Designation: C1614 – 05(Reapproved 2010)

Standard Practice for the Determination of ^{237}Np, ^{232}Th, ^{235}U and ^{238}U in Urine by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Gamma Ray Spectrometry[1]

This standard is issued under the fixed designation C1614; 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 practice covers the separation and preconcentration of neptunium-237 (^{237}Np), thorium-232 (^{232}Th), uranium-235 (^{235}U) and uranium-238 (^{238}U) from urine followed by quantitation using ICP-MS.

1.2 This practice can be used to support routine bioassay programs. The minimum detectable concentrations (MDC) for this method, taking the preconcentration factor into account, are approximately 1E-2Bq for ^{237}Np (0.38ng), 2E-6Bq for ^{232}Th (0.50ng), 4E-5Bq for ^{235}U (0.50ng) and 6E-6Bq for ^{238}U (0.48ng).

1.3 *This standard does not purport to address all of the safety problems, 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]

D1193 Specification for Reagent Water
C1475 Guide for Determination of Neptunium-237 in Soil
C859 Terminology Relating to Nuclear Materials
C1379 Test Method for Analysis of Urine for Uranium-235 and Uranium-238 Isotopes by Inductively Coupled Plasma-Mass Spectrometry
D4962 Practice for NaI(Tl) Gamma-Ray Spectrometry of Water

3. Terminology

3.1 *Definitions:*

3.1.1 Definitions not found in C859 Terminology Relating to Nuclear Materials:

3.1.2 *Instrument check standard*—standard solutions evaluated at specified intervals during batch analysis to evaluate instrument calibration stability during analysis.

3.1.3 *Internal standard*—solutions added to each calibration standard, check standard, and sample for the purpose of monitoring and correcting for instrument drift, due to aerosol transport effects, nebulizer blockage, ion sampling orifice blockage and matrix enhancement or suppression.

3.1.4 *Isobar*—any nuclide that has the same atomic mass number as another nuclide, but a different atomic number

3.1.5 *Isotope dilution analysis*—isotope ratio measurements of samples spiked with accurately known weights of individual low abundance isotopes

3.2 *Acronyms:*

ICP-MS

ICP-MS	=	Inductively Coupled Plasma-Mass Spectrometry
PHA	=	Pulse Height Analysis
LOD	=	limit of detection
MDC	=	minimum detectable concentration
LCS	=	laboratory control standard

4. Summary of Practice

4.1 An aliquot of a urine sample is spiked with ^{239}Np, ^{230}Th and ^{233}U tracers followed by wet ashing with nitric acid and hydrogen peroxide. After re-dissolution in nitric acid containing aluminum nitrate and sodium nitrite, the analytes are extracted using an extraction chromatography resin. For analysis by ICP-MS the eluent is spiked with ^{242}Pu internal standard followed by wet ashing with nitric acid and re-dissolution in 5 mL 5 % nitric acid..

4.2 ^{232}Th, ^{235}U and ^{238} U are determined using ICP-MS isotopic dilution techniques. Chemical yield (recovery) measurements indicate a typical yield of 75-85 % for these analytes. The isotopic composition of uranium is determined by ICP-MS isotopic ratio measurements. ^{237}Np is determined by ICP-MS using external standardization combined with ^{239}Np recovery measurements (85-95 %) using gamma-ray spectrometry.

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

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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.

5. Significance and Use

5.1 This practice may be used as part of a bioassay program for workers potentially exposed to nuclear material by measuring ^{237}Np, ^{232}Th and ^{235}U and ^{238}U in their urine samples. ICP-MS has been used to analyze for many actinides in high-level radioactive wastes (**1**)[3], in soils (**2**) as well as uranium in urine (Test Method C1379). ^{237}Np and ^{239}Pu analysis by ICP-MS in bioassay samples has also been reported (**3**).

5.2 Several days counting times are required for alpha-particle analysis of ^{237}Np, ^{232}Th and ^{235}U and ^{238}U whereas ICP-MS requires only four minutes per sample. Alpha-particle counting methods for neptunium may also require the use of ^{239}Pu as a radiotracer for determination of chemical yield.

5.3 ICP-MS sensitivity limits and isobaric interferences preclude accurate determination of ^{239}Pu, ^{241}Am and ^{234}U at levels present in the urine samples. ^{234}U may be estimated from the ^{235}U:^{238}U ratio by inference.

6. Interferences

6.1 ICP-MS

6.1.1 Alkali and alkaline earth salts in urine result in signal attenuation. However, in this practice neptunium, thorium and uranium are chemically separated from the salts using an extraction chromatography resin.

6.2 If ^{243}Am is added as a source of ^{239}Np, the chemical yield determination could be biased by the presence of ^{239}Np growing in from the ^{243}Am parent. The ^{243}Am should be selectively eluted from the extraction chromatography column prior to elution of the analytes.

7. Apparatus

7.1 ICP-MS, computer-controlled, equipped with a discrete dynode electron multiplier and auto-sampler.

7.2 Gamma-ray spectrometry system, see Practice D4962 for further information.

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 conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available[4].

8.2 *Purity of water*—unless otherwise noted ASTM Type I is used to prepare all solutions for ICP-MS analysis (Specification D1193).

8.3 High purity concentrated nitric acid (HNO_3), (approx. 16M).

8.4 Hydrogen Peroxide, (30 %).

8.5 *Nitric Acid (2M)*—Add 125 mL of concentrated HNO_3 to 700 mL of water, dilute to a final volume of 1000 mL, and mix.

8.6 *Nitric Acid*—Add 50mL of concentrated HNO_3 to 700 mL of water, dilute to a final volume of 1000 mL, and mix.

8.7 0.5 M Aluminum Nitrate Solution, $(Al(NO_3)_3.9H_2O)$ dissolve 187.5g of pure aluminum nitrate in 2M nitric acid and dilute to 1L with 2M nitric acid.

8.8 Sodium Nitrite, $(NaNO_2)$.

8.9 *0.1 M Ammonium Bioxalate, $(NH_4HC_2O_4)$*—dissolve 6.31g of oxalic acid dihydrate and 7.11g of ammonium oxalate monohydrate in water and dilute to 1L.

8.10 Disposable columns packed with 0.7g extraction chromatography resin[5].

8.11 *Argon Gas*—purity 99.99 % or better.

8.12 *Standard Metals Stock Solution*—a solution of beryllium, cobalt, indium, lead, and uranium, which covers the mass range that is used for tuning, detector and mass calibration and as an instrument stability check following the instrument manufacturer's recommendations.

8.13 Calibration Stock Solution containing ^{237}Np[6] in 5 % HNO_3.

8.14 ^{242}Pu Internal Standard Solution[7].

8.15 ^{230}Th Tracer[7] solution.

8.16 ^{233}U Tracer[8] solution.

8.17 ^{239}Np tracer, available as ^{243}Am daughter[7], (see 6.2).

9. Solutions

9.1 Prior to the ICP-MS analysis of the samples for ^{237}Np, ^{232}Th and ^{235}U and ^{238}U, the following QC standards, calibration standards, internal standard, and rinse solution should be prepared and included in the analytical run.

9.1.1 *Rinse Solution*—Add 2 part volume high purity concentrated HNO_3 per 100 parts water. Prepare a sufficient quantity to flush the ICP-MS and autosampler between standards and samples.

9.1.2 *^{237}Np calibration standards*—calibration standards should be prepared in 5 % HNO_3 by diluting the calibration stock solution.

9.1.3 *Calibration blank*—5 % HNO_3.

9.1.4 *^{237}Np instrument check standard*—Prepare in 5 % HNO_3. Analyze a mid-range standard (e.g. 5ng/mL) throughout the batch analysis at a minimum frequency of 10 %.

9.1.5 *Isotope dilution standards*— ^{239}Np, ^{230}Th and ^{233}U at a concentration deemed appropriate for the laboratory program.

9.1.6 Unexposed urine, spiked with ^{237}Np, ^{239}Np, ^{230}Th and ^{233}U to demonstrate the ability to quantitatively recover the radionuclides of interest.

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[3] The boldface numbers in parentheses refer to the list of references at the end of this practice.

[4] Available from American Chemical Society, 1155 Sixteenth Street, NW, Washington DC, 20036, Phone: 202-872-4600, Fax: 202-872-4615, Website: http://www.chemistry.org.

[5] TRU Resin, available from Eichrom Technologies, Inc., Darien, IL has been found suitable for this purpose.

[6] Available from Isotope Products Lab, Burbank, CA or equivalent.

[7] Available from NIST, Gaithersburg, MD or equivalent.

[8] Available from New Brunswick Lab, Argonne, IL, or equivalent.