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Standard Test Method for Uranium in Aqueous Solutions by Colorimetry¹

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1. Scope

1.1 This test method² covers the quantitative determination of uranium in known volumes of aqueous solutions that contain radioactive nuclides. These solutions arise from the processing of irradiated nuclear fuel and from laboratory studies on irradiated uranium.

1.2 The applicability of the test method is limited to solutions that contain a minimum of 30 μg of uranium per sample. It will detect as little as 0.5 μg but with lower precision. Highest precision is obtained when 50 to 75 μg of uranium is in the test sample. At concentrations above 750 $\mu\text{g/mL}$ dilutions must be made. The test method as described is limited to sample volumes of 1 mL or less, but reagent volumes can be scaled to accommodate larger sample aliquots or the sample can be concentrated by evaporation. The only known metal ion interferences are thorium and cerium(IV) when present at molar concentrations equal to or greater than the concentration of uranium. Thorium and cerium(IV) have tolerance limits greater than 1000 if the special extraction and scrub solutions are employed. Cerium(IV) present as a fission product does not interfere because its molar concentration is very low compared to uranium. The tolerance limit (no interference at the 95 % confidence limit), expressed as the weight ratio of impurity to uranium, is greater than 1000 for silver, bismuth, calcium, cadmium, cobalt, chromium, copper, iron, mercury, lanthanum, manganese, sodium, nickel, lead, strontium, and zinc. The tolerance limit is greater than 100 for barium, beryllium, potassium, magnesium, and zirconium. Plutonium does not interfere when the weight ratio of plutonium to uranium is less than two. The test method is not designed for solutions containing plutonium in the presence of large amounts of thorium or cerium(IV). The tolerance limit is greater than 100 for the following anions: acetate, borate, bromate, chloride, fluoride, ferricyanide, molybdate, oxalate, phosphate, sulfate, persulfate, thio-sulfate, and vanadate. The following anions interfere and have tolerance limits as follows: ferrocyanide 2, thiocyanate 58, and tungstate 12. The tolerance limit for free acid is 16 milliequivalents in the sample aliquot.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the*

safety problems, 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 a specific precaution statement, see Note 1.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁴

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁵

E 267 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances⁶

3. Summary of Test Method

3.1 The test method is based upon the measurement of the absorbance of the uranium-dibenzoylmethane complex at 415 nm. All the uranium in the measured volume of sample is first oxidized to uranium(VI) by potassium permanganate. An acid-deficient solution of aluminum nitrate and tetrapropylammonium nitrate serves as a salting solution to obtain quantitative extraction of uranium into a hexone solvent. Scrubbing the organic extract with an acid-deficient solution of aluminum nitrate containing tartrate, oxalate, (ethylenedinitrilo)tetraacetic acid, and ferrous sulfamate removes most interfering ions. Color development is made in the hexone phase with the addition of dibenzoylmethane in an ethyl alcohol-pyridine mixture. A portion of the solution is placed in a clean 5-cm absorption cell and its absorbance measured. The concentration of uranium in the sample is determined from two comparison standards bracketing the unknown and run concurrently, or from a standard curve.

3.2 If large amounts of thorium or cerium(IV) are present, an acid-deficient solution of aluminum nitrate without tetrapropylammonium nitrate serves as the salting solution, and then the hexone phase is scrubbed with a solution of ammonium acetate and sodium diethyldithiocarbamate. A second scrubbing with a solution of mercuric nitrate and aluminum nitrate removes the diethyldithiocarbamate which otherwise would interfere with color development. Plutonium is not eliminated by the procedure used for samples containing large amounts of thorium or cerium(IV).

¹ This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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² This test method is based on a method described by Maeck, W. J., Booman, G. L., Elliott, M. C., and Rein, J. E., *Analytical Chemistry*, Vol 31, 1959, p. 1130.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

⁶ *Annual Book of ASTM Standards*, Vol 12.02.

NOTE 1—**Caution**—Because the samples may be from irradiated fuel, the radiation hazard will require that adequate shielding be used and that proper precautions be taken to prevent ingestion or direct contact while handling these materials.

4. Photometers and Photometric Practice

4.1 Photometers and photometric practice prescribed in this test method shall conform to Practice E 60.

4.2 Use absorption cells matched to within 0.001 absorbance units; otherwise, determine corrections in accordance with Section 7.

5. Apparatus

5.1 *Shielded Facility* for sampling and diluting the solutions of the irradiated fuel.

5.2 *Spectrophotometer*.⁷

5.3 *Cells*, 5-cm path length, small volume,⁸ with TFE-fluorocarbon sleeves machined to adapt cells to the cell holder.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁹ Other grades 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type IV.

6.3 *Acetic Acid (1+9)*—Mix 10 mL of glacial acetic acid with 90 mL of water.

6.4 *Aluminum Nitrate-Ammonium Hydroxide Salting Solution*—Slurry 1050 g of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in a small amount of water. Add 135 mL of concentrated ammonium hydroxide (NH_4OH , sp gr 0.90) and dilute to about 950 mL with water. Stir to dissolve. Transfer to a separatory funnel, add 250 mL of hexone, and extract for 3 min in order to remove any uranium impurity. Filter the aqueous phase through a large, fine-porosity, sintered-glass Büchner funnel and transfer to a 1-L volumetric flask. Dilute to 1 L with water.

6.5 *Aluminum Nitrate-Tartaric Acid-Oxalic Acid-(Ethylenedinitrilo)tetraacetic Acid-Ammonium Hydroxide Scrub Solution*—Add 940 g of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 33 g of tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$), 31 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and 64 g of (ethylenedinitrilo)tetraacetic acid ($(\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$) to 100 mL of water and 150 mL of concentrated ammonium hydroxide (NH_4OH , sp gr 0.90).

Heat and stir until solution is complete, cool, and filter into a separatory funnel. Add 250 mL of hexone and extract for 3 min in order to remove any uranium impurity. Transfer the aqueous phase to a 1-L volumetric flask and dilute to 1 L with water.

6.6 *Aluminum Nitrate-Tetrapropylammonium Nitrate Salting Solution*—Slurry 1050 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a small amount of water. Add 135 mL of NH_4OH (sp gr 0.90) and 10 mL of a filtered 10% solution of tetrapropylammonium hydroxide ($(\text{C}_3\text{H}_7)_4\text{NOH}$). Dilute to about 950 mL with water. Stir until solution is complete, making sure the temperature of the solution remains below 50°C. Transfer to a separatory funnel, add 250 mL of hexone, extract for 3 min in order to remove any uranium impurity. Filter the aqueous phase through a large, fine-porosity, sintered-glass Büchner funnel and transfer to a 1-L volumetric flask. Again add 10 mL of a filtered 10% solution of $(\text{C}_3\text{H}_7)_4\text{NOH}$ and dilute to 1 L with water.

6.7 *Ammonium Acetate-Sodium Diethyldithiocarbamate Scrub Solution*—Dissolve 154 g of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) and 20 g of sodium diethyldithiocarbamate ($(\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}$) in 900 mL of water. Adjust the pH to 7 with 1+9 acetic acid, filter, and dilute to 1 L with water.

6.8 *Dibenzoylmethane-Pyridine-Ethyl Alcohol Solution*—Dissolve 0.1140 g of dibenzoylmethane ($(\text{C}_6\text{H}_5\text{CO})_2\text{CH}_2$) in 400 mL of distilled pyridine ($\text{C}_5\text{H}_5\text{N}$). Add 25 mL of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, 95%) and dilute to 500 mL with distilled pyridine. Distillation of the pyridine removes impurities which interfere. Pyridine is a highly toxic, flammable material and should be handled with caution.

6.9 *Ferrous Sulfamate Solution*—Prepare a saturated solution of 14.7 g of sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$), 26.9 g of ferrous ammonium sulfate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), and 100 mL of water. Prepare a fresh solution each week.

6.10 *Hexone (sp gr 0.80)*—Methyl isobutyl ketone.

6.11 *Mercuric Nitrate Scrub Solution*—Dissolve 0.065 g of mercuric nitrate ($\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) in 90 mL of 1+15 nitric acid. Dilute to 100 mL with 1+15 nitric acid.

6.12 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

6.13 *Nitric Acid (3+5)*—Mix 30 mL of concentrated nitric acid (HNO_3 , sp gr 1.42) with 50 mL of water.

6.14 *Nitric Acid (1+15)*—Mix 10 mL of concentrated nitric acid (HNO_3 , sp gr 1.42) with 150 mL of water.

6.15 *Potassium Permanganate Solution*—Dissolve 0.316 g of potassium permanganate (KMnO_4) in water and dilute to 1 L with water. Store in a dark bottle.

6.16 *Uranium Nitrate, Standard Solution (10.000 g U/L)*—Weigh out 11.799 g of uranium oxide (U_3O_8) (NBL CRM 129 or equivalent). Dissolve in HNO_3 (3+5) and dilute to 1 L with HNO_3 (1+15).

7. Cell Matching

7.1 Absorption cells should be matched or have correction factors determined within 0.001 absorbance unit at the working wavelength of 415 nm.

7.2 Fill two clean cells with a solution prepared by processing a uranium standard as described in Section 8, and place the cells in the spectrophotometer.

7.3 Designate the cell with the lower absorbance reading as the reference cell.

⁷ A Beckman Model B spectrophotometer obtainable from Beckman Instruments, Inc., Fullerton, CA, or equivalent has been found satisfactory for this purpose.

⁸ Absorption Cells, No. 5-997, from American Instrument Co., Silver Spring, MD, have been found satisfactory.

⁹ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United States Pharmacopeia."