Designation: C1204 – 14

Standard Test Method for
Uranium in Presence of Plutonium by Iron(II) Reduction in Phosphoric Acid Followed by Chromium(VI) Titration[1]

1. Scope

1.1 This test method covers unirradiated uranium-plutonium mixed oxide having a uranium to plutonium ratio of 2.5 and greater. The presence of larger amounts of plutonium (Pu) that give lower uranium to plutonium ratios may give low analysis results for uranium (U) (**1**)[2], if the amount of plutonium together with the uranium is sufficient to slow the reduction step and prevent complete reduction of the uranium in the allotted time. Use of this test method for lower uranium to plutonium ratios may be possible, especially when 20 to 50 mg quantities of uranium are being titrated rather than the 100 to 300 mg in the study cited in Ref (**1**). Confirmation of that information should be obtained before this test method is used for ratios of uranium to plutonium less than 2.5.

1.2 The amount of uranium determined in the data presented in Section 12 was 20 to 50 mg. However, this test method, as stated, contains iron in excess of that needed to reduce the combined quantities of uranium and plutonium in a solution containing 300 mg of uranium with uranium to plutonium ratios greater than or equal to 2.5. Solutions containing up to 300 mg uranium with uranium to plutonium ratios greater than or equal to 2.5 have been analyzed (**1**) using the reagent volumes and conditions as described in Section 10.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C852 Guide for Design Criteria for Plutonium Gloveboxes
C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

3. Summary of Test Method

3.1 Samples are prepared by dissolution techniques detailed in Practice C1168 and Ref (**2**). Aliquants containing 20 to 300 mg of uranium, as selected by the facility procedure, are prepared by weight. The sample is fumed to incipient dryness after the addition of sulfuric acid. The sample is dissolved in dilute sulfuric acid prior to titration.

3.2 Uranium is reduced to uranium(IV) by excess ferrous (iron(II)) in concentrated phosphoric acid (H_3PO_4) containing sulfamic acid. The excess iron(II) is selectively oxidized by nitric acid (HNO_3) in the presence of molybdenum(VI) catalyst. After the addition of vanadium(IV), the uranium(IV) is titrated with chromium(VI) to a potentiometric end point (**3, 4**).

3.3 A single chromium(VI) titrant delivered manually on a weight or volume basis is used. The concentration of the chromium(VI) solution is dependent upon the amount of uranium being titrated (see 7.8). Automated titrators that have comparable precisions can be used.

NOTE 1—An alternative ceric (V) sulfate or nitrate titrant may also be used, providing that the user demonstrates equivalent performance to the dichromate titrant.

3.4 For the titration of uranium alone, the precision of the modified Davies and Gray titration method has been significantly improved by increasing the amount of uranium titrated to 1 g and delivering about 90 % of the titrant on a solid mass basis followed by titration to the end point with a dilute titrant (**5**). This modification has not been studied for the titration of uranium in the presence of plutonium, and confirmation of its applicability should be obtained by the facility prior to its use.

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved June 1, 2014. Published July 2014. Originally approved in 1991. Last previous edition approved in 2008 as C1204 – 02 (2008)$^{\varepsilon 1}$. DOI: 10.1520/C1204-14.

[2] The boldface numbers in parentheses refer to the list of references at the end of this test method.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.5 The modification of the Davies and Gray titration method, as described originally in Ref (**4**), may be used instead of the method described herein, where laboratories have demonstrated no plutonium interference at the uranium to plutonium ratios and amounts titrated at that facility. If any modification is made to the procedure in Ref (**4**) for application at the facility to uranium, plutonium mixed oxides, confirmation that the modification does not degrade the analysis technique as stated should be demonstrated prior to its use.

4. Significance and Use

4.1 Factors governing selection of a method for the determination of uranium include available quantity of sample, sample purity, desired level of reliability, and equipment availability.

4.2 This test method is suitable for samples between 20 to 300 mg of uranium, is applicable to fast breeder reactor (FBR)-mixed oxides having a uranium to plutonium ratio of 2.5 and greater, is tolerant towards most metallic impurity elements usually specified for FBR-mixed oxide fuel, and uses no special equipment.

4.3 The ruggedness of the titration method has been studied for both the volumetric (**6**) and the weight (**7**) titration of uranium with dichromate.

5. Interferences

5.1 Interfering elements are not generally present in significant quantities in mixed uranium, plutonium oxide product material. However, elements that cause bias when present in milligram quantities are silver (Ag), vanadium (V), plutonium (Pt), ruthenium (Ru), osmium (Os), and iodine (I). Interference from tin (Sn), arsenic (As), antimony (Sb), molybdenum (Mo), manganese (Mn), fluorine (F), chlorine (Cl), and bromine (Br) are eliminated when the preparation procedure is followed as given (**4**, **8**, **9**, **10**, **11**, **12**) in this titrimetric method. Of the metallic impurity elements usually included in specifications for FBR-mixed oxide fuel, silver, manganese, lead (Pb), and vanadium interfere.

5.2 Other interfering metallic elements are gold (Au), mercury (Hg), iridium (Ir), and palladium (Pd). Elimination of their interference requires their separation from uranium by such techniques as ion exchange and solvent extraction (**13**, **14**).

5.3 An initial fuming with sulfuric acid removes such impurity elements as the halides and volatile metallic elements.

5.4 The effects of impurities and their removal are listed in Table A1.1 of Annex A1, and the details are given in Refs (**4**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**).

6. Apparatus

6.1 *Buret*—Polyethylene bottle (preparation instructions can be found in Appendix X1), glass weight, or volumetric.

6.2 *pH Meter,* with indicator (platinum has been found to be satisfactory) and reference (saturated calomel has been found to be satisfactory) electrodes.

NOTE 2—The indicator electrode should be changed or cleaned if there is a titration problem such as less distinct than normal end point break or end point drift, or, if desired, prior to use when more than a week has passed since its last use. Suggested cleaning procedures for platinum electrodes are detailed in Appendix X2.

NOTE 3—The reference electrode should be covered with a rubber tip or submerged in a solution (saturated potassium chloride solution for the calomel electrode) for overnight storage.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water.

7.3 *Ferrous Sulfate (1.0 M)*—Add 100 mL of sulfuric acid (H_2SO_4, sp gr 1.84) to 750 mL of water as the solution is stirred. Add 280 g of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), and dilute the solution to 1 L with water. Prepare ferrous sulfate reagent fresh on a weekly basis. See Note 6 on combination of this reagent.

7.4 *Nitric Acid (HNO_3), 8 M*—Add 500 mL of HNO_3 (sp gr 1.42) to less than 500 mL of water and dilute to 1 L.

7.5 *Nitric Acid* (8 *M*)*-Sulfamic Acid* (0.15 *M*)*-Ammonium Molybdate* (0.4 %)—Dissolve 4 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 400 mL of water, and add 500 mL of nitric acid (HNO_3, sp gr 1.42). Mix and add 100 mL of 1.5 *M* sulfamic acid solution (see 7.9) and mix.

7.6 *Orthophosphoric Acid (H_3PO_4), 85 %*—Test and treat for reducing substances prior to use (see Annex A2).

7.7 *Potassium Dichromate Solution (2 %)*—Dissolve 2 g of $K_2Cr_2O_7$ in water, and dilute to 100 g with water.

7.8 *Potassium Dichromate Titrant* (0.0045 *M* and 0.045 *M*)—Dissolve 2.65 g of reagent grade or purer grade $K_2Cr_2O_7$ in water; transfer this solution to a pre-weighed, 2-L volumetric flask and dilute to volume; this solution is for use in titration of 20 to less than 100 mg uranium aliquants. Dissolve 26.5 g of reagent grade or purer grade $K_2Cr_2O_7$ in water; transfer this solution to a pre-weighed, 2-L flask and dilute to volume; this solution is for use in titration of 100 to 300 mg uranium aliquants.

7.8.1 If potassium dichromate traceable to a national standards laboratory (for example the National Institute of Standards Technology (NIST) in the U.S. or the Federal Institute for Materials Research and Testing (BAM) in Germany) was

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[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

used, proceed as in 7.8.1.1 and 7.8.1.2 before going to 7.8.3; otherwise go to 7.8.2.

7.8.1.1 Allow the solution to equilibrate to room temperature, weigh the solution, and compute the uranium equivalent titration factor after correcting the weight of dichromate for buoyancy (see 11.1.1) and for oxidizing power (see 11.1.2).

7.8.1.2 Verify the preparation accuracy of the dichromate or ceric titrant solution by titration with a standard uranium solution (see 7.12) within laboratory accepted error limits.

7.8.2 If a reagent grade dichromate or ceric titrant was used, allow the solution to equilibrate to room temperature and standardize the dichromate solution against CRM uranium (see 7.12).

7.8.3 Store the dichromate solution in one or more borosilicate glass bottles with poly-seal tops, or equivalent containers, to prevent concentration changes due to evaporation.

7.9 *Sulfamic Acid (1.5 M)*—Dissolve 146 g of sulfamic acid (NH_2SO_3H) in water, filter the solution, and dilute to 1 L.

7.10 *Sulfuric Acid (1 M)*—Add 56 mL of H_2SO_4 (sp gr 1.84) to water, while stirring, and dilute to 1 L with water.

7.11 *Sulfuric Acid (0.05 M)*—Add 2.8 mL of H_2SO_4 (sp gr 1.84) to water, while stirring, and dilute to 1 L with water.

7.12 *Uranium Reference Solution*—Guide C1128, Section X3.4 may be used to prepare working reference solutions, or solutions may be prepared with appropriate in-house procedures from certified uranium metal.[5]

7.12.1 Clean the surface of the uranium metal, New Brunswick Laboratory CRM 112-A or its replacement,[5] following the instructions on the certificate.

7.12.2 Weigh the metal by difference to 0.01 mg making buoyancy and purity corrections detailed in 11.1.1 and 11.1.2, respectively.

7.12.3 Prepare the uranium standard solution in accordance with Guide C1128 or by the procedure approved for use by each facility. There are many methods of uranium metal dissolution that are successful; methods that reproduce the uranium assay value on the certificate of analysis for the reference material are acceptable. An example of an acceptable dissolution method is given in Appendix X4.

7.12.4 Equilibrate the uranium solution to room temperature, and weigh the solution to give the same number of significant figures as the metal weight.

7.12.5 Calculate the solution concentration in mg uranium/g uranium solution using the calculation in 11.2.2.

7.13 *Vanadyl Sulfate Dihydrate in Solution* (0.0038 *M* vanadium(IV)-0.18 *M* H_2SO_4)—Add 20 mL concentrated sulfuric acid (sp gr 1.84) to less than 980 mL water with stirring and equilibrate to room temperature. Weigh 1.5 g of vanadyl sulfate dihydrate ($VOSO_4 \cdot 2H_2O$) crystals, mix the solid with the temperature equilibrated sulfuric acid, and dilute the solution to 2 L. The vanadyl sulfate concentration should provide 75 to 125 mg $VOSO_4 \cdot 2H_2O$ per titration, but the concentration is not critical (see Refs **(6)** and **(7)**).

7.13.1 The vanadyl sulfate solution is not stable **(16)**; H_2SO_4 stabilizes the vanadium(IV) oxidation state, but the H_2SO_4 concentration is not critical. The $VOSO_4 \cdot 2H_2O$ solution should be prepared at suitable intervals to prevent vanadium(V) interference (24-h intervals for preparation are suggested).

7.13.2 Alternatively, crystalline vanadyl sulfate dihydrate (75 to 125 mg per titration) may be used with a water diluent in place of the solution (see 10.13).

8. Hazards

8.1 Since plutonium- and uranium-bearing materials are radioactive and toxic, adequate laboratory facilities, gloved boxes, fume hoods, etc., along with safe techniques, must be used in handling samples containing these materials. A detailed discussion of all precautions necessary is beyond the scope of this test method. However, personnel who handle radioactive materials should be familiar with such safe handling practices as are given in Guide C852 and Refs **(17)** and **(18)**.

8.2 *Committee C-26 Safeguards Statement:*

8.2.1 The materials (nuclear grade mixed oxides $(U, Pu)O_2$ powders and pellets) to which this test method applies are subject to nuclear safeguard regulations governing their possession and use. The analytical method in this test method meets U.S. Department of Energy guidelines for acceptability of a measurement method for generation of safeguards accountability measurement data.

8.2.2 When used in conjunction with the appropriate standard or certified reference materials (SRMs or CRMs), this procedure can demonstrate traceability to the national measurement base. However, use of this test method does not automatically guarantee regulatory acceptance of the resulting safeguards measurements. It remains the sole responsibility of the user of this test method to ensure that its application to safeguards has the approval of the proper regulatory authorities.

9. Calibration

9.1 If potassium dichromate traceable to a national standards laboratory is used, only solution preparation, verification titrations are needed. Use of an uncertified potassium dichromate requires calibration of the dichromate using a standard uranium material traceable to a national measurement base (for example, New Brunswick Laboratory's CRM 112-A uranium metal standard). See Section 9.2 below.

9.1.1 The potassium dichromate should be prepared as instructed on the certificate, weighed to 0.01 mg, and corrected for buoyancy and purity using the calculations in 11.1.1 and 11.1.2.

9.1.2 The dichromate solution concentration is calculated in mg $K_2Cr_2O_7$/g solution using the calculation in 11.2.1.

9.1.3 The titration factor (mg uranium/g dichromate solution) is calculated for the dichromate solution using the calculation in 11.3.1.

9.2 If reagent grade potassium dichromate or ceric titrant is used, the solution must be standardized against a primary uranium standard for traceability to a national measurement base.

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[5] New Brunswick Laboratory Certified Reference Materials Catalog, current issue, U.S. Department of Energy.

9.2.1 Analyze individually dispensed aliquants of the uranium reference solution in accordance with 10.3 – 10.14.4. See Appendix X3 for analysis control recommendations.

9.2.2 Calculate the uranium titration factor (mg uranium/g dichromate solution) for the standardized potassium dichromate solution using the calculation in 11.3.2.

10. Procedure

NOTE 4—Satisfactory analysis results will only be attained if the temperature of the reagents (usually at room temperature) used are >23°C (74°F).

10.1 Weigh the sample (0.5 g or more) to 0.1 mg. Dissolve the sample following the procedures in Ref **(2)** and Practice C1168.

10.2 Quantitatively transfer the weighed, dissolved sample to a weighed bottle for mixing prior to sample splitting. See 10.2.1 for plastic bottles or 10.2.2 for glass bottles.

10.2.1 A low-density polyethylene narrow mouth bottle, with a one-piece polypropylene special seal-ring screw closure to prevent leakage, may be used, or any other leak-proof bottle. If polyethylene bottles are used, long-term (weeks and months) storage will not maintain sample integrity because of transpiration through the bottle walls **(19)**.

10.2.1.1 Mix the solution by inverting and equilibrate to room temperature.

10.2.1.2 Weigh the solution to the number of significant figures equivalent to the sample weight.

10.2.1.3 Calculate the sample dilution factor (g sample/g solution). Go to 10.3.

10.2.2 Glass bottles with poly-cone seals may also be used for sample mixing.

10.2.2.1 Cover the glass bottles with parafilm during temperature equilibration, add the poly-cone seal tops to the bottles just prior to mixing to avoid pressure build-up due to radiolysis by plutonium, and mix the solution by inverting the bottle.

10.2.2.2 Continue with sample preparation as in 10.2.1.2 and 10.2.1.3 before going to 10.3.

10.3 Deliver an aliquant, weighed to 0.1 mg accuracy, containing 20 to 300 mg of uranium, into the titration vessel (400-mL beakers are satisfactory).

10.4 Add 1 mL of 1 *M* H_2SO_4 to the aliquant, and fume to near dryness.

NOTE 5—The acid tolerances **(4, 20)** for a sample aliquant to be analyzed by this test method are 4 mL H_2SO_4 (sp gr 1.84), 3 mL HNO_3 (sp gr 1.42), no HCl, and 0.5 mL free HF (sp gr 1.18). Aliquants fumed to dryness or near dryness with sulfuric acid should not require further treatment to satisfy these requirements.

10.5 Dissolve the sample in 15 mL of 0.05 *M* H_2SO_4. Use the reagent to rinse down the sides of the beaker. The total dissolution of the sample at this point is critical to accurate analysis; a wait of 30 min to 1 h is recommended to ensure total dissolution.

10.6 Add 5 mL of 1.5 *M* sulfamic acid to the beaker, and mix by swirling. Use the reagent to rinse the sides of the beaker.

10.7 Add 40 mL of H_3PO_4 (85 %), treated with dichromate (see Annex A2), directly into the sample. The splashing of any solution onto the side of the beaker should be avoided.

10.8 Add 7 mL of ferrous solution, and swirl briefly. Do not allow the ferrous solution to touch the sides of the beaker while dispensing this reagent.

NOTE 6—The ferrous reagent may be combined with the H_3PO_4 in 10.7 and added as a combined reagent.

10.9 Add a TFE-fluorocarbon coated magnet without splashing, place the beaker on a magnetic stirrer, and initiate stirring at a slow rate (avoid splashing) for 5 min.

10.9.1 If a visible precipitate is present at the end of 5 min, increase the stirring time to 7 to 8 min.

10.9.2 If a precipitate is still visible after 7 to 8 min, prepare a new sample, but increase the 0.05 *M* H_2SO_4 to 25 mL and the H_3PO_4 to 65 mL.

10.10 Add 10 mL of nitric-sulfamic-molybdate solution. Use the solution to rinse down the sides of the beaker.

10.11 Mix the solution at a moderate stirrer speed. Immediately upon disappearance of the black color, begin timing the oxidation period (3 min).

10.12 Weigh the dichromate solution in the weight buret if a gravimetric titration is to be used; otherwise, zero the buret.

10.13 Stop the stirring, add 100 mL of the vanadyl sulfate solution or water diluent if solid vanadyl sulfate is used.

10.13.1 If vanadyl sulfate is added as a solid (75 to 125 mg), add it after the diluent.

10.13.2 Use the vanadyl sulfate solution or diluent to rinse the sides of the beaker.

10.14 Increase the rate of stirring to form a vortex in the solution.

10.14.1 Insert the electrodes into the solution, and titrate rapidly with dichromate to a potential of 450 to 480 mV versus a calomel reference electrode or the equivalent voltage for other reference electrodes. If the polyethylene weight buret is used, remove the reduced size tip used in the final end point approach before beginning the addition of dichromate.

10.14.2 Decrease the rate of dichromate additions to large drops, 1 to 2 drop portions; titrate to a potential of 500 mV or the equivalent for reference electrodes other than calomel.

10.14.3 Begin smaller drop-size additions (for the polyethylene weight buret, place the micro-tip on the weight buret), and titrate to the potential break, or if a second derivative technique is to be used, skip to 10.14.4.

10.14.3.1 The maximum time elapsed between the addition of the vanadyl sulfate or diluent and the completion of 99 + % of the titration should be 7 min.

10.14.3.2 Better precision will be attained if the time is limited to 3 to 5 min elapsed time.

10.14.3.3 The variation in the final potential readings to maintain acceptable precision should be 590 mV ± 20 mV or equivalent potentials for reference electrodes other than the calomel.

10.14.4 If a double derivative end point is used instead of a fixed end point, titrate near the potential break (550 to 580 mV or equivalent) using small drops and recording each buret and potential reading. Record one drop reading past the end point, and calculate the end point using a double derivative technique.

10.14.4.1 The precautions in 10.14.3.1 and 10.14.3.2 regarding the time limits for the titration apply up to completion of 99 + % of the titration.

10.14.4.2 The double derivative end point approach may require more than 7 min, but since 99 + % of the uranium has been titrated, the additional time will not significantly affect the final results.

10.14.5 Alternative end point procedures used in manual or automated titration systems, which have been demonstrated to give comparable accuracy, are also acceptable.

11. Calculation

11.1 *Buoyancy and Purity Corrections*—If potassium dichromate traceable to a national standards laboratory is used for standard solution preparation, corrections for buoyancy and purity should be applied to the solid material weight. If NBL standard uranium metal (CRM 112-A or its replacement) is used to prepare a standard uranium solution, corrections for buoyancy and purity should be applied to the metal weight.

11.1.1 The buoyancy correction is made using the following formula:

$$W_v = W_o\left[1 + (1/D_o - 1/D_w)D_a\right] \quad (1)$$

where:

W_v = weight of the object in vacuum, g,
W_o = weight of the object in air, g,
D_o = density of the object in air,
D_w = density of the weights of the balance in air, and
D_a = density of air at the temperature and pressure at which the weight of the object was determined.

11.1.2 The purity correction is made using the following formula:

$$W_c = (W_v)(PF) \quad (2)$$

where:

W_c = corrected weight of material, g,
W_v = buoyancy corrected weight of material, g,
PF = purity factor stated on certificate, %/100.

11.2 *Concentration Calculations*—Calculations of concentrations for standard solutions of potassium dichromate and of uranium are made using the buoyancy and purity corrected weights for the solids.

11.2.1 The concentration of the standard potassium dichromate solution is calculated using the following equation:

$$C_c = (D_c)/L \quad (3)$$

where:

C_c = concentration of $K_2Cr_2O_7$, mg $K_2Cr_2O_7$/g dichromate solution,
D_c = corrected weight of $K_2Cr_2O_7$ solid, mg, from 11.1.2 for $K_2Cr_2O_7$, (1000 mg/g) W_c, and
L = $K_2Cr_2O_7$ solution weight, g dichromate solution.

11.2.2 The concentration of the standard uranium solution is calculated using the following equation:

$$C_u = (D_u)/Q \quad (4)$$

where:

C_u = concentration of uranium solution, mg uranium/g uranium solution,
D_u = corrected weight of uranium metal, mg, from 11.1.2 for uranium metal, (1000 mg/g) W_c, and
Q = standard uranium solution weight, g uranium solution.

11.3 *Uranium Titration Factor*—The titration factor is calculated in mg uranium/g dichromate solution.

11.3.1 For the standard potassium dichromate solution, the uranium titration factor is calculated from the potassium dichromate concentration factor and is based on the reaction of potassium dichromate with uranium(IV):

$$2\ \mathrm{Cr(VI)\ from\ K_2Cr_2O_7} + 3\ \mathrm{U(IV)} \longrightarrow 2\ \mathrm{Cr(III)} + 3\ \mathrm{U(VI)} \quad (5)$$

Since 3 mol of uranium(IV) react with 1 mol of $K_2Cr_2O_7$, the multiplier for the potassium dichromate to uranium conversion is the following:

$$\frac{(\text{molecular weight uranium})\ (3)}{(\text{molecular weight } K_2Cr_2O_7)} = 2.42734 \quad (6)$$

for CRM 112-A (238.0287 g/mol) and $K_2Cr_2O_7$ (294.1844 g/mol). The uranium titration factor (mg uranium/g dichromate solution) is calculated for the standard potassium dichromate concentration using the following equation:

$$T = (C_c)(M) \quad (7)$$

where:

T = titrant factor for potassium dichromate titration of uranium(IV), mg uranium/g dichromate solution,
C_c = concentration of potassium dichromate solution from 11.2.1, mg $K_2Cr_2O_7$/g dichromate solution, and
M = multiplier for the conversion of potassium dichromate to uranium concentration defined for the reaction of the titration and the atomic weight of the standard uranium, no units, (2.42734 for CRM 112-A).

11.3.2 When a potassium dichromate solution is standardized against a standard uranium solution, the titration factor is calculated directly from the standardization titration. Calculate the titration factor (mg uranium/g dichromate solution) using the following equation:

$$T = (C_u)(G)/(W) \quad (8)$$

where:

T = titrant factor for potassium dichromate titration of uranium(IV), mg uranium/g dichromate solution,
C_u = concentration of standard uranium solution from 11.2.2, mg uranium/g uranium solution,
G = weight of standard uranium solution in the aliquant of CRM 112-A uranium metal or its replacement, g uranium solution,
W = weight of potassium dichromate solution used as titrant, g dichromate solution.

11.4 The weight of uranium calculated for samples using the uranium titration factor calculated in 11.3 must be corrected for atomic weight differences between the sample and CRM 112-A or its replacement.

11.4.1 *Sample Result*—Calculate the uranium content of the original sample by the following equation:

$$U = TWR/FS \tag{9}$$

where:

U = milligrams uranium per gram sample,
T = titrant factor, mg uranium/g dichromate solution, as calculated in 11.3.1 or 11.3.2,
W = weight of potassium dichromate solution, g dichromate solution,
R = ratio of atomic weight of uranium in sample to atomic weight of CRM 112-A or its replacement,
F = factor for sample dilution, weight in grams of original sample initially dissolved per total grams of sample solution, and
S = weight of sample solution aliquant analyzed, g.

12. Precision and Bias

12.1 The uranium titration factor (see 11.3), and so the calibration of this test method, is based on CRM 112-A (uranium reference material or its replacement) or on SRM 136e (potassium dichromate reference material or its equivalent).

12.2 In 1.1 a precaution for use of this test method was given when amounts of plutonium are present in a sample so that the ratio of uranium to plutonium is less than 2.5, for example, 60 % uranium to 24 % plutonium gives a uranium to plutonium ratio of 2.5. When smaller amounts of plutonium are present in a sample, uranium to plutonium ratios greater than 2.5 result, for example, 60 % uranium to 20 % plutonium gives a uranium to plutonium ratio of 3.0; as percent plutonium approaches zero, the uranium to plutonium ratio approaches infinity. The amounts of reagents used in this test method are known to be sufficient for the quantities of uranium stated in 4.2 together with quantities of plutonium to give a ratio of 2.5 or greater. Therefore, this test method as written applies to uranium to plutonium ratios of 2.5 and greater. The precision and bias have been determined on materials at the lower uranium to plutonium ratio and so at the worse case end of the analysis range. This test method has also been used for the determination of uranium only, that is, the uranium to plutonium ratio approaches infinity, with equal or better success.[6]

12.3 This test method has been used for the mixed (U, Pu)O_2 Safeguards Analytical Laboratory Evaluation (SALE) materials analyses (63 to 66 % uranium) with a uranium to plutonium ratio of 2.6 to 3.0. The uranium analysis values determined, using this test method, were for two different mixed oxide pellets, Material 1 (with a reference value of 65.903 % uranium) and Material 2 (with a reference value of 63.756 % uranium). The 95 % Confidence Intervals (CI) of the means stated for the (Pu, U)O_2 SALE materials' reference value uranium concentrations were each from – 0.05 % to + 0.05 % (**21**). For the Material 1 reference value determination, 3 dissolutions and 18 titrations were performed with one outlier; for the Material 2 reference value determination, 13 dissolutions and 26 titrations were performed with two outliers.

12.3.1 These two materials were analyzed for the SALE Program over a 3-year period by a total of four analysts at a single facility.[6] Material 1 was dissolved and analyzed in duplicate a total of 8 times; three different analysts were involved in the analysis of Material 1 during the 3-year period. Material 2 was dissolved and analyzed in duplicate 10 times by a total of three different analysts over the 3-year period. The calculation of the bias and precision includes any variation due to dissolution because of the manner in which the data were collected. The quality control standards (QCs), which were aliquants of CRM 112-A with a certified value of 99.975 ± 0.006 weight % uranium, were analyzed using the same method as the samples (except with no variation due to dissolution and with no plutonium present) and bracketed the sample analyses. A total of 32 different QC aliquants were analyzed;[6] the SALE material data is published and compared with analyses by other laboratories in Ref (**21**). The analyzed values for SALE Material 1 relative to the reference value gave, where $n = 16$, a mean relative difference of 0.072 %, with a 95 % CI of 0.020 % to 0.124 %; an Analysis of Variance (ANOVA) F test showed statistically significant month-to-month variation for Material 1 analyses. The analyzed values for SALE Material 2 relative to the reference value gave, where $n = 20$, a mean relative difference (defined as 100 (observed value – reference value)/reference value) of – 0.005 %, with a 95 % CI from – 0.025 % to 0.016 %; the ANOVA F test showed no statistically significant month-to-month variation for Material 2 analyse. Although it appears that Material 1 may have been inhomogeneous, sufficient data to substantiate inhomogeneity is not available. Therefore, the data for Materials 1 and 2, analyzed by this technique, were evaluated as two separate data sets. The data from Material 1, which gave the greater bias and worse-case precision, were used to establish the statistical characteristics of the analysis technique.

12.4 ANOVA results from analysis of the data gave an estimated mean relative bias of 0.072 % which is statistically significant at the 0.05 level. The reproducibility (one standard deviation) of the analysis technique is 0.066 % of the reference value.

13. Keywords

13.1 chromium titration; Davies and Gray titration; mixed oxide (MOX); modified Davies and Gray titration; uranium; uranium in plutonium

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:C26-1001.

ANNEXES

(Mandatory Information)

A1. INTERFERENCES IN THE URANIUM TITRATION WITH TREATMENT STRATEGY

A1.1 See the following Table A1.1 on elemental interference.

TABLE A1.1 Elemental Interference in the Uranium Titration with Treatment Strategy

Element(s)	Treatment Strategy
Al	filter residue and ignite at 900°C; combine with solution, and fume with 1 + 1 sulfuric acid **(4)**
Zr-Mo	fume sample in 1 + 1 sulfuric, concentrated nitric and hydrofluoric acids **(4)**
V, Bi	reduce the sample size **(4)**
Zr	add 1 to 2 mL of hydrofluoric acid to the sample before titrating **(4)**
As, Sb, Sn	add potassium dichromate to sample prior to reduction step **(8)**[A]
Ru, Os	fume sample three times with perchloric acid **(9)**
Mo, Cl, Br, F	fume sample with sulfuric or perchloric acid, or both **(4, 9, 10)**
I	add bromine water to sample, evaporate, fume with sulfuric or perchloric acid **(8)**
Tc	fume sample with sulfuric or perchloric acid to dryness; flame walls of beaker to ensure dryness **(15)**
Hg, Pt, Pd	use a copper column separation **(13)**
> 10 % Au	reduce the gold to metal and separate **(8)**
Am, Sb, As, Br, Cl, Fe, Au, Pb, Mn, Hg, Mo, Np, Os, Pd, Pt, Pu, Ru, Ag, Th, Sn, V, Zr	use the tributyl phosphate/cyclohexane extraction technique **(14)**

[A] Oxidizes elements listed to noninterfering oxidation state which the ferrous ion is not capable of reducing.

A2. TREATMENT OF PHOSPHORIC ACID TO OXIDIZE REDUCING SUBSTANCES

A2.1 Add 1 mL of 2 % potassium dichromate solution (prepared in 7.7) to a 5-pt (2.366 L) bottle of phosphoric acid for oxidation of reducing impurities. If the resulting bottle of phosphoric acid does not maintain a light yellow, straw color over 2 to 3 h, add an additional 1 mL of 2 % dichromate and allow the solution to sitlor, the phosphoric is acceptable for use. If the solution is light green in color, do not use the phosphoric acid or any other phosphoric acid bottles with the same preparation lot number (**8**, **22**, **23**, **24**)

A2.2 Alternatively, add 2 drops of 2 % potassium dichromate solution (prepared in 7.7) to 40 mL of phosphoric acid prior to addition to the sample for titration. It is suggested that, prior to using a new preparation lot of phosphoric acid, one bottle be tested either by the ACS[7] test for reducing substances in phosphoric acid or by the test in A2.1.

APPENDIXES

(Nonmandatory Information)

X1. POLYETHYLENE BOTTLE WEIGHT BURET PREPARATION

X1.1 A 125-mL polyethylene bottle with a detachable tip drawn by heating low density polyethylene tubing, 5⁄32 in. inner diameter and 1⁄4 in. outer diameter, and pulling to a fine tip which is attachable to the bottle's own normal tip for the final end point approach in the dichromate titration of uranium (**25**) has been found to allow dichromate additions by weight with good precision and accuracy. A tip drawn small enough to deliver about 5 mg of dichromate solution per drop has been found to allow acceptable rates of dichromate addition near the end point.

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[7] *ACS Specifications for Reagent Chemicals and Standards*, 4th Ed., American Chemical Society, Washington, DC, 1968, pp. 346–347.

X2. PLATINUM ELECTRODE TREATMENTS

X2.1 A routine platinum electrode cleaning treatment and the treatment for restoring fast response to a sluggish platinum electrode is flaming to white heat and immersion in concentrated nitric acid followed by another flaming and nitric acid immersion.

X2.2 An alternate cleaning method for the platinum electrodes is to soak the electrode in hydrofluoric acid prior to flaming and nitric acid immersion as detailed in X2.1.

X2.3 If rising results over a day's analyses occur repeatedly after routine cleaning, a sodium bisulfate fusion of the platinum electrode may be needed. After the sodium bisulfate fusion and flaming, again perform the routine cleaning as detailed in X2.1.

X3. TITRANT SOLUTION STANDARDIZATION

X3.1 Standardize reagent grade or better potassium dichromate or ceric titrant against CRM 112-A uranium metal or its replacement.

X3.2 The standard deviation of the mean for the titrant standardization $\left(s / \sqrt{n}\right)$ should be well within the accepted laboratory error limits for the uranium titration when $n = 10$). Example: To maintain an accepted laboratory precision on the uranium titration of $s = 0.10$, the recommended acceptable precision on the titrant standardization is $s = 0.05$ for $n = 10$ so that the accuracy of the standardized titrant standard solution will have a minimal effect on the titration results.

X4. DISSOLUTION OF URANIUM METAL

X4.1 The following method has been used successfully for dissolution of 20 to 40 g of uranium metal.

X4.2 Place the clean, weighed metal in a dry, weighed 2-L flask, and add 100 mL of 8 *M* nitric acid.

X4.3 Place a small funnel, sitting on a glass bend, in the mouth of the 2-L flask, and place the flask on a hot plate at about 75°C until dark brown fumes are seen.

X4.4 Lower the hot plate temperature to about 65°C, and heat for 6 h. Swirl the solution occasionally during this stage of dissolution.

X4.5 Remove the flask from the hot plate, and add 50 mL of 8 *M* nitric acid.

X4.6 Return the solution to the hot plate with the funnel in the mouth of the flask, turn the temperature of the hot plate to about 75°C, and leave the solution for 8 h.

X4.7 Add 50 mL of 8 *M* nitric acid to the flask, turn the hot plate to about 85°C, and leave the solution on the hot plate for 4 h with occasional swirling. Visually check for completeness of dissolution.

X4.8 If dissolution is complete, dilute to 2 L with water and allow the solution to equilibrate.

X4.9 Otherwise, continue heating until dissolution is complete.

X4.10 The amount of nitric acid needed is dependent upon the amount of uranium being dissolved. If insufficient nitric acid was available for dissolution, the surface of the metal may become passive, and complete dissolution will not be possible; in that case the solution must be discarded and a new solution prepared.

X4.11 Weigh the equilibrated solution, make buoyancy and purity corrections to the uranium metal weight, and calculate the concentration of the uranium solution.

X4.12 Thoroughly mix the uranium solution, separate into multiple borosilicate bottles with polycone seals for long-term storage, or aliquant into beakers for storage.

X4.13 Aliquants may be stored after drying as the nitrate or fuming in sulfuric acid. The aliquants must meet the acid tolerances specified for this test method (see Note 5). If the samples reabsorb water, fume the aliquants again before use.

X4.14 A suitable time period for dissolution of stored, dried aliquants before titration must be used; 30 min to 1 h is suggested. Dried aliquants that are not allowed adequate dissolution time may give low titration results.

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