Standard Test Method for Isotopic Uranium in Water by Radiochemistry[1]

1. Scope

1.1 This test method covers the determination of alpha-particle-emitting isotopes of uranium in water by means of chemical separations and alpha pulse-height analysis (also known as alpha-particle spectrometry). Uranium is chemically separated from a water sample by coprecipitation with ferrous hydroxide, anion exchange, and electrodeposition. The test method applies to soluble uranium as well as to any uranium that might be present in suspended matter in the water sample. This test method is applicable for uranium processing effluents as well as substitute ocean water. When suspended matter is present, an acid dissolution step is added to assure that all of the uranium dissolves. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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

1.3 *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.* Specific warning statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C859 Terminology Relating to Nuclear Materials
C1163 Practice for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride
D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3084 Practice for Alpha-Particle Spectrometry of Water
D3370 Practices for Sampling Water from Closed Conduits
D3648 Practices for the Measurement of Radioactivity
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D7282 Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminologies C859 and D1129. For terms not included in these reference may be made to other published glossaries.[4,5]

4. Summary of Test Method

4.1 The water sample to be analyzed is acidified and ^{232}U is added to serve as an isotopic tracer before any additional operations are performed. If the sample is a seawater sample, or if it contains carbonate or bicarbonate ions, the sample must be boiled under acidic conditions to convert these ions to carbon dioxide gas which is then expelled from the solution. Carbonate ions must not be present during the precipitation step because they complex the uranium and prevent its coprecipitation. The uranium is coprecipitated from the sample with ferrous hydroxide. This precipitate is dissolved in concentrated hydrochloric acid, or is subjected to an acid dissolution with concentrated nitric and hydrofluoric acids if the hydrochloric acid fails to dissolve the precipitate.

4.2 The uranium is separated from other radionuclides by adsorption on anion-exchange resin from 8 *M* hydrochloric acid, followed by elution with 0.1 *M* hydrochloric acid. The uranium is electrodeposited onto a stainless steel disk. Isotopic uranium radioactivities are measured by alpha pulse-height

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

Current edition approved Jan. 1, 2015. Published January 2015. Originally approved in 1980. Last previous edition approved in 2009 as D3972 – 09. DOI: 10.1520/D3972-09R15.

[2] 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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Parker, S. P., ed., *Dictionary of Chemical Terms*, McGraw-Hill Book Co., New York, NY, 1985.

[5] IUPAC, "Glossary of Terms Used in Nuclear Analytical Chemistry," *Pure and Applied Chemistry*, Vol 54, 1982, pp. 1533–1554.

TABLE 1 Relevant Properties of Uranium Isotopes of Interest in Environmental Waters[A]

Isotope	Half Life Years	Principal Alpha Energies in MeV (Abundance)
^{232}U	68.9	5.320(68.6) 5.262(31.4)
^{233}U	1.592×10^5	4.824(83.3) 4.782(14.1)
^{234}U	2.455×10^5	4.774(72.5) 4.722(27.5)
^{235}U	7.038×10^8	4.596(5.6) 4.307 (57) 4.366 (17) 4.214(6.4)
^{236}U	2.342×10^7	4.493 (74) 4.445 (26)
^{238}U	4.468×10^9	4.198 (77) 4.151 (23)

[A] *Table of Isotopes*, Eighth Edition, Vol. 11, Richard B. Firestone, Lawrence Berkeley National Laboratory, University of California, 1996.

analysis with a silicon surface-barrier or ion-implanted detector and a multichannel analyzer.

4.3 When ^{232}U is used as the tracer, the other isotopes of uranium listed in Table 1 can be detected in the alpha-particle spectrum of an unknown sample. From the alpha energies given in the table, it can be seen that the alpha energy of ^{232}U is more than 0.40 MeV higher than the energy of any other uranium isotope. Thus, there should be little interference from tailing of the ^{232}U into the lower energy alpha peaks. ^{233}U and ^{234}U usually cannot be resolved because their principal alpha energies differ by only 0.04 MeV. ^{235}U and ^{236}U peaks can be resolved only with difficulty. The alpha peaks from other combinations of uranium isotopes can be resolved unless the quality of the finally prepared sample is poor.

5. Significance and Use

5.1 This test method was developed to measure the radioactivity of uranium isotopes in environmental waters or waters released to the environment, and to determine whether the uranium-isotope concentrations are below the maximum amounts allowable by any regulatory statute.

6. Interferences

6.1 Thorium, polonium, plutonium, and americium were found not to interfere in this uranium determination.[6] The only possible alpha-emitting isotopes that might interfere, based on the chemistry of this test method, are ^{231}Pa (3.28×10^4 y half-life) and ^{237}Np (2.16×10^6 y half-life). These isotopes, however, are not likely to be present in environmental water samples. Protactinum-231 has the following alpha energies in MeV, the abundance being given in parentheses: 5.013 (25.4 %), 5.03 (23 %), 4.951 (22.5 %), 5.059 (11 %), and 4.734 (8.4 %). Thus, from Table 1, it is seen that ^{231}Pa can interfere with the determination of ^{233}U or ^{234}U. However, when the 4.951 to 5.059 MeV ^{231}Pa peaks can be resolved from the uranium peaks, a correction can be made. Neptunium-237 has alpha emission energies ranging from 4.639 to 4.873 MeV, with 72 % found between 4.771 and 4.788 MeV. Conventional analytical equipment would not be able to resolve these peaks from normal ^{234}U emissions. If Np-237 is suspected to be present in the sample, a separate ^{237}Np analysis would be required to make the appropriate correction to the ^{234}U result.

6.2 When measuring very low concentrations of uranium isotopes in environmental samples, detector backgrounds and laboratory blanks must be well known. Blank determinations are made to ascertain that any contamination from reagents, glassware and other laboratory apparatus is small compared to the activity in the sample that is being analyzed. A blank determination should be made in exactly the same way as the sample determination.

7. Apparatus

7.1 *Centrifuge,* 250-mL centrifuge bottle or tube capacity.

7.2 *Ion Exchange Column,* glass or plastic, approximately 13-mm inside diameter and 150 mm long with a glass-wool plug or plastic frit and a 100- to 150-mL reservoir.

7.3 *Electrodeposition Apparatus,* consisting of a 0 to 12-V, 0 to 2-A power supply (preferably constant current) and an electrodeposition cell. The cathode is an approximately 20-mm diameter stainless steel disk polished to a mirror finish. The anode is approximately 1-mm diameter platinum wire with an approximately 8-mm diameter loop at the end of the wire parallel to the cathode disk. Cooling of the electrolyte during electrodeposition to at least 50°C is recommended. See references in Section 8 of Practice D3084 for more details.

7.4 *Alpha Pulse-Height Analysis System,* consisting of a silicon surface-barrier or ion-implanted detector, supporting electronics, and pulse-height analyzer. A system capable of giving a resolution of 30 keV FWHM or better, when measured with a high-quality source, is recommended. The counting efficiency of the system should be greater than 15 %, and the background in the energy region of each peak should be less than ten counts in 60 000 s.

8. Reagents and Materials

8.1 *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.[7] Other grades may be used provided it is first ascertained that

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[6] Bishop, C. T., Casella, V. R., and Glosby, A. A., “Radiometric Method for the Determination of Uranium in Water: Single-Laboratory Evaluation and Interlaboratory Collaborative Study,” *U.S. Environmental Protection Agency Report*, EPA *600/7-79-093*, April 1979.

[7] *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 *Annual 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.

the reagent is of sufficiently high purity to permit its use without reducing the precision, or increasing the bias, of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specifications D1193, Type III, as a minimum.

8.3 *Radioactive Purity of Reagent*—Radioactive purity shall be such that the measured results of blank samples do not exceed the calculated probable error of the measurement or are within the desired precision.

8.4 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

8.5 *Ammonium Hydroxide Solution* 0.15 *M* (1+99)—Mix 1 volume of concentrated NH_4OH (sp gr 0.90) with 99 volumes of water. This solution is 0.15 *M*.

8.6 *Anion-Exchange Resin*—Strongly basic, styrene, quaternary ammonium salt, 4 % crosslinked, 100 to 200 mesh, chloride form.

8.7 *Electrolyte*—Dissolve 132 g of ammonium sulfate in water and dilute to 1 L. Slowly add concentrated NH_4OH or concentrated H_2SO_4 while stirring to adjust the pH of the solution to 3.5. The solution is 1 *M* in $(NH_4)_2SO_4$.

8.8 *Ethyl Alcohol* (C_2H_5OH)—Make slightly basic with a few drops of concentrated NH_4OH per 100 mL of alcohol. Anhydrous denatured ethanol is acceptable.

8.9 *Ferric Chloride Carrier Solution* (20 mg Fe/mL)—Dissolve 9.6 g of $FeCl_3 \cdot 6H_2O$ in 100 mL of 0.5 *M* HCl.

8.10 *Filter paper,* ashless, medium porosity.

8.11 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.12 *Hydrochloric Acid* 8 *M* (2+1)—Mix 2 volumes of concentrated HCl (sp gr 1.19) with 1 volume of water. This solution is 8 *M*.

8.13 *Hydrochloric Acid* 0.5 *M* (1+23)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 23 volumes of water.

8.14 *Hydrochloric Acid* 0.1 *M* (1+119)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 99 volumes of water. This solution is 0.1 *M*.

8.15 *Hydrofluoric Acid* (sp gr 1.2)—Concentrated hydrofluoric acid (HF).

8.16 *Hydroiodic Acid* (sp gr 1.5)—Concentrated hydroiodic acid (HI).

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

8.18 *Sodium Hydrogen Sulfate—Sulfuric Acid*—Dissolve 10 g of sodium hydrogen sulfate in 100 mL of water and then carefully add 100 mL of concentrated H_2SO_4 (sp gr 1.84) while stirring. This solution contains about 5 g of $NaHSO_4$ per 100 mL of 9 *M* H_2SO_4.

8.19 *Sodium Hydrogen Sulfite* ($NaHSO_3$).

8.20 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

8.21 *Sulfuric Acid* 1.8 *M* (1+9)—Cautiously add with stirring 1 volume of concentrated sulfuric acid (sp gr 1.84) to 9 volumes of water. This solution is 1.8 *M*.

8.22 *Thymol Blue Indicator Solution*—Dissolve 0.04 g of the sodium salt of thymol blue in 100 mL of water.

8.23 *Uranium-232 Solution, Standard* (about 0.2 Bq/mL).

9. Precautions

9.1 Hydrofluoric acid (HF) is very hazardous and should be used in a well-ventilated hood. Wear rubber gloves, safety glasses or goggles, and a laboratory coat. Avoid breathing any HF fumes. Clean up all spills promptly and wash thoroughly after using HF. Ready availability of a topical fluoride binding agent, such as calcium gluconate gel, is strongly recommended in the event of skin contact with HF.

10. Sampling

10.1 Collect the sample in accordance with Practices D1066, D3370, and Specification D1192 as applicable. Preserve the sample by adjusting the pH to 1 with concentrated HCl if the sample is not to be analyzed within 24 h. Record the volume of the sample and the volume of acid added.

11. Calibration and Standardization

11.1 Standardized ^{232}U is required as a tracer. Before standardization, this isotope must be separated from its radioactive descendents by anion exchange or some other means of chemical separation. See Practices D3084 and D3648 for general guidance concerning the standardization of tracers, and the energy and efficiency calibrations of the detector. The pulse-height analyzer should be set to accept pulses from alpha particles of approximately 3.5 to approximately 9.0 MeV in energy.

12. Procedure

12.1 *Coprecipitation:*

12.1.1 Measure the volume of approximately 1 L of the water sample to be analyzed and transfer to a 2-L beaker.

12.1.2 If the sample has not been acidified, add 5 mL of concentrated HCl.

12.1.3 Add a magnetic stirring bar, mix the sample completely, and check the acidity with pH-indicating paper or strip. If the pH is greater than 1, add concentrated HCl with mixing until it reaches this value.

12.1.4 Add approximately 0.2 Bq of standardized ^{232}U tracer with a calibrated pipet or by weight.

12.1.5 If the sample is a seawater or if it may contain carbonate ions, it must be boiled for approximately 5 min. Check the pH again after boiling and if it is greater than 1, add concentrated HCl with mixing to bring the pH back to 1.

12.1.6 Add approximately 500 mg of $NaHSO_3$ and 2 mL of ferric chloride carrier solution.

12.1.7 Cover the sample with a watch glass and heat the sample to boiling for 10 min.

12.1.8 Without removing the watch glass, add concentrated NH_4OH from a polyethylene squeeze bottle with the delivery tube inserted under the watch glass at the beaker pouring lip.

Continue adding concentrated NH_4OH until a light permanent turbidity is produced, and then add an excess of 10 mL. Boil the solution for an additional 10 min.

12.1.9 Add another 1 mL of concentrated NH_4OH and continue to stir the sample for 30 min without heating.

12.1.10 Allow the sample to settle (approximately 30 min) and decant the supernate, being careful not to remove any precipitate.

12.1.11 Slurry the remaining precipitate and supernate, and transfer to a centrifuge bottle or tube.

12.1.12 Centrifuge the sample and pour off the remaining supernate. Discard the supernates to waste.

12.1.13 Attempt to dissolve the precipitate with a minimum volume of concentrated HCl. If the precipitate dissolves completely, add a volume of concentrated HCl equal to twice the volume of the sample solution and dilute to 100 to 150 mL with 8 *M* HCl (2+1), or otherwise adjust the acidity to 8 *M* HCl, and then proceed to 12.3. If the precipitate does not dissolve in HCl, evaporate to dryness, heat to 450°C for a few hours, and proceed to 12.2.

12.2 *Acid Dissolution of Residue:*

12.2.1 Transfer the residue to a 250-mL TFE-fluorocarbon beaker and add 60 mL of concentrated HNO_3 and 30 mL of concentrated HF. (**Warning—**See Section 9.)

12.2.2 Stir and heat on a magnetic stirrer hot plate for about 2 h at a temperature near boiling. If the volume drops below about 25 mL, add equal volumes of concentrated HNO_3 and concentrated HF, cooling the sample before adding.

12.2.3 Remove the sample from the hot plate and cool to about 40°C. Add 20 mL of concentrated HCl and slowly take the sample to dryness on the hot plate. Remove the beaker from the hot plate as soon as the sample has dried.

12.2.4 Cool the sample to near room temperature. Add 50 mL of 8 *M* HCl and boil gently for a few minutes.

12.2.5 Filter through an ashless filter paper of medium porosity. Wash the paper with about 10 mL of 8 *M* HCl, combining the wash water with the filtrate. Discard filter paper. Take this solution and proceed with 12.3.

12.3 *Anion-Exchange Separation:*

12.3.1 Prepare the column by slurrying the anion-exchange resin with 8 *M* HCl and pouring it into a column of the kind specified in Section 7. The height of the resin bed should be approximately 80 mm, or greater for samples which had originally contained suspended matter. Operate the column at a maximum flow rate of 2 mL/min.

12.3.2 After the resin has settled, pass the sample solution through the anion-exchange resin column into a beaker.

12.3.3 After the sample has passed through the column, elute the iron (and plutonium, if present) with 6 resin-bed volumes of freshly prepared 8 *M*HCl containing 1 mL of concentrated HI per 9 mL of 8 *M* HCl.

12.3.4 Wash the column with an additional two resin-bed volumes of 8 *M* HCl. Discard the eluants from steps 12.3.1 – 12.3.4 to waste.

12.3.5 Place a clean, 50-mL glass beaker under the column. Elute the uranium with 6 resin-bed volumes of 0.1 *M*HCl.

12.3.6 Evaporate the sample to about 20 mL and add 5 mL of concentrated HNO_3.

12.3.7 Evaporate the sample to near dryness.

12.4 *Electrodeposition:*[8]

12.4.1 Add 2 mL of a 5 % solution of $NaHSO_4{\cdot}H_2O$ in 9 *M* H_2SO_4 to the sample.

12.4.2 Add 5 mL of concentrated HNO_3, mix well, and evaporate to dryness, but do not bake.

12.4.3 Dissolve the sample in 5 mL of the electrolyte, warming to hasten the dissolution.

12.4.4 Transfer the solution to the assembled electrodeposition cell using an additional 5 to 10 mL of the electrolyte in small increments to rinse the sample container.

12.4.5 Add 3 or 4 drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 *M* H_2SO_4 (1+9) (or concentrated NH_4OH) dropwise until this color is obtained.

12.4.6 Place the platinum anode into the solution so that it is approximately 10 mm above the stainless steel disk that serves as the cathode.

12.4.7 Connect the electrodes to the source of current, turn the power on, and adjust the power supply to give a current of 1.2 A. (Constant current power supplies will require no further adjustments during the electrodeposition.)

12.4.8 Continue the electrodeposition for a total of 1 h.

12.4.9 Add 1 mL of concentrated NH_4OH and continue the electrodeposition for 1 min.

12.4.10 Remove the anode from the cell and then turn off the power.

12.4.11 Discard the solution in the cell and rinse the disk 2 or 3 times with 0.15 *M* NH_4OH (1+99).

12.4.12 Disassemble the cell and wash the disk with ethyl alcohol.

12.4.13 Touch the edge of the disk to a tissue to absorb the alcohol from the disk.

12.4.14 Dry the disk and label it for counting. The sample should be counted as soon as practicable and definitely within a week, because ^{232}U descendents grow into the sample and possibly interfere with the activity measurements of certain uranium isotopes.

12.5 *Alpha Pulse-Height Analysis:*

12.5.1 Count the samples with the alpha pulse-height analysis system. See Practices D3084 and D7282 for guidance on the setup and calibration of the instrument, and additional quality assurance measures.

12.5.2 Check the alpha pulse-height spectrum and its analysis for peaks at the ^{232}U, ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U alpha energies, or a combination thereof, and determine the total counts in each peak. Where two isotopes are close in energy, complete resolution probably will not be possible. This is true, for example, when ^{234}U and ^{233}U are present in the same sample.

12.5.3 Make the necessary background correction for each peak.

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[8] As an alternate to electrodeposition, the purified uranium fraction may be prepared for alpha spectroscopy analysis by lanthanide coprecipitaion using Test Method C1163 for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride, provided that the peak resolution and tracer recovery meet the laboratory's acceptance criteria for those parameters.

13. Calculation

13.1 Calculate the concentrations of each of the uranium isotopes (i) in the aliquant of water taken for analysis as follows:

$$AC_i = R_{n,i} \times (AC_t \times V_t / R_{n,t}) / V_a \tag{1}$$

where:

AC_i = activity concentration of the uranium isotope in the water, Bq/L,
$R_{n,i}$ = net sample count rate in the energy region of interest in the alpha spectrum, in counts per second,
AC_t = activity concentration of the ^{232}U tracer at the time of the count, Bq/mL,
V_t = ^{232}U tracer added, mL,
$R_{n,t}$ = net sample count rate in the ^{232}U tracer energy region of the alpha spectrum, in counts per second, and
V_a = volume of water sample taken for analysis, L.

13.2 The absolute counting efficiency of the alpha spectrometer, ε, must be determined if it is desired to calculate the uranium recovery of the analytical procedure. Calculate this efficiency as follows:

$$\varepsilon = R_{n,s} / AC_s \tag{2}$$

where:

$R_{n,s}$ = net counting rate of a standard source in the energy region of the calibrated alpha-particle emitter, cps, and
AC_s = absolute alpha-particle emission rate of the calibrated alpha-particle emitter, α/s.

13.2.1 The standard source may be any combination of alpha emitters with alpha-particle emission energies in the approximate range of the isotopes to be analyzed, provided that the peaks are well resolved. The standard source must be in the same geometrical (for example, sample deposit diameter relative to the diameter of the calibration standard, distance from the detector) arrangement as are used for the sample being analyzed. Further guidance on the calibration of the detection system can be found in Test Method D7282.

13.3 Calculate the fractional uranium recovery, Y, as follows:

$$Y = R_{n,t} / (AC_t \times V_t \times \varepsilon) \tag{3}$$

13.4 The result of the measurement of the activity concentration for each isotope (i) has a "counting uncertainty" that is due to the statistically random nature of radioactive decay and nuclear measurements. When it is calculated at the one-sigma confidence interval, this value is known as the "standard uncertainty," $u_c(R_{n,i})$ and is calculated in activity concentration units:

$$u_c(R_{n,i}) = ((R_{g,i}/t_a) + (R_{b,i}/t_b))^{1/2} \times (AC_t \times V_t / R_{n,t}) / V_a \tag{4}$$

where:

$R_{g,i}$ = gross count rate for each individual isotope (i), in counts per second,
$R_{b,i}$ = method background count rate for each isotope region of interest, in counts per second,
t_a = count duration for the sample analysis, in seconds, and
t_b = count duration of the background determination, in seconds.

Similarly, the tracer measurement has a standard uncertainty, $u_c(R_t)$:

$$u_c(R_t) = ((R_t/t_a) + (R_{b,t}/t_b))^{1/2} \times (AC_t \times V_t / R_{n,t}) / V_a \tag{5}$$

where:

R_t = gross count rate for the ^{232}U tracer, in counts per second, and
$R_{b,t}$ = method background count rate for the tracer region of interest, in counts per second.

13.5 In addition to the counting uncertainty, the laboratory should consider other systematic sources of measurement uncertainty and propagate these uncertainty contributions with the counting uncertainty to determine the total combined uncertainty of the measurement. Calculated at the one sigma confidence interval, the "combined standard uncertainty" $u_c(AC_i)$, is calculated in activity concentration units:

$$u_c(AC_i) = (u_c^2\,(R_{n,i}) + u_c^2\,(R_t) + AC_i^2) \times (u_r^2(AC_t) + u_r^2(V_t) + u_r^2(V_a) + u_r^2\,(\ldots))^{1/2} \tag{6}$$

where:

$u_r(AC_t)$ = standard relative uncertainty in the concentration of the ^{232}U tracer solution,
$u_r\,(V_t$ = standard relative uncertainty in the volume of the ^{232}U tracer solution,
$u_r(V_a)$ = standard relative uncertainty in the volume of the sample,
$u_r\,(\ldots)$ = any additional standard relative uncertainty that has been determined or estimated.

13.6 The Critical Level Concentration (L_c) in the sample is defined as the upper limit of activity that can be expected to be reported in a blank sample, at the 95 % confidence interval.

For isotope (i):[9]

$$L_{c,i} = [1.35 \times (t_a/t_b) + 1.65 \times (R_{b,i} \times t_a \times (1 + t_a/t_b))^{1/2}] / t_a / \varepsilon / Y / V_a \tag{7}$$

13.7 Similarly, Minimum Detectable Concentration (MDC) of analyte in the sample is defined as that amount of activity that must be present in the sample, in order to be distinguishable from a blank sample analysis, at the 95 % confidence interval.

For isotope (i), the a priori calculation of the MDC requires an estimate of the expected chemical yield, based on typical results observed in utilizing this method:[10]

$$MDC_i = [2.71 \times (1 + t_a/t_b) + 3.29 \times (R_{b,i} \times t_a \times (1 + t_a/t_b))^{1/2}] / t_a / \varepsilon / Y / V_a \tag{8}$$

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[9] This equation is based on the traditional critical level equation, $L_{c,i} = 1.65 \times (R_{b,i} \times t_a \times (1 + t_a / t_b))^{1/2} / t_a / \varepsilon / Y / V_a$, with consideration for the expected error rates in very low-background counting systems, such as alpha spectrometry.

[10] This equation is based on the traditional MDC equation, $MDC_i = [3.29 \times (R_{b,i} \times t_a \times (1 + t_a / t_b))^{1/2} + 2.71] / t_a / \varepsilon / Y / V_a$, with consideration for the increased calculated Critical Level described in the previous equation.

TABLE 2 Precision and Bias for Uranium-234, Uranium-235, and Uranium-238

Uranium-234 (+ 233)					Uranium-235 (+ 236)					Uranium-238				
	Recovered Bq/L	Bias, %	Precision			Recovered Bq/L	Bias, %	Precision			Recovered Bq/L	Bias, %	Precision	
			S(o)	S(t)				S(o)	S(t)				S(o)	S(t)
26.83	27.527	+2.6	1.9084	1.7570	2.17	1.866	–14	0.1917	0.3915	34.75	37.877	+0.9	1.4361	1.9552
0.936	0.918	–1.9	0.0223	0.0458	0.0438	0.0407	–6.9	0.0032	0.0057	0.936	0.889	–0.5	0.0161	0.0436
0.227	0.2247	–0.1	0.0047	0.0059	0.0017	0.00068	–60	0.00015	0.00033	0.028	0.027	–2.4	0.0026	0.0022
0.028	0.0275	–1.5	0.00236	0.0019	0.0013	0.0011	–11	0.00075	0.00067	0.0017	0.0020	+19	0.00069	0.00069

14. Precision and Bias[11]

14.1 A limited collaborative test of this test method was conducted with the uranium isotopes ^{234}U, ^{235}U, and ^{238}U. Eight laboratories participated by processing samples at four levels. Outlier results from laboratories were rejected as per the statistical tests outlined in Practice D2777. Of these four reference samples, two were prepared from actual environmental samples, one was prepared from a substitute ocean water sample, and one was prepared from a sample containing sediment.

14.2 A collaborative study of this test method showed that the precision and bias values presented in Table 2 were present based on the recovery from known additions of uranium isotope.

15. Quality Control

15.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test:

15.2 *Calibration and Calibration Verification:*

15.2.1 *Detector Efficiency*—While not required to determine the activity of the sample, the detector efficiency is necessary to determine the ^{232}U tracer chemical yield. The detector efficiency should be verified monthly or prior to use, whichever is longer, using a source traceable to a National Standardizing Laboratory such as NIST or NPL.

15.2.2 *Standardization (Yield)*—The yield of the ^{232}U tracer should be calculated for each sample and associated QC sample. The standard uncertainty in the yield determination should be less than 5 % (approximately 400 net counts). The yield should be reported along with the analytical data.

15.3 *Initial Demonstration of Laboratory Capability:*

15.3.1 If the laboratory or analyst has not performed the test before, a precision and bias study must be performed to demonstrate laboratory capability.

15.3.2 Analyze seven replicates of a standard solution prepared from an IRM (independent reference material) containing ^{234}U and ^{238}U at concentrations sufficient to minimize the counting uncertainty to less than 2 % at two sigma. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The matrix and chemistry of the solution should be equivalent to the samples.

15.3.3 Calculate the mean and standard deviation of the seven replicate values and compare to the acceptable ranges of precision and mean bias of 10 % and ±10 % respectively, based on a review of the collaborative study data. This study should be repeated until the precision and bias are met. Test Method D5847 should be consulted on the manner by which precision and mean bias are determined from the initial demonstration study.

15.4 *Laboratory Control Sample:*

15.4.1 To ensure that the test method is in control, analyze an LCS with each batch of no more than 20 samples. The activity added to reagent water should be appropriate for the type of samples analyzed and allow sufficient precision to ensure a meaningful assessment of accuracy. The LCS must be taken through all the steps of the analytical method including sample preservation and pretreatment. The laboratory shall develop acceptance criteria for the LCS and the results obtained for the LCS shall fall within those acceptance criteria.

15.4.2 If the result is not within these limits, reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

15.5 *Method Blank (Blank)*—Analyze the reagent water test blank with each batch of not more than 20 samples. The concentration of analytes found in the blank should be less than the L_c. If the concentration of the analytes is found above this level the results must be flagged and a comment made in the case narrative, if appropriate.

15.6 *Matrix Spike (MS):*

15.6.1 The performance of a matrix spike analysis with every batch is not required given the use of a tracer with each sample. The tracer chemical yield would indicate any problems with interferences in a specific sample matrix.

15.7 *Duplicate:*

15.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of no more than 20 samples. Calculate the Duplicate Error Ratio (DER) as a measure of the statistical agreement between the two results to ensure they agree within a 99.7 % confidence level.

$$DER = \mid AC_{i,sample} - AC_{i,duplicate} \mid / sqrt\left(u_c^2\left(AC_{i,sample}\right) + u_c^2\left(AC_{i,duplicate}\right)\right) \quad (9)$$

If the calculated DER exceeds 3.0, the sample and duplicate results do not agree within a 99.7 % confidence interval. In this case the samples in the batch must be reanalyzed, or the results must be flagged with an indication that they do not meet the performance criteria of the method.

15.7.2 In those cases where there is insufficient sample volume to allow performance of a duplicate sample analysis, a

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[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1073. Contact ASTM Customer Service at service@astm.org.

duplicate LCS (LCS-D) shall be performed. The LSC/LSC-D pair shall meet the same acceptance criteria as a sample/duplicate pair.

15.8 *Independent Reference Material (IRM):*

15.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted on at least single-blind basis (if practical) to the laboratory at least twice per year. The IRM should be traceable to a National Standardizing Laboratory such as NIST or NPL. The concentration of analyte in the traceable reference material should be appropriate to the typical purpose for which the method is used. The value obtained shall demonstrate acceptable performance as defined by the program or the outside source.

16. Keywords

16.1 alpha-particle spectrometry; isotopes; radioactivity; radiochemistry; uranium; water

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