



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.

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:

- D 1129 Terminology Relating to Water²
- D 1193 Specifications for Reagent Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
- D 3370 Practices for Sampling Water²
- D 3648 Practices for the Measurement of Radioactivity³

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)⁴

¹ This test method is under the jurisdiction of ASTM Committee D-19 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 11.01.

³ *Annual Book of ASTM Standards*, Vol 11.02.

⁴ The boldface numbers in parenthesis refer to the list of references at the end of the text.

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 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 ^{253}U will not be resolved by the spectrometer; however, their activity will be included in the total uranium ROI.

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

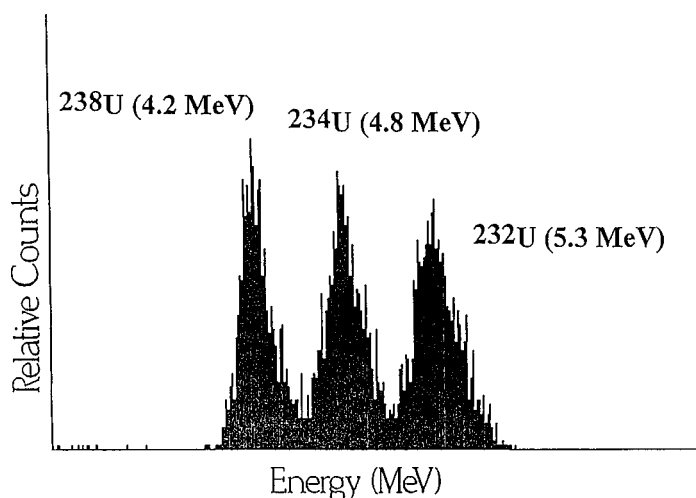


FIG. 1 Alpha Energy Spectrum of Natural Uranium and ²³²U Tracer Measured on a High-Resolution Alpha-Liquid-Scintillation Spectrometer

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 (cpm) 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 cpm to 0.1 cpm.

6. Interferences

6.1 During the development work on this method, less than 1% of ²⁴¹Am, ²³⁸Pu, ²¹⁰Po, ²²⁶Ra, ²²²Rn, and ²³⁰Th 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 ²³⁰Th and ²³⁸Pu 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.

6.4 ²³⁴U and ²³⁸U may exist in the ²³²U 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 volt @ 1 ma), or integral to the spectrometer, see item 7.10.

7.7 *Sample*, counting reference, normal uranium.⁵ This counting reference sample is an approximately 50/50 mix of ²³⁸U and ²³⁴U 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.

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

7.9 *Sparging Gas Conditioner*⁶—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

⁵ The sole source of supply of the ²³⁸U and ²³⁴U 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.

⁶ 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.