Designation: C 1473 – 05

Standard Test Method for Radiochemical Determination of Uranium Isotopes in Urine by Alpha Spectrometry[1]

This standard is issued under the fixed designation C 1473; 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 is applicable to the determination of uranium in urine at levels of detection dependent on sample size, count time, detector efficiency, background, and tracer yield. It is designed as a screening tool for detection of possible exposure of occupational workers.

1.2 This test method is designed for 50 mL of urine. This test method does not address the sampling protocol or sample preservation methods associated with its use.

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.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 1000 Test Method for Radiochemical Determination of Uranium Isotopes in Soil by Alpha Spectrometry

C 1163 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride

C 1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry

D 1193 Specification for Reagent Water

D 3084 Practice for Alpha-Particle Spectrometry of Water

D 3648 Practices for Measurement of Radioactivity

3. Summary of Test Method

3.1 A urine sample with ^{232}U tracer solution added is wet-ashed with nitric acid and hydrogen peroxide to destroy organic material. The uranium-bearing solution is converted to a hydrochloric acid medium. Uranium is absorbed on an anion exchange column from a 9 *M* hydrochloric acid solution and eluted with 0.1 *M* hydrochloric acid solution. The separated uranium is prepared for alpha spectrometric measurement either by electrodeposition onto a metal disk or coprecipitation with neodymium fluoride and filtration onto a membrane filter.

4. Significance and Use

4.1 This test method is used to detect possible exposures to uranium isotopes from occupational operations.

5. Interferences

5.1 The presence of ^{232}U in the urine sample will be masked by the tracer addition. The alpha energies of ^{233}U and ^{234}U cannot be fully resolved by alpha spectrometric measurement. A table of uranium isotope alpha energies is given in Appendix X1. If neptunium is present in the sample in the plus four oxidation state, it will co–elute with the uranium.

6. Apparatus

6.1 *Alpha Spectrometry System*—Refer to Test Methods C 1000, C 1163, D 3084, and D 3648 for guidance.

6.2 *Electrodeposition Apparatus*—Refer to Practice C 1284 for guidance.

6.3 *Neodymium Fluoride Precipitation*—Refer to Test Method C 1163 for guidance.

6.4 *Borosilicate Beakers or Flasks*, 250 mL.

6.5 *Borosilicate Beakers*, 150 and 250 mL.

6.6 *Borosilicate Graduated Glass Cylinders*, 5, 25, 100, and 1000 mL.

6.7 *Ion Exchange Columns*, disposable polypropylene, with polyethylene frit, ≥5-mL capacity.[3]

6.8 *Ion Exchange Column Reservoir*, funnel, polypropylene, 100-mL capacity.

NOTE 1—See Fig. 1 for a typical ion exchange column-reservoir setup.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that the reagents conform to the specifications of the Committee on

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

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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] Various column configurations are available from Bio-Rad Laboratories, Life Science Group, Hercules, CA; Whatman LabSales, Hillsboro, OR; and Perkin Elmer L:ife Sciences, Akron, OH.

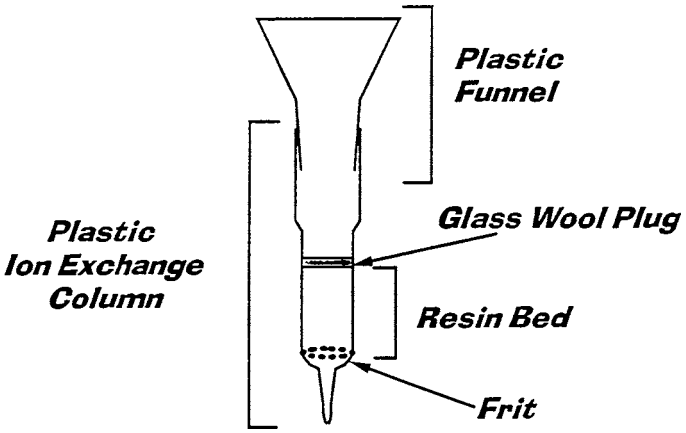

FIG. 1 Typical Ion Exchange Column Arrangement

Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification D 1193.

7.3 Reagent purity shall be such that the measured radioactivity of blank samples is minimized.

7.4 *Anion Exchange Resin*—Analytical grade, Type 1, 8 % cross linked, 100-200 mesh, chloride form.[5]

7.5 *Hydrochloric Acid (9 M)*—Mix 750 mL of concentrated HCl with water and dilute to 1 L.

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

7.7 *Hydrochloric Acid (0.1 M)*—Mix 8.3 mL of concentrated HCl with water and dilute to 1 L.

7.8 *Hydrogen Peroxide* (30 %).

7.9 *Nitric Acid (8 M)*—Mix 500 mL of concentrated nitric acid with water and dilute to 1 L.

7.10 *Nitric Acid (sp gr 1.4)*—Concentrated nitric acid (HNO_3).

7.11 *Uranium-232*, standard solution.[6]

8. Hazards

8.1 **Warning**—Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques must be used in this procedure. Site-specific policies for the handling of biological materials must be adhered to. Extreme care should be exercised in using hydrofluoric and other hot, concentrated acids. The use of proper gloves is recommended.

[4] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[5] Resin available from Bio-Rad Laboratories, (Hercules, CA) and Eichrom Technologies, Inc. (Darien, IL).

[6] Uranium-232 traceable to a national standards organization.

9. Sampling

9.1 Collect the urine sample in accordance with the site-specific protocol.

9.2 Preserve the urine sample in accordance with the site-specific protocol.

10. Calibration and Standardization

10.1 If a traceable standard ^{232}U solution is not available for use as a tracer, standardize a freshly prepared sample of ^{232}U; for guidance refer to Practice D 3648. A ^{232}U standard may also be used to determine the detection efficiency of the α-spectrometry system which, in turn, can be used to calculate the chemical yield of each sample and the lower limit of detection (LLD) of this test method.

11. Procedure

11.1 *Sample Preparation*:

11.1.1 Measure 50 mL of urine in a 100-mL graduated cylinder.

11.1.2 Transfer the urine to a 250-mL beaker or flask.

11.1.3 Rinse the cylinder twice with 5 mL of 8 *M* HNO_3 and add the rinsings to the beaker or flask.

11.1.4 Add an appropriate amount of ^{232}U tracer solution to the sample (ca. 0.02 Bq or as prescribed in the site-specific protocol) and swirl the vessel to mix.

11.1.5 Evaporate the contents of the vessel to near dryness on a medium hot plate.

11.1.6 Remove the vessel from the hot plate and cool for 1 min.

11.1.7 Add 10 mL of concentrated HNO_3 to the vessel. Swirl to mix.

11.1.8 Return the vessel to the hot plate and evaporate the solution to near dryness.

11.1.9 Remove the vessel from the hot plate and allow to cool for 1 min.

11.1.10 Slowly add 10 to 15 mL of 30 % hydrogen peroxide to the vessel to cover the residue. Swirl the vessel to mix.

11.1.11 Return the vessel to the hot plate and evaporate the solution to near dryness.

11.1.12 Repeat 11.1.9 and 11.1.10.

11.1.13 Return the vessel to the hot plate and evaporate the solution to obtain a white sample residue.

11.1.14 Remove the vessel from the hot plate and allow to cool for 1 min.

11.1.15 Add 10 to 15 mL of concentrated HCl to the vessel and swirl to mix.

11.1.16 Return the vessel to the hot plate and evaporate the solution to near dryness.

11.1.17 Remove the vessel from the hot plate and allow to cool for 1 min.

11.1.18 Repeat 11.1.15-11.1.17 twice more. Proceed to 11.1.19.

11.1.19 Add 75 mL of 9 *M* HCl to the vessel and heat gently to dissolve the residue.

11.1.20 Remove the vessel from the hot plate and cool to room temperature.

11.2 *Anion Exchange Separation*:

11.2.1 Measure 3 mL of settled, water slurried anion exchange resin.

11.2.2 Place a 250-mL beaker under an empty column. Transfer the resin to the column with water. Allow the water to drain from the column.

11.2.3 Insert a glass wool plug on the top of the resin bed.

11.2.4 Pour 30 mL of 9 *M* HCl into the ion exchange column reservoir and allow the acid to drain through to condition the resin column.

11.2.5 Transfer the sample solution to the ion exchange column reservoir. Pass the sample solution through the resin column.

11.2.6 Rinse the sample vessel with 10 mL of 9 *M* HCl and add the rinse to the column reservoir. Repeat the rinse once and allow the solution to drain to the top of the glass wool plug.

11.2.7 Wash the resin column with 30 mL of 9 *M* HCl and allow the acid to drain from the column.

11.2.8 Remove the beaker containing the combined waste and wash solutions from beneath the resin column. Discard the combined solutions in accordance with the site-specific disposal requirements for acids.

11.2.9 Place a clean 150-mL beaker under the resin column.

11.2.10 Elute the uranium from the resin column by pouring 50 mL of 0.1 *M* HCl into the column reservoir and allowing it to drain through.

11.2.11 Place the beaker containing the eluted uranium on a hot plate and evaporate the solution to just dryness. Remove the beaker from the hot plate and cool for 1 min.

11.2.12 Add 2 to 3 mL of concentrated HNO_3 to the beaker.

11.2.13 Repeat 11.2.11 and 11.2.12 until the residue is white.

11.2.14 Remove the beaker from the hot plate and cool for 1 min.

11.2.15 Add 5 mL of concentrated HCl to the beaker and evaporate to dryness. Remove the beaker from the hot plate and cool for 1 min.

11.2.16 Repeat 11.2.15 twice more.

11.3 *Electrodeposition or Neodymium Fluoride Precipitation*:

11.3.1 For electrodeposition, refer to Practice C 1284.

11.3.2 For neodymium fluoride precipitation, refer to Test Method C 1163.

11.4 *Alpha Spectrometry Measurement*:

11.4.1 Measure the sample overnight (1000 min) or longer in an alpha spectrometry system.

11.4.2 Measure the background and reagent blank activity for the regions of interest. Correct each uranium isotope activity for background and reagent blank activity.

12. Calculation

12.1 Refer to Test Method C 1000 for calculation of activity.

TABLE 1 Summary of Precision and Bias Data

	Sample Type	
	Blind Quality Control	Reference
Number of analyses	103	140
Concentration ^{234}U (Bq L^{-1})	0.17	0.025
Precision, %	30	11
Bias, %	4	1.5
Concentration ^{238}U (Bq L^{-1})	0.042	0.058
Precision, %	20	15
Bias, %	7	6
	Reagent Blanks	
Number of analyses	80	
	mean ± SD	
^{234}U	0.0007 ± 0.0013	
^{238}U	0.0008 ± 0.0013	

12.2 Calculate the lower limit of detection (LLD)[7] in becquerels at the 95 % confidence limit, as follows, assuming equal counting times for the background and sample:

$$LLD_{95\,\%} = \frac{2.71 + 4.66\,S_B}{(Y)\,(T_b)\,(E)} \quad (1)$$

where:

S_B = standard deviation of the detector background for the region of interest, counts,
T_b = background counting time, s,
Y = radiometric yield of the uranium-232 tracer, and
E = counting efficiency for the alpha spectrometry detector.

12.2.1 Typical values for these parameters are as follows:

S_B = 1 count per 60 000 s,
T_b = T_s = 60 000 s,
Y = 75 % (0.75 in the preceding LLD calculation), and
E = 30 % (0.30 in the preceding LLD calculation).

13. Precision and Bias

13.1 *Precision*—Replicate reference samples, blind quality control (QC) samples, and reagent blanks were analyzed at the Westinghouse Savannah River Company Radiobioassay Laboratory. These analyses were performed over a 12-month period by several analysts as blind samples in the routine sample stream. The results of these studies are summarized in Table 1.

13.2 *Bias*—The bias is defined as follows:

Bias, % = 100* (observed value-known value)/known value averaged over the entire data set

The uncertainty in the NIST standard of 2 % is included in this estimate.

14. Keywords

14.1 alpha spectrometry; ion exchange separation; uranium; urine

[7] Available from "Upgrading Environmental Radiation Data," U.S. Environmental Protection Agency, EPA 520/1-80-012, August 1980.

APPENDIX

(Nonmandatory Information)

X1.

TABLE X1.1 Properties of Uranium Isotopes of Interest in Environmental Samples[A]

Isotope	Half-Life, years	Alpha Energies, MeV (abundance)
^{232}U	68.9	5.320 (68.6 %), 5.263 (31.2 %)
^{233}U	1.592×10^5	4.825 (84.4 %), 4.783 (13.2 %)
^{234}U	2.454×10^5	4.776 (72.5 %), 4.723 (27.5 %)
^{235}U	7.037×10^8	4.395 (85 %), 4.370 (6 %), 4.597, (5 %)
^{236}U	2.342×10^7	4.494 (74 %), 4.445 (26 %)
^{238}U	4.468×10^9	4.196 (77 %), 4.147 (23 %)

[A] Available from Browne, E., and Firestone, R. B., *Table of Radioactive Isotopes*, (V. S. Shirley, Ed.), John Wiley and Sons, Inc., 1986.