Designation: C 1379 – 04

Standard Test Method for Analysis of Urine for Uranium-235 and Uranium-238 Isotopes by Inductively Coupled Plasma-Mass Spectrometry[1]

This standard is issued under the fixed designation C 1379; 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 the determination of the concentration of uranium-235 and uranium-238 in urine using Inductively Coupled Plasma-Mass Spectrometry. This test method can be used to support uranium facility bioassay programs.

1.2 This method detection limits for ^{235}U and ^{238}U are 6 ng/L. To meet the requirements of ANSI N13.30, the minimum detectable activity (MDA) of each radionuclide measured must be at least 0.1 pCi/L (0.0037 Bq/L). The MDA translates to 47 ng/L for ^{235}U and 300 ng/L for ^{238}U. Uranium– 234 cannot be determined at the MDA with this test method because of its low mass concentration level equivalent to 0.1 pCi/L.

1.3 The digestion and anion separation of urine may not be necessary when uranium concentrations of more than 100 ng/L are present.

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.*

NOTE 1—**Warning:** The ICP-MS is a source of intense ultraviolet radiation from the radio frequency induced plasma. Protection from radio frequency radiation and UV radiation is provided by the instrument under normal operation.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 1310 Test Method for Determining Radionuclides in Soils by Inductively Coupled Plasma-Mass Spectrometry Using Flow Injection Preconcentration

C 1345 Test Method for Analysis of Total and Isotopic Uranium and Total Thorium in Soils by Inductively Coupled Plasma-Mass Spectrometry

D 1193 Specification for Reagent Water

2.2 *Other Documents:*

ANSI N13.30 Radiological Measurement Quality

DOE Order 5480.11 Radiological Measurements Quality

3. Terminology

3.1 *Definitions:*

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

3.2 *Acronyms:Acronyms:*

3.2.1 *AMU, n*—atomic mass unit

3.2.2 *CB, n*—calibration blank

3.2.3 *COC, n*—chain of custody

3.2.4 *CVS, n*—calibration verification standard

3.2.5 *ICS, n*—instrument check standard

3.2.6 *IDL, n*—instrument detection limit

3.2.7 *LCS, n*—laboratory control sample

3.2.8 *MDA, n*—minimum detectable activity

3.2.9 *m/e, n*—mass/charge ratio

3.2.10 *RMDA, n*—required minimum detectable activity

3.2.11 *% RDS, n*—percent relative standard deviation—(1 Standard Deviation / Mean) * 100

4. Summary of Test Method

4.1 A urine sample is digested and wet oxidized with concentrated nitric and hydrochloric acids to solubilize uranium and to destroy the organic matter. Uranium is selectively separated from the chloride salts by an anion exchange resin and is eluted with dilute nitric acid. The ^{235}U and ^{238}U isotopes are determined by ICP-MS.

5. Significance and Use

5.1 DOE Order 5480.11 and ANSI N13.30 require that internal dose assessments be made as part of the bioassay program for nuclear facility workers. For indirect bioassay of uranium workers, the uranium isotopes must be measured

[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee D26.05 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

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along with the total uranium in urine samples. The RMDA for each uranium isotope is 0.1 pCi/L.

5.2 This method is applicable for measuring ^{235}U and ^{238}U at the RMDA. Because of extremely low mass concentration (because of the high specific activity), ^{234}U cannot be measured without additional sample preconcentration.

NOTE 2—Column chromatography separations and concentration of ^{234}U using manual or flow-injection preconcentration followed by ICP-MS isotopic determination are described in Test Methods C 1310 and C 1345. These methods focus on environmental soil sample analysis, but with some development, may be applicable to digested urine samples. The ^{234}U concentration can be calculated based on an enrichment gradient for workers in uranium enrichment plants, and internal dose assessments can be made.

NOTE 3—Use of high resolution ICP-MS may also be used to obtain lower detection limits, see 1.

6. Interferences

6.1 No known isobaric elemental interferences occur for determining ^{235}U and ^{238}U using this test method.

NOTE 4—Bismuth, such as found in antacids (for example, Pepto Bismol) may interferes with the analysis by using binding sites on the resin or biasing the internal standard measurement on the ICP-MS analysis.

7. Apparatus

7.1 Inductively Coupled Plasma-Mass Spectrometer, computer-controlled, multi-channel peristaltic pump, and an autosampler (2, 3, 4).

7.2 Appropriate sized disposable graduated test tube with cap that will accommodate the autosampler.

7.3 Twelve-mL disposable polyethylene column or suitable size with frit.

7.4 Vacuum manifold chamber with regulator valve, vacuum gage, vacuum relief valve, and a vacuum manifold beaker rack (optional).

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.[3] Other grades of reagents 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 ASTM, Type I water as defined in Specification D 1193.

8.3 *Nitric Acid* (sp gr 1.42)—concentrated nitric acid (HNO_3).

8.4 *Hydrochloric Acid* (sp gr 1.18)—concentrated hydrochloric acid (HCl).

8.5 *Nitric Acid* (8M)—Add 500 mL of concentrated HNO^3 to 500 mL of water, and mix.

8.6 *Nitric Acid* (0.8 M)—Add 50 mL of concentrated HNO_3 to 950 mL of water, and mix.

8.7 *Nitric Acid* (0.01 M)—Add 1.25 mL of 8M HNO_3 to 950 mL of water, and dilute to a final volume of 1000 mL, and mix.

8.8 *Hydrochloric Acid* (6 M)—Add 500 mL of concentrated HCl to 500 mL of water, and mix.

8.9 *Argon Gas*—purity 99.99 % or better recommended.

8.10 *Standard Metals Stock Solutions*— Prepare or purchase certified traceable stock or equivalent certified solutions of beryllium, bismuth, cobalt, indium, lanthanum, lead, magnesium, and uranium to be used for the tuning solution, calibration, spiking, mass calibration, and internal standard, or as recommended by the manufacturer..

8.11 *Isotopic Stock Solution*—Prepare two uranium isotopic stock solutions each containing 100,000 ng/L of total uranium purchased from a nationally recognized standards body such as NBL, NBL CRM U030–A (3 % ^{235}U) and NBL CRM U150 (15 % ^{235}U) uranium reference materials, or equivalent, are recommended.

8.12 *Calibration Stock Solution*—Prepare a uranium calibration stock solution containing 100,000 ng/L of total uranium containing 50%^{235} U, such as NBL CRM U500 (50 % ^{235}U).

8.13 The mass calibration and stability check of ICP-MS will require the preparation of a tuning solution that follows the instrument manufacturer's recommended operating conditions.

8.13.1 The tuning stock solution can be prepared by adding an aliquot each of stock standard solutions of the elements recommended by the ICP-MS instrument manufacturer to water and 5 parts volume concentrated HNO_3 per 100 parts water to the recommended concentration.

8.13.2 The daily tuning solution should be prepared by diluting an aliquot of the tuning stock solution (see 8.13.1) and 1 part volume concentrate HNO_3 per 100 parts water. The daily tuning solution concentration for each analyte should be the instrument manufacturer's suggested operating concentration.

8.14 Prior to the ICP-MS analysis for total uranium and isotopic concentration, the following QC standards, calibration standards, internal standard, and rinse solution are recommended and should be included in the analytical run (see Appendix X1 for a suggested QC protocol for this practice).

8.14.1 *Rinse Solution*—Add 1 part concentrated HNO_3 to 100 parts water. Prepare a sufficient quantity to flush the ICP-MS and autosampler between calibration standards, QC samples, and samples.

8.14.2 *Uranium Calibration Standards*—A minimum of four calibration standards should be prepared containing 50 ng/L, 500 ng/L, 1000 ng/L, and 2000 ng/L total uranium by diluting the uranium calibration stock solution (see 8.12). These calibration standards shall be prepared in 1 part volume concentrated HNO_3 per 100 parts water and contain 50 % ^{235}U and ^{238}U isotopic content.

8.14.3 *Instrument Check Standard (ICS)*—The ICS should be prepared by diluting a NBL CRM U150 uranium stock

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, Washington, D. C. 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. Pharmaceutical Convention (USPC), Rockville, MD.

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solution (see 8.11) to a total uranium concentration of 100 ng/L (15 ng/L ^{235}U and 85 ng/L ^{238}U). Prepare this solution in 1 part volume concentrated HNO_3 per 100 parts water.

8.14.4 *Calibration Verification Standard (CVS)*—The CVS should be prepared by diluting the NBL CRM U030 uranium stock solution (see 8.11). The CVS is used for initial and continuing calibration verification. Prepare the CVS at a concentration of 400 ng/L total uranium (12 ng/L ^{235}U and 388 ng/L ^{238}U). Prepare the verification standard in 1 part volume concentrated HNO_3 per 100 parts water.

NOTE 5—Improved precision of the diluted standards prepared in 8.14.2-8.14.4 may be obtained by preparing an intermediate dilution (~20 times) of the stock solutions in 8.11 and 8.12. Gravimetric preparation of these dilutions is recommended.

8.14.5 *Calibration Blank*—Prepare the calibration blank in 1 part volume concentrated HNO_3 per 100 parts water.

8.14.6 *Internal Control Sample*—An aliquot of an internal urine control of known concentration to the analyst should be obtained from a second additional laboratory source. The laboratory control sample is treated exactly as a sample including exposure to all labware, equipment, and reagents. The internal control sample is used to check laboratory analytical performance against established limits.

8.14.7 *Laboratory Control Sample (LCS)*—Prepare this control by adding an aliquot of the uranium isotopic standards (see 8.11) to water to yield an isotopic concentration within the calibration range. The LCS is treated exactly as a sample, including exposure to all labware, equipment, and reagents. The LCS is used to determine whether method performance is within accepted control limits.

8.14.8 *Laboratory Reagent Blank (preparation blank)*—An aliquot of water that is treated exactly as a sample, including exposure to all labware, equipment, and reagents that are used with other samples. The laboratory reagent blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or apparatus.

8.14.9 The recommended concentration for the bismuth internal standard solution is 20,000 ng/Bi/L. The bismuth internal standard stock solution should be prepared by adding the required volume of the bismuth standard stock solution (see 8.10) to approximately 100 mL of water. Add 2 parts concentrated HNO_3 per 100 parts water, and dilute solution with water for the final volume.

8.15 Anion exchange resin, 50–100 or 100–200 mesh (chloride form).[4]

9. Sampling, Test Specimens, and Test Units

9.1 Urine samples are to be refrigerated at 4°C until analysis. Preservatives may be used if deemed necessary to ensure stability (1).

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

10. Calibration and Standardization

10.1 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.

10.2 Set up the necessary instrument software files for data acquisition, calculation, QA and QC data requirements, archival data storage, analytical report preparation, and report verification, etc.

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

10.4 Introduce the daily tuning solution (see 8.13.2) and set the mass controls to transmit the first mass m/e 209(Bi) and m/e 238(U), and tune the instrument for optimized response.

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

10.6 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.

10.7 Determine the instrument stability before analyzing any samples. The stability is determined by analyzing the tuning solution at least ten times with a relative standard deviation of less then 5 % for ^{209}Bi and ^{238}U isotopes.

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

11. Procedure

11.1 *Glassware Preparation*:

11.1.1 Add 5 mL of 8M HNO_3 and 6M HCl to each beaker, cover each beaker with a watch glass, and place the beakers on a hot plate.

11.1.2 Heat the beakers to boiling for approximately 5 to 10 minutes, then remove the beakers and allow to cool to room temperature.

11.1.3 Rinse the beakers and watch glasses with water and air dry.

11.2 *Sample Preparation*:

11.2.1 Transfer 20 mL of the urine sample into a beaker.

11.2.2 Add 5 mL of concentrated HNO_3 to the beaker and cover the beaker with a watch glass, and digest on a hot plate at 95°C.

11.2.3 Remove the watchglass after 15 to 20 minutes and allow the samples to evaporate to dryness, but do not allow overheating to the point of ignition of the organic residue.

NOTE 6—Do not allow sample to burn or bake while on the hot plate. If the sample is allowed to burn, cool the beaker and repeat the acid addition and heating step prior to continuing to the next step.

11.2.4 Remove the urine sample from the hot plate, allow to cool, and add 3 mL of concentrated HCl to each beaker.

11.2.5 Place the beakers back on the hot plate and evaporate each sample to dryness.

11.2.6 Repeat Steps 11.2.4 and 11.2.5 once more.

[4] AG MP-1 Macroporous Anion Resin available from Bio-Rad Co, 300 Reggata Blvd., Richmond CA 94804, has been found to perform satisfactorily.

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11.2.7 Remove the urine samples from the hot plate, allow to cool, and add 10 mL of 6M HCl to each beaker.

11.3 *Column Preparation*:

11.3.1 Prepare the anion exchange resin by equilibrating with water overnight.

11.3.2 Place one polyethylene disposable column for each sample prepared onto the vacuum manifold chamber.

11.3.3 Add approximately 0.75 gram of resin to each column.

11.3.4 Wash each column with 15 mL of 0.8M HNO_3.

11.3.5 Use the vacuum only if the flow of the wash solution or sample in the column becomes obstructed. Do not let the vacuum pressure exceed 2 inches of Hg. The flow rate of the sample through the column should not exceed 4 mL/minute.

11.3.6 Condition each column by passing 10mL of 6M HCl through it.

11.4 *Ion Exchange Separation of Uranium*:

11.4.1 Transfer the prepared sample (see 11.2.7) to the conditioned column funnel.

11.4.2 Allow the sample solution to flow through the column.

11.4.3 Rinse each beaker with 10 mL of 6M HCl and pour the rinseate onto the appropriate column.

11.4.4 Place the beaker for each sample into the vacuum manifold beaker rack and place the rack into the vacuum chamber.

11.4.5 Add 25 mL of 0.8M HNO_3 to the column and elute the uranium.

11.4.6 Remove the beakers from the vacuum manifold, place them on a 95°C hot plate, and reduce the volume to 1 to 2 mL.

11.4.7 Remove the beaker from the hot plate and cool.

11.4.8 Prepare and label an appropriate sized disposable graduated test tube for each sample prepared.

11.4.9 Pipet 1 mL of the 20 ug Bi/L internal standard solution (see 8.4.10) into each graduated test tube.

11.4.10 Add 5 mL of 0.01M HNO_3 to the beaker and transfer the sample solution to a graduated test tube.

11.4.11 Wash the beaker with 2 mL of 0.01M HNO_3 and add the washings to the sample solution.

11.4.12 Dilute the sample solution to 10 mL with 0.01M HNO_3.

11.4.13 Cap and mix each sample.

11.5 *Analysis of Samples for ^{235}U and ^{238}U*:

11.5.1 Analyze the prepared samples and the included quality control samples following the ICP-MS and data system operations described in the site-specific laboratory operating procedure.

11.5.2 Ensure that all instrument set-up (see Section 9), Calibration and Standardization (see Section 10), and required laboratory-specific QC protocol have been followed. A suggested QC sample protocol is given in Appendix X1.

12. Calculation of Results

12.1 Configure the computer to calculate and report the ^{235}U and ^{238}U concentrations as required.

12.2 Configure the computer to subtract any uranium concentration of the initial calibration blank from all standards and quality control samples.

12.3 The computer is configured to subtract the preparation blank from all samples prepared in Section 11.

12.4 Apply the appropriate dilution factor for any samples that required additional dilution.

12.5 The data package for ^{235}U and ^{238}U concentrations should be prepared in accordance with the program statement of work.

13. Precision and Bias

13.1 The precision and bias were determined using NBL uranium isotopic standards CRM U030–A and CRM U150. The precision and bias results were obtained from internal known controls which were blank urine samples spiked with CRM U030–A and CRM U150. The internal known controls were then prepared as routine urine samples. The controls were prepared by four technicians over an eighteen week period. NBL CRM U030–A was used for levels 1 through 4. The total uranium concentration levels for levels 1 through 4 were 250, 500, 750 and 1000 ng/L, respectively. NBL CRM U150 was used for levels 5 and 6. The total uranium concentration levels for 5 and 6 were 250 and 500 ng/L, respectively. See Tables 1 and 2 for the ^{235}U and ^{238}U precision, bias, and concentration results.

14. Keywords

14.1 bioassay; inductively coupled plasma-mass spectrometry; total uranium concentration; urine analysis

TABLE 1 U-235 Internal Known Control

Level	Concentration	% RSD	Bias %	Number of Samples
1	7.5	19	–0.4	30
2	15.0	20	–0.9	30
3	22.5	11	–3.2	30
4	30.0	9	–4.0	30
5	37.5	9	–4.9	30
6	75.0	11	–6.0	30

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TABLE 2 U-238 Internal Known Control

Level	Concentration	% RSD	Bias %	Number of Samples
1	252.5	12	–10	30
2	486.0	12	–14	31
3	727.5	9	–17	30
4	970.0	8	–15	32
5	212.5	12	–13	30
6	425.0	15	–10	30

APPENDIX

(Nonmandatory Information)

X1. QUALITY ASSURANCE AND QUALITY CONTROL

X1.1 The following quality control is recommended for the determination of ^{238}U and ^{235}U.

X1.2 The instrument should be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. After the initial calibration blank, a calibration blank should be measured at an 8 % frequency during the analytical run and at the end of the analytical run.

X1.3 The calibration should be verified using an initial and continuing calibration verification standard (CVS). The verification standard should be made immediately after the calibration, and at an 8 % frequency during the analytical run and at the end of the analytical run. The percent recovery control limits for the verifications should be 80 % to 120 %.

X1.4 The instrument calibration also should be verified using an instrument check standard (ICS). The instrument calibration should be verified using an initial and continuing verification. The instrument verification should be made after the calibration and at an 8 % frequency during the analytical run and at the end of the run. The percent recovery control limits for the instrument standard are 80 % to 120 %.

X1.5 Two method blanks should be analyzed with each sample group. The first reagent blank will normally be blank subtracted from each sample in an analytical batch. If the difference of ^{238}U concentration of the two method blanks is >20 ng/L, use the lesser of the two method blanks for the blank correction.

X1.6 A laboratory control sample should be analyzed with each sample group. The percent recovery limits for the laboratory control sample are 70 % to 130 %.

X1.7 Duplicate samples or replicate spike samples should be analyzed when submitted by the customer to determine sampling precision. When duplicates are not submitted, replicates should be analyzed at an 8 % frequency on a randomly chosen sample from a batch of samples. The relative percent difference between replicates should be < 25 %.

X1.8 Matrix spikes should be analyzed with each group of samples or at 15 % frequency. The percent recovery control limits should be 70 % to 130 %.

X1.9 An internal control should be analyzed with each sample group. The blind control should be submitted by a quality control group internal to the laboratory.

X1.10 If the QC for the analytical run is not within established control limits, re-analyze the samples or qualify the results with the appropriate flags, or both.

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(**2**) Jarvis, K. E., Gray, A. L., and Houk, R. S., *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie, 1992.

(**3**) *Inductively Coupled Plasma-Mass Spectrometry,* Method 6020, USEPA, "SW-846 Test Methods for Evaluating Solid Wastes," Third Edition, Agency, November 1990. Available from US Department of Commerce, National Technical Information Service, Springfield, VA 22161.

(**4**) ASTM Special Technical Publication 1291: *Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations*, Morrow, R. W. and Crain, J. S., eds, American Society for Testing Materials, January 1996.

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