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.

Current edition approved Oct. 1, 2010. Published October 2010. Originally approved in 2005. Last previous edition approved in 2005 as C1614-05. DOI: 10.1520/C1614-05R10.

[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.

---

[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.

9.1.7 ^{242}Pu internal standard for spiking into each blank, standard and sample.

10. Sampling, Test Specimens

10.1 Collect urine samples from individuals and store until analysis. Preservatives may be used if deemed necessary to ensure stability.

10.2 All chain of custody requirements described in laboratory-specific operating procedures must be followed.

11. Calibration and Standardization

11.1 Follow the instrument manufacturer's operating manual and laboratory-specific operating procedures for initial start-up and optimization of the ICP-MS and the associated computer control system and peripheral equipment

11.2 Set up the necessary instrument software files for data acquisition, calculation, quality assurance and quality control data requirements, archival data storage, analytical report preparation, and report verification.

11.3 The instrument, data acquisition, and reporting parameters shall be determined to meet customer statement of work requirements.

11.4 Introduce the recommended tuning solution and tune the instrument for optimum response for ^{238}U.

11.5 Check the mass calibration and resolution with the daily tuning solution and elements recommended as per the manufacturer's instrument specifications.

11.6 Make necessary adjustments in the instrument controls to ensure that all of the above operating parameters (mass calibration, mass resolution, resolution, and baseline) are within previously established laboratory limits. Use the appropriate concentrations for each of the calibration functions suggested by the instrument manufacturer.

11.7 Determine the instrument stability before analyzing any samples. The stability is determined by analyzing five 60 second replicates of the daily tuning solution to meet a relative standard deviation of less than 2 % for ^{59}Co, ^{115}In, ^{208}Pb and ^{238}U isotopes.

11.8 If the relative standard deviation for these isotopes during instrument stability testing is greater than 2 %, determine the cause of the instability, correct the problem, and rerun the stability check.

11.9 Calibrate for ^{237}Np to cover the required analytical range, e.g. 0-10ng/mL. No calibration is required for thorium and uranium since isotopic dilution is used to determine the concentration.

12. Procedure

12.1 Sample Preparation

12.1.1 Add known amounts of ^{239}Np, ^{230} Th and ^{233}U to 250mL urine before wet-ashing with a mixture of 15mL high purity concentrated HNO_3 and 1mL 30 % H_2O_2 followed by slowly evaporating the sample to dryness.

12.1.2 Allow to cool and redissolve the sample residue after wet ashing in 10-20mL aluminum nitrate solution (8.7).

12.1.3 Add sufficient sodium nitrite (8.8) to each sample adjust the oxidation state of Np to Np(IV).

12.1.4 Load the sample onto the disposable extraction chromatography resin column and wash with at least 20mL of 2 M HNO_3 before eluting the isotopes of interest with 20mL ammonium bioxalate solution (8.9).

12.1.5 Spike each sample with a known quantity of ^{242}Pu before drying and wet-ashing to remove the bioxalate.

12.1.6 Redissolve the sample residue after ashing in 5 mL 5 % HNO_3 before analysis by gamma-ray spectrometry (^{239}Np) and ICP-MS. This solution results in a 50× preconcentration from the original sample.

12.2 Gamma-ray spectrometry of ^{239}Np

12.2.1 ^{239}Np gamma rays are counted using a gamma-ray spectrometer as described in Guide C1475.

12.3 ICP-MS Analysis of ^{232}Th, ^{237} Np, ^{235}U and ^{238}U

12.3.1 Ensure that all instrument set-up, calibration and standardization (see Section 11), and required laboratory-specific QC protocol has been followed.

12.3.2 To ensure that the ICP-MS provides requisite sensitivity, 3-sigma detection limits for each of the isotopes may determined by collecting a series of five individual acquisitions of one-minute duration.

12.3.3 Analyze the standards, prepared samples, and prepared LCS following the ICP-MS and data systems operations described in the site-specific laboratory operating procedures.

13. Calculation of Results

13.1 Determine the chemical recovery fraction for each sample and control from the following equation for each tracer:

$$\text{Chemical recovery} = \frac{(\text{concentration of tracer measured})}{(\text{concentration of tracer added})} \times 100\,\% \quad (1)$$

13.2 Gamma-ray analysis of ^{239}Np

13.2.1 ^{239}Np chemical recovery is calculated from the gamma-ray counts as described in Guide C1475. Chemical recoveries are typically between 85 – 95 %.

13.3 ICP-MS Analysis of ^{237}Np

13.3.1 ^{237}Np concentration is calculated from a ^{237}Np calibration curve with ^{242}Pu being used as an internal standard.

13.3.2 The true ^{237}Np concentration (measured by ICP-MS) is corrected by ^{239}Np chemical recovery (measured by gamma-ray).

13.3.3 Determine the final Np-237 result according to the following equation:

$$3\text{Final Result} = \text{T/Chemical Recovery} \quad (2)$$

Where T = measured ICP-MS concentration in the sample (ng/mL).

13.4 ICP-MS Analysis of ^{232}Th and ^{235}U and ^{238}U

13.4.1 The ICP-MS data should include the following ratios: $^{230/232}$Th, $^{235/233}$U, $^{238/233}$U, $^{235/238}$U, and the following concentrations: ^{230}Th (based on the ^{230}Th/^{242}Pu internal standard), ^{233}U, ^{237}Np. The $^{230/232}$Th, $^{235/233}$ U, $^{238/233}$U, $^{235/238}$U ratios are used to determine the ^{232}Th, ^{235}U, ^{238}U

concentrations. The ^{230}Th and ^{233}U concentrations may be used to determine chemical yield. **Chemical recoveries are between 75 – 85 %.**

13.4.2 ^{232}Th and ^{235}U and ^{238}U concentrations are calculated by isotope dilution from the isotope ratio measurements of ^{232}Th/^{230}Th, ^{235}U/^{233}U and ^{238}U/^{233}U. Human urine should not contain any ^{233}U (or ^{230Th}) , therefore isotope dilution formula for ^{238}U is:

$$M = n(R_M - R_S)M \quad (3)$$

where M is the total mass of ^{238}U in the sample (pg), n is the number of moles of ^{233}U (pmol) in the added spike, R_M and R_S are the molar ratios ^{238} U/^{233}U in the resulting mixture and added spike, respectively, and M is the molar mass of the isotope ^{238}U (pg pmol^{-1}). The same calculation can be applied to ^{232} Th and ^{235}U using ^{230}Th and ^{233}U respectively (4).

13.4.3 ^{235}U and ^{238}U isotopic ratios may also be determined (Table X1.1).

14. Precision and Bias

14.1 Data for each sample was obtained from four one-minute scanning acquisitions between m/z 229 to m/z 243. Each one-minute acquisition consisted of data summed from 1000 sweeps of the quadrupole over the specified mass range.

14.2 *Limits of detection*—the one-minute acquisition 3 sigma LODs are ~0.01pg/mL for each of the isotopes in solution which corresponds to 1E-3Bq for ^{237} Np, 2E-7Bq for ^{232}Th, 4E-6Bq for ^{235}U and 6E-7Bqfor ^{238}U respectively.

14.3 The minimum detectable concentrations for this method, taking the preconcentration factor into account, are approximately 1E-2Bq for ^{237}Np, 2E-6Bq for ^{232}Th, 4E-5Bq for ^{235}U and 6E-6Bqfor ^{238}U.

14.4 The results from a series of 12 occupationally exposed urine samples containing ^{237}Np and natural thorium and uranium isotopes are listed in Table X1.2. The ^{237}Np results compared favorably with alpha-particle spectrometry determinations made on the same samples. ^{232}Th levels are below the alpha-particle spectrometry detection limits; therefore no comparison data is available.

14.5 The isotopic composition of uranium detected in each of the four one-minute determinations made on each of the twelve samples is corrected for detector system dead time and for mass discrimination. The mass discrimination of the spectrometer is calculated from the analysis of SRM U500[7]. The dead time of the multiplier and counting system is determined from the analysis of U005[7] and U020[7]. The measured isotopic ratios of the twelve samples unambiguously identify the uranium as being of natural isotopic composition (average ^{235}U/ ^{238}U = 0.007252 +/- 0.000081).

15. Keywords

15.1 Bioassay; urine; neptunium; thorium; uranium; mass; inductively coupled plasma-mass spectrometry; gamma-ray spectrometry; isotope ratio; isotope dilution; extraction chromatography.

APPENDIX

(Nonmandatory Information)

X1.

TABLE X1.1 ^{235}U/^{238}U Isotope Ratio

Sample	1	2	3	4	Mean	% RSD
29056	0.00723	0.00722	0.00714	0.00708	0.00717	1
29057	0.00713	0.00707	0.0071	0.00705	0.00709	0.5
29058	0.00704	0.00697	0.00701	0.00697	0.007	0.5
29060	0.00723	0.00713	0.00708	0.00714	0.00714	0.9
29063	0.00726	0.00679	0.00689	0.00712	0.00701	3
29068	0.00713	0.00717	0.00707	0.00709	0.00712	0.6
29073	0.00741	0.00727	0.00712	0.00721	0.00725	1.7
29081	0.00717	0.00728	0.00715	0.00733	0.00723	1.2
29087	0.00685	0.00741	0.00686	0.00744	0.00714	4.6
29093	0.00663	0.00736	0.00818	0.00665	0.0072	10.2
29107	0.00659	0.00763	0.0075	0.00706	0.00719	6.6
29101	0.00722	0.007	0.00733	0.00724	0.0072	1.9

TABLE X1.2 Actinide Measurements by ICP-MS and Alpha Spectrometry

Sample	^{237}Np (ICP-MS) (Bq)	^{237}Np (ICP-MS) ng	^{237}Np (PHA) (Bq)	^{237}Np (PHA) ng	^{232}Th (ICP-MS) (Bq)	^{232}Th (ICP-MS) ng	^{235}U (ICP-MS) (Bq)	^{235}U (ICP-MS) ng	^{238}U (ICP-MS) (Bq)	^{238}U (ICP-MS) ng
29056	5.7500E-01	22.0	6.3333E-01	24.3	4.9500E-05	12.2	5.67E-03	70.9	1.22E-01	9835.2
29057	5.9667E-01	22.9	6.8167E-01	26.1	4.0833E-05	10.1	3.65E-03	45.6	7.87E-02	6324.5
29058	2.9833E-01	11.4	3.0000E-01	11.5	4.0167E-05	9.9	9.65E-04	12.1	2.08E-02	1674.9
29060	2.9833E-01	11.4	3.1833E+00	122.1	1.6317E-04	40.4	1.22E-03	15.2	2.62E-02	2103.7
29063	9.8333E-02	3.8	9.5500E-02	3.7	3.8667E-05	9.6	2.42E-04	3.0	5.22E-03	419.4
29068	1.4167E-01	5.4	1.7000E-01	6.5	4.4500E-05	11.0	3.00E-04	3.8	6.48E-03	521.2
29073	8.6667E-02	3.3	8.7167E-02	3.3	4.0167E-05	9.9	1.31E-04	1.6	2.82E-03	226.4
29081	1.1333E-01	4.3	1.4400E-01	5.5	5.6000E-05	13.8	1.88E-04	2.4	4.07E-03	326.9
29087	8.8333E-02	3.4	8.4333E-02	3.2	3.6500E-05	9.0	1.14E-04	1.4	2.47E-03	198.3
29093	3.3333E-02	1.3	3.3333E-02	1.3	4.2333E-05	10.5	4.80E-05	0.6	1.04E-03	83.3
29107	3.5000E-02	1.3	3.5333E-02	1.4	5.9333E-05	14.7	7.00E-05	0.9	1.51E-03	121.4
29101	1.1333E-01	4.3	1.1300E-01	4.3	5.5500E-05	13.7	1.42E-04	1.8	3.07E-03	246.5
Spike-1[A]	0	0	n/a	N/a	3.2667E-05	8.1	1.30E-05	0.2	2.80E-04	22.5
Spike-2[A]	0	0	n/a	N/a	2.9833E-05	7.4	8.22E-06	0.1	1.78E-04	14.3

[A] Unexposed urine samples spiked with ^{239}Np to determine chemical recovery. The thorium and uranium data represent the upper limit for the method blank.

References

(1) W.F. Kinard, N.E. Bibler, C.J, Coleman, R.A. Dewberry, W.T. Boyce, and S.B. Wyrick, "Applications of ICP-MS to the Determination of Actinides and Fission Products in High Level Radioactive Wastes at the Savannah River Site," ASTM Publication STP 1291, 48, (1995).

(2) M. Hollenbach, J.Grohs, M. Kroft and S.Mamich, "Determination of ^{230}Th, ^{234}U and ^{240}Pu by ICP-MS Using Flow Injection Preconcentration," ASTM Publication STP 1291, 99, (1995).

(3) E.J. Wyse and D.R. Fisher, "Radionuclide Bioassay by ICP-MS," Rad. Prot. Dosimetry, 55(3), 199-206, (1994).

(4) Max Haldimann, Michel Baduraux, Alan Eastgate, Pascal Froidevaux, Sine`ad O'Donovan, Danielle Von Gunten and Otmar Zoller, Determining Picogram Quantities Of Uranium In Urine By Isotope Dilution Inductively Coupled Plasma Mass Spectrometry. Comparison With A-Spectrometry, J. Anal. At. Spectrom., 2001, 16, 1364–1369