Designation: C1844 – 16

Standard Test Method for Determination of Uranium in Urine by Inductively Coupled Plasma Mass Spectrometer Following Nitric Acid Dilution[1]

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C859 Terminology Relating to Nuclear Materials
D1193 Specification for Reagent Water

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 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 M nitric acid (this is a 2 % by volume dilution of typical, 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, 50, 100, and 200 ng/L Uranium Standards prepared in 0.32 M 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

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[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] 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.

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 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 M nitric acid, UHP. The ^{235}U to ^{238}U 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 concentration 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 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 ICPMS 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 ratio of ^{234}U and ^{236}U to ^{235}U is 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 value. A highly enriched uranium reference material (NBS 930, 93.28 % mass ^{235}U, 1.08 % mass ^{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 to 10 mL; 100 to 1200 µL; 20 to 300 µL; 5 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, (16 M, ~70 % mass).

8.4 Dilute nitric acid, 0.32 M, 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 standards,* traceable to a national standards body such as the National Institute for Standards and Technology (NIST):
8.5.1 Certified uranium standard (calibration), 1000 µg/mL, used for preparation of calibration stock solutions and subsequent calibration standards.

8.5.2 Certified uranium standard (QC), 1000 µg/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 µg/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 µg/mL, for Calibration Standards (it is recommended to prepare every 6 months). Add ~50 mL of dilute nitric acid, 0.32 M, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.5 mL of certified uranium standard (calibration), 1000 µg/mL, into the flask and dilute to volume with dilute nitric acid, 0.32 M, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

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

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

8.9 Uranium Stock Solution, 5 µg/L, for Calibration Standards (it is recommended to prepare every 3 months). Add ~50 mL of dilute nitric acid, 0.32 M, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.1 mL of the Uranium Stock Solution, 5 µg/mL, for Calibration Standards into the flask and dilute to volume with dilute nitric acid, 0.32 M, UHP. Mix thoroughly and transfer to a labelled 125 mL bottle.

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

8.11 Thorium Internal Reference Standard, 2 µg/L. Add ~50 mL of dilute nitric acid, 0.32 M, UHP to a thoroughly cleaned 100 mL volumetric flask. Pipet 0.1 mL of the Thorium Internal Reference Standard Stock Solution, 2 µg/mL into the flask and dilute to volume with dilute nitric acid, 0.32 M, 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 M, 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 M, UHP. During preparation of the working standards, the uranium containing solutions should always be the last reagent to be added to the tube to avoid possible contamination of samples.

11.3 It is recommended that every tenth urine sample and the final urine sample to be analyzed should be prepared both as a normal urine sample (see Section 12) and as a spiked sample with a spike concentration of 50 ng/L uranium in the final analytical solution (see 11.9).

11.4 A 50 ng/L Uranium Instrument Quality Control Sample is prepared and analyzed after the calibration standards.

11.5 Preparation of Uranium Calibration Standard, 0 ng/L.
11.5.1 Label a 50 mL screw cap sample tube.
11.5.2 Pipet 10 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.
11.5.3 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

11.6 Preparation of Uranium Calibration Standard, 50 ng/L.
11.6.1 Label a 50 mL screw cap sample tube.
11.6.2 Pipet 9.9 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.
11.6.3 Pipet 0.1 mL of Uranium Stock Solution, 5 µg/L, for Calibration Standards into the 50 mL tube.
11.6.4 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

11.7 Preparation of Uranium Calibration Standard, 100 ng/L.

11.7.1 Label a 50 mL screw cap sample tube.

11.7.2 Pipet 9.8 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

11.7.3 Pipet 0.2 mL of Uranium Stock Solution, 5 µg/L, for Calibration Standards into the 50 mL tube.

11.7.4 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

11.8 Preparation of Uranium Calibration Standard, 200 ng/L.

11.8.1 Label a 50 mL screw cap sample tube.

11.8.2 Pipet 9.6 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

11.8.3 Pipet 0.4 mL of Uranium Stock Solution, 5 µg/L, for Calibration Standards into the 50 mL tube.

11.8.4 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

11.9 Preparation of uranium spiked urine samples.

11.9.1 Label a 50 mL screw cap sample tube with the sample number and a spike identifier (for example, a + symbol may be added to the sample number).

11.9.2 Pipet 9.0 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

11.9.3 Pipet 0.5 mL of the appropriate urine sample into the 50 mL tube.

11.9.4 Pipet 0.5 mL of Uranium Instrument Quality Control/Spike Solution, 1 µg/L into the 50 mL tube.

11.9.5 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

11.10 Preparation of Uranium Instrument Quality Control Sample, 50 ng/L.

11.10.1 Label a 50 mL screw cap sample tube.

11.10.2 Pipet 9.5 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

11.10.3 Pipet 0.5 mL of Uranium Instrument Quality Control/Spike Solution, 1 µg/L into the 50 mL tube.

11.10.4 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

12. Procedure

12.1 Samples are prepared as described below. The laboratory may choose to prepare different volumes of sample where appropriate by altering the volume of reagents in equal proportion and adjusting the volume of the sample container accordingly.

12.2 Take an appropriate number of 50 mL screw cap sample tubes and label with sample details. One tube is required for each sample in a batch, any spiked samples (prepared as described in 11.9) and a method blank.

12.3 For the preparation of each sample:

12.3.1 Pipet 9.5 mL of dilute nitric acid, 0.32 M, UHP into the labelled 50 mL tube.

12.3.2 Pipet 0.5 mL of the appropriate urine sample into the 50 mL tube.

12.3.3 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

12.4 For the preparation of the method blank:

12.4.1 Pipet 10 mL of dilute nitric acid, 0.32 M, UHP into the labelled 50 mL tube.

12.4.2 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

NOTE 3—A method blank would ideally contain the same matrix as the samples to be measured; however, the matrix will vary between samples due to differences in the composition of urine. Use of dilute nitric acid from the same batch used for sample preparation with no added urine provides consistency for all measurements and has been found to be acceptable.

12.5 Prepare the ICP-MS for analysis in accordance with the manufacturer's instructions. Conduct any necessary tuning and performance checks.

12.6 The ICP-MS must be set up to measure total uranium in a mass range that encompasses isotopes from ^{234}U to ^{238}U.

12.7 Take the four sample bottles containing the calibration solutions described in paragraphs 11.5 – 11.8 and the sample bottle containing the Instrument Quality Control sample described in 11.10 and place them in appropriate positions for calibration and quality control. The four calibration samples would typically be positioned as the first four samples for measurement, followed by the method blank described in 12.4 and then the Instrument Quality Control Sample.

NOTE 4—This method uses a three point calibration plus blank; however, fewer calibration points may be used if shown to produce the required measurement performance.

12.8 Provide the instrument with an appropriate quantity of the internal reference standard described in 8.11.

12.9 Position the bottles containing the samples and spiked samples for measurement after the standards. It is recommended that a spiked sample be positioned after every ten samples and at the end of the run.

12.10 Program the instrument and auto-sampler software to initially calibrate the instrument against the four calibration standards and then to measure the uranium concentration in the Instrument Quality Control sample, method blank and in each of the samples. The internal reference standard should be analyzed with every sample and the instrument programmed to use the measurement to automatically correct for instrumental variation.

NOTE 5—Use of an internal reference standard is recommended (see definition in 3.2.1). The internal reference standard is added to the sample using the dedicated injection and mixing system on the instrument, where available. Alternatively, an appropriate aliquot of the internal reference standard could be added manually to each sample. The laboratory may choose to omit the internal reference standard if it is satisfied that deviations caused by factors such as matrix effects or instrumental drift are adequately catered for within the allowed uncertainty for the method. The laboratory may also choose to use an alternative to thorium as the internal reference if shown to be suitable, as noted in 8.6.

12.11 Also use the instrument software to automatically subtract the concentration of uranium measured in the method blank from the concentration measured in each of the samples to give blank corrected values.

12.12 Check that regression coefficients for instrument calibration and the measurements for the instrument quality control sample and the spiked samples are within statistical parameters considered acceptable by the laboratory. If controls are acceptable then accept the measurement results.

NOTE 6—The levels of uranium being measured are extremely low and hence even low levels of cross-contamination can result in elevated results that would indicate exposure to a high internal radiation dose. It is therefore recommended that analysis of any sample containing concentrations of uranium above the level that the user of the data considers to be significant should be repeated together with a spiked sample before final confirmation of the result. The repeat sample should be prepared from the original urine sample.

NOTE 7—It is recommended that the measured value of the method blank be checked and that if this deviates from zero by a pre-determined value, for example ±4 ng/L, then the run be repeated with a new method blank.

12.13 Any sample that has been confirmed to contain concentrations of uranium above the level that the user of the data considers to be significant should be set aside for further analysis by the method described in Part B to determine the enrichment of the uranium.

13. Calculation or Interpretation of Results

13.1 If the ICP-MS is set up as described in Section 12 then it will provide blank corrected results for uranium as a mass per volume concentration. The concentration of contaminant relative to the original uranium mass is calculated as:

$$\text{Concentration of Uranium in Urine (mass/volume)} = 20 \times A \qquad (1)$$

where:

A = measured concentration of uranium (such as 50 ng/L).

14. Precision and Bias

14.1 Table 1 presents data generated by measuring 12 dilutions of the same urine sample on the same measurement run, spiked to contain uranium at a concentration of 50 ng/L (equivalent to 1 µg/L in the original urine). The relative standard deviation for repeatability calculated from these data is 1.3 %. The relative bias is –1.5 %.

14.2 A total of 246 different urine samples were spiked to contain uranium at a concentration of 50 ng/L (equivalent to 1 µg/L in the original urine) over a six month period. The data were generated in the same laboratory using the same instrument but with multiple analysts for both sample preparation and instrument operation. The full data are not presented here but have been statistically analyzed, giving a relative standard deviation of 2.9 %. The relative bias was –0.8 %.

14.3 Table 2 presents data generated by measuring 12 samples on four different days with each sample prepared independently. Each sample was spiked to contain uranium at a concentration approximately five times the Limit of Detection. The values presented have been measured without blank correction. A Limit of Detection of 3.1 ng/L in the analytical solution has been calculated from these data using the following equation:

$$\text{Limit of Detection} = \sqrt{2} \times 3.6 \times s \qquad (2)$$

where:

3.6 = two times the Student's t value for a probability of 0.05 and 11 degrees of freedom,
$\sqrt{2}$ = accounts for the enhanced error for normal measurements obtained through subtracting a method blank measurement from the sample measurement, and
s = calculated standard deviation.

The equivalent Limit of Detection in a urine sample is 20 times this value, that is 62 ng/L. This is considered to be conservative as the standard deviation used was calculated from measurements made on samples containing uranium above the estimated limit of detection, rather than on blank samples or samples containing uranium close to the limit of detection.

TABLE 1 Measurement of Samples for Repeatability at 50 ng/L Concentration

Measurement	Measured Sample Uranium (ng/L)	Measured Blank Uranium (ng/L)	Corrected Value Uranium (ng/L)
Measurement 1	48.237	-1.016	49.253
Measurement 2	48.110	-1.016	49.126
Measurement 3	47.957	-1.016	48.973
Measurement 4	48.093	-1.016	49.109
Measurement 5	48.350	-1.016	49.366
Measurement 6	49.076	-1.016	50.092
Measurement 7	48.894	-1.016	49.910
Measurement 8	48.518	-1.016	49.534
Measurement 9	48.683	-1.016	49.699
Measurement 10	46.594	-1.016	47.610
Measurement 11	47.940	-1.016	48.956
Measurement 12	48.199	-1.016	49.215
Mean			49.24
Standard Deviation			0.63

PART B – DETERMINATION OF THE ENRICHMENT OF URANIUM DETECTED IN URINE SAMPLES

15. Apparatus

15.1 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.

15.2 Required apparatus is:

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

TABLE 2 Measurement of Spiked Samples at 5× Limit of Detection

Sample	Date of Analysis	Measured Sample Uranium (ng/L)
LOD Sample 1	26 March 2008	14.901
LOD Sample 2	26 March 2008	14.318
LOD Sample 3	26 March 2008	14.928
LOD Sample 4	27 March 2008	15.050
LOD Sample 5	27 March 2008	15.325
LOD Sample 6	27 March 2008	16.297
LOD Sample 7	28 March 2008	16.107
LOD Sample 8	28 March 2008	15.504
LOD Sample 9	28 March 2008	15.765
LOD Sample 10	31 March 2008	15.055
LOD Sample 11	31 March 2008	14.424
LOD Sample 12	31 March 2008	15.072
Mean		15.23
Standard Deviation		0.61

15.2.2 Calibrated and checked balance to read to 0.01 g intervals or less.

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

15.2.4 *Volumetric flask,* 100 mL.

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

15.2.6 *Sample bottles,* 125 mL, 1 L.

15.2.7 *Aspirator bottle,* 10 L.

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

15.2.9 *Plastic Pasteur Pipets,* 1 mL.

16. Reagents and Materials

16.1 *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.

16.2 *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.

16.3 UHP concentrated nitric acid (HNO_3), density 1.42 g/mL, (16 M, ~70 % by mass).

16.4 Dilute nitric acid, 0.32 M, UHP (a 2 % by volume dilution of the acid listed in 16.3). 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.

16.5 *Certified standards,* traceable to a national standards body such as the National Institute for Standards and Technology (NIST).

16.5.1 Certified uranium enrichment standard (calibration), 1 µg/mL, used for preparation of calibration standard. This standard is used for calibration and mass bias correction and a high enrichment standard in the region of 50 % ^{235}U is recommended.

16.5.2 Certified uranium enrichment standard (Instrument QC), 1 µg/mL used for instrument quality control and independent from the standard in 16.5.1. A low enrichment standard in the region of 5 % ^{235}U is recommended for this standard.

16.5.3 Certified uranium enrichment standard (Method QC), 1 µg/mL used for spike solutions and independent from the standard in 16.5.1 and 16.5.2. A standard with an enrichment close to that which workers may be exposed to is recommended. A natural (0.71 % ^{235}U) standard is suitable for facilities processing low enriched uranium.

16.6 Uranium Enrichment Calibration Standard stock solution at 4 µg/L. Label a 150 mL sample bottle, place the bottle on a balance and tare. Weigh 100.4 g (99.6 mL) of dilute nitric acid, 0.32 M, UHP into the 150 mL bottle. Pipet 0.4 mL of the certified uranium enrichment standard (calibration), 1 µg/mL into the 150 mL bottle. Place a screw top lid tightly onto the bottle and mix thoroughly by inversion.

16.7 Uranium Enrichment Standard stock solution (Instrument QC) at 4 µg/L. Label a 150 mL sample bottle, place the bottle on a balance and tare. Weigh 100.4 g (99.6 mL) of dilute nitric acid, 0.32 M, UHP into the 150 mL bottle. Pipet 0.4 mL of the certified uranium enrichment standard (instrument QC), 1 µg/mL into the 150 mL bottle. Place a screw top lid tightly onto the bottle and mix thoroughly by inversion.

16.8 Uranium Enrichment Standard stock solution (Method QC) at 4 µg/L. Label a 150 mL sample bottle, place the bottle on a balance and tare. Weigh 100.4 g (99.6 mL) of dilute nitric acid, 0.32 M, UHP into the 150 mL bottle. Pipet 0.4 mL of the certified uranium enrichment standard (method QC), 1 µg/mL into the 150 mL bottle. Place a screw top lid tightly onto the bottle and mix thoroughly by inversion.

17. Hazards

17.1 Key hazards are as identified in Section 9.

18. Calibration and Standardization

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

18.2 An Instrument Quality Control Sample is prepared and analyzed after the calibration standard. A Method Quality Control Sample is prepared and analyzed after the urine samples.

18.3 Preparation of Uranium enrichment calibration blank.

18.3.1 Label a 50 mL screw cap sample tube.

18.3.2 Pipet 10 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

18.3.3 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

18.4 Preparation of Uranium enrichment calibration standard at 200 ng/L.

18.4.1 Label a 50 mL screw cap sample tube.

18.4.2 Pipet 9.5 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

18.4.3 Pipet 0.5 mL of Uranium Enrichment Calibration Standard stock solution at 4 µg/L into the 50 mL tube.

18.4.4 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

18.5 Preparation of uranium enrichment Instrument QC standard at 200 ng/L.

18.5.1 Label a 50 mL screw cap sample tube.

18.5.2 Pipet 9.5 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

18.5.3 Pipet 0.5 mL of Uranium Enrichment Standard stock solution (instrument QC) at 4 µg/L into the 50 mL tube.

18.5.4 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

18.6 Preparation of uranium enrichment Method QC sample at 200 ng/L.

18.6.1 Label a 50 mL screw cap sample tube.

18.6.2 Pipet 7.5 mL of dilute nitric acid, 0.32 M, UHP into the 50 mL tube.

18.6.3 Pipet 2.0 mL of urine that is essentially free from uranium into the 50 mL tube. A source of urine could be the sample with the lowest measured concentration of uranium from the most recent run of samples measured by the method described in Part A.

18.6.4 Pipet 0.5 mL of Uranium Enrichment Standard stock solution (method QC) at 4 µg/L into the 50 mL tube.

18.6.5 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

19. Procedure

19.1 Samples are prepared as described below. The laboratory may choose to prepare different volumes of sample where appropriate by altering the volume of reagents in equal proportion and adjusting the volume of the sample container accordingly.

19.2 Take an appropriate number of 50 mL screw cap sample tubes and label with sample details. One tube is required for each sample in a batch.

19.3 For the preparation of each sample:

19.3.1 Pipet 8.0 mL of dilute nitric acid, 0.32 M, UHP into the labelled 50 mL tube.

19.3.2 Pipet 2.0 mL of the appropriate urine sample into the 50 mL tube.

19.3.3 Place a screw top lid tightly onto the sample tube and mix thoroughly by inversion.

19.4 Prepare the ICP-MS for analysis in accordance with the manufacturer's instructions. Conduct any necessary tuning and performance checks.

19.5 Set up the sample run with the blank and calibrations standards first, then the instrument QC sample followed by the samples to be measured and finally the method QC sample.

19.6 The ICP-MS must be set up to make separate measurements of the ^{235}U and ^{238}U isotopes. The measurement of the calibration blank provides a baseline for peak measurement on all subsequent measurements, including the calibration standard. Subtraction should be carried out automatically by the ICP-MS software so that net peak measurements are used for subsequent determination.

NOTE 8—The treatment of the calibration blank within the instrument software may vary between instruments. Some instruments, in particular multi collector ICP-MS, may not require the use of a calibration blank.

19.7 Having measured the ^{235}U and ^{238}U isotope peaks, the instrument software is then used to calculate an initial value for the ratio of the ^{235}U to ^{238}U in the sample. The measurement of the ^{235}U to ^{238}U ratio made on the uranium enrichment calibration standard is used together with the known ratio for the standard to calculate a mass bias factor. This is used to modify the initial value for the ratio and provide a final, corrected isotopic ratio for the sample. The calculations are described in 20.1 but would typically be programmed into the instrument software so that the final result after mass bias correction is reported.

19.8 Check that the results for the Instrument and Method QC samples are within statistical parameters considered acceptable by the laboratory. If controls are acceptable, then accept the measurement results.

20. Calculation or Interpretation of Results

20.1 The ICP-MS software should be used to automatically correct for mass bias as described in 19.7. The calculations are:

Ratio Correction Factor = Measured Calibration Ratio / Known Calibration Ratio.
and
Correct Sample Ratio = Measured Sample Ratio / Ratio Correction Factor

20.2 If the ICP-MS is set up as described then it will provide mass bias corrected results for the isotopic ratio of ^{235}U to ^{238}U.

20.3 The isotopic proportion of ^{235}U to ^{238}U may be calculated as follows:

$$^{235}\text{U (isotopic \%)} = 100\% \times B/(1 + B) \tag{3}$$

where:

B = ^{235}U isotopic ratio measured in the sample.

20.4 The isotopic proportion may be converted to a mass ratio as follows:

$$^{235}\text{U(mass \%)} = (100\ \% \times C \times D)/((C \times D) + ((100\ \% - C) \times E)) \tag{4}$$

where:

C = ^{235}U (isotopic %) calculated in 20.3,
D = atomic mass of ^{235}U, taken as 235.0439, and
E = atomic mass of ^{238}U, taken as 238.0508.

20.5 If it is assumed that the proportion of minor isotopes in the uranium is low then the mass percentage of ^{235}U to ^{238}U calculated in 20.4 is approximately equal to the mass percentage of ^{235}U to total uranium. The approximate mass/volume concentration of ^{235}U in the sample may therefore be calculated as:

$$^{235}\text{U (concentration)} = F \times G/100\% \tag{5}$$

where:

F = ^{235}U (mass %) calculated in 20.4, and
G = total uranium mass/volume concentration measured by the method in Part A.

NOTE 9—The proportion of minor isotopes (^{232}U, ^{234}U, and ^{236}U) in most uranic material will be very low so that values calculated for the proportion of ^{235}U to ^{238}U will be approximately equal to the proportion of ^{235}U to total uranium, that is, the enrichment. The contribution made by minor isotopes may become significant for reprocessed uranium enriched to high levels.

21. Precision and Bias

21.1 Table 3 presents data generated by ten samples at each of two different enrichments. The measurements were made over a period of four months in samples spiked with 200 ng/L uranium, (equivalent to 1 µg/L in the original urine sample). The relative standard deviation for the sample at 0.71 % enrichment was 8.7 %. The relative standard deviation for the sample at 0.20 % was 46 %.

21.1.1 *Discussion*—The concentration of ^{235}U in a sample decreases as the enrichment decreases for samples of constant uranium concentration, resulting in a lower peak height for measurements of ^{235}U on the ICP-MS. It is therefore expected that the relative standard deviation should increase as the

TABLE 3 Measurement of Spiked Samples for Uranium Enrichment (by mass)

Sample	A Sample 0.71 % ^{235}U	B Sample 0.20 % ^{235}U
Enrichment Sample 1 (A and B)	0.71 %	0.22 %
Enrichment Sample 2 (A and B)	0.66 %	0.17 %
Enrichment Sample 3 (A and B)	0.69 %	0.19 %
Enrichment Sample 4 (A and B)	0.68 %	0.16 %
Enrichment Sample 5 (A and B)	0.71 %	0.31 %
Enrichment Sample 6 (A and B)	0.72 %	0.52 %
Enrichment Sample 7 (A and B)	0.70 %	0.31 %
Enrichment Sample 8 (A and B)	0.84 %	0.33 %
Enrichment Sample 9 (A and B)	0.77 %	0.17 %
Enrichment Sample 10 (A and B)	0.61 %	0.15 %
Mean	0.71 %	0.25 %
Standard Deviation	0.06 % absolute	0.12 % absolute

enrichment decreases for samples containing low concentrations of uranium. The precision improves significantly for depleted uranium measurements with higher starting concentrations of uranium, for example at 5 µg/L in the starting urine sample and for higher uranium enrichments.

21.2 A total of 25 different urine samples were spiked with a 0.71 % enrichment uranium reference material to contain uranium at a concentration of 200 ng/L (equivalent to 1 µg/L in the original urine) over a 21 month period. The data were generated in the same laboratory using the same instrument but with multiple analysts for both sample preparation and instrument operation. The full data are not presented here but have been statistically analyzed, giving a mean of 0.71 % and a relative standard deviation of 8.6 %, in line with the precision data presented in 21.1.

21.3 The limit of detection cannot be determined in a conventional way as it is not appropriate to measure the enrichment of a blank sample. The limit of detection will depend on the enrichment of the sample, the total concentration of the uranium in the sample and the precision of the measuring instrument, particularly at low count values. The concentration of ^{235}U for the B samples measured in Table 3 is 0.4 ng/L (equivalent to 2 ng/L in the original urine sample). The high relative standard deviation reported for these samples when compared with the equivalent. A samples measured at 0.71 % enrichment suggests that this falls between the minimum detectable amount and the limit of detection for individual uranium isotopes for the instrument used to generate the data.

22. Keywords

22.1 dosimetry; enrichment; inductively coupled plasma – mass spectrometer; uranium; urine