Designation: D 3972 – 02

An American National Standard

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

This standard is issued under the fixed designation D 3972; 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 (ε) indicates an editorial change since the last revision or reapproval.

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 *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:*

C 859 Terminology Relating To Nuclear Materials[2]
D 1066 Practice for Sampling Steam[3]
D 1129 Terminologies Relating to Water[3]
D 1192 Guide for Equipment for Samping Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[3]
D 3084 Practice for Alpha-Particle Spectrometry of Water[4]
D 3370 Practices for Sampling Water[3]
D 3648 Practices for the Measurement of Radioactivity[4]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[4]

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms used in this test method, refer to Terminologies C 859 and D 1129. For terms not included in these reference may be made to other published glossaries.[5,6]

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 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.

[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.

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[2] *Annual Book of ASTM Standards*, Vol 12.01.

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

[4] *Annual Book of ASTM Standards*, Vol 11.02.

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

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

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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.

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.[7] The only possible alpha-emitting isotope that might interfere, based on the chemistry of this test method, is ^{231}Pa (3.28×10^4 y half-life). This isotope, however, is not likely to be present in environmental water samples. ^{231}Pa 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.

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 D 3084 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.[8] Other grades may be used provided it is first ascertained that 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 D 1193, 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.

[7] 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.

[8] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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.

10. Sampling

10.1 Collect the sample in accordance with Practices D 1066 and D 3370 and Specification D 1192 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 D 3084 and D 3648 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*:

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 D 3084 for guidance.

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 and blank correction for each peak.

13. Calculation

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

$$A_{a,i} = C_{n,i} A_t V_t / C_{n,t} V_a \quad (1)$$

where:

$A_{a,i}$ = concentration of the uranium isotope in the water, Bq/L,
$C_{n,i}$ = net sample occurs in the energy region of interest in the alpha spectrum,
A_t = concentration of the ^{232}U tracer, Bq/mL,
V_t = ^{232}U tracer added, mL,
$C_{n,t}$ = net sample counts in the ^{232}U tracer energy region of the alpha spectrum, and
V_a = volume of water sample taken for analysis, L.

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

$$E = R_{n,r} / A_r \quad (2)$$

where:

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

13.2.1 The standard source may be any alpha emitter with an alpha-particle energy between 4.0 and 5.5 MeV, provided that its peak is well resolved. The standard source must be in the same chemical form and 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.

13.3 Calculate the uranium recovery in percent, *Y*, as follows:

$$Y = \frac{(C_{n,t}/t)\,(100)}{A_t V_t E} \quad (3)$$

where:

t = counting duration, s.

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

The other terms are as defined for Eq 1 and Eq 2.

13.4 See Section 9 of Practices D 3648 with regard to overall uncertainty in a measurement.

13.5 The minimum detectable activity (MDA) of a given uranium isotope, can be calculated from some typical parameters that have been observed in utilizing this test method. The MDA is defined as that amount of activity which in the same counting time gives a count that is different from the background count by two times the standard deviation of the background count. See Section 9 of Practice D 3648 for the equation used. For example, in the analysis of a water sample where typical conditions would be 75 % recovery of the uranium, a 60 000-s counting time, a 25 % alpha spectrometer counting efficiency and an 8.3×10^{-5} cps (5 counts/1000 min) background, the MDA is approximately 5.6×10^{-4} Bq (becquerel = 1 disintegration/s). The lowest detectable concentration of uranium in a water sample, however, depends not only on the MDA, but also on the volume of water taken for analysis, and on the blank values observed in the laboratory where the analysis is to be performed. In many cases the reagent blank is a factor of ten higher than the instrument background and is then the controlling factor for the lowest detectable concentration of uranium in water.

13.6 The total propagated uncertainties (1 σ) for the individual uranium isotope concentrations are calculated as follows:

$$\sigma_{A_{a,i}}\,(Bq/l) = A_{a,i}\,(Bq/l) * [(\sigma_{cn,i}/C_{n,i})^2 + (\sigma_{A_t}/A_t)^2 + (\sigma_{v_t}/V_t)^2 + (\sigma_{cn,t}/C_{n,t})^2 + (\sigma_{va}/V_a)^2]^{1/2} \quad (4)$$

where:

$\sigma_{cn,\,i}$ = one sigma uncertainty of the net sample counts in the energy region of interest in the alpha spectrum,

σ_{A_t} = one sigma uncertainty of the concentration of the ^{232}U tracer, Bq/mL,

σ_{V_t} = one sigma uncertainty in the volume of ^{232}U tracer added, mL,

$\sigma_{cn,\,t}$ = one sigma uncertainty of the net sample counts in the ^{232}U tracer energy region of the alpha spectrum, and

σ_{V_a} = one sigma uncertainty of the volume of water sample taken for analysis.

The standard deviation for the net counts in the regions of interest are calculated from:

$$\sigma_c = (C + C_b)^{1/2} \quad (5)$$

where:

C = the gross counts in the region of interest, and

C_b = the expected background counts for the same counting duration in the region of interest.

13.7 The *a priori* minimum detectable concentration (MDC) is calculated as follows:

$$MDC(Bq/L) = \frac{\{2.71 + 4.65 * [(B)^{1/2}]\} * 100}{t * Y * E * V_s} \quad (6)$$

where:

t = the counting duration, s,

Y = the uranium recovery in percent, and

E = the absolute counting efficiency of the alpha spectrometer, and other terms are as defined in 13.1 and 13.6.

14. Precision and Bias [9]

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 D 2777. 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 the National Institute of Standards and Technology.

15.2.2 *Standardization (Yield)*—The yield of the ^{232}U tracer should be calculated for each sample and associated QC sample. The two sigma uncertainty of the yield should be less than 10 % (approximately 400 net counts). The yield should be reported along with the analytical data.

15.3 *Initial Demonstration of Laboratory Capability*:

[9] Supporting data are available from ASTM Headquarters, Request RR: D19–1073.

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 D 5847 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 insure a meaningful assessment of accuracy. The LCS must be taken through all the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the limit of ± 25 % of the expected value.

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 half the MDC. If the concentration of the analytes is found above this level the results must be flagged.

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 statistical agreement between the two results to insure they agree within a 99 % confidence level. This calculation is performed using the determined uncertainty associated with each result.

15.7.2 In those cases where there is insufficient sample volume to allow performance of a duplicate sample analysis, a duplicate LCS (LCS-D) shall be performed.

15.7.3 If the result is not within these limits, all samples in the batch must be reanalyzed or the results must be flagged with an indication that they do not fall within the performance criteria of the test method.

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 once per quarter. 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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