



Designation: ~~C1267-06~~ Designation: C1267 - 11

## Standard Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium<sup>1</sup>

This standard is issued under the fixed designation C1267; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method, commonly referred to as the Modified Davies and Gray technique, covers the titration of uranium in product, fuel, and scrap materials after the material is dissolved. The test method is versatile and has been ruggedness tested. With appropriate sample preparation, this test method can give precise and unbiased uranium assays over a wide variety of material types (1, 2).<sup>2</sup> Details of the titration procedure in the presence of plutonium with appropriate modifications are given in Test Method C1204.

1.2 Uranium levels titrated are usually 20 to 50 mg, but up to 200 mg uranium can be titrated using the reagent volumes stated in this test method.

1.3

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 safeguard and safety precaution statements, see Section 4.

### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>3</sup>

C696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets

C799 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions

C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials

C1204 Test Method for Uranium in Presence of Plutonium by Iron(II) Reduction in Phosphoric Acid Followed by Chromium(VI) Titration

C1346 Practice for Dissolution of UF<sub>6</sub> from P-10 Tubes

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

2.2 *NIST Standard:*<sup>4</sup>

SRM 136e Potassium Dichromate (Oxidimetric Standard)

2.3 *NBL Standard:*<sup>5</sup>

CRM 112A Uranium Metal Standard

### 3. Summary of Test Method

3.1 Samples are prepared by dissolution techniques detailed in Practices C1346, C1347, or Refs (2), (3), and (4). Appropriate uncertainties for sampling and weight determination should be applied to the overall precision and bias calculations for the final result. Aliquants containing 20 to 200 mg of uranium are prepared by weight. The sample is fumed to dryness after the appropriate acid treatment. The sample is dissolved in dilute nitric acid or water prior to titration.

3.2 Uranium is reduced to uranium(IV) by excess iron(II) in concentrated phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) containing sulfamic acid. The excess iron(II) is selectively oxidized by nitric acid (HNO<sub>3</sub>) in the presence of a molybdenum(VI) catalyst. After the addition

<sup>1</sup> 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 July 1, 2006. Published July 2006. Originally approved in 1994. Last previous edition approved in 2006 as C1267 - 06. DOI: 10.1520/C1267-06.10.1520/C1267-11.

<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

<sup>3</sup> 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.

<sup>4</sup> Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.

<sup>5</sup> New Brunswick Laboratory (NBL) Certified Reference Materials Catalog (U.S. Department of Energy), http://www.nbl.doe.gov.

of a vanadium(IV) solution, the uranium(IV) is titrated with chromium(VI) to a potentiometric end point.

3.3 The chromium(VI) titrant may be delivered manually on a weight or on a volumetric basis as specified by the facility titration procedure.

3.3.1 If the titrant is delivered on a volumetric basis, corrections to the volume of titrant may be needed to adjust for the difference between the temperature of preparation and the ambient temperature.

3.3.2 Automated titrators are facility specific and are not explicitly addressed in this test method. However, automated titrators which have comparable bias and precision may be used.

3.3.3 There is an alternate, high precision ( $\sim 0.005\%$  RSD) modified Davies and Gray titration, which is similar to the method covered in this procedure. In the high precision method, the amount of uranium titrated is increased and about 90 % of the titrant is delivered on a solid weight basis followed by titration to the end point with a dilute titrant. Details of this alternate method are available in Ref (5).

#### 4. Significance and Use

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

4.2 This uranium assay method is referenced in the Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets (Test Methods C696) and in the Test Methods for Chemical, Mass Spectrometric, and Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions (Test Methods C799). This uranium assay method may also be used for uranium hexafluoride and uranium ore concentrate. This test method determines 20 to 200 mg of uranium; is applicable to product, fuel, and scrap material after the material is dissolved; is tolerant towards most metallic impurity elements usually specified in product and 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.

4.4 *Committee C26 Safeguards Statement:*

4.4.1 The materials (nuclear grade uranium in product, fuel, and scrap) to which this test method applies are subject to nuclear safeguard regulations governing their possession and use. The analytical method in this standard meets U.S. Department of Energy guidelines for acceptability of a measurement method for generation of safeguards accountability measurement data.

4.4.2 When used in conjunction with the appropriate certified reference materials (SRM<sup>6</sup> or CRM), this procedure can demonstrate traceability to the national measurement base. However, use of the 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 assure that its application to safeguards has the approval of the proper regulatory authorities.

#### 5. Interferences

5.1 Interfering elements are not generally present in product and fuel material in quantities which cause interference in the titration.

5.1.1 Of the metallic impurity elements usually included in specifications for product and fuel, silver, manganese, and vanadium (in the V oxidation state) interfere when present in amounts of 10 mg or greater of impurity per 100 mg of uranium (2, 8).

5.1.2 Silver and vanadium (in the V oxidation state) cause positive bias when present in milligram quantities in the sample. The aliquant treatment adjusts the oxidation state of any vanadium(V) present in the sample (2). To remove silver, the sample must be treated prior to titration (8).

5.1.3 Manganese was originally found to cause a negative bias (2), but this bias is eliminated when the titration aliquant preparation procedure is followed as given (9, 10) in this titrimetric method.

5.2 Interferences with the Modified Davies and Gray titration, which may be present in some uranium materials, have been systematically studied.

5.2.1 The non-interference of copper, titanium, cobalt, nickel, cerium, and samarium was demonstrated (11) at the 50 mg impurity level for 100 mg of uranium.

5.2.2 The effects of the following elements in milligram quantities were studied: silver, gold, lead, iodine, arsenic, antimony, and bismuth (8).

5.2.2.1 Gold, lead, arsenic(V), antimony(V), and bismuth do not interfere when present in amounts of 10 mg for 100 mg of uranium.

5.2.2.2 Silver, iodine, arsenic(III), and antimony(III) interfere seriously in the determination of uranium and must be eliminated prior to titration.

5.2.3 The effects of impurities on the titration of uranium continued with the platinum metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum), chloride, bromide (12), fluoride (13), and technetium (14).

5.2.3.1 Ruthenium, palladium, osmium, iridium, and platinum cause serious positive errors in the determination of uranium. Rhodium alone among the platinum metals does not cause any significant error.

<sup>6</sup> SRM is a registered trademark.

5.2.3.2 Chloride and bromide interfere with the assay through their effect on the platinum indicator electrode.

5.2.3.3 Small amounts of fluoride, less than 400 mg as hydrofluoric acid (HF) or 600 mg if HNO<sub>3</sub> is present, can be tolerated by the titration.

5.2.3.4 Technetium, found in high temperature reactor grade recycle (htgr) fuel, interferes with the titration and must be removed before titration.

5.3 The removal of certain interferences in the modified Davies and Gray titration has also been studied.

5.3.1 The initial fuming of titration aliquants with sulfuric acid removes impurity elements such as the halides and volatile metallic elements (2, 12, 13).

5.3.2 Arsenic(III) and antimony(III) can be eliminated in the H<sub>3</sub>PO<sub>4</sub> by potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) oxidation prior to its addition to the titration medium (8).

5.3.3 Elimination of interferences in the titration by mercury, platinum, and palladium by means of a copper column was evaluated (15).

5.3.4 Elimination of interferences by solvent extraction of the uranium from the impurities has also been studied (16).

5.4 A list of impurities with brief references to their treatment for elimination is given in Table A1.1 in Annex A1, and the details are given in Refs 2, 8, 9, 10, and 12-16.

## 6. Apparatus

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

6.2 *pH Meter*, with indicator (a 16-gauge platinum wire has been found to be satisfactory) and reference (saturated calomel has been found to be satisfactory) electrodes.

6.2.1 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 wire electrodes are detailed in Appendix X2.

6.2.2 Asbestos and glass bead tipped saturated calomel electrodes can be placed directly in the titration solution. Glass frit tipped saturated calomel electrodes may have a faster leak rate and may need to be used with a separator tube containing the electrolyte to prevent titration problems due to chloride.

6.2.3 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.

6.3 *Magnetic Stirrer and TFE-Fluorocarbon Coated Magnet*.

## 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.<sup>7</sup> 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 Heptahydrate* (FeSO<sub>4</sub>·7 H<sub>2</sub>O, 1.0 M)—Add 100 mL of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to 750 mL of water as the solution is stirred. Add 280 g of FeSO<sub>4</sub>·7 H<sub>2</sub>O, and dilute the solution to 1 L with water. Prepare the FeSO<sub>4</sub>·7 H<sub>2</sub>O reagent fresh, weekly. See the Note 5 in 10.8 on combination of this reagent with the H<sub>3</sub>PO<sub>4</sub>.

7.4 *Nitric Acid* (HNO<sub>3</sub>, 8 M)—Add 500 mL of HNO<sub>3</sub> (sp gr 1.42) to <500 mL of water, and dilute to 1 L.

7.5 HNO<sub>3</sub>, 1 M—Add 64 mL of HNO<sub>3</sub> (sp gr 1.42) to <900 mL of water, and dilute to 1 L.

7.6 HNO<sub>3</sub> (8 M)—Sulfamic Acid (NH<sub>2</sub>SO<sub>3</sub>H, 0.15 M)—Ammonium Molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, 0.4 %)—Dissolve 4 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in 400 mL of water, and add 500 mL of HNO<sub>3</sub> (sp gr 1.42). Mix and add 100 mL of 1.5 M NH<sub>2</sub>SO<sub>3</sub>H solution (see 7.10) and mix.

7.7 *Orthophosphoric Acid* (H<sub>3</sub>PO<sub>4</sub>), 85 %—Test for reducing substances prior to use (see Annex A2).

7.8 *Potassium Dichromate* (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) Solution (2 %)—Dissolve 2 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water, and dilute to 100 g with water.

7.9 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.0045 M)—Dissolve 2.65 g of reagent grade or purer grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water; transfer this solution to a pre-weighed, 2-L volumetric flask or suitable alternative and dilute to volume, or use equivalent weight/volume ratios for larger quantities of solution.

7.9.1 If National Institute of Standards and Technology (NIST) standard reference material K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (SRM 136e or its equivalent) was used, proceed as in 7.9.1.1 and 7.9.1.2 before going to 7.9.3; otherwise go to 7.9.2.

7.9.1.1 Allow the solution to equilibrate to room temperature, obtain the weight of the solution. Compute the dichromate concentration (11.2.2) and the uranium titration factor (11.3.2) after correcting the weight of dichromate for buoyancy (11.1.2) and for purity (11.1.3).

<sup>7</sup> *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.

7.9.1.2 As a good quality practice, a check on the material handling of the  $K_2Cr_2O_7$  solution within laboratory accepted uncertainties may be done by titration with a working reference uranium solution. For guidance in the preparation of a working reference uranium solution, see Guide C1128. If the titrations do not agree within laboratory accepted uncertainties, verification titrations for SRM 136e or its equivalent may be done using New Brunswick Laboratory (NBL) CRM 112-A uranium metal or its equivalent,<sup>5</sup> prepared in 7.12, or the  $K_2Cr_2O_7$  solution should be discarded.

7.9.2 If a reagent grade  $K_2Cr_2O_7$  was used, allow the solution to equilibrate to room temperature and standardize the  $K_2Cr_2O_7$  solution against CRM 112-A uranium metal or its equivalent prepared in 7.12 (see Appendix X3). Compute the uranium titration factor as in 11.3.3.

7.9.3 Store the  $K_2Cr_2O_7$  solution in one or more borosilicate glass bottles with a poly-seal top or an equivalent container to prevent concentration changes due to evaporation.

7.10  $NH_2SO_3H$  (1.5 M)—Dissolve 146 g of  $NH_2SO_3H$  in water, filter the solution, and dilute to 1 L.

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

7.12 *Uranium Standard (CRM) Solution:*

7.12.1 Clean the surface of the uranium metal (CRM 112-A or its equivalent) following the instructions on the certificate.

7.12.2 Obtain the weight of the metal by difference to 0.01 mg making buoyancy and purity corrections detailed in 11.1.2 and 11.1.3, respectively.

7.12.3 Prepare the uranium standard solution. There are many successful methods of uranium metal dissolution (none is specified on the CRM 112-A certificate); methods which reproduce the uranium assay value on the certificate are acceptable. An example of an acceptable method is given in Appendix X4.

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

7.12.4.1 Calculate the solution concentration in mg U/g uranium solution using the calculation in 11.2.3.

7.12.4.2 As a good quality practice, a check on the material handling of the uranium solution within laboratory accepted uncertainties may be done by titration with a working reference  $K_2Cr_2O_7$  solution. For guidance in the preparation of a working reference  $K_2Cr_2O_7$  solution, see Guide C1128. If the titrations do not agree within laboratory accepted uncertainties, verification titrations for CRM 112-A or its equivalent may be done using  $K_2Cr_2O_7$  SRM 136e or its equivalent, as prepared in 7.9, or the uranium solution should be discarded.

7.13 *Vanadyl Sulfate Dihydrate*—( $VOSO_4 \cdot 2H_2O$ ) *Solution* (0.0038 M—0.18 M  $H_2SO_4$ )—Add 20 mL concentrated  $H_2SO_4$  (sp gr 1.84) to <980 mL water with stirring; equilibrate to room temperature. Weigh 1.5 g of  $VOSO_4 \cdot 2H_2O$  crystals, mix the solid with the temperature equilibrated  $H_2SO_4$  solution, and dilute the solution to 2 L. The  $VOSO_4 \cdot 2H_2O$  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  $VOSO_4 \cdot 2H_2O$  solution is not stable (17);  $H_2SO_4$  stabilizes the V(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 V(V) interference (24 h intervals for preparation are suggested) since this solution is added after the aliquant treatment stage.

7.13.2 Alternatively, crystalline  $VOSO_4 \cdot 2H_2O$  (75 to 125 mg per titration) may be used with a water diluent in place of the solution (see 10.13).

NOTE 1—There is more than one crystalline form of vanadyl sulfate; there are problems with slow dissolving forms particularly when the vanadyl sulfate is added as a solid. Since vendors are now selling vanadyl sulfate with an unspecified hydration number, that is,  $VOSO_4 \cdot xH_2O$ , note that the material should be bright blue in color and have a wet appearance. The difficult-to-dissolve crystalline form is light blue and dry in appearance.

## 8. Hazards

8.1 Since enriched uranium-bearing materials are radioactive and toxic, adequate laboratory facilities and fume hoods 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 the safe handling practices of the facility.

8.2 In the absence of data about the bioavailability of the chromium(VI) in  $K_2Cr_2O_7$ ,<sup>8</sup> the facility policy for handling of  $K_2Cr_2O_7$  should be followed. In some facilities  $K_2Cr_2O_7$  has been identified as a “select carcinogen” as a conservative policy.

**8.3 Warning**—Hydrofluoric acid is highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from the other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left untreated. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personnel protective equipment to protect from skin and eye contact is essential. Acute exposure to HF can cause painful and severe burns upon skin contact that require special medical attention. Chronic or prolonged exposure to low levels on the skin may cause fluorosis.

<sup>8</sup> *Overall Evaluations of Carcinogenicity: An Updating of International Agency for Research on Cancer (IARC) Monographs*, Supplement 7, World Health Organization, International Agency for Research on Cancer, 1987, p. xvii.

## 9. Calibration

9.1 Traceability to a national or international measurement base may be demonstrated by the use of standard reference materials, for example, NIST standard SRM 136e or its equivalent (potassium dichromate), or NBL standard CRM 112-A (uranium metal standard).

9.2 The standard  $K_2Cr_2O_7$  should be prepared as instructed on the certificate; the weight should be obtained to 0.01 mg and corrected for buoyancy and purity using the calculations in 11.1.2 and 11.1.3.

9.2.1 If a  $K_2Cr_2O_7$  solution is prepared from the solid  $K_2Cr_2O_7$ , the solution should be equilibrated to room temperature, and the weight should be obtained to give a number of significant figures equal to that of the solid's weight.

9.2.2 The  $K_2Cr_2O_7$  solution concentration is calculated in mg  $K_2Cr_2O_7$ /g  $K_2Cr_2O_7$  solution using the calculation in 11.2.2. The titration factor (mg uranium/g  $K_2Cr_2O_7$  solution) is calculated for the  $K_2Cr_2O_7$  solution using the calculation in 11.3.2.

9.3 If reagent grade  $K_2Cr_2O_7$  is used, the material must be standardized against the NBL uranium metal standard (CRM 112-A or its equivalent) to provide traceability to the national measurement base.

NOTE 2—**Caution:** Satisfactory analysis results will only be attained if the temperature of the reagents (usually at room temperature) used are within the range of 23 to 31°C.

9.3.1 Analyze individually dispensed aliquants of the uranium reference solution per 10.3-10.14.4. See Appendix X3 for analysis control recommendations.

9.3.2 Calculate the uranium titration factor (mg U/g  $K_2Cr_2O_7$  solution) for the standardized  $K_2Cr_2O_7$  solution using the calculation in 11.3.2.

## 10. Titration Procedure

NOTE 3—**Caution:** Satisfactory analysis results will only be attained if the temperature of the reagents (usually at room temperature) used are within the range of 23 to 31°C.

10.1 Obtain the weight of the sample (0.5 g or more) to 0.1 mg. When necessary, especially for oxides, include errors due to weight determination in the calculation of the overall measurement uncertainty. Dissolve the sample following the procedures in Practices C1346, C1347, or Refs 2-4.

10.2 To prepare aliquants, quantitatively transfer the dissolved sample with an accurately determined weight to a bottle with an accurately determined weight for mixing prior to sample splitting.

10.2.1 A low-density polyethylene narrow mouth bottle with a one-piece polypropylene seal-ring screw closure to prevent leakage, or any other leak-proof bottle may be used. If polyethylene bottles are used, long-term (weeks and months) storage will not maintain sample integrity because of bottle respiration (18).

10.2.2 Equilibrate the solution to room temperature, and weigh the solution to the number of significant figures equivalent to the sample's weight.

10.2.3 Invert and shake the solution to insure a homogeneous solution prior to aliquanting.

10.2.4 Calculate the sample dilution factor (g sample/g solution).

10.3 Deliver an aliquant, with a weight determined to 0.1 mg accuracy, containing 20 to 100 mg of uranium, into the titration vessel (400-mL beakers have been found to be satisfactory).

10.4 Add 1 mL of 1 M  $H_2SO_4$  to the aliquant, unless the sample contains elements which form insoluble sulfates, for example, calcium and aluminum, and fume to dryness. For specific elemental interference treatments, see Annex A1 and the references cited therein.

NOTE 4—The maximum acid contents (2, 19) for a sample aliquant to be analyzed by this method are 4 mL  $H_2SO_4$  (sp gr 1.84), 3 mL  $HNO_3$  (sp gr 1.42), 5 mL  $HClO_4$  (sp gr 1.67), no HCl, and 0.5 mL free (that is, not complexed such as with zirconium in U-Zr alloys) HF (sp gr 1.17). Aliquants which are fumed to dryness with sulfuric acid should not require further treatment to satisfy these requirements.

10.5 Dissolve the sample in 15 mL of water or in 15 mL of 1 M  $HNO_3$  using the water or 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 insure total dissolution.

10.6 Add 5 mL of 1.5 M  $NH_2SO_3H$  to the beaker, and mix by swirling. Use this solution 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 5 mL of  $FeSO_4 \cdot 7 H_2O$  solution, and swirl briefly. Do not allow the  $FeSO_4 \cdot 7 H_2O$  solution to touch the sides of the beaker while dispensing this reagent.

NOTE 5—The  $FeSO_4 \cdot 7 H_2O$  solution 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 30 s.

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 of 3 min; the solution may or may not be stirred during the 3 min time period.

10.12 Obtain the weight of the dichromate 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  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  solution, or add the diluent (water) if crystalline  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  is used.

10.13.1 If crystalline  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  (75 to 125 mg) is used, add it after the diluent.

10.13.2 Use the  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  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  $\text{K}_2\text{Cr}_2\text{O}_7$  to a potential of 450 to 480 mV versus a calomel reference electrode or to 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  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

10.14.2 Decrease the rate of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution additions to large drops, one to two drop portions; titrate to a potential of 500 mV or to the equivalent for reference electrodes other than calomel.

10.14.3 Begin smaller  $\text{K}_2\text{Cr}_2\text{O}_7$  solution 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  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  solution or diluent and the completion of 99 + % of the titration should not exceed 5 min.

10.14.3.2 The best 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  $590 \text{ mV} \pm 20 \text{ mV}$  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 5 min, but since 99 + % of the uranium has been titrated, the additional time will not significantly affect the final results.

10.14.4.3 Better precision will be obtained if the total titration time is limited to 10 min or less.

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:

11.1.1 When NIST standard  $\text{K}_2\text{Cr}_2\text{O}_7$  (SRM 136e or equivalent) is used for standard solution preparation, corrections for buoyancy and purity should be applied to the solid material's weight. If NBL standard uranium metal (CRM 112-A or equivalent) is used to prepare a standard uranium solution, corrections for buoyancy and purity should be applied to the metal's weight.

11.1.2 The buoyancy correction is made using the following formula:

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

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.

11.1.3 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, and

$PF$  = purity factor stated on certificate, %/100.

### 11.2 Concentration Calculations :

11.2.1 Calculations of concentrations for standard solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  and of uranium are made using the buoyancy and purity corrected weight for the solids.

11.2.2 The concentration of the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is calculated using the following equation:

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

where:

$C_c$  = concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$ , mg  $\text{K}_2\text{Cr}_2\text{O}_7$ /g  $\text{K}_2\text{Cr}_2\text{O}_7$  solution,

$D_c$  = corrected weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  solid in mg from 11.1.3 for  $\text{K}_2\text{Cr}_2\text{O}_7$ , (1000 mg/g)  $W_c$ , and

$L$  =  $\text{K}_2\text{Cr}_2\text{O}_7$  solution weight, g  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

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