



Designation: C1844 – 24

Standard Test Method for Determination of Uranium in Urine by Inductively Coupled Plasma Mass Spectrometer Following Nitric Acid Dilution¹

This standard is issued under the fixed designation C1844; 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 uranium in urine by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after dilution in nitric acid. The method is presented in two parts. Part A describes a method for determination of total uranium in urine that does not distinguish between uranium isotopes. Part B describes a method that determines the ratio of ^{235}U to ^{238}U (the enrichment) in samples that Part A has shown to contain levels of uranium that the user of the data considers to be significant. The measurement in Part B may be combined with the measurement in Part A to calculate a ^{235}U concentration. The enrichment measurement may in turn be used to estimate levels of minor uranium isotopes, in particular ^{234}U , that are important for calculating the internal radiation dose received by an individual exposed to uranium. The estimation of minor isotope concentrations and the calculation of internal dose does not form part of this standard.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards*:²

C859 Terminology Relating to Nuclear Materials

D1193 Specification for Reagent Water

2.2 *ISO Standards*:³

ISO 17034 General Requirements for the Competence of Reference Material Producers

3. Terminology

3.1 *Definitions*—For definitions of other standard terms in this test method, refer to Terminology **C859**.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *internal reference standard*—a solution containing non-analyte elements that is analyzed by the ICP-MS alongside all samples. The signal is used to correct for small matrix effects and instrumental drift during the run to give a more precise measurement. The element or elements are selected such that they are not present in the unknown samples at significant concentrations, are within the general mass range of the measured analytes and have similar chemical behaviors in the instrument.

3.2.2 *method blank*—a solution which in so far as is practical duplicates the preparation process of the sample to be analyzed and passes through the same measurement process but does not initially contain significant quantities of any of the analytes to be measured.

3.2.2.1 *Discussion*—The method blank does not initially contain significant quantities of analyte, hence the value of any analyte measured may be assumed to be due to interference, matrix effects or contamination introduced as a consequence of sample processing. If the contribution of such factors is

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

evaluated to be representative to the measurement of the unknown samples in the batch then subtracting the measured value for the method blank from the value measured on the genuine sample will eliminate these interferences, typically providing a better estimate for the true value of the quantity of analyte in the sample.

3.2.3 *spike*—a known quantity of analyte added to a sample which is used to evaluate losses during the sample preparation process or biases during measurement.

4. Summary of Test Method

4.1 For the determination of total uranium in urine: samples of urine are initially diluted by a factor of 20 with 0.32 mol/L nitric acid (this is a 2 % by volume dilution of concentrated nitric acid). The diluted sample is then analyzed for total uranium using an ICP-MS. Prior to analysis of samples the instrument is calibrated using 0 ng/L, 50 ng/L, 100 ng/L, and 200 ng/L uranium standards prepared in 0.32 mol/L nitric acid, that has been prepared using ultra high purity (UHP) concentrated acid. The Certified Reference Materials used for standard preparation typically contain natural uranium. A method blank is run after the calibration and all subsequent results are blank corrected. A 50 ng/L Uranium Instrument Quality Control Sample is also analyzed after the calibration in order to maintain quality control of the instrument. An on-line internal reference standard of 2 µg/L thorium is analyzed with every sample in order to correct results for minor matrix effects and instrumental variation between samples, in particular for instrumental drift.

4.2 For the determination of the ^{235}U to ^{238}U isotope mass ratio in urine: samples that have been shown to contain levels of uranium that are sufficiently high to allow enrichment to be determined and that the user of the data considers to be significant are diluted by a factor of 5 with 0.32 mol/L nitric acid, UHP. The ^{235}U to ^{238}U isotope mass ratio in the diluted sample is measured on an ICP-MS which has been calibrated for mass bias parameter using a 200 ng/L solution of a uranium reference material with certified enrichment level. A 200 ng/L Uranium Instrument Quality Control Sample is analyzed after the calibration in order to maintain quality control of the instrument. At the end of the measurement run a method quality control sample in a urine matrix is also measured.

4.3 The mass density of ^{235}U may be calculated using the results from the two determinations.

NOTE 1—A lower dilution factor than the 20 used for total uranium measurement may be used for the determination of the ^{235}U to ^{238}U isotope mass ratio as any interference from the matrix should affect each isotope equally.

5. Significance and Use

5.1 It is common practice within the nuclear industry for internal dose assessment to be made as part of a bioassay program for nuclear facility workers. For indirect bioassay of workers that may be exposed to uranium at enrichments that may differ from natural then the ^{235}U concentration must be measured in addition to the total uranium isotopes so that an estimate of uranium enrichment may be made for use in the dose assessment.

5.2 The enrichment measurement may also be of value in tracing the source of uranium exposure should significant uranium levels be detected in a sample.

5.3 A modern, quadrupole ICP-MS should be capable of delivering performance characteristics close to those claimed in this test method; however, older models or those where performance has deteriorated over time may be unable to do so. It is the responsibility of the user to validate the performance of their equipment.

6. Interferences

6.1 No isobaric elemental interferences have been identified when employing this method in uranium processing facilities; however, interferences can be envisaged for facilities also processing transuranic elements such as plutonium. In such instances, the facility will need to determine whether the quantity present could result in interference that is significant.

6.2 It is possible that significant quantities of minor uranium isotopes, such as ^{234}U and ^{236}U could result in a bias on the ^{235}U to ^{238}U ratio measured in part B. The isotope mass ratios of $m(^{234}\text{U})/m(^{235}\text{U})$ and $m(^{236}\text{U})/m(^{235}\text{U})$ are low for unirradiated uranium at all enrichments and will make no significant contribution to the ^{235}U measurement. The ratio may be significantly higher for reprocessed uranium; however, even in this case any bias is likely to be less than 10 % of the ^{235}U isotope mass fraction value. A highly enriched uranium reference material, National Bureau of Standards (NBS) Standard Reference Material (SRM) 930 (93.28 % isotope mass fraction ^{235}U , 1.08 % isotope mass fraction ^{234}U) was measured repeatedly during the validation of the method and the results for the ^{235}U enrichment level agreed with the certified value to well within the uncertainty for the method.

PART A – DETERMINATION OF TOTAL URANIUM IN URINE

7. Apparatus

7.1 Equipment materials must be compatible with nitric acid. Each type of container should be tested to ensure that it does not contain leachable uranium that might affect the measurement by soaking in dilute nitric acid and measuring the uranium content of the acid after leaching.

7.2 Required apparatus is:

7.2.1 ICP-MS controlled by computer and fitted with associated software and peripherals. A compatible autosampler is highly recommended.

7.2.2 *Pipets*, variable volume, in appropriate sizes such as 1 mL to 10 mL; 100 µL to 1200 µL; 20 µL to 300 µL; 5 µL to 100 µL used with polyethylene pipette tips.

7.2.3 *Volumetric flask*, 100 mL.

7.2.4 *Graduated cylinder*, 100 mL or 250 mL.

7.2.5 *Sample bottles*, 125 mL, 1 L, 2 L.

7.2.6 *Aspirator bottle*, 10 L.

7.2.7 *Screw cap sample tubes*, 50 mL (polypropylene centrifuge tubes have been found to be suitable).

7.2.8 *Plastic Pasteur Pipets*, 1 mL.

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water in conformance with Specification D1193, Type 1.

8.3 UHP concentrated nitric acid (HNO_3), density 1.42 g/mL, ($c = 16 \text{ mol/L}$, $\omega = \sim 70 \%$).

8.4 Dilute nitric acid, $c = 0.32 \text{ mol/L}$, UHP (a 2 % by volume dilution of the acid listed in 8.3). Add approximately 9 L of water to a 10 L Aspirator Bottle. Add 200 mL of concentrated nitric acid, UHP to the aspirator bottle using a graduated cylinder and dilute to 10 L with water. Mix thoroughly before use.

8.5 *Certified Reference Materials*, procured from a national standards body such as the National Institute for Standards and Technology (NIST) or from a reference material producer that is ISO 17034 accredited:

8.5.1 Certified uranium standard (calibration), 1000 $\mu\text{g/mL}$, used for preparation of calibration stock solutions and subsequent calibration standards.

8.5.2 Certified uranium standard, quality control (QC), 1000 $\mu\text{g/mL}$ used for preparation of quality control/spike solutions, and independent from the standard in 8.5.1.

8.5.3 Certified thorium standard, 1000 $\mu\text{g/mL}$, used for preparation of an internal reference standard. An element other than thorium may be used as the internal reference in which case this standard would be substituted by an equivalent certified standard containing the element to be used.

8.6 Uranium Stock Solution, 5 $\mu\text{g/mL}$, for Calibration Standards (it is recommended to prepare every 6 months). Add $\sim 50 \text{ mL}$ of dilute nitric acid, 0.32 mol/L, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.5 mL of certified uranium standard (calibration), 1000 $\mu\text{g/mL}$, into the flask and dilute to volume with dilute nitric acid, 0.32 mol/L, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

8.7 Uranium Quality Control Spike Solution, 1 $\mu\text{g/mL}$, (it is recommended to prepare every 6 months). Add $\sim 50 \text{ mL}$ of dilute nitric acid, 0.32 mol/L, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.1 mL of certified uranium standard (QC), 1000 $\mu\text{g/mL}$, into the flask and dilute to volume with dilute nitric acid, 0.32 mol/L, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

8.8 Thorium Internal Reference Standard Stock Solution, 2 $\mu\text{g/mL}$, (it is recommended to prepare every 6 months). Add $\sim 50 \text{ mL}$ of dilute nitric acid, 0.32 mol/L, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.2 mL of certified thorium standard, 1000 $\mu\text{g/mL}$, into the flask and dilute to volume with dilute nitric acid, 0.32 mol/L, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

8.9 Uranium Stock Solution, 5 $\mu\text{g/L}$, for Calibration Standards (it is recommended to prepare every 3 months). Add

$\sim 50 \text{ mL}$ of dilute nitric acid, 0.32 mol/L, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.1 mL of the Uranium Stock Solution, 5 $\mu\text{g/mL}$, for Calibration Standards into the flask and dilute to volume with dilute nitric acid, 0.32 mol/L, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

8.10 Uranium Instrument Quality Control/Spike Solution, 1 $\mu\text{g/L}$, (it is recommended to prepare every 3 months). Add $\sim 50 \text{ mL}$ of dilute nitric acid, 0.32 mol/L, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.1 mL of the Uranium Quality Control Spike Solution, 1 $\mu\text{g/mL}$, into the flask and dilute to volume with dilute nitric acid, 0.32 mol/L, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

8.11 Thorium Internal Reference Standard, 2 $\mu\text{g/L}$. Add $\sim 50 \text{ mL}$ of dilute nitric acid, 0.32 mol/L, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.1 mL of the Thorium Internal Reference Standard Stock Solution, 2 $\mu\text{g/mL}$ into the flask and dilute to volume with dilute nitric acid, 0.32 mol/L, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

NOTE 2—Instructions for the preparation and use of reference materials and standards throughout this method are based upon the concentrations given for the certified standards. The laboratory may choose to use different concentrations and preparation schemes to prepare standards and spikes that suit its purposes. It is the responsibility of the laboratory to adjust dilutions to deliver the required concentration of uranium or internal reference standard.

9. Hazards

9.1 Strong acids are used to prepare solutions used in this analysis. Safety glasses and gloves must be worn when handling these solutions.

9.2 Fumes and splashes of urine present a possible biological hazard. Gloves should be worn when handling urine samples. Work should be carried out in a dedicated area, preferably within a fume hood, which should be cleaned regularly. Samples and waste items contaminated with urine should be disposed of appropriately.

9.3 The ICP-MS is a source of intense ultra-violet radiation from the radio frequency induced plasma. Protection from radio frequency radiation and UV radiation is provided by the instrument under normal operation.

10. Preparation of Apparatus

10.1 All flasks to be used for preparation of stock solutions and quality control spike solutions should be left soaking in dilute nitric acid, 0.32 mol/L, UHP. Before use, the flasks should be rinsed three times with demineralized water.

11. Calibration and Standardization

11.1 Standards and blanks are prepared as described below. The laboratory may choose to prepare different volumes of these materials at different concentrations and in containers of different volume where appropriate to the requirements of the laboratory and the measurement to be performed.

11.2 Calibration standards are prepared in dilute nitric acid, 0.32 mol/L, UHP. During preparation of the working standards, the solutions containing uranium should always be the last reagent to be added to the tube to avoid possible contamination of samples.