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Roger C. Ingle

FOREWORD

This standard supersedes the May 1977 issue of RDT F 11-1T and incorporates those changes that were approved for publication in this revision. These changes are identified by the following marginal notations:

C	Change approved 3-27-85
D	Deletion approved 3-27-85
N	Addition approved 3-27-85

Editorial changes that were made during preparation of this revision are not identified.

The methods in this revision are presented in one of the following forms:

1. Referenced to appropriate ASTM standard(s),
2. Referenced to appropriate ASTM standard(s) with additional requirements, or
3. Kept intact as existing in the May 1977 issue.

Seven methods are in Category 3 because either they do not exist in current ASTM standards (5 are of this type) or the F 11-1T method is more suited than the corresponding ASTM method for the required application. In addition, four methods were eliminated from the May 1977 issue and one ASTM method was added.

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ANALYTICAL CHEMISTRY METHODS FOR MIXED OXIDE FUEL

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ANALYTICAL CHEMISTRY METHODS FOR MIXED OXIDE FUEL

1. SCOPE

This standard provides analytical chemistry methods for the analysis of materials used to produce mixed oxide fuel. These materials are ceramic fuel and insulator pellets and the plutonium and uranium oxides and nitrates used to fabricate these pellets.

2. APPLICABLE DOCUMENTS

The following documents are a part of this standard to the extent specified herein. The issue of a document in effect on the date of the invitation to bid, including any amendments or other published changes also in effect, shall apply unless otherwise specified. Where this standard appears to conflict with the requirements of a reference document, such conflict shall be brought to the attention of the purchaser for resolution.

2.1 NE Standards.

NE F 2-6T Qualification and Control of Analytical Chemistry Laboratories for Mixed Oxide Fuel Analysis

2.2 American Society for Testing and Materials (ASTM) Standards.

ASTM C 696¹ Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets

ASTM C 697¹ Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets

ASTM C 698¹ Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides [(U,Pu)O₂]

ASTM C 759¹ Standard Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions

ASTM C 799¹ Standard Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions

¹Annual Book of ASTM Standards, Part 45

3. GENERAL REQUIREMENTS

3.1 Analytical Methods. The analytical methods referenced or found in this standard describe acceptable equipment and procedures for use by trained analysts. Other methods approved by the purchaser may be used. Identification of brand names and model numbers are for information; equivalent equipment may be used instead.

3.2 Laboratory Qualification. Analytical laboratories shall be qualified to perform analyses in accordance with the requirements of NE F 2-6.

3.3 Calibration. Calibration of all methods referenced in ASTM standards and calibration standards used shall be in accordance with NE F 2-6.

3.4 Tolerances. Unless otherwise specified, all values for measurements stated in this standard (volume, weight, time, temperature, etc.) are nominal values. The actual measurements used, however, shall be within $\pm 5\%$ of the stated value. For example, "add 20 mL" means that a volume between 19 and 21 mL shall be added. Required tolerances are specified in one of the two following ways:

1. Tolerance limits are given with the value. For example, 15 ± 0.1 mL, $1 \text{ h} \pm 10$ min, or "take a 50 mg sample weighed to the nearest 0.1 mg."
2. When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL.

4. PLUTONIUM BY COULOMETRY

This method for determining plutonium in plutonium dioxide, mixed oxide, and plutonium nitrate solutions shall be in accordance with ASTM C 697, C 698, and C 759, respectively.

5. PLUTONIUM BY AMPEROMETRY

5.1 Application. This method is applicable to the determination of plutonium in samples of plutonium oxide, mixed oxide powder and pellets, and plutonium nitrate solutions. From 5 to 20 mg of plutonium are required for each titration.

5.2 Summary. A solid sample is dissolved either by fusion with sodium bisulfate or by heating in nitric acid with a trace of hydrofluoric acid. The fused sample is dissolved in sulfuric acid, after which the plutonium is oxidized to plutonium(VI) with excess silver(II) oxide and the excess silver(II) is reduced by heating. The nitric acid

dissolved sample and other plutonium nitrate solutions are fumed with sulfuric acid to remove the nitrate before the plutonium is oxidized. After the oxidation of plutonium and reduction of excess silver(II), the solution is adjusted to about 3M in sulfuric acid. Excess standardized ferrous ammonium sulfate is added and the excess iron(II) is back titrated with standard potassium dichromate using amperometric end point detection. The indicating electrode is a rotating platinum microelectrode that is used in conjunction with a saturated mercurous sulfate reference electrode as the counter electrode.

5.3 Interferences. Ions that are oxidized by silver(II) and are reduced by iron(II), such as chromium, manganese, and vanadium cause a high bias. A 0.1 % (by weight) positive error will result from 150 μ g of chromium or 100 μ g of manganese per gram of sample. These two constituents of stainless steel are the most probable interferences. Metals precipitated by sulfate may remove some plutonium from solutions, causing low results. Iron and uranium do not interfere.

5.4 Apparatus.

1. Amperometric end point detector. See Fig. 1.
2. Analytical balance, readable to at least 0.1 mg.
3. Digital voltmeter.¹
4. Flasks, Erlenmeyer, fused quartz, 50 mL, with a fused quartz cover glass.
5. Magnetic stirrer.
6. Muffle furnace.
7. Recorder.²
8. Reference electrode, saturated mercurous sulfate. See Fig. 2.
9. Rotating platinum electrode.³

¹Hewlett-Packard Model 3440A, with a HP DC Multi-Function Unit (Model 344A), has been found satisfactory.

²A Hewlett-Packard, Model 7100B, has been used successfully.

³E. H. Sargent and Co., Model S 30420 has been used for this method. Before use, each new electrode should be examined for hairline cracks in the glass. Such cracks will cause an electrode to malfunction.

HEDL 7608-227.3

Fig. 1. Amperometric End Point Detector.

- A. PLATINUM WIRE
- B. 125 ml ERLLENMEYER FLASK
- C. ULTRA-FINE FRIT

Fig. 2. Reference Electrode.

10. Synchronous electrode rotator.¹
11. Weighing buret, drop dispenser bottle, 60 mL volume, polyethylene.

5.5 Reagents and Standards.

1. Acid mixture, 12M nitric acid-0.5M hydrofluoric acid.
2. Argentic oxide.
3. Ferrous ammonium sulfate, 0.05 milliequivalent per gram of solution in 0.5M sulfuric acid.

This solution must be standardized each day used because iron(II) is gradually oxidized by air (see 5.6).

4. Nitric acid, 1M.
5. Sodium bisulfate, fused.
6. Sulfuric acid, 0.25M, 0.5M and 9M.
7. Potassium dichromate standard.

This standard is a solution of potassium dichromate in 0.5M sulfuric acid at a concentration of about 0.05 milliequivalent of chromium(VI) per gram of solution. It is prepared from NBS potassium dichromate, SRM 136 or its replacement, as follows:

- a. To a tared 1 litre volumetric flask, add about 2.5 g of NBS SRM 136 weighed to the nearest 0.1 mg.
- b. Add 500 mL of 0.5M sulfuric acid and let the potassium dichromate dissolve.
- c. Dilute to volume with 0.5M sulfuric acid and mix thoroughly.
- d. Weigh the flask and solution to the nearest 0.1 g and calculate milliequivalents per gram of solution using 5.8.1.
- e. Store in 20 mL screw cap bottles with polyseal liners in caps. Seal caps with tape until used.

¹E. H. Sargent and Co., Model S 76485, 600 rpm, has been used successfully.

8. Calibration standard.

The calibration standard is a solution of plutonium prepared from either NBS plutonium metal (SRM 949) or NBS plutonium sulfate tetrahydrate (SRM 944). Plutonium metal is dissolved in 6M hydrochloric acid and the sulfate is dissolved by fusion with sodium bisulfate. The final concentration of plutonium in either standard is about 5 mg/mL prepared as follows:

a. Plutonium metal.

Take one unit of NBS SRM 949, or its replacement, and carefully transfer it to a tared 100 mL volumetric flask. Rinse the container with 1M hydrochloric acid, transferring the rinses to the flask. Add 10 mL of 1M hydrochloric acid and let the metal dissolve. Dilute to volume with 1M hydrochloric acid and mix thoroughly. Weigh the flask and solution to the nearest 0.1 mg.

b. Plutonium sulfate.

Carefully transfer one unit of NBS SRM 944, or its replacement, to a 50 mL quartz Erlenmeyer flask. Weigh the container before and after transfer to obtain the weight of the standard transferred to the flask. Follow Steps 2 through 5 of 5.7.2. Quantitatively transfer the dissolved melt to a tared 100 mL volumetric flask, rinsing the Erlenmeyer flask with 0.25M sulfuric acid. Dilute to volume with 0.25M sulfuric acid and mix thoroughly. Weigh the flask and solution to the nearest 0.1 mg.

c. Store 5 mL portions of the standard solution either in sealed glass ampoules or in small screw cap vials with polyseal liners in the caps.

d. Calculate the milligrams of plutonium per gram of solution using 5.8.2.

5.6 Calibration. Calibration involves standardization of the ferrous ammonium sulfate solution with the calibration standard (plutonium solution). The iron(II) solution is standardized each 8-h shift during which plutonium analyses are made because iron(II) is slowly oxidized by air. Standardize as follows:

1. Weigh, to the nearest 0.1 mg, three portions of the calibration standard containing about 10 mg of plutonium into separate 50 mL beakers.

- a. For a standard prepared from plutonium metal, start at Step 7 of 5.7.1 and continue through Step 11. Omit Step 11 of 5.7.4.
 - b. For a standard prepared from plutonium sulfate, add 0.25M sulfuric acid to a volume of 10 mL. Proceed with the oxidation and titration in accordance with 5.7.3 and 5.7.4, omitting Step 11 of 5.7.4.
2. Calculate the end point and the milliequivalents of iron(II) per gram of ferrous ammonium sulfate solution using 5.8.3 and 5.8.4.
 3. Calculate the average and relative standard deviation from the results of the three titrations.*

The relative standard deviation should be $\leq 0.1\%$. If it is $> 0.2\%$, investigate and correct the problem before continuing with the analysis.

5.7 Analysis. Samples already in solution form as the nitrate or chloride are analyzed by starting at Step 6 of 5.7.1.

5.7.1 Sample Dissolution in Acid.

1. Add a portion of sample, weighed to the nearest 0.1 mg, to a 150 mL beaker.

Select an amount of sample to give a plutonium concentration of 3 to 5 mg/mL in a 60 mL volume.

2. Add 20 mL of the acid mixture; cover the beaker with a watch glass and heat on a hot plate until dissolution is complete.

The solution must be examined carefully to determine if dissolution is complete. It is difficult to detect small amounts of residue in the highly colored solution. Add additional amounts of the acid mixture, if necessary, until the dissolution is complete.

If the solution should evaporate to dryness during the dissolution, add 20 mL of the acid mixture and heat to redissolve the sample.

*The standard deviation (s) expressed as a percentage of the average ($\bar{x}$) of the quality measured; or expressed as an equation: relative standard deviation = $(s/\bar{x}) (100)$.

3. Remove the beaker from the hot plate and let the solution cool to room temperature.
4. Quantitatively transfer the solution to a tared 60 mL weighing buret using 1M nitric acid to rinse the beaker.
5. Dilute to about 60 mL with 1M nitric acid, mix thoroughly, and weigh.
6. Add an aliquot, weighed to the nearest 0.1 mg, containing 20 mg of plutonium to a 50 mL beaker.

Use a volume aliquot if the original sample is a solution of plutonium.
7. Add about 0.5 mL of 9M sulfuric acid and evaporate to dryness on a hot plate.
8. Raise the temperature of the hot plate and continue heating until all of the sulfuric acid is gone; remove the beaker from the hot plate.
9. Let the beaker cool to room temperature and then add 10 mL of 0.25M sulfuric acid, rinsing down the sides of the beaker as the acid is added.
10. Swirl the beaker until the residue is completely dissolved.
11. Proceed with the oxidation of the plutonium in accordance with 5.7.3.

5.7.2 Sample Dissolution by Fusion.

1. Add a portion of sample, weighed to the nearest 0.1 mg, to a 50 mL fused quartz Erlenmeyer flask.

Select an amount of sample to give a plutonium concentration of 3 to 5 mg/mL in a 60 mL volume.
2. Add 10 to 12 g of fused sodium bisulfate to the flask and cover with a fused quartz cover glass.
3. Place the flask in a muffle furnace and heat at about 625°C for 30 min.
4. Remove the flask from the furnace and cool to room temperature.
5. Dissolve the melt in 30 mL of 0.5M sulfuric acid, swirling the flask occasionally to aid dissolution.

6. Quantitatively transfer the solution to a tared 60 mL weighing buret using 0.5M sulfuric acid to rinse the flask.
7. Dilute to about 60 mL with 0.5M sulfuric acid, mix thoroughly, and weigh.
8. Add an aliquot, weighed to the nearest 0.1 mg, containing 5 to 20 mg of plutonium to a 50 mL beaker and add 0.25M sulfuric acid to a volume of 10 mL.
9. Proceed with the oxidation of the plutonium in accordance with 5.7.3.

5.7.3 Oxidation of Plutonium.

1. Add a stirring bar to the 50 mL beaker.
2. Put the beaker on the magnetic stirrer and, while the solution is being stirred, add 25 mg portions of argentic oxide every 15 to 30 s until excess oxide has been added.

Excess argentic oxide is indicated by a brownish-black color in the solution along with a black precipitate. Fused samples (5.7.2) require more argentic oxide for complete oxidation than samples dissolved in acid (5.7.1).

3. Remove the beaker from the stirrer and let the solution stand for at least 30 min.

The black precipitate and color of the solution must persist during the 30-min period. If not, insufficient argentic oxide was added.

4. Add sufficient 0.5M sulfuric acid to bring the volume of solution to about 20 mL, rinsing the sides of the beaker while adding the acid.
5. Place the beaker on the hot plate and heat the solution until all of the black precipitate disappears.
6. Remove the beaker from the hot plate and let it cool to room temperature.
7. Rinse down the sides of the beaker with 0.5M sulfuric acid, but do not let the volume exceed 25 mL.
8. Proceed with the titration in accordance with 5.7.4.

5.7.4 Amperometric Titration.

1. Place the 50 mL beaker into position so that the electrodes are immersed in the solution.

The apparatus is arranged so that the beaker sits on a magnetic stirrer. The stirring bar from the oxidation of the plutonium should still be in the beaker. It is assumed at this point that the apparatus is completely assembled ready to operate.

2. Turn on the rotating platinum electrode.
3. Add 10 mL of 9M sulfuric acid.
4. Turn on the magnetic stirrer and wait until the solution is thoroughly mixed.

It is important that the speed of the stirrer is the same from titration to titration.

5. Turn on the digital voltmeter and the electrode switch; turn the I/E switch to the E position.
6. Adjust the voltage to 600 mV and then turn the I/E switch to the I position; turn on the recorder.

The current being observed at this point is the residual current, which must be below 0.2 μ A and preferably below 0.1 μ A. If the initial current is above 0.2 μ A, the desired current will often be attained by waiting a few minutes. Should a residual current above 0.2 μ A persist, investigate and correct the problem before continuing the titrations.

The recorder is used to monitor the current during the titration. The current at each step of the titration can be read from the chart produced or from the digital voltmeter.

7. Add standardized ferrous ammonium sulfate solution from a weighing buret until a current reading of 25 to 30 μ A is attained.

This addition gives an excess of iron(II).

The weighing buret must be weighed before and after the addition to get the weight of solution added. Weigh to the nearest 0.1 mg.

8. Titrate the excess iron(II) with standard potassium dichromate solution, adding the solution from a weighing buret.

The first titration point taken (current reading versus weight of potassium dichromate solution added) should be between 9 and 12 μ A. The last point must be above 1 μ A and preferably below 3 μ A.

The weighing buret must be weighed before the first addition of potassium dichromate solution and after each addition. Weigh to the nearest 0.1 mg.

The dichromate solution in the weighing buret must not be used for more than three consecutive days, after which any remaining solution must be discarded.

When refilling the weighing buret, rinse several times with fresh dichromate solution before refilling.

9. Turn the I/E switch to the E position after the titration is complete; turn off the electrode switch and the rotating platinum electrode.
10. Remove the 50 mL beaker and rinse the electrodes thoroughly with 0.5 M sulfuric acid.
11. Calculate the end point and concentration of plutonium in the sample using 5.8.3 and either 5.8.5 or 5.8.6 as appropriate.

5.8 Calculations

5.8.1 Potassium Dichromate Standard. Calculate the milliequivalents per gram of solution using Equation 1.

$$C_{Cr} = \frac{D}{EW_{Cr}} \quad (1)$$

where

C_{Cr} = milliequivalents per gram of solution,
 D = milligrams of potassium dichromate used,
 E = 49.0320, equivalent weight of potassium dischromate, and
 W_{Cr} = grams of final solution.

5.8.2 Plutonium Standard. Calculate the concentration of plutonium in the solution using Equation 2 or 3.

1. Plutonium Metal, SRM 949.

$$C_{Pu} = \frac{M}{W_{Pu}} \quad (2)$$

where

C_{Pu} = milligrams of plutonium per gram of solution,

M = milligrams of plutonium metal used, and

W_{Pu} = grams of final solution.

2. Plutonium Sulfate, SRM 944.

$$C_{Pu} = \frac{SF}{W_{Pu}} \quad (3)$$

where

C_{Pu} = milligrams of plutonium per gram of solution,

S = milligrams of plutonium sulfate used,

F = 0.4750, gravimetric factor for plutonium in the sulfate compound, and

W_{Pu} = grams of final solution.

5.8.3 End Point. Calculate the end point of the titration using Equation 4.

$$EP = (B_0 - B_2) + \frac{(C_2)(B_1 - B_2)}{(C_1 - C_2)} \quad (4)$$

where

EP = end point in grams of dichromate solution added,

B_0 = initial weight of dichromate weighing buret (grams),

B_1 = weight of buret at first titration point (grams),

B_2 = weight of buret at second titration point (grams),

C_1 = current reading at first titration point (microamperes), and

C_2 = current reading at second titration point (microamperes).

5.8.4 Iron Standardization. Calculate the milliequivalents per gram of ferrous ammonium sulfate solution using Equation 5.

$$C_{Fe} = \frac{(2)(W)(C_{Pu}) + (A_1)(EP)(C_{Cr})}{(A_1)(P)} \quad (5)$$

where

C_{Fe} = milliequivalents per gram of solution,
 W = grams of aliquot taken from calibration standard,
 C_{Pu} = milligrams of plutonium per gram of calibration solution,
 A_1 = atomic weight of plutonium in calibration standard,
 EP = end point of titration,
 C_{Cr} = milliequivalents per gram of dichromate solution, and
 P = grams of excess ferrous ammonium sulfate solution.

5.8.5 Solid Samples. Calculate the concentration of plutonium in mixed oxide and plutonium oxide samples using Equation 6.

$$Pu = \frac{[(P)(C_{Fe}) - (EP)(C_{Cr})] AW_3}{2W_1W_2} \times 100 \quad (6)$$

where

Pu = weight percent of plutonium in sample,
 P = grams of excess ferrous ammonium sulfate solution,
 C_{Fe} = milliequivalents per gram of iron solution,
 EP = end point in grams of potassium dichromate solution from back titration,
 C_{Cr} = milliequivalents per gram of dichromate solution,
 A = atomic weight of plutonium in sample,
 W_1 = sample weight, milligrams,
 W_2 = grams of sample aliquot taken, and
 W_3 = grams of total sample solution.

5.8.6 Solution Samples. Calculate the concentration of plutonium in plutonium nitrate or chloride solutions using Equation 7.

$$Pu = \frac{[(P)(C_{Fe}) - (EP)(C_{Cr})] A}{2V} \quad (7)$$

where

Pu = grams of plutonium per litre of solution,
 P = grams of excess ferrous ammonium sulfate solution,
 C_{Fe} = milliequivalents per gram of iron solution,
 EP = end point in grams of potassium dichromate solution from back titration,
 C_{Cr} = milliequivalents per gram of dichromate solution,
 A = atomic weight of plutonium in sample, and
 V = millilitres of sample aliquot taken.

5.9 Precision. The relative standard deviation of the method is 0.1 %.

6. URANIUM BY COULOMETRY

This method for determining uranium in uranium dioxide, mixed oxide, and uranium nitrate solutions shall be in accordance with ASTM C 698.

7. URANIUM BY VOLUMETRIC ANALYSIS

This method for determining uranium in uranium dioxide and uranium nitrate solutions shall be in accordance with ASTM C 696 and C 799 respectively.* This method is applicable for determining uranium in mixed oxide by dissolving the sample using 5.7.2 in this standard as follows:

7.1 At Step 1 (5.7.2), use a portion of sample that will give a uranium concentration of about 15 mg/mL in a 60-mL volume,

7.2 At Step 8 (5.7.2), transfer an aliquot of dissolved sample containing about 120 mg of uranium to a 400-mL beaker,

7.3 Continue by following ASTM C 696, beginning at Step 5 of the Basic Procedure and adding 3 mL of H_2SO_4 . (13.1.5 in ASTM C 696-80.)

An automatic titrator and buret have been used successfully with this method, such as the Metrohm E-526 Titration-Controller and the Metrohm E-535 Digital Buret.

8. OXYGEN-TO-METAL RATIO

This method for determining oxygen-to-metal ratio in uranium dioxide and mixed oxide shall be in accordance with ASTM C 698.

9. PLUTONIUM AND URANIUM ISOTOPIC COMPOSITION

This method for determining the isotopic contents of plutonium and uranium contained in mixed oxide and the individual oxides and nitrate solutions shall be in accordance with ASTM C 696, C 697, C 698, C 759, and C 799, as appropriate.

*Uranium by Ferrous Sulfate Reduction in Phosphoric Acid and Dichromate Titration Method.

10. FLUORIDE

This method for determining fluoride in uranium dioxide, plutonium dioxide, and mixed oxide shall be in accordance with ASTM C 696, C 697, and C 698, respectively.

C

11. CHLORIDE

This method for determining chloride in plutonium dioxide and mixed oxide shall be in accordance with ASTM C 697 and C 698, respectively. This method, as given in either ASTM C 697 or C 698, is applicable for determining chloride in uranium dioxide.

D

12. NITRIDE NITROGEN

This method for determining nitride nitrogen in mixed oxide and in uranium dioxide shall be in accordance with ASTM C 698. This method is not applicable to plutonium dioxide.

C

13. TOTAL NITROGEN

13.1 Application. This method is applicable to the determination of total nitrogen in samples of uranium oxide and mixed oxide powder and pellets, and plutonium dioxide. From 5 to 2500 μ g of nitrogen can be determined in a 0.1 g sample.

13.2 Summary. Powdered or small pieces of sample are fused at about 2600°C in a graphite crucible. The nitrogen is released in its elemental form and it is measured by gas chromatography, which is based upon the differences in thermal conductivity of gases.

13.3 Interferences. Nitrogen from the atmosphere will enter the nitrogen analyzer if the sample is improperly loaded and this will cause a high result. Ammonia, nitrates, and other nitrogen-containing compounds from extraneous sources will cause high results.

13.4 Apparatus.

1. Nitrogen analyzer, LECO UO14 sp Nitrogen Determinator, Model No. 875-034 or its equivalent.
2. Remote furnace, LECO Model No. 375-492 or equivalent.
3. Tin capsule, LECO No. 501-059 or equivalent.

13.5 Reagents and Standards.

1. Anhydron, LECO No. 501-171 or equivalent.
2. Ascarite, 20-30 mesh, LECO No. 183-001 or equivalent.

3. Ascarite, 8-20 mesh, LECO No. 501-166 or equivalent.
4. Helium, ultra-high purity, 99.995% minimum.
5. Molecular sieve, 5A, 20-30 mesh.
6. Phosphorus pentoxide, LECO No. 765-278 or equivalent.
7. Rare earth oxide, LECO No. 501-170 or equivalent.
8. Sulfur absorber, LECO No. 763-770 or equivalent.
9. Calibration standards.

Steel standards are used to calibrate the "SLOPE" adjustment and they are: NBS SRM 346 and 133; and LECO No. 501-551, No. 501-552, and No. 501-553.

Standards used to prepare a calibration curve shall be as specified by NE F 2-6. These standards are uranium and plutonium oxide materials to which known amounts of nitrogen have been added.

13.6 Calibration. * Calibration consists of calibrating the "SLOPE" adjustment and preparing a calibration curve. Calibrate as follows:

1. Prepare the instrument for analysis. The analyzer must conform to the following:
 - a. Be sure that the water supply to the coolant circulator has not been shut off or disconnected; then turn on the coolant circulator power switch.
 - b. "DVM ON" switches must be on.
 - c. "AUX FURN ON" indicator must be on.
 - d. The "FUNCTION SWITCH" switch must be in the "OPERATE" position.
 - e. The two circuit breakers must be on.
 - f. The "STD-BY" indicator must be green.

*Calibration is based upon the LECO U014 sp Nitrogen Determinator, Model No. 875-034. If another analyzer is used, follow the manufacturer's recommended procedure.

- g. The "HELIUM BLANKET" indicator must be off.
 - h. The coolant circulator power switch must be on.
 - i. The furnace must be empty and closed.
 - j. The "OVEN INDICATOR" must be cycling on and off and the oven temperature must be approximately 45°C.
 - k. The helium regulator must be set for 40 psig (280 kPa).
 - l. Both the "MEASURE FLOW" and the "REFERENCE FLOW" rotometers must indicate the approximate flows.
- 2. Turn the "FUNCTION SELECT" switch to the "DVM ZERO" and adjust the DVM zeros if necessary.
 - 3. Depress the "STD-BY" switch. Turn the "FUNCTION SELECT" switch to the "OPERATE" position for approximately 30 s. Then turn the "FUNCTION SELECT" switch to the "INTEG CHECK" position and note the time. At the end of 1 min, note the reading.

The DVM reading must not change more than ± 0.001 during this period. If it does, refer to the electronic checkout in the instruction manual for the LECO U014 sp Nitrogen Determinator.

- 4. Depress the "STD-BY" switch. Turn the "FUNCTION SELECT" switch to the "OPERATE" position.

The "STD-BY" indicator should turn green.

- 5. Open the furnace.

The "PURGE" indicator will turn white and the "STD-BY" indicator will go off.

Inspect the interior of the upper electrode cavity with a mirror and flashlight to make sure that no deposits of graphite or other material are present. Also inspect the lower electrode. The bottom interior of the lower cup must be free from all metal or graphite particles. A small gas jet is ideal for cleaning the bottom interior of the lower electrode. Use the proper brush and precaution should be taken to prevent scratching of the electrodes or the O-rings.

Do not insert your fingers or any metallic object into the safety thermostat mounted on the outside of the upper electrode. When power is applied, there is 115 V on these connections.

6. Place a LECO crucible on the lower electrode assembly using tweezers.

To avoid contamination, do not touch the crucibles with your fingers.

7. Close the furnace.

The "PURGE" indicator will turn green.

The furnace must be kept closed at all times except when cleaning the interior of the furnace or loading the crucible. The furnace must be cleaned before each analysis.

8. Depress the "OUT-GAS" switch.

The "OUT-GAS" indicator will be white during the outgas period and the "PURGE" indicator will be off.

The crucible current value is indicated on the "FURNACE POWER" meter and during out-gas, the value should be between 1000 and 1050 A. If not, refer to the procedure described in the installation section of the instruction manual.

9. The following procedure will compensate for a normal nitrogen blank:

- a. Repeat Steps 4 through 8.
- b. The "OUT-GAS" indicator must be green.
- c. The empty out-gassed crucible must be left in the furnace. Do not put a sample into the crucible at this time.
- d. Depress the "ANALYZE" switch.

The "ANALYZE" indicator will turn white and the "OUT-GAS" indicator will go off.

When the "ANALYZE" indicator goes off, the "NITROGEN" indicator will turn green. The "BLANK" control must be adjusted before the "NITROGEN" indicator turns green.

- e. Adjust the "NITROGEN BLANK" control while the "NITROGEN" indicator is white to maintain all zeros on the "NITROGEN" DVM.
- f. Repeat this procedure with a minimum of three crucibles to establish the proper "NITROGEN BLANK" setting.

10. The following describes the procedure for calibration of the "SLOPE" adjustment.

- a. Repeat Steps 4 through 6.
- b. Place a steel calibration standard of a weight between 0.300 and 0.699 g into the loading head.

Be sure to handle the sample only with tweezers.

The sample form must be such that it can be contained in a cylinder 6 mm in diameter and 8 mm high.

- c. Turn the "SAMPLE WEIGHT COMPENSATOR" switches to the value of the weighed sample.
- d. Close the furnace.
- e. Depress the "OUT-GAS" switch.
- f. Push the "SAMPLE DROP" button after the "OUT-GAS" indicator turns green.

This lets the standard fall into the crucible.

- g. Depress the "ANALYZE" switch.

The "OUT-GAS" indicator will go off and the "ANALYZE" indicator will turn white.

The crucible current value should be slightly lower than during outgas (approximately 30 A lower). If the current is considerably lower, the sample may not have fallen into the crucible--check the loading head cavity.

- h. Note the reading when the "NITROGEN" indicator turns green, but do not adjust the slope control.
- i. Repeat this procedure for a minimum of three standards to determine the average reading.
- j. If the average reading is within the tolerance stated for the sample, no adjustment should be made. If the average reading is above or below tolerance for the nitrogen standard value, adjust the slope control to bring the average value within the tolerance.

The slope adjustment can be made only when the "NITROGEN" indicator is white.

Never attempt to open or close the furnace during "OUT-GAS" or "ANALYZE" (indicators white) because the furnace electrodes or the a-c switch will be severely damaged.

11. Prepare a calibration curve by repeating Step 10, except use a uranium or plutonium oxide calibration standard instead of a steel standard at Step 10b. The oxide is placed into a tin capsule; the ends are pinched closed and the capsule is placed into the loading head.

- a. Analyze at least five portions of the oxide standard to produce calibration points ranging between 10 and 300 μg of nitrogen.

The amounts of standard taken should be between 0.30 and 0.60 g.

- b. Determine a tin capsule blank using an empty capsule at Step 10b; make at least three determinations and calculate an average blank.
- c. Subtract the average blank from each standard readout and prepare a calibration curve by plotting the net readouts versus micrograms of nitrogen using linear graph paper.

A new calibration curve is not required each time nitrogen analyses are made, although at least one point on the curve must be checked during each 8-h shift in which analyses are made. The method is in calibration if the result falls within $\pm 5\%$ of the curve. A new curve is required if two consecutive results fall outside $\pm 5\%$.

13.7 Analysis.*

1. Repeat Steps 4 through 6 of 13.6.
2. Place a sample weighing between 0.30 and 0.60 g into the loading head.

The sample form must be such that it can be contained in a cylinder 6 mm in diameter and 8 mm high.

Weigh powdered samples in tin capsules; pinch the ends in.

Contamination of samples with nitrogen from air can be eliminated by weighing in an argon atmosphere.

*This procedure is based upon the LECO U014 sp Nitrogen Determinator, Model No. 875-034. If another analyzer is used, follow the manufacturer's recommended procedure.

For samples containing less than 0.5 % nitrogen, the 0 to 1000 µg/g range should be used; for more than 0.5 % the 0 to 10 000 µg/g range should be used.

3. Turn the "SAMPLE WEIGHT COMPENSATOR" switch to 0.5.
4. Close the furnace.
5. Depress the "OUT-GAS" switch.
6. Push the "SAMPLE DROP" button after the "OUT-GAS" switch turns green.

This lets the sample fall into the crucible.

7. Depress the "ANALYZE" switch.

The "OUT-GAS" indicator will go off and the "ANALYZE" indicator will turn white.

The fusion current should be between 950 and 1000 A, which requires the highest transformer tap setting possible without causing crucible breakdown.

If current drops to zero during analysis, discard the result and repeat the analysis.

As soon as the "NITROGEN" indicator turns green, the impulse furnace may be opened and the used crucible removed. The furnace can be cleaned and next sample introduced into the loading head.

When the "NITROGEN" indicator turns green, the micrograms of nitrogen will be displayed on the DVM.

13.8 Calculations. Calculate the concentration of nitrogen in the sample using Equation 8.

$$\text{Nitrogen} = \frac{(A-B)}{2W} \quad (8)$$

where

Nitrogen = nitrogen content (micrograms per gram),
 A = micrograms of nitrogen determined from the DVM readout and the calibration curve,
 B = average tin capsule blank (micrograms of nitrogen), and
 W = sample weight (grams).

13.9 Precision. A pooled relative standard deviation of 12 % was obtained from the analysis of 22 standards with the amount of nitrogen taken for analysis ranging between 5 and 300 μ g.

14. TUNGSTEN

The method for the determining tungsten in mixed oxide shall be in accordance with ASTM C 698. This method is applicable for determining tungsten in uranium dioxide and plutonium dioxide.

C

15. SULFUR BY SPECTROPHOTOMETRY

This method for determining sulfur in mixed oxide shall be in accordance with ASTM C 698. This method is applicable for determining sulfur in plutonium dioxide and in uranium dioxide with the following exception:

C

15.1 At Step 8 of the Procedure, disregard the last sentence for uranium dioxide (do not heat and do not add hydroxylamine). (68.8 in ASTM C 698-80a)

16. SULFUR BY IODOMETRY

16.1 Application. This method is applicable to the determination of sulfur in samples of uranium oxide, plutonium oxide, and mixed oxide powder and pellets. Twenty to over 1000 μ g of sulfur per gram of sample can be determined, depending upon sample size.

16.2 Summary. Sulfur is determined by igniting the sample between 1600 and 1700°C in a stream of oxygen. The sulfur dioxide formed is swept from the combustion chamber into an acid solution containing potassium iodide and the blue iodine-starch complex. The sulfur dioxide, which reduces iodine, is automatically titrated with standard potassium iodate solution using a colorimetric end point monitor.

16.3 Interferences. Interferences are not expected. Chemical calibration corrects for a low bias inherent with the method.

16.4 Apparatus.

1. Crucibles, ceramic with porous covers, LECO 528-031 or equivalent.
2. Induction furnace, LECO 521-400 or equivalent.
3. Scoop, to contain about 0.25 cm^3 (250 mm^3).
4. Sulfur titrator, LECO Automatic Sulfur Titrator, Model 532-000 or equivalent.

16.5 Reagents and Standards.

1. Copper, ring, LECO 550-184 or equivalent.
2. Hydrochloric acid, 0.18N.
3. Iron, granular, LECO 501-76 or equivalent.
4. Oxygen, ultra high purity grade or equivalent.
5. Potassium iodate solution, 0.0888 g/L.
6. Starch solution, arrowroot, LECO 501-061 or equivalent.

Prepare by making a slurry of 1 g of starch in 25 mL of water. Add the slurry to 75 mL of boiling water and let boil for 1 min. Let the solution cool for several minutes. Dissolve 3 g of potassium iodide in the solution and mix thoroughly. This solution will remain stable for about 1 week, unless stored under refrigeration. The starch solution must be discarded when the starch-iodine color takes on a reddish tinge.

7. Tin, granular, LECO 501-77 or equivalent.
8. Calibration standards.

Standards shall be as specified by NE F 2-6. These standards are uranium and plutonium oxide materials to which known amounts of sulfur have been added.

16.6 Calibration. To determine a calibration factor, analyze a portion of a calibration standard containing about 200 μ g of sulfur using 16.7. Calculate the calibration factor using 16.8.1. If the calibration factor is within 0.90 ± 0.05 , the calibration is satisfactory. If not, investigate and correct the problem before proceeding with the analysis. Generally two calibration standards are analyzed during each 8-h shift in which sulfur analyses are made. The first standard run conditions the instrument.

16.7 Analysis.* Care must be taken to avoid sulfur contamination of reagents and laboratory equipment.

1. Turn on the sulfur titrator and let it warm up for 15 min.

*This procedure is based upon the LECO Automatic Sulfur Titrator, Model 532-000. If another analyzer is used, follow the manufacturer's recommended procedures.

2. Place 3 scoops of tin and 1 scoop of iron into each of two clean crucibles.
3. Add about 1 g of sample that has been crushed and weighed to the nearest 0.01 g to one of the crucibles.

The second crucible without sample is used to determine a blank.

4. Tap each crucible several times to settle the powder and add one copper ring to each crucible.
5. Rinse the titration cell with the 0.18N hydrochloric acid and fill the cell one-half full with hydrochloric acid.
6. Add 5 mL of the starch solution to the cell.
7. Turn on the oxygen to flow through the system at 1 L/min.
8. Fill the buret with the 0.0888 g/L of potassium iodate solution and set the mode switch to "end point."
9. Turn the mode switch to "off" when the buret reading stabilizes.

The solution in the titration cell should be dark blue and it can be used without changing for several samples, depending upon the amount of sulfur titrated each time.

The mode switch should always be in the "off" position when changing the solution in the titration cell.

10. Turn on the power switch to the induction generator and let it warm up for 5 min.
11. Place a porous cover on each crucible and take each crucible through Steps 12, 13, 14, and 15.
12. Refill the buret with the potassium iodate solution.
13. Place a crucible into the furnace and set the mode switch to "titrate."
14. Turn on the furnace and let the sample burn for 4.5 min.
15. Turn off the furnace; read and record the buret reading.

The mode switch can be left in the "titrate" position between samples.

16.8 Calculations. Calculate the calibration factor and percent sulfur in the sample using 16.8.1 and 16.8.2. The titrator is designed to read percent sulfur directly when a 1-g sample and a concentration of 0.444 g/L potassium iodate solution is used. In this method, the concentration of the potassium iodate solution is reduced by a factor of 5 (0.0888 g/L) to give larger buret readings during titrations. Therefore, a denominator of 5 is used in each equation.

16.8.1 Calibration Factor.

$$F = \frac{Sc - b}{5s} \quad (9)$$

where

F = calibration factor,
Sc = buret reading from the analysis of the calibration standard,
b = buret reading from the blank, and
s = micrograms of sulfur taken with the calibration standard.

16.8.2 Concentration of Sulfur.

$$\text{Sulfur} = \frac{A - b}{5WF} \times 10^4 \quad (10)$$

where

Sulfur = micrograms of sulfur per gram of sample,
A = buret reading from sample analysis,
b = buret reading from the blank,
F = calibration factor, and
W = sample weight (grams).

16.9 Precision. The pooled relative standard deviation obtained over a 2-year period from mixed oxide standards was 7.4 %.

17. PHOSPHORUS

17.1 Application. This method is applicable to the determination of phosphorus in samples of uranium dioxide powder and pellets, plutonium dioxide powder, and mixed oxide powder and pellets. Between 0.5 and 10 µg of phosphorus are required for an analysis.

17.2 Summary. Samples are dissolved in nitric and hydrofluoric acids and fumed with perchloric acid. Phosphorus is separated from uranium and plutonium and measured spectrophotometrically as the blue reduced form of heteropoly molybdophosphoric acid. Separation is accomplished by extracting the heteropoly molybdophosphoric acid into n-butanol.

17.3 Interferences. Interfering elements include arsenic, cerium, germanium, gold, tantalum, and tin. Silicon present as silica is a major interference and it is removed with hydrofluoric acid. Care must be taken to prevent contamination from extraneous phosphorus.

17.4 Apparatus.

1. Diamond (Plattner) mortar.
2. Heat lamp.
3. Platinum crucibles, 8 mL.
4. Spectrophotometer, UV to visible range, using 10 mm matched cells.

17.5 Reagents and Standards.

1. Ammonium molybdate, 4 % in 0.6M sulfuric acid.
Prepare fresh daily to minimize phosphorus contamination.
2. n-Butanol.
3. Ethanol, 100 %.
4. Hydrochloric acid, 12M (37 %).
5. Hydrofluoric acid, 28M (48 %).

CAUTION: Hydrofluoric acid causes severe and slow healing burns.

6. Nitric acid, 15.6M (70 %).
7. Perchloric acid, 11.6M (70 %).
8. Stannous chloride.

Dissolve 1 g of stannous chloride dihydrate in 3 mL of 12M hydrochloric acid and dilute to 100 mL with 0.6M sulfuric acid. Prepare fresh daily.

9. Sulfuric acid, 18M (96 %) and 0.6M.
10. Calibration standards.

Standards shall be as specified by NE F 2-6. These standards are uranium and plutonium oxide materials to which known amounts of phosphorus have been added.

17.6 Calibration. Calibration shall be in accordance with NE F 2-6. Using at least five calibration points ranging between 0.5 and 10 μ g of phosphorus, calibrate the method as follows:

1. Analyze weighed portions of the calibration standards and a reagent blank according to 17.7. If the measured absorbance of the reagent blank is greater than 0.015, replace each reagent individually to determine the source of contamination. Subtract the absorbance reading of the reagent blank from the absorbance reading of each standard.
2. Prepare a calibration curve by plotting the absorbance versus micrograms of phosphorus or use a least-squares analysis to obtain the linear calibration equation ($y = Ax + B$) that best fits the calibration data. In this equation, y is the absorbance; x is the micrograms of phosphorus; A is the slope; B is the intercept on the y-axis (B should be approximately zero).

17.7 Analysis. Cleanliness in this determination is extremely important to avoid contamination from extraneous phosphorus. As a minimum effort, rinse all glassware with 18M sulfuric acid and then with large amounts of distilled water. Clean platinum dishes with fine sand and rinse with distilled water. Be especially careful to remove powder from protective gloves by washing them with a nonphosphorus-containing soap and water.

1. Transfer a 50 mg portion of sample weighed to the nearest 0.1 mg into one of two 8-mL platinum crucibles.

A 50 mg sample is satisfactory for concentrations of 10 to 200 μ g of phosphorus per gram of sample.

The second crucible, which is used for the measurement of the reagent blank, is taken through Steps 2 through 15.

If the sample is not in powdered form, crush to a fine powder* using the diamond (Plattner) mortar.

2. Add 3 mL of 15.6M nitric acid, 1 drop of 28M hydrofluoric acid, and 0.2 mL of 11.6M perchloric acid.
3. Heat to fumes of perchloric acid under a heat lamp.

Perchloric acid is recommended rather than sulfuric acid because the latter causes low and erratic results.

*Particles should be no larger than those passing a No. 100 screen (U. S. Standard Sieve Series).

4. Add 1 mL of distilled water and decant the solution into a second 8-mL platinum crucible.

Avoid carrying any undissolved sample along with the solution.

5. Repeat Steps 2 through 4 until the sample completely dissolves.

Steps 2 through 4 must be repeated the same number of times for the reagent blank as for the sample.

6. Add 10 drops of 28M hydrofluoric acid and fume the solution to near dryness.

The hydrofluoric acid is used to volatilize any interfering silica that may be present.

7. Dissolve the residue in 1 mL of 0.6M sulfuric acid and quantitatively transfer the solution to a separatory funnel with 7 mL of 0.6M sulfuric acid.

8. Add 2 mL of 4 % ammonium molybdate and shake the separatory funnel for 10 min.

Shaking for 10 min allows time for the formation of the heteropoly acid of phosphate and molybdate ions.

9. Add 5 mL of n-butanol; shake for 2 min to mix phases, allow the phases to separate and discard the aqueous (lower) phase.

The yellow heteropoly acid extracts into the n-butanol phase.

10. Add 5 mL of 0.6M sulfuric acid; shake for 1 min; allow the phases to separate and discard the aqueous (lower) phase.

The 0.6M sulfuric acid removes excess ammonium molybdate from the n-butanol.

11. Repeat Step 10.

12. Add 2 mL of 1 % stannous chloride solution; shake for 1 min and allow the phases to separate and discard the aqueous phase.

The yellow heteropoly acid reduces to the intense blue form.

13. Transfer the n-butanol phase to a 5 mL volumetric flask; rinse the sides of the separatory funnel with ethanol and transfer the rinses to the flask.

Because butanol is soluble in water, its volume is about 4 mL at the time of transfer to the volumetric flask. Rinsing with ethanol, which is highly miscible with both n-butanol and water, ensures a quantitative transfer.

14. Dilute to volume with ethanol.

15. Measure the absorbance at 725 nm in a 10-mm cell using ethanol as the reference solution.

17.8 Calculations. Calculate micrograms of phosphorus per gram of sample using 17.8.1 or 17.8.2. The equation used depends upon the technique used for calibration (see 17.6, Step 2).

17.8.1 Calibration Curve. Using the absorbances measured for the sample and reagent blank, obtain the micrograms of phosphorus for each from the calibration curve. Calculate the concentration of phosphorus in the sample using Equation 11.

$$\text{Phosphorus} = \frac{s-b}{W} \quad (11)$$

where

Phosphorus = micrograms of phosphorus per gram of sample,
s = micrograms of phosphorus from sample measurement,
b = micrograms of phosphorus from reagent blank measurement, and
W = sample weight (grams).

17.8.2 Least-Squares Calibration. Use Equation 12 to calculate the concentration of phosphorus in the sample.

$$\text{Phosphorus} = \frac{S-B}{AW} \quad (12)$$

where

Phosphorus = micrograms of phosphorus per gram of sample,
S = (absorbance of sample) - (absorbance of reagent blank),
A&B = constants determined from calibration equation ($y = Ax + B$), and
W = sample weight (grams).

17.9 Precision. The relative standard deviation ranges between 10 % for about 10 μg of phosphorus per gram to about 4 % for 100 μg of phosphorus per gram.

18. URANIUM IMPURITY

This method for determining uranium in plutonium dioxide shall be in accordance with ASTM C 759* with the following additions:

18.1 Apparatus.

1. Platinum dishes, 30-mL.

18.2 Reagents.

1. Hydrofluoric acid, 28M (48 %).
2. Nitric acid, 15.6M (70 %).
3. Sulfuric acid, 6M.

18.3 Analysis.

1. Quantitatively transfer to one of two 30-mL platinum dishes a 70 mg sample weighted to the nearest 0.1 mg.

A 70 mg sample is satisfactory for concentrations of 150 to 3000 μ g of uranium per gram.

The second dish, which is used for the measurement of the reagent blank, is taken through Steps 2 through 7.

2. Add 10 mL of 15.6M nitric acid, 3 or 4 drops of 28M hydrofluoric acid, and 0.5 mL of 6M sulfuric acid.
3. Heat under a heat lamp to fumes of sulfuric acid.

This dissolves the sample and volatilizes nitrate.

4. Add 2 mL of water to the residue, mix, and decant the solution into a 50 mL beaker.

Avoid carrying any undissolved sample along with the solution.

5. Repeat Steps 2 and 3 until the sample is completely dissolved.

Decant the solution into the same 50-mL beaker each time.

Steps 2 and 3 must be repeated the same number of times for the reagent blank as for the sample.

*Uranium by Arsenazo I Spectrophotometric Method.

6. Evaporate the combined solutions to dryness in the 50-mL beaker.
7. Continue by following the method in ASTM C 759 beginning at Step 5 of the Procedure. (38.5 in ASTM C 759-79)

18.4 Calculation.

1. Change the equation in ASTM C 759 as follows:

$$R = (Y-B)/AW$$

where,

R = micrograms of uranium per gram of sample, and
W = weight of sample in grams.

19. GENERAL METALLIC IMPURITIES BY CARRIER DISTILLATION SPECTROSCOPY

This method for determining trace metallic impurities in uranium dioxide, plutonium dioxide, and mixed oxide shall be in accordance with ASTM C 696, C 697, and C 698, respectively. As a minimum, the following 24 elements shall be determined in the three oxides: Ag, Al, Be, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ta, Ti, V, and Zn. A direct reading spectrograph of comparable quality may be substituted for the equipment listed in the ASTM Standards. If that is done, follow the directions given by the manufacturer as stated in the ASTM C 698 method, equipment item 5 (Spectrograph) under Apparatus. (97.5 in ASTM C 698-80a)

20. IMPURITIES BY SPARK-SOURCE MASS SPECTROGRAPHY

This method for determining trace impurities in uranium dioxide, plutonium dioxide, and mixed oxide shall be in accordance with ASTM C 696, C 697, and C 698, respectively.

21. RARE EARTHS

This method for determining rare earths in uranium dioxide, plutonium dioxide, and mixed oxide shall be in accordance with ASTM C 696, C 697, and C 698, respectively.

22. CARBON

This method for determining carbon in mixed oxide shall be in accordance with ASTM C 698. This method is applicable also for determining carbon in uranium and plutonium dioxides.

23. WATER

This method for determining water (moisture) in mixed oxide shall be in accordance with ASTM C 698. This method is applicable also for determining water in uranium and plutonium dioxides.

24. GAS CONTENT

This method for determining gases in uranium dioxide and mixed oxide pellets shall be in accordance with ASTM C 698.

25. TOTAL VOLATILES

25.1 Application. This method is applicable to the determination of total volatiles in samples of plutonium dioxide powder. The lower limit of the method is controlled by the sensitivity of the balance used for the weight measurement and by the weight of sample taken for an analysis.

25.2 Summary. Total volatile material is determined by measuring the weight loss of a sample when heated to constant weight at $950 \pm 25^\circ\text{C}$ in air.

25.3 Interferences. Interferences are not anticipated because only a weight change occurring under the prescribed conditions of the method is measured.

25.4 Apparatus.

1. Analytical balance capable of providing a standard deviation in weighing of 0.2 mg or less over a range of 0.5 to 50 g.
2. Desiccator.
3. Furnace capable of sustained operation at 950°C with a temperature control of $\pm 10^\circ\text{C}$.
4. Platinum crucibles, 5 mL capacity.

25.5 Reagents and Standards. None required.

25.6 Calibration. Calibration standards are not available for this method. Calibration of the analytical balance shall be in accordance with NE F 2-6.

25.7 Analysis. Constant weight, as used in this procedure, is defined as a maximum difference of 0.2 mg between two successive weighings.

1. Transfer about 1 g of sample to a crucible that has been tared to constant weight at $950 \pm 25^\circ\text{C}$.

Larger amounts of sample may be used to improve precision. Also, larger amounts may be desirable should the ignited material be required for other analyses.

2. Weight the crucible and sample to the nearest 0.2 mg.
3. Place the crucible in a cold or warm (about 110°C) furnace.

Loss by spattering may occur when a moisture laden sample is placed into a hot furnace.

4. Raise the temperature to about 110°C ; hold at this temperature for 30 min and then raise the temperature to $950 \pm 25^\circ\text{C}$ for 1 h.

Heating too rapidly may cause loss of sample from spattering through rapid volatilization of water.

5. Remove the crucible from the furnace; let cool for a few minutes and then place in a desiccator for final cooling to room temperature.

Atmospheric water and gas may be reabsorbed should the sample be allowed to cool to room temperature in the glove box atmosphere.

6. Weigh the crucible and sample to the nearest 0.2 mg.
7. Replace the crucible in the furnace at 950°C for 20 min; remove cool, and weigh as in Steps 5 and 6.
8. Repeat Step 7 until constant weight is obtained.

25.8 Calculation. Calculate the weight percent of the total volatiles in the sample using Equation 13.

$$\text{Total Volatiles} = \frac{S-B}{S-C} \times 100 \quad (13)$$

where

Total Volatiles = weight percent in sample,
S = grams of original sample plus tared crucible,
B = grams at constant weight of ignited sample plus crucible, and
C = grams at constant weight (tare) of crucible.

25.9 Precision. For 1 g samples when using a balance with a standard deviation of 0.2 mg, the relative standard deviation is 1.2 and 6 % for total volatile contents of 2.5 and 0.5 % (by weight) respectively.

26. FREE ACID

This method for determining free acid in plutonium nitrate and uranium nitrate solutions shall be in accordance with ASTM C 759 and C 799, respectively.

27. UNDISSOLVED SOLIDS

27.1 Application. This method is applicable to the determination of undissolved solids in samples of uranyl nitrate and plutonium nitrate solutions.

27.2 Summary. After vigorously mixing the sample, a 10-mL volume is removed and passed through a tared filter. The filter is washed with nitric acid followed by a water wash, dried, and weighed.

27.3 Interferences. There are no interferences as such. The major source of error is associated with sampling the shipping container to obtain a representative sample.

27.4 Apparatus.

1. Analytical balance capable of weighing to 0.1 mg.
2. Filter, 5 μ m pore size.
3. Filter, 10 $\pm$ 2 μ m pore size.
4. Pipet, 10 mL, with a tip opening of about 0.5 mm.

27.5 Reagents and Standards

1. Distilled water filtered through a 5 μ m filter before use.
2. Nitric acid, 6M* filtered through a 5 μ m filter before use.

27.6 Calibration. Calibration standards are not available for this method. Calibration of the balance shall be as specified by NE F 2-6.

*The specification range for nitric acid in plutonium nitrate solutions is usually between 2 and 10M.

27.7 Analysis.

1. Prepare a 10 μ m filter by washing it twice with 5 mL of filtered 6M nitric acid, rinsing twice with 5 mL of filtered distilled water, drying at 110° C, and weighing to the nearest 0.1 mg.
2. Mix the sample by shaking the container vigorously for 30 s.
3. Immediately transfer 10.0 mL of the sample to the tared filter.

Vacuum can be used to hasten filtering.

4. Wash the filter once with 5 mL of filtered 6M nitric acid and then twice with 5 mL of filtered distilled water.
5. Dry the filter at 100°C and weight to the nearest 0.1 mg.

27.8 Calculation. Calculate micrograms of undissolved solids per gram of metal (uranium or plutonium) using Equation 14.

$$\mu\text{g Solids/g} = \frac{10^8 (C-T)}{M} \quad (14)$$

where

C = grams of filter plus solids,
 T = tare weight of filter, (grams), and
 M = grams of metal per litre of solution.

27.9 Precision. The precision, exclusive of sampling, depends primarily upon the precision of weighing.

28. ENTRAINED ORGANICS

28.1 Application. This method is applicable to the determination of entrained organics in samples of uranyl nitrate and plutonium nitrate solutions.

28.2 Summary. Entrained organic materials are extracted from the aqueous nitrate solution with carbon tetrachloride and are measured by infrared spectrophotometry using the alkane carbon-hydrogen stretching frequency at 0.342 μ m/m. The measured organic compounds, as defined by the calibration of this method, are tributyl phosphate (TBP) and dodecane as a 30 % TBP-dodecane solution. A solution of TBP (30 %) in a mixture of normal paraffin hydrocarbons, which has an average molecular weight approximating dodecane, is commonly used in chemical processing plants for the production of plutonium nitrate.

28.3 Interferences. No interferences are expected. The major source of error is associated with sampling the shipping container to obtain a representative sample.

28.4 Apparatus.

1. Infrared spectrophotometer with cells having a known light path of about 0.5 mm.
2. Extraction vessel, separatory funnel, 30 mL with a Teflon stopcock.

28.5 Reagents and Standards.

1. Carbon tetrachloride.

CAUTION: Carbon tetrachloride is toxic; avoid inhalation and repeated or prolonged contact with the skin.

2. Tributyl phosphate solution, 30 % TBP in dodecane.
3. Calibration standards.

A series of five standards ranging from 1000 to 5000 μL of 30 % TBP-dodecane per litre of carbon tetrachloride. Prepare by pipetting 100, 200, 300, 400, and 500 μL of the TBP solution into separate 100 mL volumetric flasks containing 50 mL of carbon tetrachloride. Dilute to volume with carbon tetrachloride and mix.

28.6 Calibration. The calibration shall be verified at least once a week during periods when samples are analyzed. Calibrate the method as follows:

1. Analyze a 10 mL portion of each calibration standard according to 28.7.
2. Prepare a calibration curve of absorbance versus microlitres of 30 % TBP-dodecane per litre of solution.

28.7 Analysis.

1. Mix the sample by shaking the container vigorously for 30 s.
2. Immediately transfer 10.0 mL of sample to the extraction vessel.
3. Pipet 10.0 mL of carbon tetrachloride into the extraction vessel.

4. Stopper the vessel and shake it vigorously for 2 min.
5. Allow the phases to separate.
6. Measure the absorbance of the carbon tetrachloride phase at 0.342 mm/m using carbon tetrachloride as the reference solution.

28.8 Calculations. Using the measured absorbance for the sample, obtain microlitres of organics per litre of nitrate solution directly from the calibration curve. Report ppm ($\mu\text{L}/\text{L} = \text{ppm}$).

If the ratio of sample to carbon tetrachloride used in the extraction is changed from 1:1, correct the result accordingly.

28.9 Precision. The precision of this method has not been established.

29. SURFACE AREA

This method for determining surface area of uranium dioxide powder shall be in accordance with ASTM C 696. This method is applicable also to plutonium dioxide and mixed oxide powders, as long as proper precautions are taken when handling powders containing plutonium.

30. AMERICIUM-241

This method for determining Americium-241 in plutonium nitrate solutions shall be in accordance with ASTM C 759. (94 in ASTM C 759-79.) This method is applicable also for determining Americium-241 in plutonium dioxide and mixed oxide once those oxides are dissolved, which can be done by following the procedure in 5.7.1 of this standard.

END

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