NIST Special Publication 260
NIST SP 260-250

Certification of Standard Reference Material® 1641f Mercury in Water

Colleen E. Bryan Sallee
Therese A. Butler
Jenna R. Klingsick
John L. Molloy
James H. Yen

This publication is available free of charge from:
https://doi.org/10.6028/NIST.SP.260-250

NIST | NATIONAL INSTITUTE OF
STANDARDS AND TECHNOLOGY
U.S. DEPARTMENT OF COMMERCE

Page Intentionally Blank

Certification of Standard Reference Material® 1641f Mercury in Water

Colleen E. Bryan Sallee
Therese A. Butler
Jenna R. Klingsick
John L. Molloy
Chemical Sciences Division
Material Measurement Laboratory

James H. Yen
Statistical Engineering Division
Information Technology Laboratory

NIST Technical Series Policies
[Copyright, Fair Use, and Licensing Statements](#)
[NIST Technical Series Publication Identifier Syntax](#)

Publication History
Approved by the NIST Editorial Review Board on 2024-11-13

How to Cite this NIST Technical Series Publication

NIST Author ORCID iDs
Bryan Sallee CE: 0000-0002-2334-3925
Butler TA: 0009-0005-7294-3539
Klingsick JR: 0009-0000-8793-1016
Molloy JL: 0009-0003-8901-5494
Yen JH: 0000-0001-5242-7629

Contact Information

Abstract

Standard Reference Material (SRM) 1641f Mercury in Water 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 1641f consists of ten 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. This publication documents the production, analytical methods, and computations involved in characterizing this product.

Keywords

Table of Contents

List of Tables

List of Figures

Acknowledgments

1. Introduction

Even very low levels of mercury are toxic. Accurate measurements of mercury are necessary for informed decision-making. The National Institute of Standards and Technology (NIST) has developed a series of Standard Reference Materials® (SRMs®) for the metrologically traceable calibration of instruments and measurement procedures used to determine mercury in a variety of matrices. Standard Reference Material® 1641f (SRM® 1641f) is the sixth renewal of the 1641 series of NIST SRMs intended for use in determining mercury content of natural waters [1-6].

Although SRM 1641 was certified 5-March-1975, accessible digital sales information begins in May 1990. More than 2100 units of the series were purchased from that date through 2024. The proportions of these sales to customers in the US, Canada, Europe, Asia, and the rest of the world are displayed in Fig. 1 as functions of calendar year.
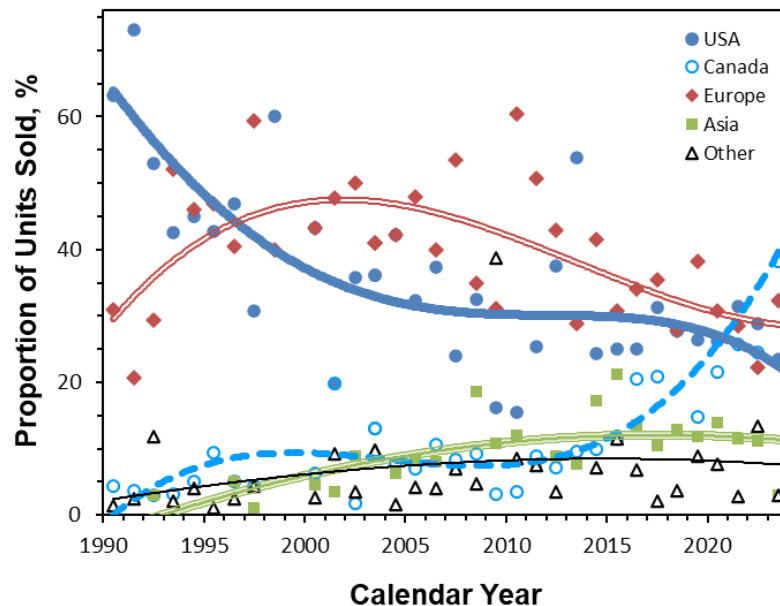
Fig. 1. Location of Customers for SRMs 1641.

The solid circles and the thick trendline display the proportion of sales to customers within the USA. Open circles and dashed line display the proportion sold to customers in Canada. Solid diamonds and the double-line display the proportion of units sold to customers in Europe. Solid squares and the triple-line display the proportion solid to customers in Asia. The open triangles and thin single-line display the proportion of units sold to customers elsewhere.

2. Production

All units of SRM 1641f Mercury in Water were prepared and packaged by NIST staff in Gaithersburg, MD. One SRM unit consists of ten ampoules each containing approximately 10 mL of dilute Hg in an acidic aqueous solution.

2.1. Reagents

Mercury: SRM 3133 Mercury (Hg) Standard Solution, Lot No. 160921, having a certified value of mercury of (10.004 ± 0.040) mg/g in an aqueous solution containing about 10 % by mass nitric acid [7] is the source of mercury for making SRM 1641f.

High-Purity Water (H_2O): College of American Pathologists (CAP) Type III grade or better, generated in the mechanical equipment penthouse of NIST's Advanced Chemical Sciences Laboratory.

Concentrated Nitric Acid (HNO_3): Fisher Scientific Trace Metal Grade.

Concentrated Hydrochloric Acid (HCl): Fisher Scientific Trace Metal Grade.

10 % Volume Fraction Nitric Acid: Concentrated HNO_3 diluted 1:10 by volume with high-purity water.

2 % Volume Fraction Nitric Acid: Concentrated HNO_3 diluted 1:50 by volume with high-purity water.

2.2. Equipment

50 L container: low-density polyethylene carboy.

Sartorius Combics 1: Serviced and calibrated annually. Prior to performing a particular weighing, the calibration was verified using either a 5 kg standard mass (for weighing the empty carboy) or the sum of the 5 kg standard mass and a 10 kg standard mass (for weighing the filled carboy). Both standard masses are traceable to the Internation system of Units (SI) through the standard mass set maintained by the Chemical Sciences Division (CSD).

Mettler-Toledo AB304-S/FAC: Serviced and calibrated annually. The calibration was verified using a 50 g standard mass that is traceable to the SI through the standard mass set maintained by CSD's Inorganic Chemical Metrology Group. All weighings were to the nearest 0.1 mg.

2.3. Preparation Procedure

The carboy was cleaned by soaking for several days in 10 % volume fraction HNO_3, followed by rinsing with copious amounts of high-purity water. The carboy was then filled with high-purity water and allowed to stand for 24 h, rinsed again with copious amounts of high-purity water, and allowed to dry in a vertical, laminar-flow hood. The empty, dry carboy was weighed to the nearest 0.1 g on the Combics 1 balance.

A solution of approximately 200 µg/g Hg was prepared from SRM 3133 and high purity water. Twenty-six milliliters of this solution were quantitatively transferred into the carboy containing 50 L of 0.5 mol/L HNO$_3$/0.5 mol/L HCl solution. The carboy was reweighed on the Combics 1 balance, and the Hg mass fraction of the solution was calculated. Material was mixed in the 50 L carboy for approximately 1 week.

2.4. Packaging

The SRM solution was packaged in Wheaton No. 51 ten-milliliter borosilicate glass ampoules by NIST Office of Reference Materials (ORM). Prior to filling, each ampoule was cleaned in high-purity water and air-dried in a Class 100 clean area.

The Cozzoli ampouling machine in ORM was used on the first day to fill ampoules of SRM 1641f. This machine stopped functioning after producing 2288 ampoules. These ampoules were stored in 15 boxes of 144 ampoules and 1 box of 128 ampoules.

The ROTA ampouling machine in ORM was used the following day to complete the production of SRM 1641f, producing 2128 ampoules. These ampoules were stored in 14 boxes of 144 ampoules and 1 box of 112 ampoules.

2.5. Gravimetric Preparative Value

The mass fraction of Hg in the SRM 1641f solution, w_{1641f}, was calculated from the mass fraction mercury of SRM 3133 and various solution masses, all corrected for buoyancy according to formula (1):

$$w_{1641f} = \frac{(w_{3133})(m_{3133})(m_{spike})}{(m_{spike\_soln})(m_{1641f})} \qquad (1)$$

where w_{3133} is the certified Hg mass fraction of SRM 3133 (Lot No. 160921), m_{3133} is the mass of SRM 3133 used in the first dilution to prepare the intermediate spiking solution, m_{spike_soln} is the total mass of the spiking solution, m_{spike} is the mass of the intermediate spiking solution used in the second (final) dilution step to prepare the candidate SRM 1641f solution, and m_{1641f} is the total mass of the final solution. Table 1 lists the input values and the estimated mercury mass fraction of the final solution. Table 2 describes the basis of the standard uncertainty estimates.

Table 1. Results of Gravimetric Preparation of SRM 1641f.

Factor	Value	u^a	v^b	units	c^c	units	cu^d	units
w_{3133}	10004000	40000.0	11.8	ng/g	2.0 10^{-5}	1	0.81	ng/g
m_{3133}	1.0174	8.0 10^{-4}	large	g	200	ng/g^2	0.16	ng/g
m_{spike}	25.5256	8.0 10^{-4}	large	g	3.9 10^{-6}	ng/g^2	3.2 10^{-9}	ng/g
m_{spike_soln}	51.5995	8.0 10^{-4}	large	g	0.0041	ng/g^2	3.3 10^{-6}	ng/g
m_{1641f}	50049.6	0.11	large	g	0.0020	ng/g^2	0.00023	ng/g
w_{1641f}	100.6	0.8	12.7	ng/g				

a   standard uncertainty associated with the value of the factor
b   number of degrees of freedom associated with the standard uncertainty
c   sensitivity coefficient calculated from the first derivatives of Eq. 1.
d $u \times c$, the fractional influence the input factor has on the standard uncertainty of the output result

Table 2. Uncertainty Components for the Gravimetric Preparation of SRM 1641f.

Factor	Description	Basis
w_{3133}	Mass fraction of SRM 3133, Lot No. 160921	The uncertainty of SRM 3133 was taken from the certificate of analysis, which also gives the degrees of freedom.
m_{3133}	Mass of SRM 3133 added in first dilution	Taken from specifications for the AB304-S balance, which give the readability, reproducibility, and linearity of the balance for measurements of up to 50 g as 0.01 mg, 0.009 mg, and 0.02 mg, respectively. The standard uncertainty of a single measurement is estimated as one-third of the square root of the sum of the squares of these specifications. The standard uncertainty of the sum of the two weighings is the standard uncertainty of a single weighing multiplied by the square root of 2.
m_{spike}	Mass of spiking solution added in second (final) dilution	Same as above
m_{spike_soln}	Final mass of the intermediate spiking solution	Same as above
m_{1641f}	Final mass of the SRM 1641f solution	The Combics 1 balance has a readability to 0.1 g and the IS 64 weighing platform lists a linearity of 0.3 g. The repeatability has been taken from the last three yearly calibrations, with the higher of the "as found" and "as left" values being used in order to have a conservative estimate of typical performance.
w_{1641f}	Hg Mass Fraction of the SRM 1641f solution	Computed as the square root of the sum of the squares of the standard uncertainties for the mass fraction of the solution.

Note: the mercury mass fraction in the solution used to prepare the SRM 1641f ampoules is not necessarily the same as the mass fraction delivered by the solution in the ampoules since minor evaporation may occur while transferring the solution for ampouling. The mercury mass fractions delivered by the ampoules filled by the Cozzoli and ROTA machines must be determined by direct measurement of the solution as delivered to the customer.

3. Direct Combustion Atomic Absorption Spectrometry (DC-AAS)

The mercury mass fraction and homogeneity of the two sets of SRM 1641f Mercury in Water ampoules was investigated using direct combustion atomic absorption spectrometry (DC-AAS) [8]. The metrologically traceable measurement results are suitable for helping to assign the mercury value.

The mass fraction of total mercury in the samples was determined with a DMA-80 direct Hg analyzer (Milestone Scientific, Shelton, CT) [9]. The DMA-80 is an atomic absorption spectrophotometer based on mercury vaporization, amalgamation, desorption, and analysis of samples using an absorbance spectrophotometer and external calibration.

Samples are first dried at 200 °C and then heated to 650 °C, causing organic materials to be decomposed and mercury to be vaporized in a carrier gas of oxygen which is introduced into a quartz catalyst tube. A continuous flow of oxygen carries the decomposition products through a hot catalyst bed where halogens, nitrogen, and sulfur oxides are trapped. All mercury species are reduced to mercury oxide and are then carried along with reaction gases to a gold amalgamator where the mercury is deposited on gold-covered molecular sieves. All non-mercury vapors and decomposition products are carried out of the system with the continuous gas stream. The mercury deposits are then desorbed as the amalgamator is heated. Vaporized mercury is transported to the spectrophotometer for analysis.

The spectrophotometer uses a mercury vapor lamp as its light source. Light from the lamp is directed through an excitation filter before it irradiates the vaporized mercury contained in a cuvette block with a dual-cell arrangement. The detector utilizes two sequential cells positioned along the optical path of the spectrophotometer: one for low concentration samples (cell 1) and the other for high concentration samples (cell 2). Light which is not absorbed by the mercury vapors then passes through an emission filter before being measured by the detector. Absorbance is measured at 253.7 nm as a function of mercury content.

3.1. Materials

One unit of SRM 3133 Mercury Standard Solution (Lot No. 160921), obtained from ORM, was used to make the calibration curve solutions. Two randomly selected adjacent ampoules from each of the eight boxes from each ampouling machine were received from ORM. Two ampoules from a unit of SRM 1641e Mercury in Water, obtained from ORM, were used as the control material. Five empty quartz weigh boats were used as procedural blank samples.

3.2. Measurement Procedure

3.2.1. External Calibration

The external calibration curve is constructed utilizing peak area (absorbance) and mercury mass. The curve for the analysis of the SRM 1641f assessment materials was prepared by gravimetrically aliquoting different masses (between 0.0493 g and 0.2019 g) of an 102.53 ng/g aqueous dilution of SRM 3133 and an aqueous solution of 5 % mass fraction nitric acid and 3 % mass fraction hydrochloric acid into quartz sample boats.

The calibrants were prepared and analyzed two days before the SRM 1641f assessments. Calibration functions are known to be stable for up to 1 month. Table 3 identifies the calibrants, the mass of mercury delivered to the weigh boat, and the measured cell 1 peak area. The relationship between peak area in cell 1, A_{Hg}, and mercury mass, m_{Hg}, is shown in Fig. 2.

Table 3. DMA-80 Calibrants.

Calibrant ID	m_{WS}, g [a]	w_{WS}, ng/g [b]	m_{Hg}, ng [b]	A_{Hg} [d]
0 ng	1	0	0	0.0015
5 ng	0.0493	102.53	5.0545	0.501
10 ng	0.1008	102.53	10.3347	0.9526
15 ng	0.1513	102.53	15.5122	1.3523
20 ng	0.2019	102.53	20.7001	1.6803

a   mass of working standard aliquot (the 0 ng calibrant is a clean empty quartz weigh boat, 1 g nominal mass)
b   mass fraction of mercury in the working standard
c   mass of mercury delivered to the weigh boat, $m_{\text{Hg}} = m_{\text{WS}} \times w_{\text{WS}}$
d   measured mercury peak area in cell 1 (low concentration) of the DMA-80

The {mercury mass, cell 1 peak area} calibration points relevant for evaluating the SRM 1641e and 1641f materials are well estimated using a second-order (quadratic) polynomial model:

$$A_{\text{Hg}} = a \times m_{\text{Hg}}^2 + b \times m_{\text{Hg}} + c \qquad (2)$$

Unrestricted regression analysis yields a value for c of (0.0020 ± 0.0045) peak area units. Since this interval encompasses zero, the c coefficient was forced to be zero yielding model parameters: a = (-0.001104 ± 0.000034), b = (0.10407 ± 0.00061), and c = 0. The root mean square deviation (RMSD), *aka* "standard estimate of error", of the model is 0.0041 peak area units.
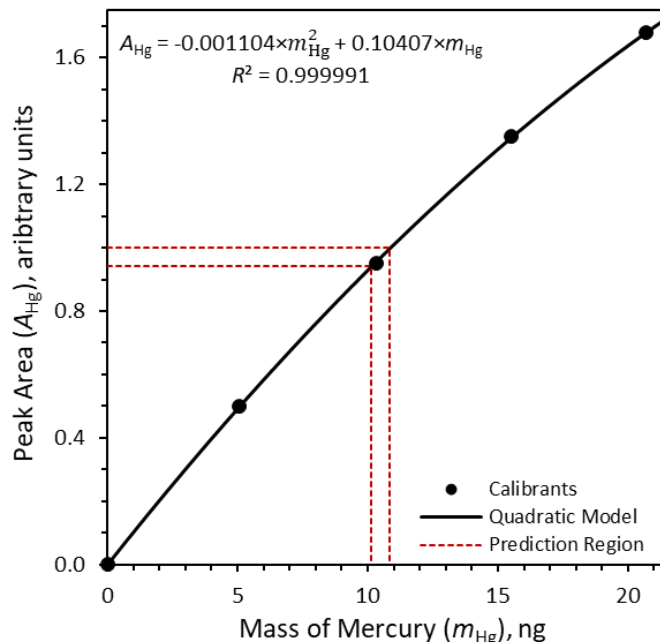
Fig. 2.Calibration Function.

The solid black symbols represent the {mercury mass, cell 1 peak area} measurements of the five calibrants used to estimate mercury in the SRM 1641e and 1641f materials. The black curve represents a best-fit second-order polynomial (quadratic) function through these points. The dashed red lines bound the region of this function used to evaluate mercury in the SRM 1641e and 1641f materials.

3.2.2. Sample Analysis

Mercury was measured in the SRM 1641e and 1641f samples by weighing approximately 100 mg of material into pre-cleaned quartz weigh boats and placing them into the instrument's 40 position auto-sampler rotor. A single replicate was measured from each ampoule of candidate SRM 1641f. The SRM 1641e control samples and procedural blanks (empty quartz weigh boats) were bracketed between blocks of SRM 1641f samples to verify instrument calibration and monitor instrumental drift. The method parameters for all calibration, blank, and sample materials were: 90 s ramp to 200 °C, 30 s hold; 90 s ramp to 650 °C, 180 s hold.

The order of sample analysis was designed to minimize correlation with the ampoule production order and to facilitate comparison between the solutions in the ampoules filled using the Cozzoli and ROTA machines. The five columns to the left in Table 4 identify the samples, their within-machine ampoule production order, the analysis run order, and sample aliquot mass. The two columns to the right in Table 4 list the measured cell 1 peak areas and the calculated mercury mass fractions; the calculations are described below.

Table 4. Analysis Order and Results of DC-AAS Analysis.

Sample	Code	Ampoule Order [a]	Run Order [b]	m_{sample} g [c]	A_{Hg} [d]	w_{Hg} ng/g [e]
Instrument Blank			1			
Quartz Blank-0			2	1	0.0016 [f]	-
SRM 1641e-A1			3	0.1039	0.9710	101.01
SRM 1641e-B1			4	0.1042	0.9897	102.94
SRM 1641f Cozzoli Box 1-66	C-B01-A066	66	5	0.1038	0.9714	101.15
SRM 1641f ROTA Box 6-143	R-B06-A143	863	6	0.1036	0.9725	101.48
SRM 1641f Cozzoli Box 13-102	C-B13-A102	1830	7	0.1040	0.9644	100.13
SRM 1641f ROTA Box 6-144	R-B06-A144	864	8	0.1038	0.9826	102.49
SRM 1641f Cozzoli Box 7-83	C-B07-A083	947	9	0.1007	0.9336	99.65
SRM 1641f ROTA Box 10-20	R-B10-A020	1316	10	0.1034	0.9582	99.97
SRM 1641f Cozzoli Box 1-65	C-B01-A065	65	11	0.1035	0.9738	101.73
SRM 1641f ROTA Box 15-11	R-B15-A011	2027	12	0.1036	0.9783	102.17
Quartz Blank-1			13	1	0.0053	0.051
SRM 1641e-A2			14	0.1039	0.9946	103.83
SRM 1641f Cozzoli Box 11-9	C-B11-A009	1449	15	0.1033	0.9499	99.08
SRM 1641f ROTA Box 1-1	R-B01-A001	1	16	0.1037	0.9659	100.59
SRM 1641f Cozzoli Box 5-47	C-B05-A047	623	17	0.1043	0.9550	98.73
SRM 1641f ROTA Box 5-61	R-B05-A061	637	18	0.1032	0.9565	99.96
SRM 1641f Cozzoli Box 15-130	C-B15-A130	2146	19	0.1031	0.9610	100.59
SRM 1641f ROTA Box 15-10	R-B15-A010	2026	20	0.1029	0.9880	104.04
SRM 1641f Cozzoli Box 4-51	C-B04-A051	483	21	0.1031	0.9597	100.44
SRM 1641f ROTA Box 12-124	R-B12-A124	1708	22	0.1031	0.9752	102.29
Quartz Blank-2			23	1	0.0048	0.046
SRM 1641e-B2			24	0.1033	0.9705	101.53
SRM 1641f Cozzoli Box 7-84	C-B07-A084	948	25	0.1034	0.9724	101.66
SRM 1641f ROTA Box 9-36	R-B09-A036	1188	26	0.1031	0.9812	103.02
SRM 1641f Cozzoli Box 4-52	C-B04-A052	484	27	0.1031	0.9694	101.60
SRM 1641f ROTA Box 12-125	R-B12-A125	1709	28	0.1034	0.9724	101.66
SRM 1641f Cozzoli Box 13-101	C-B13-A101	1829	29	0.1036	0.9774	102.06
SRM 1641f ROTA Box 10-21	R-B10-A021	1317	30	0.1034	0.9841	103.06
SRM 1641f Cozzoli Box 16-18	C-B16-A018	2178	31	0.1035	0.9805	102.53
SRM 1641f ROTA Box 3-33	R-B03-A033	321	32	0.1029	0.9884	104.08
Quartz Blank-3			33	1	0.0050	0.048
SRM 1641e-A3			34	0.1027	0.9940	104.97
SRM 1641f Cozzoli Box 11-8	C-B11-A008	1448	35	0.1033	0.9684	101.28
SRM 1641f ROTA Box 3-34	R-B03-A034	322	36	0.1023	0.9579	101.01
SRM 1641f Cozzoli Box 5-48	C-B05-A048	624	37	0.1006	0.9392	100.43
SRM 1641f ROTA Box 5-62	R-B05-A062	638	38	0.0997	0.9470	102.30
SRM 1641f Cozzoli Box 15-129	C-B15-A129	2145	39	0.1033	0.9735	101.89
SRM 1641f ROTA Box 9-37	R-B09-A037	1189	40	0.1032	0.9813	102.93
SRM 1641f Cozzoli Box 16-17	C-B16-A017	2177	41 [g]	0.1037	0.9600	99.89
SRM 1641f ROTA Box 1-2	R-B01-A002	2	42 [g]	0.1035	0.9858	103.17
Quartz Blank-4			43 [g]	1	0.0052	0.050
SRM 1641e-B3			44 [g]	0.1035	0.9845	103.01

a ampoule production order is equal to (Box number – 1) × 144 + within-box ampoule location

b analysis run order, related to the sample position on the 40-position autosampler plate

c mass of sample aliquot delivered to the weigh boat

d measured mercury peak area in cell 1 (low concentration) of the DMA-80

e mass fraction of mercury in the sample

f not included since run before mercury in water samples

g loaded into positions 1 to 4 of the 40-position auto sampler after the original samples were analyzed

3.2.3. Calculations for Mean Procedural Blank

While five quartz blanks were analyzed, the peak area for Blank-0 was three-fold lower than that of the later blanks, since mercury in water samples had not been analyzed yet on the instrument. The relationship used to estimate each of the four representative quartz blanks is:

$$w_{\text{Hg},i} = \frac{-b \pm \sqrt{b^2 + 4\,a\,A_{\text{Hg,i}}}}{2\,a\,m_{\text{blank}}} \tag{3}$$

where: $w_{\text{Hg},i}$ is the apparent mass fraction of mercury in the blank,
a and b are the parameter values of the quadratic model,
A_{Hg} is the measured mercury peak area in cell 1, and
m_{blank} is the 1 g nominal mass of the quartz blank.

The mean blank and its standard uncertainty are calculated from the measurements of these four quartz blanks:

$$\overline{w}_{\text{blank}} = \sum_{i=1}^{4} w_{\text{Hg,i}} \Big/ 4 = 0.049 \text{ ng/g} \tag{4}$$

$$u(\overline{w}_{\text{blank}}) = \sqrt{\frac{\sum_{i}^{4}\left(w_{\text{Hg,i}} - \overline{w}_{\text{blank}}\right)^2}{4-1}} \Big/ \sqrt{4} = 0.001 \text{ ng/g} \tag{5}$$

3.2.4. Calculation for SRM 1641e and 1641f

The relationship used to calculate each of the SRM 1641e and 1641f samples is:

$$w_{\text{Hg}} = \frac{-b \pm \sqrt{b^2 + 4\,a\,A_{\text{Hg}}}}{2\,a\,m_{\text{sample}}} - \overline{w}_{\text{blank}} \tag{6}$$

where: w_{Hg} is the mass fraction of mercury in the sample,
a and b are the parameter values of the quadratic model,
A_{Hg} is the measured mercury peak area in cell 1,
m_{sample} is the mass of the sample aliquot, and
$\overline{w}_{\text{blank}}$ is the mean procedural blank as described above.

3.2.5. Uncertainties

The uncertainty in the DC-AAS mercury measurements of the SRM 1641e and 1641f materials involves contributions from the five sources listed in Table 5.

Table 5. Uncertainty Sources for DC-AAS Measurements.

Source	Basis	Component [a]	v [b]
Repeatability	Measurement variability of n_1 replicate samples	A_1	$n_1 - 1$
Procedural blank	Measurement variability of n_2 representative procedural blanks	A_2	$n_3 - 1$
Weighing	Measurement variability due to weighing on a four-place balance, estimated as 0.1 %	B_1	large
Primary standard	The standard uncertainty from the Certificate of Analysis for SRM 3133 is: $u = U_{95}/k = 0.040/2.183 = 0.018$ ng/g. This propagates to its dilutions as $100*u/10.004 \approx 0.2$ %.	B_2	11.8
Calibration model	Root mean square deviation (RMSD) of the quadratic calibration model using n_3 calibrants	B_3	$n_3 - 2$

a   Type A components of uncertainty are evaluated by the statistical analysis of series of observations.
    Type B components are evaluated by means other than the statistical analysis of series of observations.
b   Effective degrees of freedom, a measure of the uncertainty in the variance of a value.

The standard uncertainty in the mercury mass fraction of a given material is calculated by combining the individual uncertainty components in quadrature.

$$u\left(w_{\mathrm{Hg}}\right) = \sqrt{\sum_{i=1}^{n_A} u(A_i)^2 + \sum_{i=1}^{n_B} u(B_i)^2} \tag{7}$$

For these DC-AAS measurements, n_A is 2, n_B is 3.

3.3. SRM 1641e DC-AAS Measurements

The mean of the six mass mercury fraction measurements for the SRM 1641e ampoules (three aliquots each from two ampoules) is 102.9 ng/g; the standard deviation is 1.5 ng/g. Table 6 lists the uncertainty components and their relative contributions to the total variance.

Table 6. Uncertainty Components for the DC-AAS Analysis of SRM 1641e Control Material.

Component	Calculation	u ng/g	Variance % [a]
$u(A_1)$	$1.5/\sqrt{6}$	0.61	57
$u(A_2)$	Eq.5	0.01	0.0
$u(B_1)$	0.001×102.9	0.10	2
$u(B_2)$	0.002×102.9	0.20	6
$u(B_3)$	Eq. 6 with $A_{\mathrm{Hg}} \pm 0.004$ [b]	0.48	35
$u(w_{\mathrm{Hg}})$		0.81	

a   Percent of total variance, $100 \times (u(\text{component})/u(w_{\mathrm{Hg}}))^2$
b   Estimated as one-half of the difference between the result of Eq. 6 using $A_{\mathrm{Hg}} + 0.004$ and $A_{\mathrm{Hg}} - 0.004$.

The certified mass fraction value of mercury in SRM 1641e is (0.1016 ± 0.0017) mg/kg, where the 0.0017 is an expanded uncertainty defined as $U_{95} = 2u$. The measured mercury mass fraction value of 102.9 ng/g and standard uncertainty of 0.8 ng/g thus overlaps with the certified value of 101.6 ng/g and its standard uncertainty of 0.9 ng/g.

3.4. SRM 1641f DC-AAS Measurements

The mean of the 32 mercury mass fraction measurements of the SRM 1641f ampoules analyzed is 101.5 ng/g; the standard deviation is 1.4 ng/g. Table 7 lists the uncertainty components and their relative contributions to the total variance. Measurement repeatability is a significant component of the combined uncertainty, but the calibration RMSD is the largest component.

Table 7. Uncertainty Components for the DC-AAS Analysis of SRM 1641f Ampoules.

Component	Calculation	u ng/g	Variance %[a]
$u(A_1)$	1.4/√32	0.24	17
$u(A_2)$	Eq.5	0.01	0.0
$u(B_1)$	0.001 × 101.5	0.10	3
$u(B_2)$	0.002 ×101.5	0.20	12
$u(B_3)$	Eq. 6 with $A_{Hg} \pm 0.004$	0.48	68
$u(w_{Hg})$		0.58	

a   Percent of total variance, $100 \times (u(\text{component})/u(w_{Hg}))^2$
b   Estimated as one-half of the difference between the result of Eq. 6 using A_{Hg} + 0.004 and A_{Hg} - 0.004.

The estimated mercury mass fraction of the SRM 1641f ampoules is 101.5 ng/g with a standard uncertainty of 0.6 ng/g. The uncertainty is associated with about 6 degrees of freedom.

3.4.1. Comparison Between Results for Cozzoli and ROTA Ampoules

Sample heterogeneity across the entire material needed to be tested due to the Cozzoli machine breaking during day one of filling ampoules and the ROTA machine was then used on day two to complete filling the ampoules in order to determine if these factors impact heterogeneity.

The mean of the sixteen mercury mass fraction measurements of the SRM 1641f ampoules filled by the Cozzoli machine (one aliquot from each ampoule) is 100.8 ng/g; the standard deviation is 1.1 ng/g. The mean of the sixteen mercury mass fraction measurements of the SRM 1641f ampoules filled by the ROTA machine (one aliquot from each ampoule) is 102.1 ng/g; the standard deviation is 1.3 ng/g.

The contents of the ampoules filled using the Cozzoli and ROTA machines have significantly different mean mass fractions of mercury. A two-sample t-test rejects the null hypothesis of no difference in means with a p-value of 0.004. A 95 % confidence interval for the true difference in means (ROTA - Cozzoli) is (0.47, 2.22) ng/g, which does not contain zero.

Checking on conditions pertaining to the appropriateness of a t-test, the results for both the Cozzoli and ROTA ampoules are approximately normally distributed, as confirmed by a Shapiro-Wilk test for normality. As a further check on the results, a nonparametric Wilcoxon rank sum test rejected the hypothesis of no difference (same median) with a p-value of approximately 0.006.

An additional component of uncertainty is necessary to adequately account for this observed difference between the ampoules filled using the two machines. Treating the two mean values

as a sample from a N(μ,σ^2) distributions [10], the relative magnitude of this component is estimated as the standard deviation of this sample of means divided by the overall mean.

$$u_{\text{rel}} = 100\,\frac{0.92}{101.5} = 0.91 \cong 1\ \%\tag{8}$$

3.5. Homogeneity and Trend Analysis

Analysis of variance does not show any significant box effects for the mercury mass fraction results for either the Cozzoli or ROTA ampoules. Graphic analysis (see Fig. 3) does not indicate that any of the results would be considered outliers or that there is any significant temporal trends with regard to the production sequences. There does appear to be a weak upward trend with regard to the analysis run order that modestly impacts measurement repeatability.
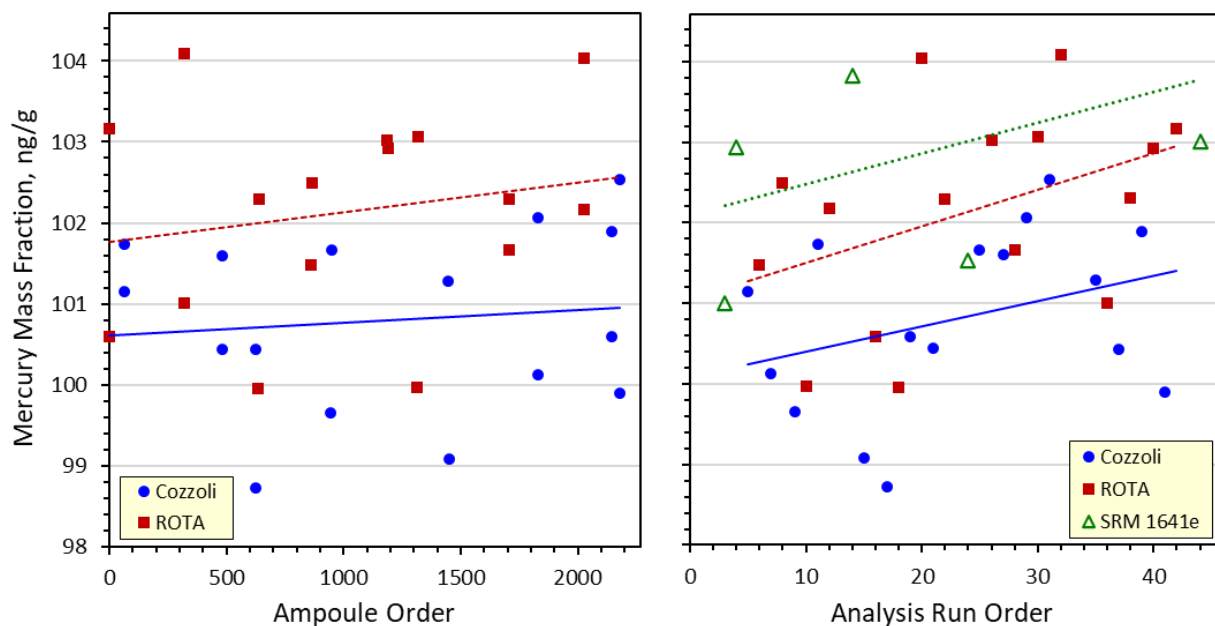
Fig. 3. DC-AAS Results as Functions of Ampoule Production Order and Analysis Run Order.

Each symbol represents one DC-AAS estimate of mercury mass fraction. The solid circles mark estimates for SRM 1641f ampoules filled by the Cozzoli machine, solid squares mark estimates for SRM 1641f ampoules filled by the ROTA machine, and open triangles mark estimates for aliquots of ampoules of SRM 1641e. The lines represent linear trend lines with respect to either the ampoule production order or the DC-AAS analysis order. Solid lines span the SRM 1641f Cozzoli ampoule estimates, dashed lines span the SRM 1641f ROTA ampoule estimates, and the dotted line spans the SRM 1641e estimates.

3.6. Metrological Traceability

The DC-AAS mass fraction results are traceable to the SI through the gravimetric procedures used in the preparation of the external calibration solutions from the SRM 3133 Mercury Standard Solution.

4. Isotope Dilution Cold-Vapor Inductively Coupled Plasma Mass Spectrometry (ID-CV-ICP-MS)

The mercury mass fraction of the two sets of SRM 1641f Mercury in Water ampoules was investigated using isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS). The metrologically traceable measurement results are suitable for helping to assign the mercury value.

This method was developed at NIST in 2000 [11]. It is based on reduction of Hg(II) in acidic solution with tin (II) chloride, and transfer of the resulting "cold vapor" to an inductively coupled plasma mass spectrometer (ICP-MS) for measurement. The method is extremely sensitive, permitting quantitation down to approximately 10 pg/g, in any matrix. This is possible because the transfer of mercury in the gas phase is highly efficient and selective. The process is illustrated in Fig. 4.
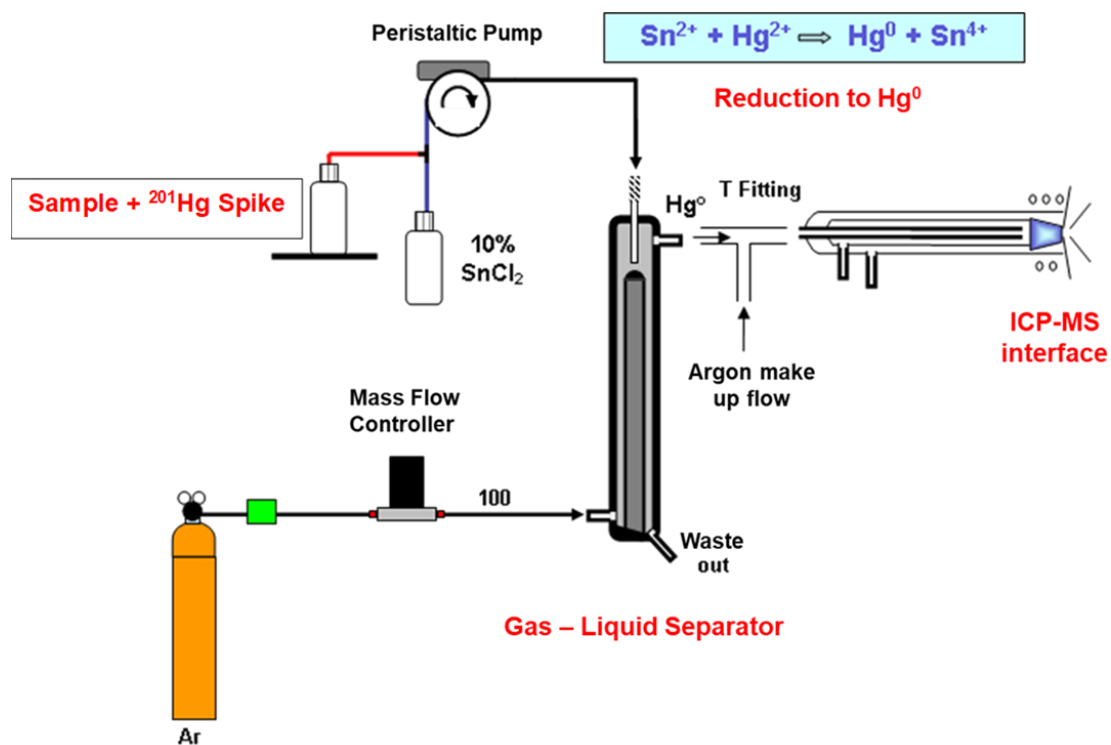
Fig. 4. Configuration for measurements by ID-CV-ICP-MS.

The $^{201}Hg^{2+}$ isotopically spiked sample is dynamically reduced with $SnCl_2$. Hg^0 vapor is separated from the liquid and swept into the ICP-MS for analysis.

Sample aliquots containing mercury are equilibrated with an enriched isotopic spike and the ratio of the spike isotope to a reference isotope is measured by ICP-MS. The measured ratio is used as an input variable for the isotope dilution equation, from which highly accurate data can be obtained for the target analyte. A quadrupole ICP-MS system can be cycled relatively rapidly between isotopes, and therefore the attainable isotope ratio measurement repeatability is of the order of (0.1 to 0.3) %. Because isotope dilution is employed, matrix effects are not a significant factor. However, spectral interferences must be accounted for and eliminated if necessary.

The cold vapor generation process combined with isotope dilution approaches provides both excellent measurement precision and trueness. It is therefore the method of choice for SRM value assignment measurements for mercury.

Note: The ID-CV-ICP-MS analyses of the Cozzoli and ROTA ampoules were accomplished in two sessions, separated by about seven months. However, the session designs were identical, were executed by the same analyst using the same equipment and produced the same type of results. The two sessions are discussed here as if they were conducted in parallel.

4.1. Materials

One unit of SRM 3133 Mercury Standard Solution (Lot No. 160921) was used as the primary standard. The isotopic spiking solution "Hg-201 spike (Batch 180691)" was purchased from the National Isotope Development Center (NIDC) (Oak Ridge, TN). Two sets of three ampoules from a unit of SRM 1641e Mercury in Water were used as the control material.

A solution of 3 % high purity HNO_3 and 2 % high purity HCl, both purchased from Fisher Scientific (Suwanee, GA), was prepared in high purity deionized water (18.3 Ω).

Two sets of eight SRM 1641f ampoules were obtained from ORM. The Cozzoli ampoules analyzed in the initial session were pulled from boxes 1, 3, 5, 6, 9, 10, 12, and 15. The ROTA ampoules analyzed in the later session were pulled from boxes 1, 4, 5, 7, 11, 13, 15, and 16. The ampoule pulled from each box was adjacent to the ampoules pull from measurement by DC-AAS.

4.2. Measurement Procedure

4.2.1. Session Design

The sessions were designed to optimize the analytical system for accurate isotope dilution measurements. The mass fraction of total Hg in SRM 1641f was well known through the gravimetric preparation and DC-AAS measurements described in Sections 2.5 and 3. The isotope dilution measurement system was designed to optimize sample mass and amount of added ^{201}Hg spike. Six procedural blank measurements were considered sufficient for these determinations. The spike to sample ratio (^{201}Hg/^{202}Hg^{+2}) provided a compromise between reducing the effects of error magnification, ICP-MS instrument background, and minimizing ICP-MS detector dead-time resulting from a measured isotope ratio differing from unity.

4.3.1. Sample Preparation

Single aliquots from each ampoule of SRM 1641f and duplicate aliquots from each ampoule of SRM 1641e, each of 0.25 g nominal mass, were accurately weighed by difference into acid-cleaned 50 mL polypropylene centrifuge tubes using a calibrated four-place analytical balance. They were then spiked with an accurately weighed aliquot of ^{201}Hg. The samples were then diluted with the 3 % HNO$_3$/2 % HCl solution to approximately 0.2 ng/g ^{201}Hg. Analytical measurements were completed within one day of dilution to reduce the risk of external contamination and Hg losses from the solutions during storage.

In addition to the SRM 1641e and 1641f samples, six procedural blanks each containing only a small aliquot of ^{201}Hg spike, were carried through the entire sample processing and measurement scheme.

4.3.2. Sample Analysis

Mercury vapor was generated using tin (II) chloride reductant (10 % mass fraction in 7 % volume fraction HCl) and separated from the liquid phase using a commercial (Teledyne CETAC, Omaha, NE) glass reaction/separator cell. The vapor was transferred to Thermo Electron X Series II ICP-MS (Thermo Fisher Scientific, Waltham, MA) with 1/16" (1.6 mm) i.d. Viton tubing, using an argon carrier gas flow rate of approximately 100 mL/min. This gas stream was mixed with the plasma injector gas stream using a plastic T piece. The ICP-MS was operated in a dry plasma mode, which necessitated slight re-tuning of the ion lenses relative to an aqueous aerosol sample introduction system.

All samples were transferred to the instrument in manual sequence, and the timing of the sample uptake was adjusted to allow sufficient time to measure the instrument background prior to measurement of the sample. The ^{201}Hg and ^{202}Hg isotopes were monitored for a duration of 60 s in a pulse counting Time-Resolved-Analysis mode (TRA) to recover the individual ion count rates. The isotope-time profiles were downloaded as comma-separated values (CSV) files to a Microsoft Excel spreadsheet for calculation of background corrected ^{201}Hg/^{202}Hg ratios using Isotope Dilution Assistant (IDA) v0.9 [12]. The instrument detector dead-time was 33 ns.

The working ^{201}Hg isotopic spike solution was prepared by accurate gravimetric dilution of a master stock solution, which was calibrated by reverse isotope dilution using the high-purity primary standard SRM 3133. Stock solutions were prepared by serial dilution. Four spike calibration mixtures (approximately 0.2 ng/g ^{201}Hg) were prepared from these stock solutions (approximately 50 ng/g ^{201}Hg), and these were measured using cold-vapor ICP-MS, under the same conditions as the samples (double ID-MS).

4.3.3. Calculation

The relationship used to calculate each of the SRM 1641e and 1641f samples from the ID-CV-ICP-MS measurements is:

$$m_{\text{Hg}} = \frac{m_s \, K}{m_{\text{sample}}} \, \frac{A_s - B_s \, F \, R}{B \, F \, R - A} \tag{9}$$

where: m_{Hg} is the mass fraction of mercury in the sample,

m_s is the mass of ^{201}Hg spike added (µg),

m_{sample} is the mass of sample aliquot taken (g),

K = 0.997847 is the natural to spike (^{202}Hg/^{201}Hg) atomic weight ratio [13,14]

A_s = 2.62 atom % is the fractional abundance of the reference isotope (^{202}Hg) in the spike,

B_s = 96.17 atom % is the fractional abundance of the spike isotope (^{201}Hg) in the spike,

B = 13.17 atom % is the natural fractional abundance of the spike isotope (^{201}Hg) [15],

A = 29.74 atom % is the natural fractional abundance of the reference isotope (^{202}Hg) [15],

F = 1 is the discrimination correction factor for measured ratio R, and

R is the detector dead-time corrected ^{202}Hg/^{201}Hg ratio.

The A_s and B_s values are specific to the NIDC "Hg-201 spike (Batch 180691)" spiking solution used in in both sessions.

The results of the ID-CV-ICP-MS analyses for the SRM 1641e and 1641f samples are listed in Table 8.

The uncertainty in the ID-CV-ICP-MS mercury measurements of the SRM 1641e and 1641f materials involves contributions from the eleven sources listed in Table 9.

4.3.4. Procedural Blanks

The ^{202}Hg counts in the two sets of six procedural blanks were about the same as the instrument background signal, yielding zero to very slightly negative m_{Hg} estimates. The sample measurement data were therefore not blank-corrected.

4.3.5. Isotopic Composition

There are no commonly recognized spectral interferences for *m/z* 201 and *m/z* 202. The isotopic composition of Hg has no significant natural variability that is measurable on a quadrupole ICP-MS. Therefore, the isotopic composition of the SRM 1641e and 1641f samples was not expected to deviate from that of the accepted natural composition.

Table 8. Results of ID-CV-ICP-MS Analyses.

	Session 1							Session 2					
Sample ID	m_{sample} g	m_{spike} g	m_{201Hg} µg	$\frac{^{202}Hg}{^{201}Hg}$	m_{Hg} µg	w_{Hg} ng/g	Sample ID	m_{sample} g	m_{spike} g	m_{201Hg} µg	$\frac{^{202}Hg}{^{201}Hg}$	m_{Hg} µg	w_{Hg} ng/g
Blank-1		0.0507	0.00227	37.94	-0.00001		Blank-1		0.0497	0.00254	39.09	-0.00001	
Blank-2		0.0508	0.00228	37.76	-0.00001		Blank-2		0.0515	0.00263	39.21	-0.00001	
Blank-3		0.0510	0.00229	38.53	-0.00001		Blank-3		0.0512	0.00262	39.08	-0.00001	
Blank-4		0.0476	0.00214	36.61	0.00000		Blank-4		0.0506	0.00259	38.10	-0.00001	
Blank-5		0.0497	0.00223	36.74	0.00000		Blank-5		0.0510	0.00261	39.06	-0.00001	
Blank-6		0.0505	0.00227	36.95	0.00000		Blank-6		0.0506	0.00259	38.93	-0.00001	
SpikeCal 1A		0.2259	0.01996	2.0110	0.04514		SpikeCal 1A		0.1976	0.02045	1.9735	0.05157	
SpikeCal 1B		0.2273	0.01993	2.0107	0.04480		SpikeCal 1B		0.1997	0.02039	1.9757	0.05096	
SpikeCal 2A		0.2284	0.01993	2.0135	0.04467		SpikeCal 2A		0.2002	0.02045	1.9737	0.05090	
SpikeCal 2B		0.2279	0.01991	2.0165	0.04481		SpikeCal 2B		0.2000	0.02040	1.9777	0.05097	
SRM 1641e-AmpA-1	0.2578	0.2851	0.01279	1.9295	0.02630	102.0	SRM 1641e-AmpA-1	0.2558	0.2541	0.01299	1.9424	0.02646	103.4
SRM 1641e-AmpA-2	0.2576	0.2844	0.01276	1.9187	0.02643	102.6	SRM 1641e-AmpA-2	0.2559	0.2549	0.01303	1.9432	0.02653	103.7
SRM 1641e-AmpB-1	0.2572	0.2843	0.01275	1.9242	0.02632	102.3	SRM 1641e-AmpB-1	0.2562	0.2552	0.01304	1.9459	0.02651	103.5
SRM 1641e-AmpB-2	0.2581	0.2841	0.01274	1.9129	0.02651	102.7	SRM 1641e-AmpB-2	0.2560	0.2553	0.01305	1.9413	0.02661	103.9
SRM 1641e-AmpC-1	0.2572	0.2841	0.01274	1.9146	0.02648	103.0	SRM 1641e-AmpC-1	0.2543	0.2555	0.01306	1.9500	0.02647	104.1
SRM 1641e-AmpC-2	0.2574	0.2843	0.01275	1.9182	0.02643	102.7	SRM 1641e-AmpC-2	0.2558	0.2546	0.01301	1.9426	0.02651	103.6
SRM 1641f-Cozzoli Box 1	0.2570	0.2842	0.01275	1.9576	0.02571	100.0	SRM 1641f-ROTA Box 1	0.2548	0.2552	0.01304	1.9684	0.02610	102.5
SRM 1641f-Cozzoli Box 4	0.2562	0.2838	0.01273	1.9580	0.02566	100.2	SRM 1641f-ROTA Box 3	0.2551	0.2543	0.01300	1.9678	0.02602	102.0
SRM 1641f-Cozzoli Box 5	0.2568	0.2839	0.01273	1.9564	0.02570	100.1	SRM 1641f-ROTA Box 5	0.2564	0.2546	0.01301	1.9640	0.02612	101.9
SRM 1641f-Cozzoli Box 7	0.2568	0.2833	0.01271	1.9597	0.02559	99.6	SRM 1641f-ROTA Box 6	0.2554	0.2535	0.01295	1.9722	0.02586	101.3
SRM 1641f-Cozzoli Box 11	0.2575	0.2838	0.01273	1.9562	0.02570	99.8	SRM 1641f-ROTA Box 9	0.2548	0.2553	0.01305	1.9788	0.02593	101.8
SRM 1641f-Cozzoli Box 13	0.2567	0.2842	0.01275	1.9569	0.02572	100.2	SRM 1641f-ROTA Box 10	0.2520	0.2540	0.01298	1.9665	0.02602	103.2
SRM 1641f-Cozzoli Box 15	0.2561	0.2833	0.01271	1.9532	0.02570	100.4	SRM 1641f-ROTA Box 12	0.2561	0.2557	0.01307	1.9674	0.02617	102.2
SRM 1641f-Cozzoli Box 16	0.2559	0.2837	0.01273	1.9627	0.02557	99.9	SRM 1641f-ROTA Box 15	0.2562	0.2544	0.01300	1.9667	0.02605	101.7
Spike Recovery-1	0.2550	0.2834	0.01271	1.8340	0.02801	109.9	Spike Recovery-1	0.2574	0.2545	0.01301	1.8671	0.02797	108.6
Spike Recovery-2	0.2553	0.2832	0.01270	1.8269	0.02814	110.2	Spike Recovery-2	0.2579	0.2550	0.01303	1.8767	0.02782	107.9
Spike Recovery-4	0.2565	0.2835	0.01272	1.8204	0.02831	110.4	Spike Recovery-3	0.2576	0.2570	0.01313	1.8716	0.02815	109.3
Spike Recovery-3	0.2552	0.2840	0.01274	1.8202	0.02836	111.2	Spike Recovery-4	0.2584	0.2548	0.01302	1.8687	0.02797	108.2

Table 9. Uncertainty Sources for ID-CV-ICP-MS Measurements.

Source	Basis	Component [a]	ν [b]
Sample replication	Measurement variability of n_1 replicate samples	A_1	$n_1 -1$
Spike calibration	Measurement variability of n_2 spike calibration mixtures	A_2	$n_2 -1$
Weighing	Measurement variability due to weighing on a four-place balance, estimated as 0.1 %	B_1	large
Primary standard	The standard uncertainty from the Certificate of Analysis for SRM 3133 is: $u = U_{95}/k = 0.040/2.183 = 0.018$ ng/g. This propagates to its dilutions as $100*u/10.004 \approx 0.2$ %.	B_2	11.8
Natural/Spike Atomic Weight Ratio (K)	Uncertainty of the IUPAC atomic weight for Hg divided by the atomic weight of the spike determined by isotopic measurements. Estimated at 0.0005 %.	B_3	large
Abundance of ^{202}Hg in spike (A_s)	Uncertainty in spike isotopic composition and relative impact on the measurement of Hg by double ID-MS. Estimated at 1.00 % for SRM 1641e and 1.01 % for SRM 1641f.	B_4	large
Abundance of ^{201}Hg in spike (B_s)	Uncertainty in spike isotopic composition and relative impact on the measurement of by double ID-MS. Estimated at 0.61 % for SRM 1641e and 0.62 % for SRM 1641f.	B_5	large
Abundance of ^{202}Hg in the sample (A)	Uncertainty of the IUPAC isotopic composition and relative impact on the measurement of Hg by double ID-MS. Estimated at 0.02 %.	B_6	large
Abundance of ^{201}Hg in the sample (B)	Uncertainty of the IUPAC isotopic composition and relative impact on the measurement of Hg by double ID-MS. Estimated at 0.02 %.	B_7	large
^{201}Hg/^{202}Hg ratio measurement (R)	Uncertainty of the dead-time corrected ICP-MS isotope ratio measurements based on pooled standard deviation of approximately 500 ratio measurement points and subtraction of the instrument blank counts on each isotope. Estimated at 0.75 %.	B_8	large
Mass discrimination correction (F)	Uncertainty of the correction factor (T/E) for the instrument mass bias/mass discrimination and the impact on the measured mass fraction of Hg using a double ID-MS approach. Estimated at 0.75 %.	B_9	large

a   Type A components of uncertainty are evaluated by the statistical analysis of series of observations.
    Type B components are evaluated by means other than the statistical analysis of series of observations.
b   Effective degrees of freedom, a measure of the uncertainty in the variance of a value.

The standard uncertainty in the mercury mass fraction of a given material is calculated using Eq. 7 where: n_A is 2, n_B is 9.

4.4. SRM 1641e ID-CV-ICP-MS Measurements

The mean of the six mass mercury fraction measurements for the SRM 1641e ampoules (two aliquots each from three ampoules) in the first session is 102.6 ng/g; the standard deviation is 0.4 ng/g. The mean of the six mass mercury fraction measurements (two aliquots each from three ampoules) in the second session is 103.7 ng/g; the standard deviation is 0.3 ng/g. The mean of the 12 mass mercury fraction measurements in the combined sessions is 103.1 ng/g; the standard deviation is 0.7 ng/g.

Table 10 lists the uncertainty components and their relative contributions to the total variance. Measurement repeatability is a minor component of the combined uncertainty.

Table 10. Uncertainty Components for the for the ID-CV-ICCP-MS Analysis of SRM 1641e Control Material.

| Component | Session 1 | | | | Session 2 | | |
	Calculation	u ng/g	Variance %[a]		Calculation	u ng/g	Variance %[a]
$u(A_1)$	0.4/√6	0.1	0.4		0.3/√6	0.1	0.4
$u(A_2)$	0.4/√4	0.2	1.5		0.6/√4	0.3	3.2
$u(B_1)$	0.001 × 101.6	0.1	0.4		0.001 × 103.7	0.1	0.4
$u(B_2)$	0.002 × 101.6	0.2	1.5		0.002 × 103.7	0.2	1.4
$u(B_3)$	0.000005 × 101.6	0.001	0.0		0.000005 × 103.7	0.001	0.0
$u(B_4)$	0.0100 × 101.6	1.0	36.5		0.0100 × 103.7	1.0	35.8
$u(B_5)$	0.0061 × 101.6	0.6	13.1		0.0061 × 103.7	0.6	12.9
$u(B_6)$	0.0002 × 101.6	0.02	0.0		0.0002 × 103.7	0.02	0.0
$u(B_7)$	0.0002 × 101.6	0.02	0.0		0.0002 × 103.7	0.02	0.0
$u(B_8)$	0.0075 × 101.6	0.8	23.4		0.0075 × 103.7	0.8	22.9
$u(B_9)$	0.0075 × 101.6	0.8	23.4		0.0075 × 103.7	0.8	22.9
$u(w_{Hg})$		1.7				1.7	

a Percent of total variance, $100 \times (u(\text{component})/u(w_{Hg}))^2$

4.5. SRM 1641f ID-CV-ICP-MS Measurements

The mean of the eight mass mercury fraction measurements for the SRM 1641f ampoules (one aliquot from each of eight ampoules) in the first session is 100.0 ng/g; the standard deviation is 0.2 ng/g. The mean of the eight mass mercury fraction measurements (one aliquot from each of eight ampoules) in the second session is 102.1 ng/g; the standard deviation is 0.6 ng/g. The mean of the combined 16 measurements is 101.0 ng/g with a standard deviation of 1.1 ng/g.

Table 11 lists the uncertainty components and their relative contributions to the total variance.

Table 11. Uncertainty Components for the ID-CV-ICCP-MS Analysis of SRM 1641f Ampoules.

| Component | Session 1 (Cozzoli Ampoules) | | | | Session 2 (ROTA Ampoules) | | |
	Calculation	u ng/g	Variance %[a]		Calculation	u ng/g	Variance %[a]
$u(A_1)$	0.2/√8	0.1	0.4		0.6/√8	0.2	1.4
$u(A_2)$	0.4/√4	0.2	1.5		0.6/√4	0.3	3.2
$u(B_1)$	0.001 × 100.0	0.1	0.4		0.001 × 102.1	0.1	0.4
$u(B_2)$	0.002 × 100.0	0.2	1.5		0.002 × 102.1	0.2	1.4
$u(B_3)$	0.000005 × 100.0	0.001	0.0		0.000005 × 102.1	0.001	0.0
$u(B_4)$	0.0101 × 100.0	1.0	36.5		0.0101 × 102.1	1.0	35.5
$u(B_5)$	0.0062 × 100.0	0.6	13.1		0.0062 × 102.1	0.6	12.8
$u(B_6)$	0.0002 × 100.0	0.02	0.0		0.0002 × 102.1	0.02	0.0
$u(B_7)$	0.0002 × 100.0	0.02	0.0		0.0002 × 102.1	0.02	0.0
$u(B_8)$	0.0075 × 100.0	0.8	23.4		0.0075 × 102.1	0.8	22.7
$u(B_9)$	0.0075 × 100.0	0.8	23.4		0.0075 × 102.1	0.8	22.7
$u(w_{Hg})$		1.6				1.7	

a Percent of total variance, $100 \times (u(\text{component})/u(w_{Hg}))^2$

4.6. Homogeneity and Trend Analysis

Graphic analysis (see Fig. 5) does not indicate that any of the results would be considered outliers. Since samples were analyzed in ampoule production order, there is no evidence of significant trends with regard to the production sequences or ICP-MS evaluations.
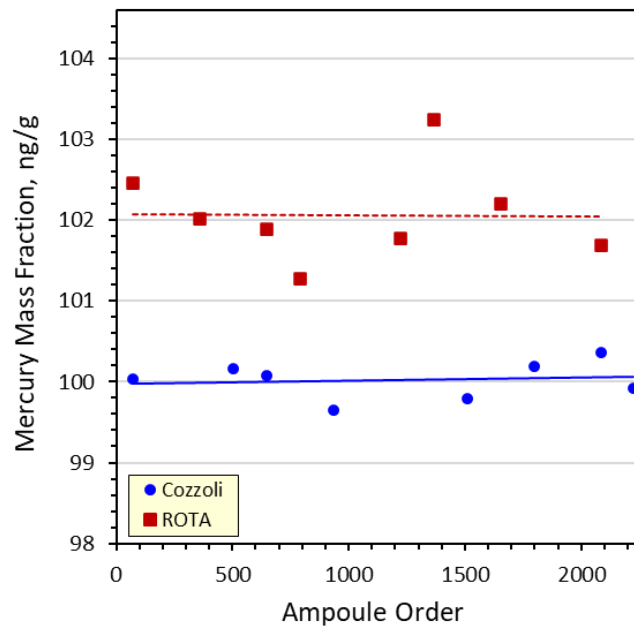

Fig. 5. ID-CV-ICP-MS Results as a Function of Ampoule Production Order.

Each symbol represents one ID-CV-ICP-MS estimate of mercury mass fraction in one SRM 1641f ampoule. The solid circles mark estimates for ampoules filled by the Cozzoli machine and solid squares mark estimates for ampoules filled by the ROTA machine. The lines represent linear trend lines with respect to ampoule production order. The solid line spans the SRM 1641f Cozzoli ampoule estimates and the dashed line spans the ROTA ampoule estimates.

4.7. Combined ID-CV-ICP-MS Result

As shown in Fig. 6, the mean DC-AAS and ID-CV-ICP-MS mercury mass fraction results for the SRM 1641e control material are systematically slightly greater than the certified value. This suggests either that the certified mass fraction interval of the SRM 1641e material was slightly low or that results for the SRM 1641e materials as reported here may be slightly high.

The estimated mercury mass fraction of the eight SRM 1641f ampoules filled using the Cozzoli machine as analyzed in Session 1 is 100.0 ng/g with a repeatability standard deviation of 0.2 ng/g and a combined standard uncertainty of 1.6 ng/g. The mercury mass fraction of the eight SRM 1641f ampoules filled using the ROTA machine as analyzed in Session 2 is 102.1 ng/g with repeatability of 0.3 ng/g and standard uncertainty of 1.7 ng/g. The mass fraction of the combined 16 ampoules is 101.0 ng/g with a standard deviation of 1.1 ng. Treating the results of the two sessions as N(μ,σ^2) distributions [10], the standard uncertainty is 1.2 ng/g. The standard uncertainties for all of the ID-CV-ICP-MS results are associated with more than 60 degrees of freedom.
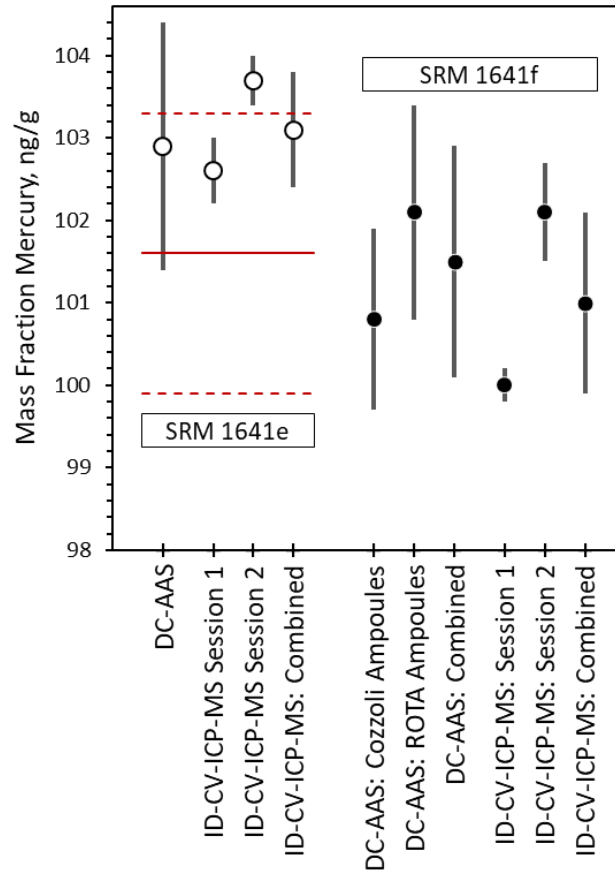
Fig. 6. Mercury Mass Fraction Results for SRM 1641e and SRM 1641f materials.

Each open circle represents a mean measured mercury mass fraction for the SRM 1641e control material. The solid horizontal line represents the SRM 1641e certified value; the dashed horizontal lines bound the 95 % level of confidence interval on the certified value. Each solid symbol represents a mean mercury mass fraction estimate for SRM 1641f. Error bars represent measurement repeatability standard deviations.

4.8. Metrological Traceability

The ID-CV-ICP-MS mass fraction results are traceable to the SI through use of a primary method based on isotope dilution mass spectrometry and correction for all known sources of analytical bias. The spike employed for the isotope dilution measurements was calibrated using the SRM 3133 Mercury Standard Solution.

5. Combined Method Result

As shown in Fig. 7, the mean DC-AAS and ID-CV-ICP-MS mercury mass fraction results for the SRM 1641f are slightly greater than the gravimetric preparation value. This suggests that possibly some solvent was lost between solution preparation and ampouling resulting in slightly greater mercury values from analytical measurement methods. The certified value for mercury in SRM 1641 combines the DC-AAS and ID-CV-ICP-MS method results and uncertainty. The mean DC-AAS result is 101.5 ng/g with a combined standard uncertainty of 0.6 ng/g that is associated with about 6 degrees of freedom. The combined ID-CV-ICP-MS result is 101.0 ng/g with a standard uncertainty of 1.2 ng/g that is associated with more than 60 degrees of freedom. Treating these as N(μ,σ^2) distributions [10], the mean of these two method estimates is 101.3 ng/g. While there is no evidence for significant ampoule production order effects, the results of the DC-AAS measurements indicate a statistically significant difference between the mean levels of Hg for the two sets of ampoules, as do the results from the ID-CV-ICP-MS evaluations. The uncertainty of the combined value is estimated using a bootstrap procedure based on a Gaussian random effects model for the between-method effects [10, 16-18] combined with a 1 % relative standard uncertainty component for inhomogeneity between filling machines. The approximate 95 level of confidence expanded uncertainty on the combined value is 2.4 ng/g. SRM 1641f has a certified mercury mass fraction of 101.3 ng/g ± 2.4 ng/g.
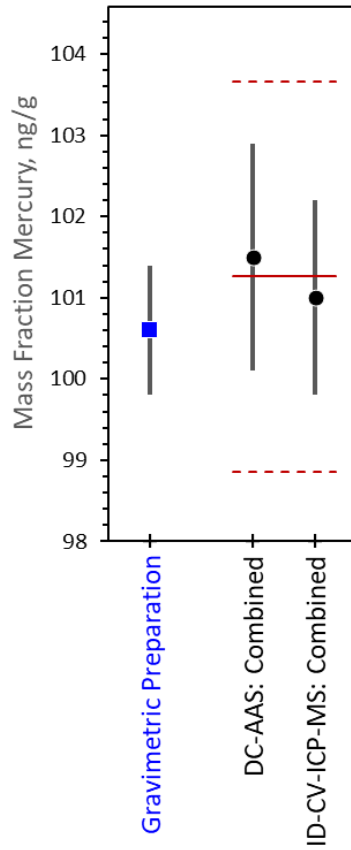
Fig. 7. Mercury Mass Fraction Results for SRM 1641f materials.

Each symbol represents a mean mercury mass fraction estimate for SRM 1641f, with the square denoting the gravimetric preparatory value and circles the combined all-ampoule distributions for the DC-AAS and ID-CV-ICP-MS analyses. The solid horizontal lines represent the proposed combined mean; the dashed horizontal lines bound the 95 % level of confidence interval that includes a between-filling machine uncertainty component. The error bars represent standard uncertainties.

References

[1]   National Bureau of Standards (5-March-1975) Certificate of Analysis, Standard Reference Material 1641 Mercury in Water - Concentrate. https://tsapps.nist.gov/srmext/certificates/archives/1641.pdf.

[2]   National Bureau of Standards (12-December-1978) Certificate of Analysis, Standard Reference Material 1641a Mercury in Water – μg/mL. https://tsapps.nist.gov/srmext/certificates/archives/1941a.pdf.

[3]   National Bureau of Standards (13-April-1983) Certificate of Analysis, Standard Reference Material 1641b Mercury in Water – μg/mL. https://tsapps.nist.gov/srmext/certificates/archives/1941b.pdf.

[4]   National Institute of Standards and Technology(14-June-1993) Certificate of Analysis, Standard Reference Material 1641c Mercury in Water (Acidified with 2% HNO_3). https://tsapps.nist.gov/srmext/certificates/archives/1941c.pdf.

[5]   National Institute of Standards and Technology(8-July-2014) Certificate of Analysis, Standard Reference Material 1641d Mercury in Water (Acidified to 2% Nitric Acid). https://tsapps.nist.gov/srmext/certificates/archives/1941d.pdf.

[6]   National Institute of Standards and Technology(22-July-2019) Certificate of Analysis, Standard Reference Material 1641e Mercury in Water. https://tsapps.nist.gov/srmext/certificates/1641e.pdf.

[7]   National Institute of Standards and Technology(22-December-2016) Certificate of Analysis, Standard Reference Material 3133 Mercury (Hg) Standard Solution. https://tsapps.nist.gov/srmext/certificates/3133.pdf.

[8]   U.S. EPA (1998) Method 7473 (SW-846): Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry," Revision 0. https://www.epa.gov/esam/epa-method-7473-sw-846-mercury-solids-and-solutions-thermal-decomposition-amalgamation-and. Accessed 9/20/2024.

[9]   Milestone (2019) Industry Report: Determination of Total Mercury in Environmental Samples. https://www.milestonesci.com/wp-content/uploads/2019/07/Industry-report-DMA-80-Environmental-USREV062019.pdf. Accessed 9/20/2024.

[10]   JCGM 100:2008 (2008) Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement. Joint Committee for Guides in Metrology. http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf. See also: Taylor BN, Kuyatt CE (1994) Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. NIST Technical Note 1297 https://doi.org/10.6028/NIST.TN.1297.

[11]   Christopher SJ, Long SE, Rearick MS, Fassett JD (2001) 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 73(10):2190-2199. https://doi.org/10.1021/ac0013002.

[12] Ragland JM (2022). Isotope Dilution Assistant (IDA) (Version 1.0) [Computer software]. https://github.com/jmr-nist-gov/IDA. Accessed 9/20/2024.

[13] IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW), molecular weight calculator. https://ciaaw.shinyapps.io/calculator/. Accessed J9/20/2024.

[14] Possolo A, van der Veen AMH, Meija J, Hibbert DB (2018) Interpreting and propagating the uncertainty of the standard atomic weights (IUPAC Technical Report). Pure Appl Chem 90:395-424. https://doi.org/10.1515/pac-2016-0402.

[15] Meija J, Coplen TB, Berglund M, Brand WA, De Bièvre P, Gröning M, Holden NE, Irrgeher J, Loss RD, Walczyk T, Prohaska T (2016) Isotopic compositions of the elements 2013 Pure and Applied Chemistry 88, 293-306. https://doi.org/10.1515/pac-2015-0503.
See also: IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW). Isotopic compositions of the elements 2021. Available online at www.ciaaw.org.

[16] JCGM 101:2008 (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. http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf.

[17] Searle SR, Casella G, McCulloch CE (1992) Variance Components. John Wiley, Hoboken, NJ. https://doi.org/10.1002/9780470316856.

[18] Efron B, Tibshirani RJ (1994) An Introduction to the Bootstrap. Chapman and Hall/CRC. https://doi.org/10.1201/9780429246593.

Appendix A. List of Acronyms and Symbols

A.1. Acronyms

CSD   Chemical Sciences Division
DC-AAS   direct combustion atomic absorption spectrometry
ICP-MS   inductively coupled plasma-mass spectrometry
ID-MS   isotope dilution mass spectrometry
ID-CV-ICP-MS   isotope dilution-cold vapor-inductively coupled plasma-mass spectrometry
IUPAC   International Union of Pure and Applied Chemistry
NIDC   National Isotope Development Center
NIST   National Institute of Standards and Technology
ORM   Office of Reference Materials
RMSD   root mean square deviation
SI   International System of Units (Système international d'unités)
SRM®   Standard Reference Material®

A.2. Symbols

a coefficient of a function
A natural fractional abundance of the reference isotope
A_{Hg} mercury peak area
A_i the ith type "A" component of uncertainty
A_s fractional abundance of the reference isotope in the spike
b coefficient of a function
B natural fractional abundance of the spike isotope
B_i the ith type "B" component of uncertainty
B_s fractional abundance of the spike isotope in the spike
c coefficient of a function
d coefficient of a function
F discrimination correction factor for measured ratio R
K natural to spike atomic weight ratio
m mass
n number
R detector dead-time corrected (reference isotope/spike isotope) ratio
$u(\cdot)$ standard uncertainty of a given quantity
$U_{95}(\cdot)$ approximate 95 % level of confidence expanded uncertainty of a given quantity
v effective degrees of freedom
w mass fraction