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Standard Test Method for Uranium in Drinking Water by High-Resolution Alpha-Liquid-Scintillation Spectrometry¹

This standard is issued under the fixed designation D 6239; 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.

~~¹Note— Added research report reference to Section 14 editorially in March 2008.~~

~~²Note— Added research report reference to Section 14 editorially in September 2008.~~

1. Scope

1.1 This test method covers determining the total soluble uranium activity in drinking water in the range of 0.037 Bq/L (1 pCi/L) or greater by selective solvent extraction and high-resolution alpha-liquid-scintillation spectrometry. The energy resolution obtainable with this technique also allows estimation of the ^{238}U to ^{234}U activity ratio.

1.2 This test method was tested successfully with reagent water and drinking water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

D 1129 Terminology Relating to Water

D 1193 Specifications for Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 3648 Practices for the Measurement of Radioactivity—Practices for the Measurement of Radioactivity

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D 7282 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 Terminology D 1129. For terms not included in this reference, refer to other published glossaries (1)³

4. Summary of Test Method

4.1 This test method is based on solvent extraction technology to isolate and concentrate uranium in drinking water for counting via a high-resolution alpha-liquid-scintillation spectrometer.

4.2 To determine total uranium, as well as limited isotopic uranium (^{238}U and ^{234}U) by activity in drinking water, a 200-mL acidified water sample is first spiked with ^{232}U as an isotopic tracer, boiled briefly to remove radon, and evaporated until less than 50 mL remain. The solution is then made approximately 0.01 M in diethylenetriaminepentaacetic acid (DTPA) and the pH is adjusted to between 2.5 and 3.0. The sample is transferred to a separatory funnel and equilibrated with 1.50 mL of an extractive scintillator containing a dialkyl phosphoric acid extracting agent. Under these conditions only uranium is quantitatively transferred to the organic phase while the extraction of undesired ions is masked by the presence of DTPA. Following phase separation, 1.00

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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 boldface numbers in parenthesis refer to the list of references at the end of the text.

mL of the organic phase is sparged with dry argon gas to remove oxygen, a chemical quench agent, and counted on a high-resolution alpha-liquid-scintillation spectrometer and multichannel analyzer (MCA).

4.3 The alpha spectrum of a sample that contains natural uranium and that is analyzed with an internal ^{232}U tracer will appear similar to the spectrum in Fig. 1. An approximate resolution of 250 keV FWHM for ^{238}U (4.2 MeV) allows resolution and analysis of the ^{238}U , ^{234}U , and ^{232}U energy spectrum peaks when their activities are of the same order of magnitude. Resolution of the ^{235}U (4.4 MeV) alpha peak is not possible, but its activity, which accounts for approximately 2.2 % of the total natural uranium activity, is included in the total uranium activity calculated when the ^{238}U and ^{234}U peaks are in the region of interest (ROI). When the ^{238}U and ^{234}U peaks are integrated separately, a portion of the ^{235}U activity will be included in the ^{238}U activity and the rest in the ^{234}U activity, depending on the exact ROIs selected. Likewise, if present, ^{236}U and ^{233}U will not be resolved by the spectrometer; however, their activity will be included in the total uranium ROI. U will not be resolved by the spectrometer; however, their activity will be included in the total uranium ROI. Fig. 2 is a flow chart that summarizes the steps required in this test method.

5. Significance and Use

5.1 This test method is a fast, cost-effective method that can yield limited isotopic activity levels for ^{238}U and ^{234}U , as well as total uranium activity. Although ^{232}U is incorporated as a tracer, uranium recoveries for this test measured during the developmental work on this test method were usually between 95 and 105%.

5.2 The high-resolution alpha-liquid-scintillation spectrometer offers a constant $(99.6 \pm 0.1)\%$ counting efficiency and instrument backgrounds as low as 0.001 counts per minute ($\text{cpm}/\text{min}^{-1}$) over a 4 to 7 MeV energy range according to McDowell and McDowell (2). Count rates for extractive scintillator blanks and reagent blanks usually range from 0.01 $\text{cpm}/\text{min}^{-1}$ to 0.1 $\text{cpm}/\text{min}^{-1}$.

6. Interferences

6.1 During the development work on this method, less than 1% of ^{241}Am , ^{238}Pu , ^{210}Po , ^{226}Ra , ^{222}Rn , and ^{230}Th present in the original sample were found to extract under the conditions described for the extraction of uranium by this procedure. Uranium extraction is quantitative at pH values from 1.0 to 5.0 but extraction of ^{230}Th and ^{238}Pu increased slightly at pH values below 2.5 and phase separation was slower and less complete at pH values above 3.5. DTPA concentration is not critical in the range of 0.001 M to 0.1 M as long as a stoichiometric excess relative to the concentration of interfering ions, especially ferric ion (Fe^{3+}), is maintained. As much as 30 mg of Fe^{3+} did not interfere with the extraction of uranium when the DTPA concentration was 0.010 M, and as much as 250 mg of Fe^{3+} did not interfere when the DTPA concentration was increased to 0.10 M. As much as 2000 mg of calcium ion (Ca^{2+}) did not present an interference in a 0.010 M DTPA solution. Sulfate ion (SO_4^{2-}) did not interfere with the extraction of uranium at concentrations as high as 1 M, but hydrogen oxalate (HC_2O_4^-) concentrations greater than 0.001 M and dihydrogen phosphate (H_2PO_4^-) concentrations greater than 0.2 M resulted in decreased uranium recovery. These concentrations, however, are several orders of magnitude higher than the normal concentration of these ions in drinking water.

6.2 Beta- and gamma-emitting radionuclide interference is minimized (typically 99.95 % rejection of beta/gamma pulses) according to McDowell and McDowell (2) by the pulse-shape discrimination of the high-resolution alpha-liquid-scintillation spectrometer.

6.3 Quenching, often a problem with liquid scintillation counting, is significantly reduced by the use of extractive scintillator technology and will only result in a normally insignificant spectral energy shift with this procedure. No alpha counts will be lost due to quenching.

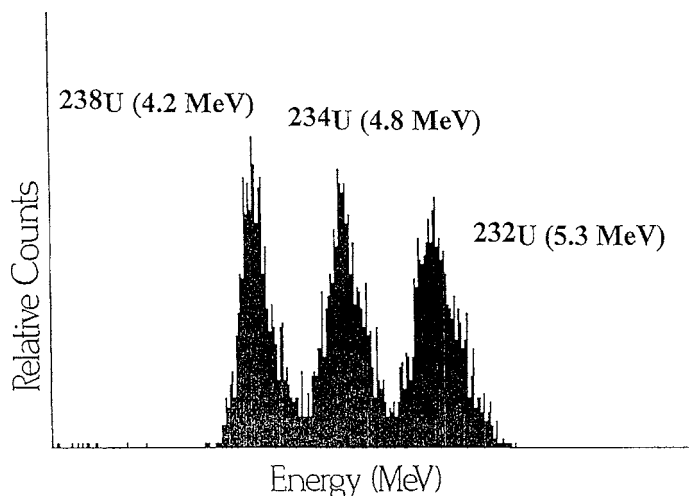


FIG. 1 Alpha Energy Spectrum of Natural Uranium and ^{232}U Tracer Measured on a High-Resolution Alpha-Liquid-Scintillation Spectrometer

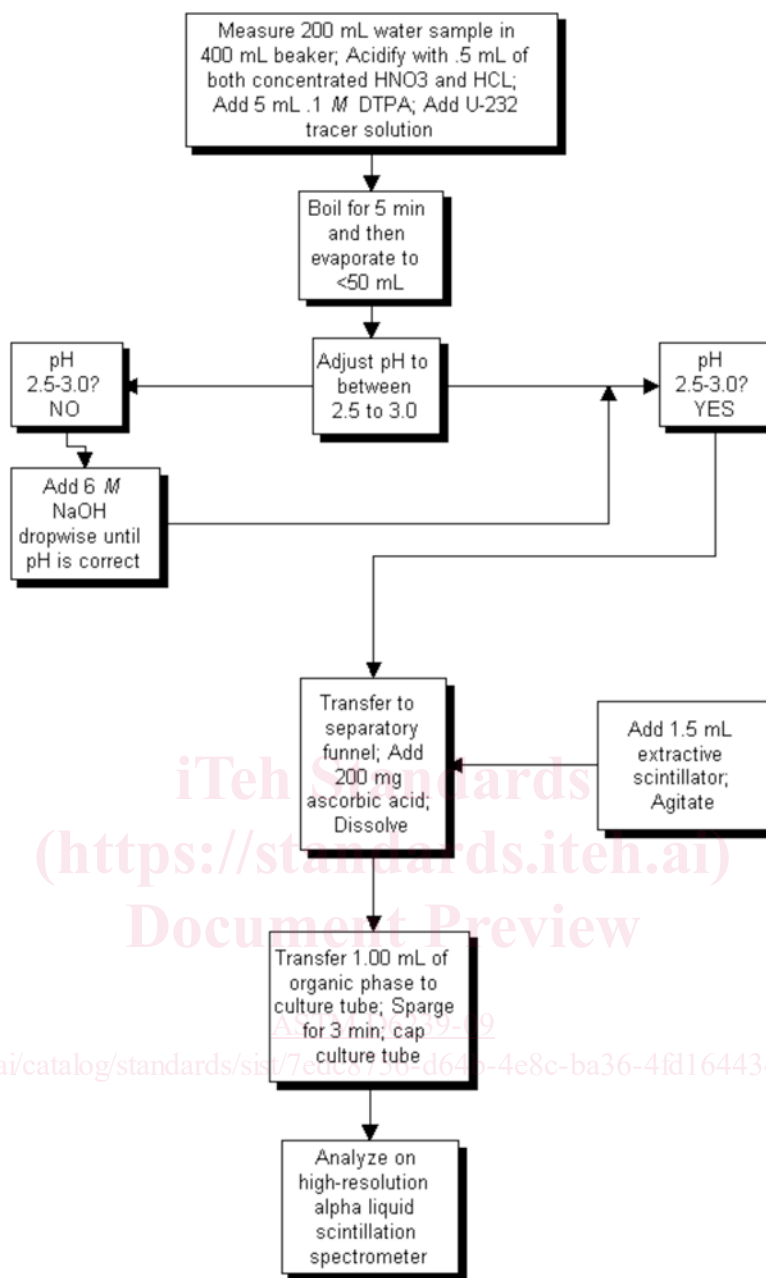


FIG. 2 Flow Chart Summary of this Test Method

6.4 ^{234}U and ^{238}U may exist in the ^{232}U tracer. The extent of the positive bias should be determined periodically.

7. Apparatus

7.1 *Caps*, vinyl or cork for culture tubes.

7.2 *Funnels*, separatory, 125-mL, pear-shaped, polytetrafluoroethylene or polypropylene.

7.3 *Meter*, pH, with gel electrode or low leak-rate reference electrode.

7.4 *Multichannel Analyzer (MCA)*, 512 channels or more, ADC/memory or better.

7.5 *NIM Bin and Power Supply*.

7.6 *Power Supply*, high voltage (+1000 voltV @ 1 mA), or integral to the spectrometer, see item 7.10.

7.7 *Sample*, counting reference, normal uranium.⁴ This counting reference sample is an approximately 50/50 mix of ^{238}U and ^{234}U by activity in 1.00 mL of the extractive scintillator solution and enclosed in a 10 by 75 mm glass culture tube and is for standardization purposes only.

⁴ The sole source of supply of the ^{238}U and ^{234}U normal uranium counting reference sample known to the committee at this time is from ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN, 37830. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

7.8 *Source*, ^{137}Cs , approximately 1.85×10^5 Bq (5 microcuries) (μCi). This item is for standardization purposes only.

7.9 *Sparging Gas Conditioner*⁵—This apparatus provides conditioned argon gas to remove oxygen, a chemical quench agent, from the sample, thus improving pulse shape discrimination and energy resolution. It consists of a specially-made glass tube, partially filled with silicone oil, that serves as a pressure-limiter, a gas drying tower filled with CaSO_4 (6 to 8 mesh) for additional drying of the argon gas, a gas washing bottle containing toluene and molecular sieve to saturate the argon with toluene and prevent sample evaporation while deoxygenating, and plastic tubing of various lengths to serve as connections between the pieces. The inlet from the compressed argon cylinder is connected to one side arm of the pressure limiter; the opposite side arm of the pressure limiter is connected to the inlet (bottom) of the gas drying tower. The outlet (top) of the drying tower is connected to the inlet (dispersion tube) of the gas washing bottle. The outlet of the gas washing bottle is connected to a disposable Pasteur pipet that serves as the sparging lance for the sample. For further information, consult the spectrometer (see 7.10) instruction manual.

7.10 *Spectrometer*, high-resolution pulse-shape discriminating alpha-liquid-scintillation spectrometer. Typical performance specifications include greater than 99 % alpha counting efficiency, 99.95 % beta/gamma rejection, energy resolution of 200 to 250 keV FWHM for the 4.78 MeV ^{226}Ra spectrum peak and instrument backgrounds of 0.001 counts per minute over a 4 to 7 MeV energy range.⁶

7.11 *Tubes*, 10 by 75 mm borosilicate glass. These tubes serve as sample-counting cells for the spectrometer (see 7.10).

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 (3). 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.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type III, or better.

8.3 *Argon Gas, Compressed*—99.999 % pure, with two-stage pressure regulator.

8.4 *Ascorbic Acid*— Reagent grade, solid ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$).

8.5 *Dialkyl Phosphoric Acid Extractive Scintillator*—See Ref (4).⁷

8.6 *Diethylenetriaminepentaacetic Acid (DTPA) (0.1 M)*—Add 3.93 g of solid DTPA ($\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$) to 50 mL of water. Adjust the pH approximately 7 by the dropwise addition of 6 M sodium hydroxide (NaOH) while stirring to complete dissolution. Dilute to 100 mL with water.

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

8.8 *Molecular Sieve*— Type 4A, activated, indicating, 4-8 mesh ($\text{Na}_{12}[\text{AlO}_2]_{12}(\text{SiO}_2)_{12} \cdot x\text{H}_2\text{O}$).

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

8.10 *Sodium Hydroxide (6 M)*—Slowly and with cooling add 240 g sodium hydroxide (NaOH) pellets to 500 mL of water and stir to dissolve. Dilute to 1 L with water.

8.11 *Toluene*—Reagent grade ($\text{C}_6\text{H}_5\text{CH}_3$).

8.12 ^{232}U *Solution, Standard* —Nominally 0.04 Bq/mL activity and standardized as per Practice D 3648.

9. Hazards

9.1 Use extreme caution when handling all acids and bases. They are extremely corrosive and skin contact could result in severe burns.

9.2 When diluting concentrated acids, always use safety glasses and protective clothing, and add the acid to the water.

9.3 Toluene is flammable. Avoid breathing vapors. Use with adequate ventilation and avoid open flames.

10. Sampling

10.1 Collect the sample in accordance with the applicable methods as described in Practice D 3370.

11. Calibration and Standardization

11.1 Use a normal uranium counting reference sample (that consists of an approximate 50/50 mixture of ^{238}U and ^{234}U , by activity) to establish an initial region of interest (ROI) on the multichannel analyzer (MCA).

⁵ The sole source of supply of the sparging gas conditioner known to the committee at this time is ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN, 37830. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

⁶ The sole source of supply of the spectrometer known to the committee at this time is ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN, 37830. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

⁷ The sole source of supply of the extractive scintillator known to the committee at this time is ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN, 37830, and may be prepared as in Ref (4). If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee.

NOTE 1—The actual ROI for any given sample may differ slightly from this initial ROI setting depending on the nature of the sample and the extractive scintillator used. This reference sample may be made using the techniques cited in Burnett and Tai (5). Set the pulse shape discriminator (PSD) of the high-resolution alpha-liquid-scintillation spectrometer prior to counting each individual sample. A 1.85×10^5 Bq (5 microcurie) ^{137}Cs gamma source may be used to aid in setting the PSD by quickly inducing a beta/gamma peak (4). For additional information, refer to the instrument instruction manual.

NOTE 2—Setting the pulse shape discriminator (PSD) is a quick, but critical procedure. Inaccurate activity determinations will result if the PSD is set improperly.

~~11.2A reagent blank, without tracer, must be made in exactly the same way as the sample determination.~~

11.2 A reagent blank is prepared without tracer for use in the background subtraction count (BSC). The reagent blank used for the BSC must closely match the associated sample test source configuration to ensure that the measurements used for background subtraction accurately reflect conditions when counting sample test sources. Refer to Practice D 7282, Section 12.1.3.

11.3 For general guidance on calibration and standardization, refer to Practice D 3648.

12. Procedure

NOTE 3—This procedure applies to analysis of water samples, whether preserved with HNO_3 or HCl or unpreserved.

12.1 Measure 200 mL of a water sample into a 400-mL borosilicate glass beaker.

12.2 Acidify the sample with 0.5 mL of concentrated nitric acid (HNO_3) and 0.5 mL of concentrated hydrochloric acid (HCl).

12.3 Add an accurately measured activity (depending on the expected uranium activity of the sample) of ^{232}U tracer solution.

NOTE 4—It is recommended that the tracer activity corresponds roughly (0.75 to 1.25 times the expected ^{234}U activity) to the ^{234}U activity so as to minimize uncertainties in determining the integral peak areas. If the approximate level of uranium activity in the sample is not known it may be estimated by the following simple screening technique: Add 40 mL of the water sample to a 100 mL beaker, boil for 5 min and let cool to room temperature. Then, follow 12.6-12.16. Calculate the ^{234}U activity (Bq/L) as in 12.18 by integrating the right-hand peak and assuming chemical recovery equals 100 % (recovery/efficiency (R) equals 0.667). Add ^{232}U tracer solution to each subsequent 200 mL sample such that the added tracer activity is equal to approximately one-fifth the activity calculated in 12.18. This amount of tracer activity should result in an energy spectrum having ^{234}U and ^{232}U peaks of approximately the same magnitude. Analyzing the sample without tracer will also show any potentially interfering radionuclides in the ^{232}U tracer ROI (such as ^{210}Po) that may result in a high yield bias and therefore a corresponding low uranium activity analysis.

12.4 Place the beaker on a hot plate, cover with a ribbed watch glass, and heat to boiling. Boil for approximately 5 min to remove radon.

12.5 Reduce the temperature and evaporate until approximately 40 mL of solution remains. Remove from heat and cool to room temperature.

12.6 Make the solution approximately 0.01 M in DTPA by adding 5 mL of 0.1 M DTPA solution.

12.7 Adjust the pH to between 2.5 and 3.0 with 6 M NaOH added dropwise while swirling the beaker. Rinse the pH electrode back into the solution with several milliliters of water.

12.8 Transfer the sample to a 125-mL, pear-shaped, polytetrafluoroethylene or polypropylene separatory funnel. Rinse the beaker twice with 5 to 10 mL of water delivered from a plastic wash bottle and transfer both rinses to the separatory funnel.

12.9 Add 200 mg of ascorbic acid and agitate to dissolve.

12.10 Using a calibrated pipet, add 1.50 mL of dialkyl phosphoric acid extractive scintillator to the separatory funnel and cap tightly. Agitate by inverting about once every second for five minutes.

12.11 Allow the phases to separate for at least 15 to 20 min, or longer if necessary. Proper phase separation is evidenced by two distinct, clear phases; the organic phase will be on top. Discard the aqueous phase.

12.12 Carefully transfer 1.00 mL of the organic phase to a 10 by 75 mm culture tube using a calibrated pipet, ensuring no water is transferred along with the organic.

12.13 Sparge the sample for three minutes with dry, oxygen-free, toluene-saturated argon (at a flow rate of approximately 10 mL/min) supplied by the sparging gas conditioner (see 7.9) using a Pasteur pipet as a sparging lance.

12.14 Cap the tube with a vinyl cap or close the tube with a cork stopper or other suitable device.

12.15 Place the counting cell in a high-resolution alpha-liquid-scintillation spectrometer. Set the instrument to acquire a pulse-shape (time) spectrum and begin acquiring a spectrum on the multichannel analyzer (MCA). Set the pulse-shape discriminator (PSD) three to five channels to the left of the minimum point between the beta/gamma peak (left) and the alpha peak (right) appearing on the MCA display. Especially on low level samples, it is sometimes helpful to use an external gamma source such as ^{137}Cs to identify the beta/gamma peak. For very low-level samples, set the PSD a few channels to the right of the beta/gamma peak.

NOTE 5—If the PSD is set too far to the left, the pulse-height spectrum will record beta/gamma pulses resulting in high background values. If the PSD is set too far to the right, some of the alpha pulses will not be recorded in the pulse-height spectrum resulting in low values for sample activity. For additional information refer to the instrument instruction manual.

12.16 Set the instrument to acquire a pulse-height (energy) spectrum on the MCA. Count until sufficient counts are obtained in the uranium peaks for the required statistical accuracy.

12.17 Integrate the ^{232}U ROI and calculate the fractional recovery/efficiency RY of ^{232}U according to Eq 1. The theoretical maximum value of RY is 0.667 if 1.50 mL of extractive scintillator solution is used and 1.00 mL of scintillator is counted.

12.18 Integrate the combined $^{238}, ^{234}\text{U}$ ROI and calculate the total uranium activity concentration in the original sample using Eq 2.

12.19 If isotopic information is desired, separately integrate the ^{238}U and ^{234}U ROIs as accurately as possible and calculate their individual activity concentrations using Eq 2.

12.20 Based on a conservative reagent blank count rate of 0.002 counts per second (cps)(s⁻¹) for the uranium ROI and a count time of 3600 s, this method will result in a sensitivity of at least 0.037 Bq/L (1 pCi/L) for total soluble uranium activity in water.

13. Calculation

13.1 The uranium activity concentration U_c in Bq/L can be calculated using the following equations:

$$RY = \frac{R_t - R_{tb}}{A_t} \quad (1)$$

(2) — AC

13.1 The fractional yield for uranium, RY , and the uranium activity concentration AC_a in becquerels per litre (Bq/L) can be calculated using the following equations:

$$RY = \frac{C_{t,n}}{AC_t \times V_t \times D_t \times t} \quad (1)$$

$$AC_a = \frac{R_a - R_b}{RYXV} \quad (2)$$

$$= C_{a,n} \times AC_t \times V_t \times DtC_{t,n} \times V_a$$

where:

$$C_{t,n} = C_{t,s} - C_{t,b} \quad (3)$$

and

$$C_{a,n} = C_{a,s} - C_{a,b} \quad (4)$$

$C_{a,n}$

where:

RY = fractional recovery/efficiency of fractional yield of ^{232}U tracer,

$R_t C_{t,n}$ = count rate in net count in the ^{232}U region of interest for the sample,

R_t = count rate in total count in the ^{232}U ROI for reagent blank (without ^{232}U region of interest for the sample),

$\frac{bC_{t,s}}{C_{t,b}}$ = total count in the ^{232}U tracer added), for the same detector used for the sample, ^{232}U region of interest for the background subtraction count (BSC) (without ^{232}U tracer added),

A_{AC_t} = activity of activity concentration of the ^{232}U tracer added (Bq), ^{232}U tracer (Bq/mL or Bq/g) on its reference date,

V_t = volume (mL) or mass (g) of ^{232}U tracer added,

D_t = decay factor for the ^{232}U tracer from its reference date to the midpoint of the counting period,

AC_a = uranium activity concentration (Bq/L), uranium activity concentration of the sample (Bq/L),

R_a = net count rate in the uranium ROI (^{234}U , ^{235}U , ^{238}U) for the sample,

$\frac{C_{a,n}}{R_b}$ = count rate in uranium ROI (total count in the uranium ROI for the sample,

$\frac{C_{a,s}}{C_{a,b}}$ = total count in the uranium ROI (^{234}U , ^{235}U , ^{238}U) for reagent blank (without ^{232}U for the BSC (without ^{232}U tracer added) for the same detector used for the sample, ^{232}U tracer added),

V_a = volume of sample analyzed (L), and

t = count time for both the sample and the BSC (s).

NOTE 6—Corrections for decay of the uranium analytes are not necessary, however, a correction for decay of the ^{232}U tracer may be required.

NOTE 7—Equations in 13.1 and 13.2 were changed to reflect the latest terminology and treatment of low background or sample count (or both) rates. The new equations are equivalent to the original equations and their use will not change the results reported in the round robin. The introduction of additional terms is consistent with D19.04 subcommittee's generic formula for alpha-emitting radionuclides. For clarity, the original method equations, updated only for terminology are included in Appendix X1.

13.2 The standard uncertainty of the ^{232}U yield, $u(RY)$, and the standard uncertainty of the uranium activity concentration, $u(AC_a)$, can be evaluated as follows:

$$u(RY) = \sqrt{\frac{u^2(C_{t,n})}{AC_t^2 \times V_t^2 \times D_t^2 \times t^2} + RY^2 \left(\frac{u^2(AC_t)}{AC_t^2} + \frac{u^2(V_t)}{V_t^2} \right)} \quad (5)$$

$$u(AC_a) = \sqrt{\frac{u^2(C_{a,n}) \times AC_t^2 \times V_t^2 \times D_t^2}{C_{t,n}^2 \times V_a^2} + AC_a^2 \left(\frac{u^2(C_{t,n})}{C_{t,n}^2} + \frac{u^2(AC_t)}{AC_t^2} + \frac{u^2(V_t)}{V_t^2} + \frac{u^2(V_a)}{V_a^2} \right)} \quad (6)$$

where:

$u(\bullet)$ = standard uncertainty of the measured quantity in parentheses (same unit of measurement as the quantity),