National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1641e

Mercury in Water

This Standard Reference Material (SRM) is intended for the calibration of instruments and techniques used for the determination of mercury in natural waters. It is designed for the preparation of calibration solutions and for use as a "spike" sample in a "method-of-additions" analytical procedure. A unit of SRM 1641e consists of 10 ampoules, each ampoule containing approximately 10 mL of solution consisting of a trace amount of mercury in approximately 3 % mass fraction nitric acid and 2 % mass fraction hydrochloric acid, equivalent to amount-of-substance concentration (molarity) values of approximately 0.5 mol/L nitric acid and 0.5 mol/L hydrochloric acid.

Certified Mass Fraction Value: The certified mass fraction of mercury is based on (1) gravimetric preparation using traceable high-purity metal and (2) cold-vapor isotope dilution inductively-coupled plasma mass spectrometry (CV-ID-ICP-MS) [1]. The certified mercury content and its estimated uncertainty are:

Table 1. Certified Mass Fraction Value of Mercury

0.1016 mg/kg ± 0.0017 mg/kg

The uncertainty in the certified value is given as an expanded uncertainty $U = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO/JCGM Guide [2] and k is a coverage factor ($k = 2$) used to obtain an approximate confidence level of 95 %. The value of u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the gravimetric preparation, ICP-MS measurement and stability assessment over the shelf life of the material.

Expiration of Certification: The certification of **SRM 1641e** is valid, within the measurement uncertainty specified, until **01 October 2019**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of the technical measurements leading to certification of SRM 1641e was provided by S.E. Long of the NIST Chemical Sciences Division.

This SRM was prepared by T.A. Butler and J.L. Molloy of the NIST Chemical Sciences Division. Stability assessment and certification analyses were performed by C.E. Bryan, B.L. Catron and S.E. Long of the NIST Chemical Sciences Division.

Statistical consultation was provided by A.M. Possolo of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 11 December 2014

Robert L. Watters, Jr., Director
Office of Reference Materials

METROLOGICAL TRACEABILITY

Metrological traceability of measurement results to a given reference must be established through an unbroken chain of calibrations and/or comparisons, each having stated uncertainties [3], using measurement standards that are appropriate for the physical or chemical property being measured. Comparisons may include validation measurements using various spectroscopic, chromatographic, or classical methods of analysis. Gravimetric or volumetric dilution is also a method of comparison, where the mass or volume of a solution before and after dilution is measured.

For this SRM, the measurand is the total concentration of mercury expressed as mass fraction, and the certified value is metrologically traceable to the SI unit of mass. This SRM can be used to establish traceability of the results of mercury measurements to NIST measurement results and standards. One approach is to calibrate analytical instruments or procedures for the determination of mercury using standards whose values are traceable to the certified value of mercury in this SRM. When the traceable values of such standards are assigned using this SRM for calibration, the uncertainties assigned to those values must include the uncertainty of the certified value of this SRM, appropriately combined with the uncertainties of all calibration measurements.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

CAUTION: This SRM is an acidic solution sealed in borosilicate glass ampoules with pre-scored stems. All appropriate safety precautions, including the use of gloves during handling, should be taken. Unopened ampoules should be stored under normal laboratory conditions in an upright position inside the original packaging supplied by NIST.

Traces of mercury vapor are present in most laboratory environments. Therefore, contamination of reagents, equipment, and common laboratory materials may cause a severe blank or background problems. Apparatus for analyses at and below the milligram-per-kilogram level must be scrupulously cleaned immediately before use, and only the purest reagents with respect to mercury should be used.

Ampoules are to be opened immediately before use by applying light pressure at the score line in the narrowest segment of the neck of the ampoule. Ampoules should not be resealed, nor stored in some other manner for subsequent use. Once ampoules are opened, the entire contents should be transferred immediately to another container and dilutions should be prepared and used without delay since stability of the dilutions cannot be guaranteed.

If desired, this SRM can be used to prepare more dilute working standard solutions. Blank determinations should be made of the diluent reagents. The user should establish internal laboratory procedures that specify a maximum shelf-life for a working standard solution. Two procedures for the preparation of working standard solutions follow.

Preparation of Standard Solutions by Mass: Diluted working standard solutions can be prepared by transferring an aliquot of the SRM to an empty, dry, pre-weighed polyethylene bottle, and then reweighing the bottle. An appropriate dilute acid must be added by mass to bring the solution to the approximate desired dilution. The dilution need not be exact since the mass of the empty bottle, mass of the bottle plus SRM aliquot, and the final diluted mass of the solution will permit calculation of the exact mass fraction (mass of mercury per mass of solution) of the working standard solution. Dilutions prepared gravimetrically as described will need no correction for temperature and no further correction for true mass fraction in vacuum.

Preparation of Standard Solutions by Volume: Volumetric dilutions are **NOT** recommended due to uncertainties in volume calibrations and variations in density. If dilutions must be made volumetrically, then they may be made by the addition of accurately measured aliquots, withdrawn from the just opened ampoule, to known volumes of an appropriate dilute acid using conventional techniques. The volumetric apparatus used should be scrupulously cleaned. The reliability of the dilution process will depend on the care exercised and on the reliability of the calibration of the volumetric apparatus used.

PREPARATION OF THE SRM SOLUTION

SRM 3133 *Mercury (Hg) Standard Solution* (Lot No. 061204) was used to prepare SRM 1641e. A solution of approximately 200 mg/kg mercury was prepared from SRM 3133 in dilute nitric acid. This solution was quantitatively transferred into a 50 L low-density polyethylene carboy containing a solution mixture of high-purity 0.5 mol/L nitric acid and 0.5 mol/L hydrochloric acid. The resulting solution was aliquoted and packaged into 10 mL borosilicate glass ampoules which were cleaned prior to use by high-purity water followed by air drying in a Class 100 clean facility.

Possible Presence of Other Elements: Studies conducted by NIST have shown that components of borosilicate glass ampoules may leach into solution. In *undiluted* solutions, Na and Si mass fractions as large as 20 mg/kg, B and La mass fractions in the range 1 mg/kg to 5 mg/kg, and Al, As, Ce, Mg, Mn, Rb, and Zn mass fractions in the range 0.05 mg/kg to 1 mg/kg have been found. Possible effects should be considered when this SRM is used.

REFERENCES

[1] Christopher, S.J.; Long, S.E.; Rearick, M.S.; Fassett, J.D.; *Development of High Accuracy Vapor Generation Inductively Coupled Plasma Mass Spectrometry and its Application to the Certification of Mercury in Standard Reference Materials*; Anal. Chem., Vol. 73, pp. 2190–2199 (2001).

[2] JCGM 101:2008; *Evaluation of Measurement Data — Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" — Propagation of Distributions using a Monte Carlo Method*; Joint Committee for Guides in Metrology (JCGM) (2008) available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Dec 2014).

[3] JCGM 200.2012; *International Vocabulary of Metrology - Basic and General Concepts and Associated Terms*, 3rd ed. (2008 version with minor corrections); Joint Committee for Guides in Metrology (JCGM) (2012); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf (accessed Dec 2014).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.