Report of Investigation

Reference Material 8610

Mercury Isotopes in UM-Almaden Mono-Elemental Secondary Standard

This Reference Material (RM) is intended for use in developing and validating methods for measuring relative differences in mercury (Hg) isotope-number ratios, $R(^{XXX}Hg/^{198}Hg)$. A unit of RM 8610 consists of four ampoules each containing approximately 5 mL of solution comprised of 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.

Reference Values: Reference values are shown in Table 1. A NIST reference value is a best estimate of the true value provided by NIST where all known or suspected sources of bias have not been fully investigated by NIST [1]. Isotopic reference values were determined from a consensus estimate among multiple laboratories and methods using a weighted means statistical model [2]. The expanded uncertainties for isotopic values were determined using a Birge ratio expansion model and a coverage factor (k) of 2.571 to provide an expanded uncertainty interval that has approximately a 95 % probability of encompassing the consensus mean [2] based on uncertainty sources evaluated by Type A methods. Type B uncertainty and uncertainty in the bias of the methods is not included. The measurand is the Hg isotope ratios as determined by the methods used. Metrological traceability is to the delta scale to report the measured isotope ratios relative to the isotope ratios in *NIST SRM 3133 Mercury (Hg) Standard Solution (Lot No. 061204)* as described in the methods described in the text. The mercury mass fraction was determined from the arithmetic mean of replicate measurements made by NIST. Expanded uncertainty of the Hg mass fraction was determined by Type A and Type B methods. These were combined in accordance with ISO/JCGM guidelines to obtain the combined standard uncertainty [3-4]. The expanded uncertainty, U, was calculated as $U = ku_c$, where k is a coverage factor used to obtain an approximate level of confidence of 95 %. The value of k was determined from Student's t distribution with ν_{eff} effective degrees of freedom. The measurand is the concentration of mercury as determined by the method described in the text. Metrological traceability is to the derived SI unit for mass fraction.

Expiration of Value Assignment: **RM 8610** is valid, within the measurement uncertainty specified, until **31 July 2026**, provided the RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Handling and Storage"). The reference values are nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Technical aspects involved in the issuance of this RM were coordinated by R.D. Day of the NIST Chemical Sciences Division.

Statistical analyses for mercury isotope values were performed by B. Toman of the NIST Statistical Engineering Division.

Mercury isotopic measurements by multi-collector inductively coupled plasma mass spectrometry were made by R.D. Day and the individuals and institutions listed in Table 2.

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

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Mercury mass fraction measurements were performed by S. Long from the NIST Chemical Sciences Division using cold-vapor isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). The raw material was acquired and provided by J. Blum and M. Johnson from the University of Michigan (Ann Arbor, MI). Final dilution and ampouling were performed at NIST Gaithersburg by T. Butler and M. Cronise.

INSTRUCTIONS FOR STORAGE AND USE

CAUTION: This RM 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. Mercury is a hazardous material and should be handled with care. Please consult the Safety Data Sheet.

STORAGE: Unopened ampoules should be stored under normal laboratory conditions in an upright position inside the original packaging supplied by NIST.

USE: 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. To minimize the potential for RM 8610 to undergo isotopic fractionation, it is recommended that the solution be transferred to a tightly sealed vial and stored in a cool, dark, place once it is opened.

Table 1. Reference Values and Expanded Uncertainties for RM 8610

	Isotope Ratios[a,b] (‰)
δ^{199}Hg	-0.17 ± 0.01
δ^{200}Hg	-0.27 ± 0.01
δ^{201}Hg	-0.46 ± 0.02
δ^{202}Hg	-0.56 ± 0.03
δ^{204}Hg	-0.82 ± 0.07
	Mass-Independent Fractionation Isotope Ratios[a,b] (‰)
Δ^{199}Hg	-0.03 ± 0.02
Δ^{200}Hg	0.00 ± 0.01
Δ^{201}Hg	-0.04 ± 0.01
Δ^{202}Hg	0.00 ± 0.02
	Mass Fraction: (mg/kg)
Hg	4.958 ± 0.073

(a) All δ values are reported in permil, ‰ (part per thousand, equal to 0.001)
(b) Relative to the isotope ratios in NIST SRM 3133 Mercury (Hg) Standard Solution (Lot No. 061204)

Table 2. Laboratories Contributing Isotopic Data and Analytical Methods

Laboratory	Point of Contact	Multi-collector ICPMS	DSN[(a)]	GLS[(b)]	Mass Bias Correction
NIST Charleston, SC	R. Day	Nu Plasma II	Aridus II or None	CETAC HGX-200	Thallium or Mercury
University of Michigan Ann Arbor, MI	J. Blum M. Johnson	Nu Plasma I	Aridus	Custom	Thallium
University of Pau/IPREM Pau, France	S. Berail D. Amouroux O. Donard	Nu Plasma I	Nu DSN 100	Custom	Thallium
GET Toulouse, France	J. Sonke, J. Masbou, L. Laffont, D. Point	Thermo-Finnigan Neptune	None	CETAC HGX-200	Mercury
Trent University Petersborough, Canada	H. Hintelmann B. Dimock	Thermo-Finnigan Neptune	Apex-q	Yes	Thallium

(a) GLS = Gas liquid separator used for cold vapor generation.
(b) DSN = Desolvation nebulizer used for thallium introduction.

PREPARATION AND ANALYSIS[(1)]

Sample Preparation: RM 8610 was prepared by J. Blum and M. Johnson (University of Michigan, Ann Arbor, MI) by dissolving mercury cinnabar ore obtained from the Almaden region of Spain in 10 % (mass fraction) nitric acid. Final dilution to the Hg mass fraction of 4.958 mg/kg in approximately 3 % mass fraction (0.5 mol/L) nitric acid and 2 % mass fraction (0.5 mol/L) hydrochloric acid were performed at NIST Gaithersburg.

Homogeneity: The homogeneity of this RM solution was assessed using cold-vapor isotope dilution inductively coupled plasma mass spectrometry and cold-vapor multi-collector inductively coupled plasma mass spectrometry. Reproducibility among vials did not exceed the reproducibility for the analytical method, indicating no detectable Hg inhomogeneity in this RM.

Analytical Methods: The δ^{xxx}Hg and Δ^{xxx}Hg values and expanded uncertainty estimates reported in Table 1 are taken from results of an inter-laboratory study involving five expert labs. These isotopic measurements were made using cold-vapor generation multi-collector inductively coupled mass spectrometry (CV-MC-ICP-MS) with minor variations on the sample introduction systems (see Table 2) [5,6,7]. Measurements were made using thallium introduced by a desolvation nebulizer for mass bias correction of mercury ratios, except data from Géosciences Environnement Toulouse (GET) (Toulouse, France), and one dataset from NIST, which used mercury and standard-sample-standard bracketing for external mass bias correction. Mercury mass fraction measurements were performed using cold-vapor ID-ICP-MS.

Reporting of Stable Isotope Values: Notation and reporting of differences in measured isotope ratios of stable mercury isotopes in RM 8610 follow the conventions outlined by Blum and Bergquist [5]. All δ values are reported in permil, ‰ (part per thousand, equal to 0.001), and are calculated relative to the reference standard NIST *SRM 3133 Mercury (Hg) Standard Solution (Lot No. 061204)* using the following equation:

$$\delta^{xxx}\mathrm{Hg}(‰) = [((^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{Sample}}/(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{SRM3133}}) - 1] * 1000$$

where

xxx is the Hg isotope 199, 200, 201, 202, or 204
$(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{Sample}}$ is the ratio of each isotope to ^{198}Hg in RM 8610
$(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{SRM3133}}$ is the average ratio of the two NIST SRM 3133 standards bracketing that sample

(1)Certain commercial instruments, materials, or processes are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments, materials, or processes identified are necessarily the best available for the purpose.

The measurement community typically calculates mass-independent fractionation (MIF) values from these δ^{xxx}Hg values, which are reported using the capital delta notation (Δ). These values were calculated using the Blum and Bergquist [6] formulas below and are provided in this report for convenience:

$$\Delta^{199}\text{Hg}(‰) = \delta^{199}\text{Hg} - (\delta^{202}\text{Hg} * 0.2520)$$
$$\Delta^{200}\text{Hg}(‰) = \delta^{200}\text{Hg} - (\delta^{202}\text{Hg} * 0.5024)$$
$$\Delta^{201}\text{Hg}(‰) = \delta^{201}\text{Hg} - (\delta^{202}\text{Hg} * 0.7520)$$

The Δ^{xxx}Hg notation describes the difference between measured δ^{xxx}Hg and the theoretically predicted δ^{xxx}Hg using mass dependent fractionation (MDF) laws.

REFERENCES

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