National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 3177

Mercuric Chloride ($HgCl_2$) Standard Solution

Lot No. 090925

This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of mercury when the chemical form of mercury is high-purity mercuric chloride (mercury (II) chloride). A unit of SRM 3177 consists of five 10 mL sealed borosilicate glass ampoules of an acidified aqueous solution prepared gravimetrically from high-purity mercury (II) chloride to contain a known mass fraction of mercury. The solution contains nitric acid at a volume fraction of approximately 3 % and hydrochloric acid at a volume fraction of approximately 4 %.

Certified Value of Mercury: 0.9981 mg/g ± 0.0044 mg/g

The certified value is based on (1) gravimetric preparation using high-purity mercury (II) chloride and (2) isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) analysis [1-3]. The isotopic spike for the ID-CV-ICP-MS analysis was calibrated against SRM 3133 Mercury Standard Solution, Lot No. 991304.

The uncertainty in the certified value is calculated as

$$U = ku_c$$

where $k = 2.120$ is the coverage factor for a 95 % confidence interval and 16 effective degrees of freedom. The quantity u_c is the combined standard uncertainty calculated according to the ISO/JCGM Guide [4]. 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, the ID-CV-ICP-MS determination, and method bias [5].

Expiration of Certification: The certification of **SRM 3177 Lot No. 090925** is valid, within the measurement uncertainty specified, until **25 September 2025**, 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 the certification of SRM 3177 was provided by S.E. Long and M.R. Winchester of the NIST Chemical Sciences Division.

This SRM was prepared by T.A. Butler of the NIST Chemical Sciences Division. The ID-CV-ICP-MS analysis was performed by S.E. Long of the NIST Chemical Sciences Division.

Statistical consultation was provided by S.D. Leigh formerly 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
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Gaithersburg, MD 20899
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Certificate Revision History on Last Page

Steven J. Choquette, 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 [6], using measurement standards that are appropriate for the physical or chemical property being measured. Comparisons may include validation measurements using various spectroscopic 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 mass fraction of mercury and the certified value is metrologically traceable to the derived SI unit for mass fraction, expressed as milligrams per gram. 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 of mercury (II) chloride contained in sealed borosilicate glass ampoules with prescored stems. Therefore, all appropriate safety precautions, including use of gloves during handling, should be taken. Unopened ampoules should be stored under normal laboratory conditions in an upright position inside the original container supplied by NIST.

Opening an Ampoule: When preparing to open an ampoule, that area of the stem where the prescored band is located ($\approx$ 5 mm below the encircling metallic band) should be carefully wiped with a clean, damp cloth and the body of the ampoule wrapped in absorbent material. Holding the ampoule steady and with thumb and forefinger grasping the stem at the metallic band, **minimal** thumb pressure should be applied to the stem to snap it. Correctly done, the stem should break easily where prescored. Use of a metal file to break the stem is **NOT** recommended.

Working Standard Solutions: After the ampoule is opened, the entire contents should be transferred immediately to another container and *working standard solutions* should be prepared. Working standard solutions in the range of 10 mg/kg to 100 mg/kg are recommended, from which more dilute standards can be prepared. 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 Working Standard Solutions by Mass: Each working standard solution should be prepared by emptying one or more ampoules of the SRM into an empty, dry, preweighed, polyethylene bottle and then reweighing the bottle. An appropriate dilute acid must be added by mass to bring the solution to the 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 Working Standard Solutions by Volume: Volumetric dilutions are **NOT** recommended due to uncertainties in volume calibrations and variations in density. However, for user convenience, a procedure for volumetric preparation that will minimize the major sources of error is given. Each working standard solution should be prepared by emptying one or more ampoules of the SRM into an empty, dry, polyethylene bottle and weighing the bottle. The solution must then be transferred to a Class A volumetric flask and the polyethylene bottle reweighed to determine the exact mass of SRM solution transferred. The solution in the flask is diluted to 99 % + volume using an appropriate dilute acid, mixed thoroughly, and the remaining few drops needed to dilute to exact volume carefully added. The concentration (in milligrams per milliliter) of the resulting working standard solution can be calculated by multiplying the mass (in grams) of the SRM solution amount by the SRM certified value (in milligrams per gram) and dividing the numerical product by the calibrated volume (in milliliters) of the flask used for dilution. If this procedure is followed, no correction for density is needed. Although the concentration of the resulting working standard solution may be an uneven fraction of the original SRM concentration, it will be known as accurately as a volumetric dilution permits.

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, Ca, Ce, Mg, Mn, Rb, and Zn mass fractions in the range 0.05 mg/kg to 1 mg/kg have been found. When diluted to prepare working standard solutions, the levels of these

elements become negligible for most purposes. Nevertheless, possible effects should be considered when this SRM is used.

NOTICE TO USERS

NIST strives to maintain the SRM inventory supply, but NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of this SRM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As such, the SRM should be used to validate the more routinely used reference materials in a laboratory. Comparisons between the SRM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the SRM and the stability of relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

REFERENCES

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

[2] Long, S.E.; Kelly, W.R.; *Determination of Mercury in Coal by Isotope Dilution Cold-Vapor Generation Inductively Coupled Plasma Mass Spectrometry*; Anal. Chem., Vol. 74, pp. 147–1483 (2002).

[3] Kelly, W.R.; Long, S.E.; Mann, J.L.; *Determination of Mercury in SRM Crude Oils and Refined Products by Isotope Dilution Cold Vapor ICP-MS Using Closed-System Combustion*; Anal. Bioanal. Chem., Vol. 376, pp. 753–758 (2003).

[4] JCGM 100:2008; *Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Jul 2019); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/pubs/tn1297/index.cfm (accessed Jul 2019).

[5] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.-K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; *An Approach to Combining Results From Multiple Methods Motivated by the ISO GUM*; J. Res. Natl. Inst. Stand. Technol., Vol. 105, pp. 571–579 (2000).

[6] 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 https://www.bipm.org/en/publications/guides/vim.html (accessed Jul 2019).

Certificate Revision History: 26 July 2019 (Change of expiration date; editorial changes); 23 June 2014 (Updated title; editorial changes); 14 November 2011 (Editorial changes); 24 March 2010 (Original certificate date).

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: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.