_3\text{O}_8$  (such as NBS SRM 950). Treat as specified on the NBS certificate for SRM 950.

NBS SRMs U-0002 through U-970. These are provided in the form of  $\text{U}_3\text{O}_8$  and are certified for isotopic distribution only. No pretreatment is necessary if one of these PRCTMs is used to prepare a WCTM for isotopic distribution by thermal ionization mass spectrometry. If they are to provide a total uranium or  $^{235}\text{U}$  concentration value, as in  $^{235}\text{U}$  concentration measurement by activation analysis and gamma ray spectrometry, the PRCTMs must be taken to a reproducible starting point (ignition at  $900^\circ\text{C}$  for 1 to 2 hr), then characterized for uranium concentration using two methods or two facilities with the measurements traceable to RCTMs (see Section 5.2.1).

Uranium dioxide ( $\text{UO}_2$ ).  $\text{UO}_2$ , even when high fired, reacts slowly with oxygen and absorbs moisture. Any  $\text{UO}_2$  SRCTM will probably be packaged under argon or nitrogen in a sealed container or packaged to contain a measured quantity of material. If packaged under nitrogen in a sealed container, use the material as received, taking the necessary precautions to guard against air oxidation and sorption of moisture. Once exposed to air, the material slowly degrades; hence, dissolve the entire contents of the package and repackage as weighed units for later use.

### 3.2 Reagents

All the required reagents are common laboratory chemicals made from Analytical Reagent Grade stock. Purify the water by distillation or deionization.

### 3.3 Apparatus

Like the reagents, most of the apparatus are common laboratory equipment. Glassware that will contact a solution should be cleaned with hot nitric acid and water and dried. If the WCTM is prepared on a concentration basis, the dissolution container should be designed to prevent mechanical loss of material. A 250-ml iodine flask fitted with a 24/40 male member air condenser and a reflux head (Figure 3-a) is satisfactory for small-scale dissolutions. Large-scale dissolutions require scaling up.

TABLE III

PREPARATION OF URANYL NITRATE WCTMs  
FOR URANIUM CONCENTRATION

---

<u>Starting Material</u>	<u>Characterization of Starting Material</u>	<u>Preparation of WCTM</u>	<u>Establishment of Uranium Concentration**</u>
RCTMs	NONE	Dissolve in $\text{HNO}_3$ , add impurities and filter.	One assay method and calculated (makeup) value based on starting material and solution weights.
Highly pure U materials other than RCTMs (<99.95% pure).	Two assay methods or one assay method and calculated purity based on complete impurity analysis.	As above.	Two assay methods, or if starting material was characterized, one assay method and calculated (makeup) value based on starting materials and solution weights.
Other U materials such as $\text{UO}_2$ powder	Two assay methods	As above.	As above.
Plant uranyl nitrate	Not applicable	Filter	Two assay methods.

---

\*\*Reference: Every WCTM prepared for uranium concentration is filtered. Figure 1 and Section 5.1 for treatment of residue.

TABLE IV

PREPARATION OF URANYL NITRATE WCTMs  
FOR URANIUM ISOTOPIC DISTRIBUTION

<u>Starting Material</u>	<u>Characterization of Starting Material</u>	<u>Preparation of WCTM</u>	<u>Establishment of Uranium Isotopic Distribution</u>
RCTMs	NONE	Dissolve in $\text{HNO}_3$ and add impurities	One assay method and calculated (makeup) value based on starting material and solution weights.
Highly pure uranium materials other than RCTMs.	Analysis by two laboratories using a single method for complete isotopic distribution. Analysis by two methods or by two laboratories using different methods for $^{235}\text{U}$ abundance only.	As above.	See "Characterization of Starting Material". If starting material was characterized, one assay method and calculated (makeup) value based on starting material and solution weight.
Plant uranyl nitrate.	Not applicable.	Filter	Analysis by two laboratories using a single method for complete isotopic distribution. Analysis by two methods or by two laboratories using different methods for $^{235}\text{U}$ abundance only.

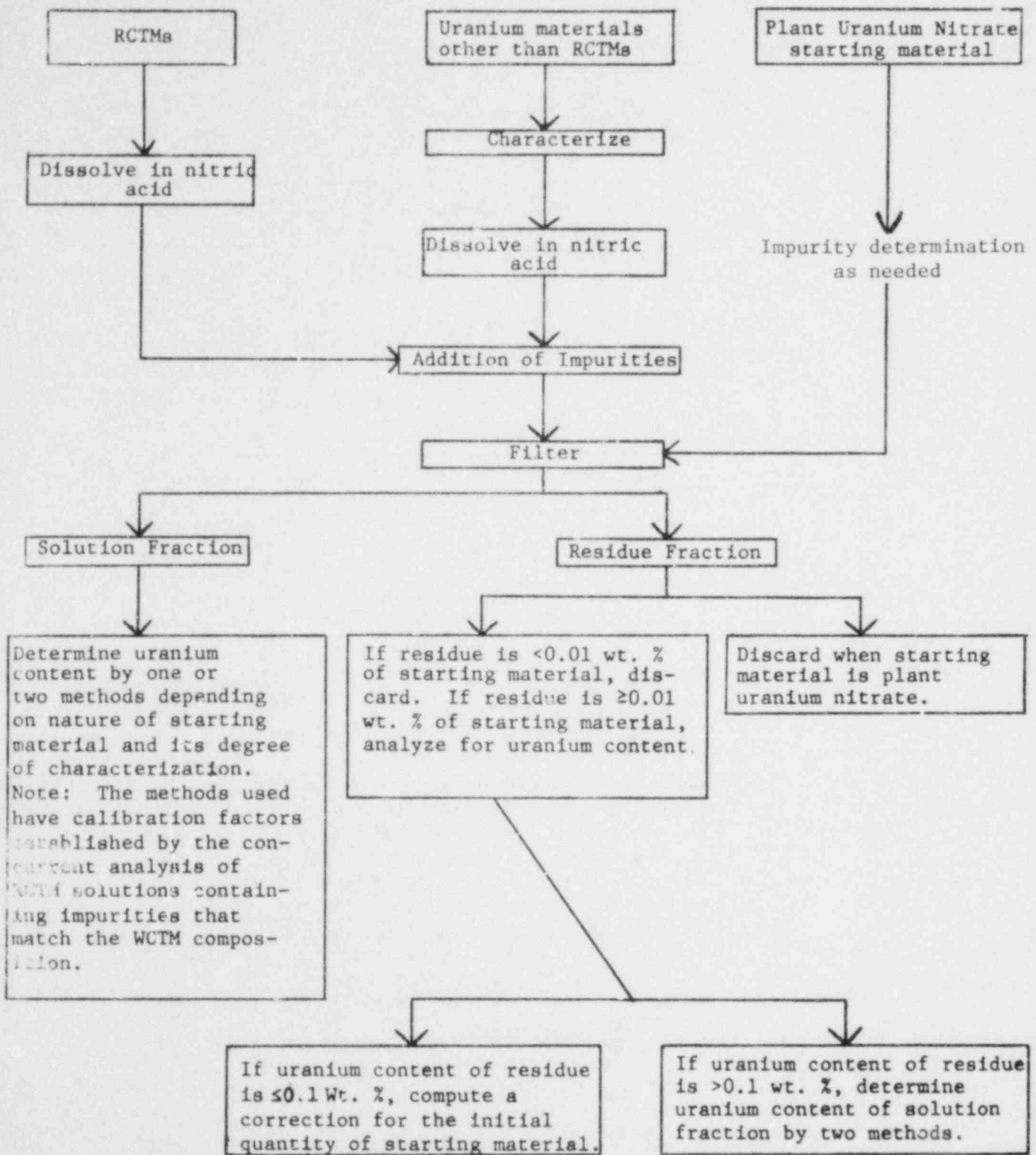


Fig. 1 General operations involved in the preparation of a uranyl nitrate concentration WCTM.

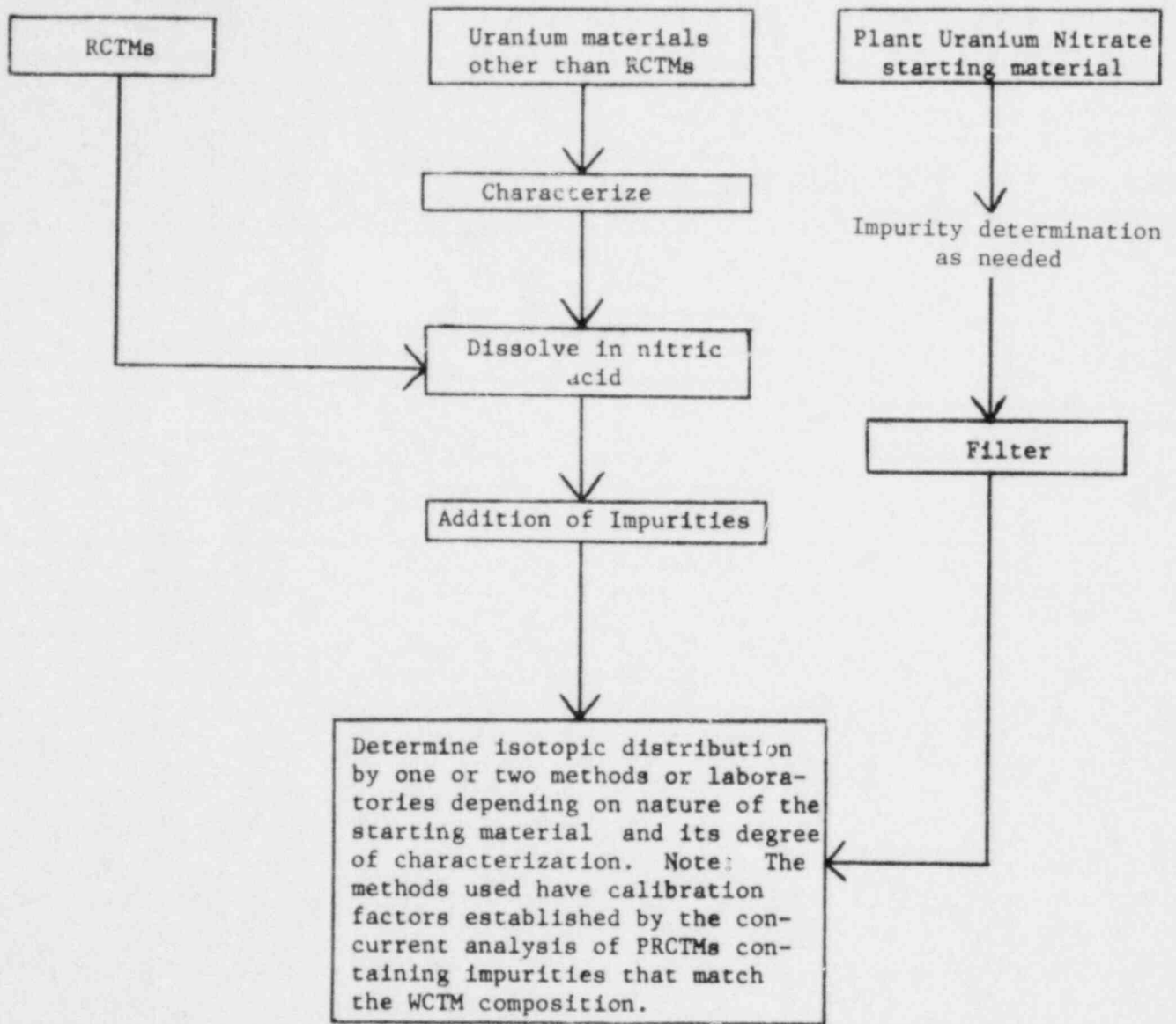
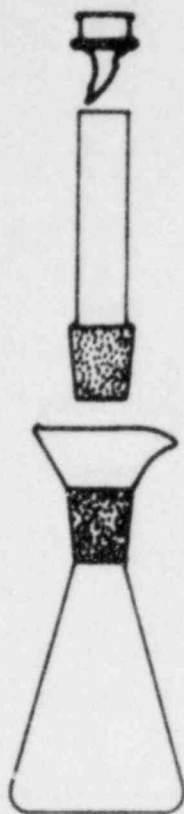
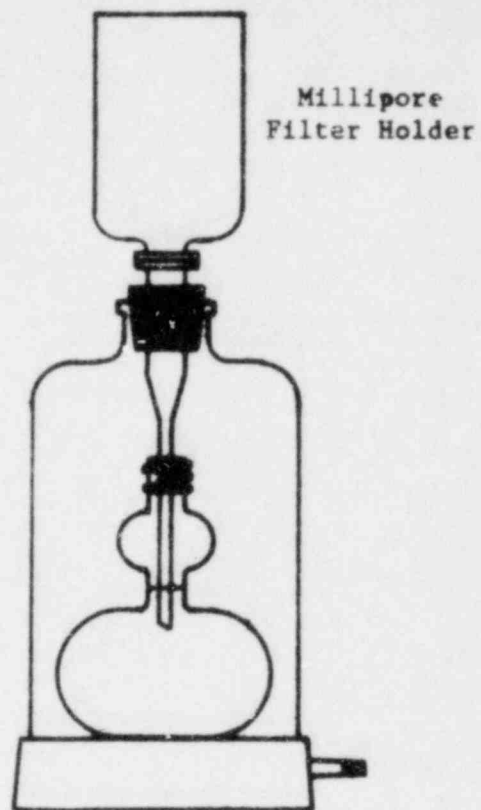


Fig. 2 General operations involved in the preparation of a uranyl nitrate isotopic distribution WCTM.



(a) Apparatus for  
Dissolution



(b) Apparatus for  
Filtration

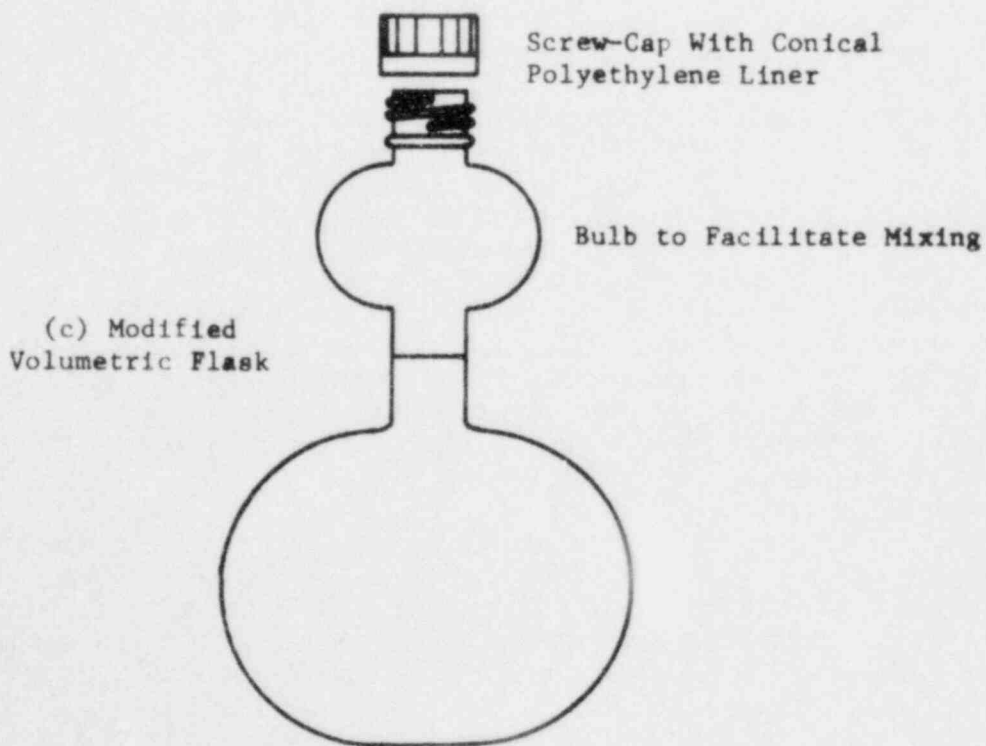


Fig. 3. Special apparatus for uranyl nitrate WCTM preparation.



Filtrations are best accomplished with a 0.45  $\mu\text{m}$  acid-resistant membrane filter held in a Millipore filter assembly with suction supplied through a Fisher filtrator or equivalent (Figure 3-b). The base of the filter holder should be narrowed and extended with small-diameter glass tubing to facilitate filtrations directly into a volumetric flask. The volumetric flask (Figure 3-c) should be short enough to facilitate weighing on a conventional single pan balance and should contain a bulb above the reference mark to facilitate mixing. Other items used to package the WCTMs are:

- a. Ampoules, trimmed stem, color-break, Kimax N-51A or equivalent; sizes according to needs.
- b. Bottles, wash, polyethylene, 4-oz and 8-oz, equipped with long, slender delivery spouts.
- c. Buret, weighing, equipped with slender delivery tip long enough to reach below the shoulder of the ampoule or bottle. Place a sleeve of polyethylene tubing on the delivery spout, about 0.5 in. from the tip, to prevent the tip from contacting the neck of the ampoule.
- d. Parafilm. This is a wax-coated film used to cover a large-opening container such as a beaker.

### 3.4 Synthesis of WCTM for Isotopic Measurement Only

3.4.1 Starting materials. At the present time, there are three principal methods for determining one or more of the uranium isotopes. These are: (a) thermal ionization mass spectrometry which determines the abundances of all uranium isotopes, (b)  $\text{UF}_6$  gas source mass spectrometry which is usually calibrated to provide  $^{235}\text{U}$  abundance, and (c) gamma spectrometry which provides  $^{235}\text{U}$  concentration only.

The NBS SRM series U-0002 through U-970 is an ideal and highly recommended series of starting materials for the preparation of thermal ionization mass spectrometry WCTMs. These same materials could be used in gas source mass spectrometry; however, the usual 1-gram sample requirement precludes their use on a routine basis and in fact, all laboratories actively using this technique should establish a series of in-house WCTMs that have been characterized against the NBS SRMs. As noted in Section 3.1.1, this series of SRMs is not certified for total uranium or  $^{235}\text{U}$  concentration and requires prior characterization if used in a way requiring these values.

Other useful starting materials would be the proposed depleted and enriched uranium metal SRCTMs or any other well characterized low and high enriched uranium materials which could be blended to provide a WCTM with a special isotopic distribution. This approach requires accurate knowledge of the quantity of each component added.

### 3.4.2 Preparation of WCTM for thermal ionization mass spectrometry

1. Weigh into a 60-ml Erlenmeyer flask a portion of the appropriate NBS SRM uranium isotopic reference material that is within + 5% of the desired amount. The uranium concentration should be controlled because the amount of uranium loaded onto the filament should be held constant in order to obtain reproducible results.
2. Dissolve the oxide in 6 M - 8 M HNO<sub>3</sub> with the aid of controlled heating.
3. When the dissolution is complete, evaporate the solution on low heat until the uranyl nitrate crystallizes.
4. Dissolve the crystals, add impurities in kind and amount comparable to the sample being analyzed, and mix thoroughly.
5. Dilute the solution to the desired concentration with the desired strength (usually 1 M) of nitric acid.
6. To prevent contamination of the entire batch of WCTM, package the solution in smaller units described in Section 4.3.

### 3.4.3 Preparation of WCTM for <sup>235</sup>U assay by gamma spectrometry

In the gamma spectrometry method for determining <sup>235</sup>U content, the sample is converted to a nitrate solution and compared to a set of uranyl nitrate WCTMs of known <sup>235</sup>U content. The WCTMs may be made from the lower members of the NBS SRM series. Because these SRMs are certified only for isotopic abundances and not for uranium concentration, their uranium contents must be established, the NBS SRMs U-0002 through U-970 can be used to prepare WCTMs for <sup>235</sup>U assay by gamma spectrometry as follows:

1. Weigh the required quantity of the ignited oxide into a 250-ml iodine flask. Fit a male member of a 24/40 joint onto the flask to minimize spatter losses.
2. Dissolve the oxide completely with 8 M nitric acid, add impurities in kind and amount comparable to the sample being analyzed, quantitatively transfer the solution to the container used for the gamma spectrometry measurement, and dilute to the reference mark; mix thoroughly.

NOTE: If low-enrichment material is to be measured for <sup>235</sup>U content using NaI(Tl) detectors, the sample and WCTMs should have the same "age to equilibrium". Appropriate purification treatment should be applied prior to dilution.



### 3.5 Synthesis of WCTM from Characterized Starting Materials for Uranium Concentration Measurement Only.

3.5.1 Starting materials. The PRCTMs certified for uranium assay are NBS 950  $U_3O_8$  and NBS SRM 960 natural uranium metal. The authors prefer the metal. Other applicable starting materials are the proposed depleted and 93%-enriched uranium metal SRCTMs and properly-characterized plant materials. All of these starting materials must be treated as described in Table II and Section 3.1.1.

#### 3.5.2 Preparation of WCTM

1. On the basis of the intended application, determine the characteristics of the WCTM, the quantity of solution to be prepared, and the mode of packaging.
2. Weigh the required quantity of properly treated starting material to the required accuracy and transfer the measured material into an Erlenmeyer flask of the type shown in Figure 3-a. Record the atmospheric pressure and temperature to permit a buoyancy correction.
3. Using an air-cooled condenser and reflux head to prevent spatter losses, dissolve the metal or oxide with 8 M  $HNO_3$ . Apply heat and replenish the 8 M  $HNO_3$  as necessary to obtain complete dissolution. (Note: NBS 950a  $U_3O_8$  contains a small amount of material that resists nitric acid attack. One drop of HF usually solubilizes this material). Examine the flask and contents critically to make sure that dissolution is complete.
4. Evaporate the solution until crystals start to form.
5. Dissolve the crystals in 1 M  $HNO_3$ .
6. Add impurities in kind and amount comparable to that of the majority of samples being analyzed and mix thoroughly. The impurities are best added as a composite solution of the appropriate salts or acids in 1 M  $HNO_3$ .
7. Filter the solution through a 0.45  $\mu m$  membrane filter into a tared (to the required accuracy) volumetric flask (Figure 3-c). Use 1 M  $HNO_3$  as a wash solution and transfer the solution quantitatively. (Note: When the filtration is performed with the recommended setup of a membrane filter supported on a Millipore filter holder, some of the uranium solution creeps to the periphery of the circular filter. To recover this uranium, remove the filter holder reservoir during the final stages of rinsing and apply the wash solution to the periphery of the filter). Reserve the filter and residue for analysis as described in Section 5.1.

8. Dilute the solution to the calibration mark and mix.
9. Dry the exterior of the flask; then weigh the flask plus contents to the required accuracy.
10. Package the solution as described in either Section 4.1 or 4.2.
11. Wrap the membrane filter containing the filtered residue from Step 7. in a small piece of ashless filter paper and ignite it to constant weight in a tared platinum crucible at 900°C. Treat the residue as described in Section 5.1.

### 3.6 Synthesis of WCTM from Characterized Starting Materials for Measurement of Both Uranium Concentration and Uranium Isotopic Distribution

3.6.1 Starting materials. Applicable starting materials are the proposed depleted uranium metal and 93%-enriched uranium metal SRCTMs, and other properly characterized materials. NBS SRMs 950 U<sub>3</sub>O<sub>8</sub> and 960 uranium metal may also be used together with the 93%-enriched uranium metal SRCTM. These SRMs are certified only for their uranium concentration and must be characterized for their isotopic distribution if they are to be blended.

#### 3.6.2 Preparation of WCTM

1. On the basis of the intended application, determine the characteristics of the WCTM, the quantity of solution to be prepared, and the mode of packaging to be used.
2. Weigh the required quantities of 93%-enriched uranium metal (or other enriched uranium material) and non-enriched uranium starting material to the required accuracy. Place the weighed pieces in the Erlenmeyer dissolution flask. Record the atmospheric pressure and temperature to permit a buoyancy correction.
3. Continue as per Section 3.5 beginning at Step 3.

### 3.7 Preparation of WCTMs from Uncharacterized Plant Material

1. Based on the types of samples being analyzed and the intended WCTM application, determine the characteristics of the WCTM, the quantity of solution to be prepared, and the mode of packaging to be used.
2. Prepare a solution approximating the requirements set forth in Step 1. (Note: If typical plant material is used to prepare the solution, impurities need not be added).
3. Filter the solution through a 0.45 µm membrane filter into a container at least 50% greater in volume than the intended

dilution. Use of a bottle or flask equipped with an air-tight screw cap is recommended. Mix the filtered solution thoroughly.

4. Depending on the intended WCTM application, package the solution according to Section 4.0.

#### 4.0 PACKAGING OF URANYL NITRATE SOLUTION WCTMs

Uranyl nitrate solution WCTMs for uranium concentration can be packaged as measured aliquots ready for immediate analysis or as unmeasured portions that are aliquotted when used. The former requires only protection against dust and accidental spill whereas the latter requires that the WCTM retain its prepared concentration until it is aliquotted for analysis. Premeasured aliquots may be stored in a test tube or beaker using a polyethylene stopper or inert plastic film to protect the sample from external contamination. Packaging in sealed glass ampoules is the recommended method for WCTMs that must be protected from evaporation; however, packaging in conical polyethylene-lined screw-cap bottles is satisfactory for short-term storage; i.e., up to at least 1-yr, if the container is not opened frequently.[3]

Uranyl nitrate solution WCTMs for isotopic measurement need only be protected from external contamination and from significant changes in concentration due to evaporation. Almost any vial, test tube, flask, or bottle with a suitable cap is acceptable; however, sealed glass ampoules provide, with only minimal added effort, the assurance of total containment and freedom from external contamination.

##### 4.1 Packaging of Measured Aliquots for Concentration Measurement on a Total Sample Basis

The aliquot weight can be determined directly or by weighing the dispensing vessel prior to and after delivery of the aliquot.[8] If the latter approach is used, exercise caution in the use of plastic dispensing bottles. Static charges can cause significant weight changes when using plastic containers. Wiping with a slightly damp towel will virtually eliminate the problem.[1] If the delivered aliquot is weighed, avoid the use of a compressive "stopper" cap; i.e., do not pressurize the container when applying the stopper. When small aliquots are being weighed, significant errors can develop due to varying air buoyancy and to evaporation.

1. Clean, dry, and label a sufficient number of suitable containers for the individual aliquots.
2. Transfer the WCTM to a weight buret and weigh. Record the weight.
3. Deliver the required amount of solution into the selected packaging container (beaker, vial, ampoule, bottle, etc.) and reweigh the weight buret. (Note: As an alternative, weigh the receiving vessel before and after delivery of the aliquot.) Record the weight and vial number.

4. Repeat steps 2. and 3. until the desired number of samples has been weighed.
5. Close each container with an appropriate closure. A piece of Parafilm is satisfactory for covering a beaker.

#### 4.2 Packaging of Unmeasured Lots for Concentration Measurement

Note: Sealed glass ampoules are recommended. Glass bottles with tight-fitting screw-cap closures are satisfactory for short-term storage. The acceptable duration of bottle storage depends on the closure and how often the container is opened. Except for short-term use, containers with friction-fit stoppers are not recommended.

1. Clean and dry the required number of ampoules.
2. Transfer the WCTM to a polyethylene wash bottle equipped with a long, slender delivery spout.
3. Deliver the required amount of solution to the ampoule without wetting the ampoule in the stem area. Prepare all individual packages in one uninterrupted sequence to minimize ampoule-to-ampoule differences. Stopper the ampoule if it is not to be sealed immediately.
4. Flame-seal each ampoule, then if desired, number and weigh each ampoule to provide a means for detecting pin-hole leaks.\*

#### 4.3 Packaging of Unmeasured Lots for Isotopic Measurement

Subdivision of the WCTM for isotopic measurements is recommended mainly to eliminate the possibility of contaminating the entire lot. Because small changes in concentration are permissible, almost any closed glass containment is acceptable. Sealed glass ampoules as described in Section 4.2, offer the advantages of total containment and freedom from external contamination for long durations.

### 5.0 ESTABLISHMENT OF WCTM VALUES

Section 2.0 presents the general considerations governing solution WCTMs, and Figures 1 and 2 outline the options for establishing the uranium concentration and isotopic values of the uranyl nitrate WCTMs. Analyses are required to characterize WCTMs prepared from uncharacterized starting materials, to characterize materials that are to be used as starting materials for WCTM synthesis, and to confirm the make-up values assigned to WCTMs synthesized from characterized starting materials. The analysis guidelines are as follows:

- a. Use one method to confirm the make-up of a WCTM synthesized from characterized materials.

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\* As a check for concentration changes during ampouling, analysis of the first and the last ampoule may be a worthwhile precaution.

- b. Use two methods or, for isotopic characterization, independent analyses by two laboratories to characterize a WCTM or intended starting material.

Option a. may be used when a RCTM or characterized uranium material is used as the starting material. As stated in Section 2.0, the minimum requirement for characterization of starting materials is analysis by two methods or, in the case of complete isotopic distribution characterization, two independent analyses. For high purity metal ( $\geq 99.95\%$  purity) one method can be the determination of total impurity content.

When option a. is used, a confirmatory analysis must be performed in which statistical tests (Section 6.0) are used to compare the confirmatory analysis and the makeup value.

Option b. must be used when an uncharacterized uranium material is selected as the starting material.

When option b. is used, analysis by two methods or, in the case of a complete isotopic distribution WCTM, two independent analyses are required for characterization. The results of these analyses are then statistically compared (Section 6.0) and used to assign the concentration or isotopic distribution values to the WCTM.

As discussed in Section 2, every analytical method used shall be calibrated at the time a WCTM is analyzed. This calibration shall be done with RCTMs that have been treated to simulate the WCTM in uranium concentration, isotopic distribution and impurity contents. Also, the number of determinations of the WCTM and RCTM shall be equal.

In addition to the above topics, this section describes the determination of the uranium 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 values.

### 5.1 Uranium Content of Filtered Residues

Each WCTM prepared for uranium concentration measurement undergoes a filtration treatment. If the starting material is other than plant material, compare the observed residue weight (see Section 3.5 step 11) with the weight of the starting material. If the residue amounts to less than 0.01 wt% of the starting material, the residue can be discarded without analysis. The residue may also be discarded without analysis if the uranium concentration value of the WCTM is to be established on the basis of two different analytical methods. If the weight of the residue is equal to or greater than 0.01 wt% of the starting material, determine the uranium content of the residue. Solubilize the residue via a pyrosulfate or bisulfate fusion, then determine the uranium by a method having a precision of at least 20% relative standard deviation. If the uranium content of the residue is found to be equal to or less than 0.1 wt%, a correction may be applied to the makeup value. If the uranium content of the residue is greater than 0.1 wt%, the uranium content of the WCTM must be established by two different analytical methods.



## 5.2 Methods for Characterization or Confirmation of Uranyl Nitrate Starting Materials and WCTMs

5.2.1 Uranium concentration. The analytical methods for determining uranium concentration are subject to diverse ion effects. If the impurity content of the material being analyzed is not known, determine the impurity content by emission spectrographic analysis, spark source mass spectrometry, or other methods that give comparable coverage. Some WCTMs and starting materials can contain organic or non-metallic impurities and should be examined by methods that will reveal their presence and quantity. Considering the impurities present, select two analytical methods, preferably those not affected by the observed impurities. Three highly recommended methods for uranium concentration are the NBL improved version of the Davies and Gray method[2], the gravimetric method based on ignition to  $U_3O_8$ [8], and controlled-potential coulometry[2]. There are several versions of the gravimetric procedure. The particular one favored by the authors is that procedure wherein the initially produced  $U_3O_8$  is cycled through a hydrogen reduction and a second ignition in air to assure proper oxide stoichiometry.\* The gravimetric method is not recommended when the impurity correction exceeds 0.1%.

Analyze the WCTM to be characterized or confirmed plus appropriate uranyl nitrate RCTMs. If a laboratory has expertise with only one method, arrange to have the WCTM analyzed by another laboratory. Perform as many analyses as are necessary to obtain the required limit of error (see Section 5.3). The number of replicates should be the same for the WCTM being confirmed or characterized and the RCTM.

5.2.2 Uranium isotopic distribution (or  $^{235}U$ ) Thermal ionization mass spectrometry must be used to determine uranium isotopic distribution. For  $^{235}U$  abundance alone, this technique or gas source mass spectrometry can be used. If the CTM is to be characterized only for its  $^{235}U$  abundance, then these two methods satisfy the requirement of analysis by two methods. However, if the CTM must be characterized for isotopic distribution, then there is but one satisfactory method and analysis by another laboratory is recommended. Again, perform as many analyses of the CTM and one or more appropriate uranium isotopic RCTMs as are necessary to obtain the required limit of error (see Section 5.3). Concurrently process an equal number of replicates of the WCTM and the RCTM. All samples should be processed identically.

## 5.3 Criteria Covering Number of Replicate Analyses

The limit of error\*\* (LE) of the uranium concentration or the isotopic distribution of the WCTM is determined by the method used to synthesize

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\* This ignition sequence assures a stoichiometric  $U_3O_8$  product. Details of this method by S. Kallman, Ledoux, and Co., Teaneck, New Jersey, are described in NUREG-75/010, "Methods for the Accountability of Uranium Dioxide", by K. Ernst et al. of the Lawrence Livermore Laboratory.

\*\* The LE of an estimator T is defined[4] as twice the standard deviation of T. The RLE, expressed as a percentage, is 100 LE/T.

or characterize the WCTM. The desired limit of error is related to the intended use of the WCTM. Specifically, the desired LE is a function of the accuracy and precision of the measurement 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 stipulated LE and Relative Limit of Error (RLE)\*. The LE of an MBA is distributed among the plant materials in that MBA in a manner determined by the individual facility.

The RLE to be associated with the WCTM value is selected, on a somewhat arbitrary basis, to be  $\leq 1/3$  of the RLE associated with the plant material to which the WCTM applies. This selection provides for attainment of satisfactory measurement precisions without an unreasonable number of replicate analyses.

When the assigned value of the WCTM is obtained by characterization, its LE is a function of the precisions of the two analytical methods used. The number of replicates of each analysis is further controlled by the following criteria:

1. For each method, the number of determinations of the WCTM and the RCTM shall be equal.
2. The average result from each method shall have an RLE that is not appreciably greater than 1.4 times the required RLE of the WCTM value.

These criteria will be met if the number of replicate analyses of the WCTM and the RCTM,  $n_i$ , is obtained by equation[1].

$$n_i = \frac{4(RSD_i)^2}{(RLE)^2} \quad (1)$$

where  $RSD_i$  = relative standard deviation of a single determination by method  $i$  expressed in %.

RLE = required relative limit of error of the WCTM value (usually set at  $1/3$  of the plant material RLE).

The use of this relationship is demonstrated by the following example.

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

for  $RSD_1 = 0.1\%$

$$n_1 = \frac{(2.0)^2 (0.1)^2}{(0.15)^2} = 1.8$$

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\* The LE of an estimator  $T$  is defined[4] as twice the standard deviation of  $T$ . The RLE, expressed as a percentage, is  $100 \frac{LE}{T}$ .

for  $RSD_2 = 0.3\%$

$$n_2 = \frac{(2.0)^2 (0.3)^2}{(0.15)^2} = 16$$

Hence, two replicate analyses of the WCTM and two analyses of the RCTM should be performed by Method 1 and 16 replicate analyses of both CTM's should be performed by Method 2. The advantage of using highly precise methods is apparent.

The actual LE assigned to the WCTM is based on precision estimates obtained from the WCTM and RCTM analyses. These estimates may differ from the precisions ( $RSD_i$ ) used in equation 1 and an adjustment in the number of replicates may be required. To obtain the required precision estimates, an absolute minimum of two analyses of each CTM by each method is necessary. However, even when Equation 1 indicates two replicates are adequate, a minimum number of five is recommended. Confidence intervals, which are a more useful measure of uncertainty than limits of error, can be very dependent on the number of analyses performed. For example, the confidence interval of an average based on two analyses of both CTM's is nearly three times larger than one based on five analyses of both CTM's. This substantial reduction in the uncertainty generally justifies the extra effort required.

The LE associated with the makeup value of a WCTM synthesized from characterized starting materials is independent of the number or types of confirmatory analyses. A method for estimating this LE is given in Section 6.3. The confirmatory analyses are run for the sole purpose of confirming the absence of a blunder during the synthesis of the WCTM. Therefore, the number of such analyses is a matter of judgement. Consideration should be given to the likelihood of a mistake occurring during the synthesis, to the consequences of assigning an erroneous value to the WCTM, and to the precision of the method used for the analyses. As discussed in section 1.0, there are extreme cases where it is unnecessary to run confirmatory analyses. On the other extreme, particularly if there is any question concerning the completeness of a transfer, the effect of a chemical treatment, the stability of the resulting solutions, etc., the value assigned to the WCTM should be determined by characterization using two different methods or laboratories.

In general, confirmatory analyses provide some assurance that no serious mistake occurred during the synthesis. The magnitude of error that will be detected by the analyses is related to the number of replicates and the precision of the analytical method. The RLE of the average result from the confirmatory analyses should be no larger than twice the required RLE of the WCTM value. This criterion, which is somewhat arbitrary, will be satisfied if the number of analyses of both the WCTM and the RCTM is calculated from

$$n_i \geq \frac{4(RSD_i)^2}{(RLE)^2}$$

where  $RSD_i$  = relative standard deviation of a single determination by method  $i$  expressed in %.



RLE = required relative limit of error of the WCTM value (usually set at 1/3 of the plant material RLE).

Note that the confirmatory analyses result and its associated RLE have no effect on the value or RLE assigned to the WCTM. The final assurance that these values are correct must come from a thorough knowledge and understanding of all operations involved in the WCTM synthesis.

## 6.0 STATISTICAL TESTS AND ASSIGNMENT OF VALUES TO WCTMs

These tests cover the modes of using two different methods of analysis and of using the makeup value and one method of analysis. Also presented are the statistical tests applied to isotopic distribution WCTMs. These tests are preceded by a definition of terminology.

### 6.1 Terminology

The three major symbols used are:

<u>Symbol</u>	<u>Definition</u>
n	Number of replicate aliquots of the WCTM (and of the RCTM) analyzed for uranium concentration or isotopic distribution by one method.
M	Mean (arithmetic average) of n results, $x_1, x_2, \dots, x_n$ .
S	Standard deviation for a single result computed by the standard formula:

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

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.

<u>Subscript</u>	<u>Material</u>	<u>Method</u>
1	RCTM	one
2	WCTM	one
3	RCTM	two
4	WCTM	two

Thus,  $M_2$  is the mean uranium (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 RCTM obtained using method two.

The number of replicate analyses is chosen so that  $n_1 = n_2$  and  $n_3 = n_4$  (Section 5.0) but the following is applicable even when the number of replicates is unequal. 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 (Section 6.2.1) shall be made to establish that the past precision is not significantly different from the present precision.

In the subsequent section, many of the statistical tests are as reported by Natrella[5].

## 6.2 Tests for Two Methods of Analyses

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

6.2.1 Tests of precision This test compares the precision of the results obtained by one method for the WCTM and the RCTM:

a. Choose a level of significance,  $\alpha$ , usually .05.

b. Calculate for Method 1,

$$F = \frac{S_1^2}{S_2^2}$$

c. 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

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

d. 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.

e. Do the same test for Method 2, for

$$F = \frac{S_3^2}{S_4^2}$$

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

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

This test is somewhat sensitive to normality. A test for non-normality is available[6]. A significant difference in precisions for only one method may indicate a difference in the impurity compositions of the WCTM and RCTM. A significant difference in precisions for both methods indicates a larger compositional difference.

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 RCTM 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 RCTM** The uranium concentration or isotopic value assigned to the WCTM shall be based directly on the RCTM. Since both the WCTM and RCTM 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 values assigned to the WCTM.  $M_1, M_2, M_3$ , and  $M_4$  are the analysis result means as defined previously.

$R$  is the uranium content of the RCTM, assumed to have insignificant error and therefore a constant for statistical calculations.

**6.2.3 Test 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  $V_2$  and  $V_4$ , are derived by propagation of error and by Satterthwaites formula[7].

The pooled variances are given by:

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

$$V_4 \approx \bar{X}_2^2 \left( \frac{S_3^2}{n_3 M_3^2} + \frac{S_4^2}{n_4 M_4^2} \right) ; f_4 \approx \frac{V_4^2}{\left( \frac{\bar{X}_4^2 S_3^2}{n_3 M_3^2} \right)^2 + \left( \frac{\bar{X}_4^2 S_4^2}{n_4 M_4^2} \right)^2}$$

$$\frac{n_3 - 1}{n_3 - 1} \quad \frac{n_4 - 1}{n_4 - 1}$$

The variance of  $(\bar{X}_2 - \bar{X}_4)$  is  $(V_2 + V_4)$  for which the associated degrees of freedom is given by [7]

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

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 WCTM population means are 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 the two means  $\bar{X}_2$  and  $\bar{X}_4$  by

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

in which,

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

$$W_4 = 1 - W_2$$

in which,

$V_2$  and  $V_4$  are the variances associated with  $\bar{X}_2$  and  $\bar{X}_4$  (See Section 6.2.3)

Calculate the standard deviation,  $S_A$ , associated with A by the approximation [8]

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

in which,

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

with associated degrees of freedom,  $n_A$ , rounded to the nearest integer, by

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

in which,

$f_2$  and  $f_4$  are the degrees of freedom associated with  $V_2$  and  $V_4$  (See Section 6.2.3)

Calculate the LE and RLE by

$$LE = 2 S_A$$

$$RLE = 100 \frac{LE}{A}$$

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

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

$$CL = A \pm t(1-\alpha/2, n_A)(S_A)$$

### 6.3 Tests for Makeup Value and One Method of Analysis

Examples of the tests presented in this section are given in Section B of the Appendix.

6.3.1 Makeup value calculation Calculate the makeup value of the WCTM by

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

in which,

$A_W$  = grams uranium per gram of solution

F = fractional uranium 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

$W_1$  = weight in grams of container

c = determined grams of uranium in filtered residue

$W_4$  = weight in grams of flask plus uranium nitrate solution

$W_3$  = weight in grams of flask

In the above relationship, no air buoyancy correction factor is shown for the solution weight (denominator). None is needed when the WCTM is used solely at the laboratory where it was prepared.

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

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

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.

LE and RLE are calculated by

$$LE = 2 S_A$$

$$RLE = 100 \frac{LE}{A}$$

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 Section 6.2.1.

- a. Choose a level of significance,  $\alpha$ , usually .05.
- b. Calculate

$$F = \frac{S_1^2}{S_2^2}$$

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

- d. 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.

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

- e. Calculate the mean value of the WCTM by

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

in which,

$\bar{X}_2$  is the value assigned to the WCTM.

$M_1$  and  $M_2$  are the analysis result means for the RCTM, and WCTM, respectively.



R is the uranium content of the RCTM, assumed to have insignificant error and therefore a constant for statistical calculations.

### 6.3.3 Test of makeup value and analysis-based mean.

- a. Calculate the approximate precisions, expressed as variances and degrees of freedom associated with  $\bar{X}_2$  by

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

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

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

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 makeup value A and the analysis-based mean  $\bar{X}_2$  test significantly different, no value can be assigned to the WCTM. Investigate for 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 Section 6.2 apply.

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

Calculate the LE and RLE associated with A by

$$LE = 2 S_A$$

$$RLE = 100 \frac{LE}{A}$$



Establish whether the RLE meets the requirement of  $< 1/3$  the 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 per Section 6.2. If this alternate approach is not feasible, the WCTM must be rejected.

#### 6.4 Tests Applied to Isotopic Distribution WCTMs

As discussed in Section 2, virtually only one method, thermal ionization mass spectrometry is used to determine uranium isotopic distribution. Thus the statistical treatment given in Section 6.3 normally will apply to establishing the isotopic distribution of a WCTM. Should a second laboratory also analyze the WCTM, then the statistical treatment given in Section 6.2 applies. If the WCTM is characterized only for  $^{235}\text{U}$  abundance, then thermal ionization and gas source mass spectrometry can be used to satisfy the requirement of analysis by two methods and the statistical treatment given in Section 6.2 applies. Examples are given in Section C of the Appendix.

#### 7.0 ACKNOWLEDGMENTS

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## APPENDIX

### A. TESTS FOR TWO METHODS OF ANALYSIS

A uranium 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 uranium nitrate as the starting material per Section 3.7 and applicable later sections. The two analytical methods used to establish the uranium concentration are redox titrimetry (termed method 1) and gravimetry (termed method 2).

#### 1. Estimated Number of Replicate Analyses of the WCTM and the Concurrently Analyzed PRCTM (Section 5.3)

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

$$RSD_{i_1} = 0.04\%$$

$$RSD_{i_2} = 0.06\%$$

Estimated number of replicate analyses is

$$n \approx \frac{4.0 (RSD_i)^2}{RLE^2}$$

$$n_1 \approx \frac{4.0 (0.04)^2}{(0.083)^2} \approx 0.93$$

$$n_2 \approx \frac{4.0 (0.06)^2}{(0.083)^2} \approx 2.09$$

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

The RCTM is prepared using NBS SRM 960 uranium metal and impurity elements were added to the analyzed aliquots to simulate the composition of the WCTM. The calculated uranium concentration (R) of the RCTM is 300.00 mg/g.

The results are:

<u>Mg U per Gram Solution</u>			
<u>Method 1</u>		<u>Method 2</u>	
<u>RCTM</u>	<u>WCTM</u>	<u>RCTM</u>	<u>WCTM</u>
300.22	303.30	300.70	304.25
300.10	303.65	300.53	303.90
300.25	303.75	300.15	300.85
299.85	303.55	300.34	303.30
299.93	303.50	300.43	303.98

2. Calculated Means and Standard Deviations (Section 6.1)

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

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

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

The values are

<u>Method 1</u>	<u>M</u>	<u>S</u>
RCTM	$M_1 = 300.070$	$S_1 = 0.1759$
WCTM	$M_2 = 303.550$	$S_2 = 0.1695$
<u>Method 2</u>		
RCTM	$M_3 = 300.430$	$S_3 = 0.2058$
WCTM	$M_4 = 303.856$	$S_4 = 0.3470$

3. F-Tests of Precisions (Section 6.2.1)

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

Method 1

$$F = \frac{S_1^2}{S_2^2} = \frac{(0.1759)^2}{(0.1695)^2} = 1.07$$

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

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

Because  $1.07 < 9.6$  and  $1.07 > 0.104$ , the precisions are not different.

#### Method 2

$$F = \frac{S_3^2}{S_4^2} = \frac{(0.2058)^2}{(0.3470)^2} = 0.35$$

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

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

Because  $0.35 < 9.6$  and  $0.35 > 0.104$ , the precisions are not different.

#### 4. Calculation of Method Means Based on RCTM (Section 6.2.2)

Calculate the two method means

$$\bar{X}_2 = M_2 (R/M_1) = 303.550 (300.00/300.070) = 303.479$$

$$\bar{X}_4 = M_4 (R/M_3) = 303.856 (300.00/300.430) = 303.421$$

#### 5. Tests of Equality of Means (Section 6.2.3)

Calculate the approximate variances and degrees of freedom for each mean.

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

$$V_2 \approx 303.479^2 \left( \frac{0.1759^2}{5(300.070)^2} + \frac{0.1695^2}{5(303.550)^2} \right)$$

$$V_2 \approx 0.01207$$

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

$$V_4 \approx 303.421^2 \left( \frac{0.2058^2}{5(300.430)^2} + \frac{0.3470^2}{5(303.856)^2} \right)$$

$$V_4 \approx 0.03255$$

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

$$f_2 \approx \frac{0.01207^2}{\left(\frac{(303.479)^2 (0.1759)^2}{5(300.070)^2}\right)^2 + \left(\frac{(303.479)^2 (0.1695)^2}{5(303.550)^2}\right)^2}$$

$$f_3 \approx 8.0$$

$$f_4 \approx \frac{V_4^2}{\left(\frac{\bar{X}_4^2 S_3^2}{n_3 M_3^3}\right)^2 + \left(\frac{\bar{X}_4^2 S_4^2}{n_4 M_4^2}\right)^2}$$

$$f_4 \approx \frac{0.03265^2}{\left(\frac{(303.421)^2 (0.2058)^2}{5(300.430)^2}\right)^2 + \left(\frac{(303.421)^2 (0.3470)^2}{5(303.856)^2}\right)^2}$$

$$f_4 \approx 6.6 \text{ or } 7 \text{ rounded to the nearest integer}$$

Compute the T statistic

$$T = \frac{\bar{X}_2 - \bar{X}_4}{\sqrt{V_2 + V_4}}, \text{ with } f \text{ degrees of freedom}$$

in which

$$T = \frac{|303.479 - 303.421|}{\sqrt{0.01207 + 0.03265}}$$

$$= 0.27$$

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

$$f \approx \frac{(0.0127 + 0.03265)^2}{\frac{(0.01207)^2}{8.0} + \frac{(0.03265)^2}{6.6}}$$



$f \approx 11.1$  or 11 rounded to the nearest integer.

Find, in a t-table

$$t(1-\alpha/2, f) = t(.975, 11) = 2.201$$

Because  $T = 0.27 < t(1-\alpha/2, f) = 2.201$

conclude that the two means are not different.

6. Assignment of WCTM Value (Section 6.2.4)

Calculate the assigned value, A

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

$$W_2 = \frac{\frac{1}{V_2}}{\left(\frac{1}{V_2} + \frac{1}{V_4}\right)} = \frac{\frac{1}{0.01207}}{\frac{1}{0.01207} + \frac{1}{0.03265}}$$

$$= 0.73010$$

$$W_4 = 1 - W_2 = 1 - 0.73010$$

$$= 0.26990$$

$$A = (0.73010)(303.479) + (0.26990)(303.421)$$

$$= 303.463$$

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

$$S_A \approx \left[ \frac{1}{W} \left\{ 1 + 4W_2W_4 \left( \frac{1}{f_2} + \frac{1}{f_4} \right) \right\} \right]^{1/2}$$

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

$$W = \left( \frac{1}{(0.01207)} + \frac{1}{(0.03265)} \right)$$

$$= 113.478$$

$$S_A \approx \frac{1}{113.478} \left\{ 1 + 4(0.73010)(0.26990) \left( \frac{1}{8.0} + \frac{1}{6.6} \right) \right\}^{1/2}$$

$$\approx 0.1036$$

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

$$\approx \frac{1}{\frac{(0.73010)^2}{8.0} + \frac{(0.26990)^2}{6.6}}$$

$$\approx 12.9 \text{ or } 13 \text{ rounded to nearest integer.}$$

Calculate the LE and RLE

$$LE = 2 S_A = 2 (0.1036) = 0.2072$$

$$RLE = 100 \frac{LE}{A} = 100 \frac{0.2072}{303.463}$$

$$= 0.068\%$$

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

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

$$t (.995, 13) = 2.160$$

$$CI = 303.463 \pm 2.160 (0.1036)$$

$$= 303.24 \text{ to } 303.69$$

mg U per gram of solution

B. TESTS FOR MAKEUP VALUE AND ONE METHOD OF ANALYSIS

A uranium 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 uranium metal per Section 3.5 and applicable later sections. The uranium content of the metal had previously established by two methods, which gave agreeing results. The method of analysis used to establish the uranium concentration of the WCTM is redox titrimetry.

1. Estimated Number of Replicate Analyses of the WCTM and Concurrently analyzed RCTM (Section 5.3)

Required RLE of WCTM is

$$\leq 1/3 \text{ of RLE of plant process Stream}$$

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

Estimated precision, as  $RSD_i$ , of method is 0.04%

Estimated number of replicate analyses is

$$n \geq \frac{4.0 (RSD_i)^2}{RLE^2}$$

$$n \geq \frac{4.0 (0.04)^2}{0.167^2} \geq 0.23$$

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

The RCTM is prepared using NBS SRM 960 uranium metal and impurity elements are added to simulate the composition of the WCTM. The calculated uranium concentration (R) of the RCTM is 0.016386 gm U per gram of solution.

The results are

Gram U per Gram Solution

<u>RCTM</u>	<u>WCTM</u>
0.01635	0.01561
0.01638	0.01557
0.01634	0.01558
0.01633	0.01563
0.01630	0.01560

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

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

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

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

The values are

RCTM

$$M_1 = 0.016340$$

$$S_1 = 0.000029$$

WCTM

$$M_2 = 0.015598$$

$$S_2 = 0.000024$$

Calculate the F ratio and compare to a tabulated F value

$$F = \frac{S_1^2}{S_2^2} = \frac{(0.000029)^2}{(0.000024)^2} = 1.46$$

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

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

Because  $1.46 < 9.6$  and  $1.46 > 0.104$ , precisions are not different

Calculate the WCTM mean

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

$$= 0.015598 (0.016386/0.016340)$$

$$= 0.015642$$

3. Makeup Value (Section 6.3.1)

The makeup data are

<u>COMPONENT</u>	<u>SYMBOL</u>	<u>VALUE</u>	<u>S</u>
Fraction U content of starting material	F	0.99975	0.000085
Air bouyancy correction	b	0.99993	0.000
Weight of container + starting material, g	W <sub>2</sub>	36.1999	0.002
Weight of container, g	W <sub>1</sub>	10.3785	0.002
Determine uranium in residue	c	0.000	0.000
Weight of flask + uranium nitrate solution, g	W <sub>4</sub>	1846.91	0.002
Weight of flask, g	W <sub>3</sub>	196.88	0.002

The WCTM is to be used solely at the laboratory where prepared, so no air bouyancy correction is required for the uranium nitrate solution weight.

Calculate the makeup value, A, and associated standard deviation, S<sub>A</sub>

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

$$A = \frac{[(0.99975)(0.99993)(36.1999 - 10.3785)] - 0.000}{1846.91 - 196.88}$$

$$A = 0.015644$$

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

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

$$S_A \approx \frac{1}{1846.91 - 196.88} \left[ (0.99993)^2 \left\{ (0.99975)^2 (0.002^2 + 0.002^2) + (36.1999 - 10.3785)^2 (0.000085)^2 \right\} + (0.000)^2 + (0.015644)^2 (0.02^2 + 0.02^2) \right]^{1/2}$$

$$\approx 2.1857 \times 10^{-6}$$

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

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

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

$$V_2 \approx (1.564 \times 10^{-2})^2 \left[ \frac{.000029^2}{5(1.634 \times 10^{-2})^2} + \frac{.000024^2}{5(1.560 \times 10^{-2})^2} \right]$$

$$V_2 \approx 2.699 \times 10^{-10}$$

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

$$f_2 \approx \frac{(2.699 \times 10^{-10})^2}{\frac{(0.015642)^2 (0.000029)^2}{5(0.016340)^2} + \frac{(0.015642)^2 (0.000024)^2}{5(0.015598)^2}}$$

$$f_2 \approx 7.8 \text{ or } 8 \text{ rounded to the nearest integer}$$

Compute the T statistic

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

$$T = \frac{|0.015642 - 0.015644|}{\sqrt{(2.1857 \times 10^{-6})^2 + (2.699 \times 10^{-10})}}$$

$$T = 0.12$$

Find, in a t table

$$t(1 - \alpha/2, f) = t(.975, 8) = 2.306$$

because  $T = 0.12 < t(1 - \alpha/2, f_2) = 2.306$ , conclude that the makeup value and the determined mean are not different.



5. Assignment of WCTM Value (Section 6.3.4)

The makeup value; 0.015644; is assigned

Calculate the LE and RLE

$$\begin{aligned}LE &= 2 S_A \\ &= 2 (2.1857 \times 10^{-6}) \\ &= 4.4 \times 10^{-6}\end{aligned}$$

$$\begin{aligned}RLE &= 100 \frac{LE}{A} \\ &= 100 \frac{4.4 \times 10^{-6}}{0.015644} \\ &= 0.028\%\end{aligned}$$

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

From (a), required RLE = 0.167%

Hence, RLE of WCTM meets the requirements.

### C. TESTS FOR URANIUM ISOTOPIC DISTRIBUTION RESULTS

A WCTM, prepared from a plant uranium nitrate, is to be characterized for isotopic distribution. This example is presented for the  $^{235}\text{U}$  value. The RLE assigned to the  $^{235}\text{U}$  fraction measurement of the stream is 0.10%. The WCTM is analyzed by the producing laboratory and an independent laboratory using thermal ionization mass spectrometry.

#### 1. Estimated Number of Replicate Analyses of the WCTM and Concurrently Analyzed RCTM (Section 5.3)

Required RLE of WCTM is

$$\leq 1/3 \text{ of RLE of plant process stream}$$

$$\leq 1/3 (0.10\%) = 0.033\%$$

The estimated precision, as  $\text{RSD}_i$ , of the measurement is

$$0.03\%$$

Estimated number of replicate analyses is

$$n \approx \frac{4.0 (\text{RSD}_i)^2}{\text{RLE}^2}$$

$$\approx \frac{4.0 (0.03)^2}{(0.033)^2} \approx 3.4$$

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

The RCTM was prepared using NBS SRM U-850 and impurity elements are added to simulate the composition of the WCTM. The certified value (R) of the  $^{235}\text{U}$  isotopic abundance is 85.137 atom %. The results obtained are tabulated below.

U Isotopic Abundance, Atom %

<u>Laboratory</u>	<u>Material</u>	<u>234</u>	<u>235</u>	<u>236</u>	<u>238</u>
Producing	RCTM	0.6528	85.100	0.3720	13.875
		0.6515	85.115	0.3710	13.862
		0.6520	85.095	0.3711	13.890
		0.6510	85.110	0.3705	13.868
		0.6505	85.105	0.3717	13.873
Producing	WCTM	0.5834	85.400	0.3647	13.652
		0.5820	85.415	0.3655	13.638
		0.5825	85.407	0.3640	13.647
		0.5835	85.412	0.3650	13.640
		0.5818	85.405	0.3645	13.649
Independent	RCTM	0.6435	85.153	0.3710	13.833
		0.6420	85.162	0.3705	13.826
		0.6442	85.148	0.3707	13.387
		0.6432	85.145	0.3701	13.842
		0.6445	85.160	0.3715	13.824
Independent	WCTM	0.5810	85.425	0.3638	13.630
		0.5822	85.419	0.3645	13.634
		0.5805	85.430	0.3650	13.624
		0.5818	85.415	0.3641	13.639
		0.5802	85.428	0.3635	13.628
NBS Values	RCTM	0.6437	85.137	0.3704	13.848

Note: All isotopic results are given. However, this example is calculated only for the  $^{235}\text{U}$  data.

2. Calculated Means and Standard Deviations (Section 6.1)

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

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

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

The values, for  $^{235}\text{U}$  atom % abundance, are

Producing Laboratory	M	S
RCTM	$M_1 = 85.105$	$S_1 = 0.008$
WCTM	$M_2 = 85.408$	$S_2 = 0.006$
Independent Laboratory		
RCTM	$M_3 = 85.154$	$S_3 = 0.007$
WCTM	$M_4 = 85.423$	$S_4 = 0.006$

3. F-Tests of Precision (Section 6.2.1)

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

Producing Laboratory

$$F = \frac{S_1^2}{S_2^2} = \frac{0.008^2}{0.006^2} = 1.78$$

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

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

Because  $1.78 < 9.6$  and  $1.78 > 0.104$ , precisions are not different.

Independent Laboratory

$$F = \frac{S_3^2}{S_4^2} = \frac{0.007^2}{0.006^2} = 1.36$$

Again, because  $1.36 < 9.6$  and  $1.36 > 0.104$ , precisions are not different.

4. Calculate of WCTM Means Based on RCTM (Section 6.2.2)

Calculate the two WCTM means

$$\bar{X}_2 = M_2(R/M_1) = 85.408(85.137/85.105) = 85.440$$

$$\bar{X}_4 = M_4(R/M_3) = 85.423(85.137/85.154) = 85.406$$

5. T Tests of Means (Section 6.2.3)

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

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

$$V_2 \approx (85.440)^2 \left[ \frac{.008^2}{5(85.105)^2} + \frac{.006^2}{5(85.408)^2} \right]$$

$$V_2 \approx 2.011 \times 10^{-5}$$

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

$$V_4 \approx (85.406)^2 \left[ \frac{.007^2}{5(85.154)^2} + \frac{.006^2}{5(85.423)^2} \right]$$

$$V_4 \approx 1.706 \times 10^{-5}$$

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

$$\frac{1}{n_1 - 1} \quad \frac{1}{n_2 - 1}$$

$$f_2 \approx \frac{(2.011 \times 10^{-5})^2}{\frac{(85.440)^2 (0.008)^2}{5(85.105)^2} + \frac{(85.440)^2 (0.006)^2}{5(85.408)^2}}$$

$$\frac{1}{5 - 1} \quad \frac{1}{5 - 1}$$

$$f_2 \approx 7.4 \text{ or } 7 \text{ rounded to the nearest integer}$$

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

$$\frac{1}{n_3 - 1} \quad \frac{1}{n_4 - 1}$$

$$f_4 \approx \frac{(1.706 \times 10^{-5})^2}{\frac{(85.406)^2 (.007)^2}{5(85.154)^2} + \frac{(85.406)^2 (0.006)^2}{5(85.423)^2}}$$

$$\frac{1}{5 - 1} \quad \frac{1}{5 - 1}$$

$$f_4 \approx 7.8 \text{ or } 8 \text{ rounded to the nearest integer}$$

Compute the T statistic.

$$T = \frac{|\bar{X}_2 - \bar{X}_4|}{\sqrt{V_2 + V_4}}, \text{ with } f \text{ degrees of freedom}$$

in which,

$$T = \frac{|85.440 - 85.406|}{(2.011 \times 10^{-5}) + (1.706 \times 10^{-5})}$$

$$T = 5.58$$

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

$$f \approx \frac{(2.011 \times 10^{-5} + 1.706 \times 10^{-5})^2}{\frac{(2.011 \times 10^{-5})^2}{7.4} + \frac{(1.706 \times 10^{-5})^2}{7.8}}$$

$$f \approx 15.0 \text{ or } 15 \text{ rounded to the nearest integer.}$$

Find in a t table

$$t(1-\alpha/2, f) = t(.975, 15) = 2.131$$

Because  $T = 5.58 > t(1-\alpha/2, f) = 2.131$ , 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 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.