



Designation: C 1476 – 00

Standard Test Method for Analysis of Urine for Technetium-99 by Inductively Coupled Plasma-Mass Spectrometry¹

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1. Scope

1.1 This test method covers the determination of the concentration of technetium-99 in urine using inductively coupled plasma-mass spectrometry (ICP-MS). This test method can be used to support uranium enrichment and reclamation facility bioassay programs.

1.2 The minimum detectable concentration for this test method, using a quadrupole ICP-MS, is approximately 1.0 ng/L (0.62 Bq/L).

2. Referenced Documents

2.1 ASTM Standards:

C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry²

C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry²

C 1128 Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials²

C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials²

C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry²

C 1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials²

D 1193 Specification for Reagent Water³

2.2 Other Standards:

ANSI N13.20 Radiological Measurement Quality⁴

Code of Federal Regulations, Title 10, 835.402⁵

HPS N13.30 Performance Criteria for Radiobioassay⁶

3. Terminology

3.1 Definitions:

3.1.1 *instrument check standard, n*—standard solutions evaluated at given intervals during batch analysis to evaluate instrument stability during analysis.

3.1.2 *internal reference standard, n*—standard solutions, containing an element with similar chemical properties to the analyte of interest, added to each calibration standard, check standard, and sample for the purpose of monitoring and correcting for fluctuations in matrix, instrument drift, nebulizer and sample orifice blockages, and aerosol transport effects.

3.1.3 *isobar, n*—any nuclide that has the same atomic mass number as another atom, but a different atomic number.

3.2 Acronyms:

3.2.1 *ICP-MS, n*—inductively coupled plasma-mass spectrometry.

3.2.2 *LOD, n*—limit of detection.

3.2.3 *LCS, n*—laboratory control standard.

3.2.4 *MDC, n*—minimum detectable concentration.

3.2.5 *%RSD, n*—percent relative standard deviation (1 standard deviation/Mean) * 100.

3.2.6 *% Bias, n*—((mean – true value)/true value) * 100.

4. Summary of Test Method

4.1 A urine sample is digested in the presence of hydrogen peroxide to decompose the organic matrix. The pertechnetate ion is selectively separated from Ruthenium, actinides, alkali, and alkaline earth metals in the sample matrix using anion exchange chromatography. The ⁹⁹Tc is eluted with warmed 3.0 M nitric acid. The ⁹⁹Tc isotope is analyzed by ICP-MS using ¹¹⁵In as the internal reference standard.⁷ The chemical recovery

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 Methods of Test.

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² *Annual Book of ASTM Standards*, Vol 12.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

⁵ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

⁶ Health Physics Society, "Performance Criteria for Radiobioassay," HPS N13.30, McLean, VA, 1996.

⁷ Crain, J., and Gallimore, D., "Inductively Coupled Plasma-Mass Spectrometry of Synthetic Elements: ⁹⁹Tc," *Applied Spectroscopy*, Vol 46, 1992, pp. 547-549.

is determined by the sample, sample spike method. Recoveries obtained from submitted samples over a one-year period averaged 89.9 %.

5. Significance and Use

5.1 Code of Federal Regulations, Title 10, 835.402 states that radiological workers who are likely to receive 100 mrem from intakes are required to be monitored for exposure. For the indirect bioassay for radiological workers exposed to nuclear material containing fission products, ^{99}Tc must be measured in urine samples.

6. Interferences

6.1 Elements or complexes having a mass-to-charge ratio (m/z) of 99 will interfere with the ^{99}Tc analysis. Interfering nuclides of mass 99 (molybdenum and ruthenium) are chemically separated using anion exchange chromatography. The presence of an interfering nuclide may be monitored by evaluating the m/z value of another isotope of the interfering element.

6.2 Alkali and alkaline earth salts can lead to unstable signals at low levels and signal attenuation at high levels. The ^{99}Tc is chemically separated from the salts using anion exchange chromatography.

7. Apparatus

7.1 *Inductively Coupled Plasma-Mass Spectrometer*, computer-controlled, multichannel peristaltic pump, and an auto-sampler.⁸

7.2 *Centrifuge Tube With Cap*, 15-mL, disposable, graduated, that will accommodate the auto-sampler for sample analysis.

7.3 *Erlenmeyer Flasks and Distillation Columns*, appropriately sized.

7.4 *Plastic Cups*, disposable, appropriately sized.

7.5 *Polyethylene Ion Exchange Column* 12-mL, disposable, or suitable size with a 30- μm porosity frit.

7.6 *Polyethylene Ion Exchange Column Funnels*.

7.7 *Centrifuge Cone*, 50 mL, disposable, graduated.

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.⁹ 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 as defined by Type I of Specification D 1193.

8.3 *Anion Exchange Resin*—100-200 mesh (chloride form).¹⁰

8.4 *Argon Gas*, purity 99.99 % or better recommended.

8.5 *Calibration Stock Solution*—Prepare a calibration stock solution containing approximately 2000 ng/L of ^{99}Tc from a certified traceable NIST or equivalent certified standard.¹¹

8.6 *Hydrochloric Acid (sp gr 1.18)*, concentrated, high-purity Baker Ultrex or equivalent, hydrochloric acid (HCl).

8.7 *Hydrochloric Acid (0.5 M)*—Add 41.7 mL of concentrated HCl to 900 mL of water, dilute to a final volume of 1000 mL, and mix.

8.8 *Hydrogen Peroxide (30 %)*, (H_2O_2).

8.9 *Nitric Acid (sp gr 1.42)*, concentrated, high-purity Baker Ultrex or equivalent, nitric acid (HNO_3).

8.10 *Nitric Acid (0.5 M)*—Add 31.3 mL of concentrated HNO_3 to 900 mL of water, dilute to a final volume of 1000 mL, and mix.

8.11 *Nitric Acid (2.5 M)*—Add 156 mL of concentrated HNO_3 to 800 mL of water, dilute to a final volume of 1000 mL, and mix.

8.12 *Nitric Acid (3.0 M)*—Add 188 mL of concentrated HNO_3 to 700 mL of water, dilute to a final volume of 1000 mL, and mix.

8.13 *Standard Metals Stock Solution*—Prepare or purchase solutions of beryllium, cobalt, indium, lead, and uranium, or equivalent combination of elements to cover the mass range, to be used as a tuning solution, detector and mass calibration standard, and stability check solution.

8.14 *^{99}Tc Spike Solution*—Prepare a ^{99}Tc spike solution containing approximately 8000 ng/L of ^{99}Tc from a certified traceable NIST or equivalent certified standard.¹¹

9. Hazards

9.1 Since ^{99}Tc is radioactive, adequate laboratory facilities along with safe handling techniques must be used. A detailed discussion of all safety precautions needed is beyond the scope of this test method. Follow site- and facility-specific radiation protection and chemical hygiene plans.

10. Sampling, Test Specimens, and Test Units

10.1 Urine samples are to be refrigerated at 4°C 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.

⁸ The VG Elemental PlasmaQuad PQ2+ ICP-MS was used to develop this test method.

⁹ *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. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

¹⁰ AG MP-1 Macroporous Anion Exchange Resin available from Bio-Rad Co., 300 Reggata Blvd., Richmond, CA 94804, has been found to perform satisfactorily. The feasibility of comparable resins for use in this test method should be demonstrated prior to utilization.

¹¹ The ^{99}Tc standard solution is available from NIST, Building 245, Room C114, Gaithersburg, MD 20899.

11. Calibration and Standardization¹²

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 (QA) and quality control (QC) 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 Instrument tuning, detector and mass calibration, and stability check functions for the ICP-MS will require a tuning solution that follows the instrument manufacturer's recommendations. Introduce the daily tuning solution and tune the instrument for optimum response on the selected peaks.

11.4.1 A stock tuning solution can be prepared by adding an aliquot of the standard metal stock solution (see 8.13) or solution as specified by the ICP-MS instrument manufacturer to water and 2 parts volume concentrated HNO₃ per 100 parts water.

11.4.2 The daily tuning, mass calibration, detector calibration, and stability check solutions should be prepared by diluting an aliquot of the stock tuning solution (see 11.4.1) and 2 parts volume concentrated HNO₃ per 100 parts water. These solutions should be prepared at analyte concentrations suggested by the instrument manufacturer.

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

11.6 Make necessary adjustments in the instrument controls to ensure that all of the preceding operating parameters (mass calibration, mass resolution, and baseline) are within previously established laboratory limits. Use the appropriate concentrations (see 11.4.2) 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 the daily tuning solution (see 11.4.2) at least 10 times with a relative standard deviation of less than 5 % on the selected peaks.

11.8 If the relative standard deviation for these isotopes during instrument stability testing was greater than 5 %, determine the cause of the instability, correct the problem, and rerun the stability check.

11.9 Prior to the ICP-MS analysis for ⁹⁹Tc, the following QC standards, calibration standards, internal standard, and rinse solution are recommended and should be included in the analytical run:

11.9.1 *Rinse Solution*—Add 2 parts volume concentrated HNO₃ per 100 parts water. Prepare a sufficient quantity to flush the ICP-MS and auto sampler between standards and samples.

11.9.2 *⁹⁹Tc Calibration Standards*—A minimum of four calibration standards should be prepared ranging from 2 to 80

ng/L ⁹⁹Tc by diluting the calibration stock solution (see 8.14). The calibration standards should be prepared in 2.5 M HNO₃ (see 8.11) to match the final acid concentration of the prepared samples.

11.9.3 *Calibration Blank*—The calibration blank should be prepared at the same acid concentration as the calibration standards, 2.5 M HNO₃ (see 8.11).

11.9.4 *Instrument Check Standard*—Prepare in accordance with 11.9.2. Analyze at minimum a low- and high-level standard throughout the analytical run at a minimum frequency of 10 %

11.9.5 *Artificial Urine*¹³—Prepare an artificial urine solution in accordance with the following instructions. Mix 16.0 parts urea, 2.32 parts NaCl, 3.43 parts KCl, 1.10 parts creatinine, 4.31 parts Na₂SO₄ (anhydrous), 0.63 part hippuric acid, 1.06 parts NH₄Cl, 0.54 part citric acid, 0.46 part MgSO₄ (anhydrous), 2.73 parts NaH₂PO₄·H₂O, 0.63 part CaCl₂·2H₂O, 0.02 part oxalic acid, 0.094 part lactic acid, 0.48 part glucose (or dextrose), 0.071 part Na₂SiO₃·9H₂O, 0.029 part pepsin, 5.0 parts concentrated HNO₃, and 961 parts water. Mix dry chemicals thoroughly before adding liquids. Stir the mixture thoroughly for approximately 2 h using a magnetic stirrer.

11.9.6 *Method Reagent Blank*—An aliquot of artificial urine that is carried through each step of the procedure. The method reagent blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. The method reagent blank is used to determine the test method MDC.

11.9.7 *Laboratory Control Sample (LCS)*—Prepare the control by adding an appropriate aliquot of the calibration stock solution (see 8.14) to an aliquot of artificial urine to give a ⁹⁹Tc concentration within the calibration range. The LCS is carried through each step of the procedure. The LCS result is used to determine if the test method performance is within acceptable control limits.

11.9.8 *Internal Reference Standard*—The recommended concentration for the working In internal reference solution is 20 000 ng/L. The recommended concentration of In within each calibration standard and sample is 200 ng/L. To prepare the working solution, add the required volume of In standard solution to approximately 100 mL of water containing 2 parts concentrated HNO₃.

12. Procedure

12.1 Sample Preparation:

12.1.1 Transfer 30 mL of the urine sample into an Erlenmeyer flask, and add 2 mL of H₂O₂. Add an additional 1 mL if the sample appears dark. Attach a distillation column to the flask.

12.1.2 Transfer 30 mL of the same urine sample into an additional Erlenmeyer flask, and add the same amount of H₂O₂ as was added to the unspiked sample (see 12.1.1). Add an appropriate amount (approximately 8000 ng/L ⁹⁹Tc) of a known concentration of ⁹⁹Tc spike solution (see 8.14). Attach a distillation column to the flask.

¹² For quality assurance guides for Nuclear Industry Analytical Laboratories see C 1009, C 1068, C 1128, C 1156, C 1210, and C 1297. For a quality assurance guide for radiological measurements see ANSI Standard N13.20.

¹³ Robinson, A. V., Fisher, D. R., and Hadley, R. T., "Technical Evaluation of Draft ANSI Standard N13.30, Performance Criteria for Radioassay," Report No. PNL-5107 (draft), Pacific Northwest Laboratory, Richland, WA, 1984.