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Comparison of mass bias correction models for the examination of isotopic composition of mercury using sector field ICP-MS†

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Six mass bias correction models, *viz.*, linear law, power law, exponential law, Russell equation, common analyte internal standardization (CAIS) and polynomial function, were evaluated for the measurement of the isotopic composition of a natural abundance mercury standard solution using a sector field ICP-MS instrument. Thallium, Os and Ir were tested as internal standards. Significant differences in resultant isotope abundances were noted when the various mass bias correction models and different internal standards were used for instrument mass bias correction. The isotopic abundances calculated from Hg ratios corrected for mass bias using a polynomial function with Os, Ir and Tl as internal standards resulted in data having the smallest relative difference (Df) from IUPAC values, which were selected as common reference points. No significant Df in results arose when the power law, exponential law and Russell equation models for mass bias correction were used in conjunction with the Tl internal standard, these exhibiting the next smallest Df values. Hg isotope abundances having the third smallest Df values arose with a linear law model. Of the three internal standards examined, use of Tl for mass bias correction provided the smallest Df values with these four models, which only require one pair of isotopes from a reference standard. The CAIS model produced the largest Df values in this study.

Introduction

Thermal ionization mass spectrometry (TIMS) remains the technique of choice for highest accuracy and precision of isotope abundance ratio determinations,[1] despite the investment of extensive sample preparation and long measurement times necessary to achieve such performance. On the other hand, inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for trace and ultra-trace element determinations since its commercialization in 1983, due to its high sensitivity, large dynamic range and multi-element capability. One of the most attractive features of ICP-MS is its capability for determination of elemental isotopic composition with high sample throughput. Unfortunately, the precision of such ratios measured by quadrupole based ICP-MS is relatively poor[2–6] and usually lies in the range of 0.05–1%. Recent developments in sector field single and multi-collector ICP-MS have brought a new dimension to this analytical field. In addition to high mass resolution and enhanced sensitivity, unique flat topped peaks produced in low resolution mode provide for a more accurate and precise isotope ratio measurement.[7–14] This has been reported to reach 0.01% precision with a single detector and as low as 0.001% with multi-collector detection, comparable to performance achieved with TIMS.

Two major effects, detector dead time and instrument mass bias, must be compensated for to achieve accurate isotope ratio measurements when using an ion counting detection system with single detector ICP-MS systems. Detector dead time is the time during which the ion counting system is unable to respond to incoming ions after the impact of a previous ion event and is a feature of both the detector itself and the ion counting electronics. This leads to counting losses that increase in magnitude as the counting rate increases, resulting in inaccurate isotope ratio measurements if not accounted for.[15–19] A recent publication by Nelms *et al.*[18] evaluated four popular dead time calculation models used for ICP-MS and concluded that all four models gave similar results for the estimation of this parameter. A method in which the dead time was derived from a plot of the measured $^{204}Pb/^{208}Pb$ ratio *versus* Pb concentration was recommended as it generated a clear, unambiguous value for the dead time and a systematic approach to deriving the uncertainty in the resulting value could be obtained. The same model was thus used in this study to determine detector dead time. Wegscheider and Meisel[19] also reported similar results, concluding that no biased dead time corrections were obtained using the investigated models.

Mass bias occurs when ions of different mass are transmitted through the mass spectrometer with different efficiencies within the ICP-MS instrument, mainly due to space charge effects, resulting in non-uniform response (sensitivity) across the mass range and inaccurate isotope ratio measurements.[20,21] In general, mass bias can be corrected using one of the following two methods. With external standardization, the isotope ratio of the analyte in a calibration solution is measured and the mass bias correction factor is calculated using the true ratio (R^{true}) divided by the experimentally determined ratio (R^{obs}). The mass bias correction factor obtained is then used for the mass bias correction of the analyte in samples. There are several drawbacks associated with this method. High concentrations of elements in the sample matrix result in increased space charge effects, which enhance the mass bias in the sample compared with that in the calibration solution, leading to inaccurate correction. Mass bias drift during data acquisition may also lead to improper correction. Furthermore, this method is not applicable to elements whose isotopic abundance varies in nature, as in the case of Pb, or for enriched isotope spikes because of a lack of standards having accurate isotopic composition.

The second method used for mass bias correction, based on internal standardization, has been used more frequently in the

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last decade for accurate isotope ratio measurements. The correction factor is determined in the sample solution either by using one or more isotope ratios of one or more reference elements added to the sample, or by using a pair of isotopes of the analyte element that are invariant in nature.

Various mathematical models have been used for extrapolating mass bias corrections in order to achieve accurate isotope ratio measurements.[17,20,21] Three commonly used standard functions include a linear law (eqn. 1), a power law (eqn. 2) and an exponential law (eqn. 3), *i.e.*:

$$R^{\text{obs}} = R^{\text{true}} (1 + \varepsilon_{\text{linear}} \Delta M) \quad (1)$$

$$R^{\text{obs}} = R^{\text{true}} (1 + \varepsilon_{\text{power}})^{\Delta M} \quad (2)$$

$$R^{\text{obs}} = R^{\text{true}} \cdot e^{\varepsilon_{\text{exp}} \cdot \Delta M} \quad (3)$$

where R^{obs} is the experimentally measured ratio, R^{true} the true ratio, ΔM the mass difference between the isotopes of interest and ε the mass bias per mass unit in each of the functions. From the above equations, it is evident that mass bias corrections are all dependent on the mass difference between the measured isotopes and not on the absolute masses, and thus may not reflect the real situation. In general, a linear law can be accurately applied to the third decimal place, a power law is good to the fourth decimal place, and an exponential law can accurately predict and correct for mass fractionation to the fifth decimal place when a proper internal standard is used.[20]

An improved model, first described by Russell *et al.*[22] and referred to as the Russell equation throughout this paper, has been used for mass bias correction for ratio measurements by several research groups.[10,12,13,23] The equation used is:

$$R^{\text{obs}} = R^{\text{true}} \cdot \left(\frac{m_2}{m_1}\right)^f \quad (4)$$

where m_1 and m_2 are the masses of the isotopes of interest for the ratio R and f is the mass bias factor. The Russell correction model generally employs one pair of isotopes of an internal reference element for the mass bias correction for the analyte. For example, Tl was used as an internal standard for mass bias correction for Pb isotope ratios measurements.[10,12]

Al-Ammar and Barnes[24] suggested that use of only one internal reference isotope pair may be insufficient to achieve absolute mass bias correction and thus proposed an alternative model (eqn. 6) called the common analyte internal standardization (CAIS) approach, based on the instrument response function:

$$S = \text{a} \ln m + \text{c} \quad (5)$$

where S is the isotope sensitivity at mass number m, and a and c are constants. The CAIS equation used for mass bias correction is given by:

$$\frac{R^{\text{true}}}{R^{\text{obs}}} = \frac{\Delta M}{S_1} \cdot \frac{\text{a}}{m_1} + 1 \quad (6)$$

where ΔM is the mass difference between the isotopes of interest, S_1 is the sensitivity of the light isotope of an element and m_1 is the mass of the light isotope. Under conditions wherein the analyte and internal reference element are close in mass and the variation of S is very small compared with the variation of m, S can be regarded as constant. The correction is obtained by measuring several internal reference isotope ratios simultaneously with the analyte followed by plotting $R^{\text{true}}/R^{\text{obs}}$ for the reference isotopes against $1/m$. The resulting linear plot is used to calculate the correction factor. By using the CAIS model, an accuracy of 0.02% was obtained for Ga, Br and Re ratio measurements.[24]

Recently, a new approach to the estimation and correction of mass bias based on a polynomial function as the instrument response has been proposed by Ingle *et al.*[21] and applied successfully to the determination of isotope ratios of Cd. The following equations were used to derive a and b values for the mass bias correction for ratio measurements:

$$R^{\text{obs}} = R^{\text{true}} \cdot \frac{\text{a}m_2^2 + \text{b}m_2 + 1}{\text{a}m_1^2 + \text{b}m_1 + 1} \quad (7)$$

$$E^{\text{obs}} = \frac{R^{\text{obs}} - R^{\text{true}}}{R^{\text{true}}} \quad (8a)$$

$$E^{\text{obs}} = \frac{\text{a}(m_2^2 - m_1^2) + \text{b}(m_2 - m_1)}{\text{a}m_1^2 + \text{b}m_1 + 1} \quad (8b)$$

where a and b are constants, m_1 and m_2 are the masses of the isotopes used in the ratio and E^{obs} is the fractional error in an isotope ratio measurement. The constants a and b were derived using the Solver optimisation function in Microsoft Excel to find values which minimise the sum of the squared differences between E^{obs} calculated from the instrument data and that predicted by eqn. 8b. The authors[21] found that this polynomial function and the Russell equation consistently provided better mass bias correction compared with the power and exponential laws for measurement of isotope ratios of Cd.

The objective of this study was to evaluate the above six mass bias correction models for application to the determination of Hg isotope ratios. Mercury was selected for this study because of current efforts in our laboratory to characterise the isotopic composition of inorganic and methylmercury calibration solutions being considered as reference material candidates. Using a natural abundance Hg standard, all models were evaluated in terms of their relative difference compared with IUPAC values. It is acknowledged that the IUPAC isotopic composition of mercury is not "absolute" and may suffer not only from systematic error due to inaccurate mass bias correction[25] but also from fractionation arising from distillation processes. Additionally, the source of mercury used in this study may itself be fractionated. Nevertheless, the focus of this study was a comparative assessment of isotopic composition arising from the application of the various mass bias correction models to converge upon a consistent set of data. The degree of divergence of the resulting sets of data (termed the "relative difference, Df") from a benchmark point selected to be the current IUPAC set, was tabulated. Clearly, there is no means of assessing the "accuracy" of the results under these conditions, but the relative performance of the mass bias correction procedures can be assessed to highlight the fact that they lead to different results.

Experimental section

Instrumentation

The SF-ICP-MS instrument used in this work was a ThermoFinnigan Element2 (Bremen, Germany), equipped with a Scott-type double pass glass spray chamber and a PFA self aspirating nebulizer (Elemental Scientific, Omaha, NE, USA) operating at 100 μl min^{-1}. A plug-in quartz torch with a sapphire injector and a Ag guard electrode were used. Optimization of the Element2 was performed as recommended by the manufacturer and typical operating conditions are summarized in Table 1.

Detector dead time was obtained using method 2 recommended by Nelms *et al.*,[18] based on plots of measured analyte isotope ratio *versus* concentration. To determine detector dead time, a $^{238}\text{U}/^{235}\text{U}$ ratio was measured in three U standard solutions at concentrations of 0.5, 1.0 and 2.5 ng ml^{-1}. A dead time of 18 ± 1 ns (one calculated uncertainty) was derived from a plot of the measured $^{238}\text{U}/^{235}\text{U}$ ratios *versus* U concentration at a slope of zero.

Table 1 ICP-MS operating conditions

Rf power	1150 W
Plasma Ar gas flow rate	15.0 l min^{-1}
Auxiliary Ar gas flow rate	1.05 l min^{-1}
Ar carrier gas flow rate	1.16 l min^{-1}
Sampler cone (nickel)	1.1 mm
Skimmer cone (nickel)	0.8 mm
Dead time	18 ns
Resolution	300
Data acquisition	E-scan, 5 runs 275 passes, 5% mass window, 0.0050 s sample time, 200 samples per peak

Reagents and solutions

Hydrochloric and nitric acids were purified in-house prior to use by subboiling distillation of reagent grade feedstock in a quartz still. High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). A 0.2 N BrCl solution was prepared in a fume hood by dissolving 27 g of KBr (Fisher Scientific, Nepean, Canada) in 2.5 l HCl then slowly adding 38 g of $KBrO_3$ while stirring. The 500 ng ml^{-1} Tl, 500 ng ml^{-1} Ir and 1 μg ml^{-1} Os standard solutions were prepared by diluting individual 1000 μg ml^{-1} stock solutions (SCP Science, Canada).

"Natural abundance" high purity Hg metal was purchased from Johnson Matthey & Co. Ltd. (London, UK). A 1000 μg ml^{-1} stock solution was prepared in 5% HCl (since Hg is known to form stable $HgCl_2$ or Hg_2Cl_2). A 2.5 μg ml^{-1} Hg standard solution was prepared by dilution of the stock solution in 1% HCl containing 0.002 N BrCl solution in order to minimize memory effects in the spray chamber.

Sample preparation and analysis procedure

Ten replicate 20 ng ml^{-1} solutions of natural abundance Hg were prepared for isotope ratio measurements to assess the mass bias correction models. A 0.2 ml volume of 2.5 μg ml^{-1} Hg along with 0.05 ml each of 500 ng ml^{-1} Ir and Tl, 0.125 ml of 1 μg ml^{-1} Os and 0.25 ml of 0.2 N BrCl solution were pipetted into a 25 ml clean glass volumetric flask and the contents were diluted with DIW to 25 ml. No significant Hg memory effect was observed when using 0.002 N BrCl in 1% HCl solution as sample matrix and wash solution; the Hg signal ($>2.5 \times 10^6$ cps) was reduced to its base line level within several minutes (<5 min) of washing.

For achieving best results, samples were introduced continuously and the following isotopes were simultaneously monitored: ^{188}Os, ^{189}Os, ^{190}Os, ^{192}Os, ^{191}Ir, ^{193}Ir, ^{195}Pt, ^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{204}Hg, ^{203}Tl, ^{205}Tl and ^{208}Pb. Data acquisition parameters are summarized in Table 1. Ten measurements were made on each sample solution. Small isobaric interferences from ^{196}Pt and ^{198}Pt on respective Hg isotopes were corrected based on the ratio measurements of $^{196}Pt/^{195}Pt$ and $^{198}Pt/^{195}Pt$ derived from a high purity Pt solution introduced on several occasions throughout a run sequence. The contribution from ^{204}Pb to ^{204}Hg was insignificant, thus the interference was corrected using the IUPAC recommended value for the ratio of $^{204}Pb/^{208}Pb$ of 0.0267.

Results and discussion

Mass bias correction with linear, power and exponential law models

As noted earlier, mass bias in ICP-MS arises primarily as a result of space charge effects and hence should be dependent on the mass of the analyte ion. This implies that the mass bias for two elements having similar mass should be similar. As a consequence, Tl was first tested as an internal reference from which mass bias correction for Hg isotope ratio measurements could be derived because ^{203}Tl and ^{205}Tl isotopes are close in mass to the isotopes of Hg. Calculated $^{196}Hg/^{200}Hg$, $^{198}Hg/^{200}Hg$, $^{199}Hg/^{200}Hg$, $^{201}Hg/^{200}Hg$, $^{202}Hg/^{200}Hg$, $^{204}Hg/^{200}Hg$ ratios were corrected for mass bias based on the $^{203}Tl/^{205}Tl$ ratio correction using linear, power and exponential law functions. Isotope abundances for Hg were then calculated and reported in Table 2. The relative difference, Df, in percent, between the measured isotope abundance and the IUPAC recommended value was calculated as follows:

$$\mathrm{Df}(\%) = \frac{A^{\mathrm{obs}} - A^{\mathrm{IUPAC}}}{A^{\mathrm{IUPAC}}} \cdot 100 \qquad (9)$$

where A^{obs} is the experimentally measured Hg isotope abundance and A^{IUPAC} is the IUPAC recommended Hg isotope abundance value. As expected, the relative difference of measured abundances decreased when power and exponential laws were used to calculate mass bias correction as compared with linear law corrections. No significant difference in Df was observed between results generated using a power law and an exponential law for mass bias correction.

For comparison, two additional pairs of isotope ratios, *i.e.*,

Table 2 Hg isotope abundances arising from a natural abundance Hg standard solution obtained using different mass bias correction models (presented as mean with one standard deviation on the last two digits of the number; $n = 10$)

Mass bias correction models	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg	$\sqrt{\sum \mathrm{Df}^2}$
IUPAC	0.153 44 ± 19	9.968 ± 13	16.873 ± 17	23.096 ± 26	13.181 ± 13	29.863 ± 33	6.865 ± 7	
Linear ($^{203}Tl/^{205}Tl$)	0.153 21 ± 46	10.0072 ± 97	16.9030 ± 72	23.1207 ± 87	13.1857 ± 48	29.796 ± 15	6.8343 ± 77	
Df (%)	−0.15	0.39	0.18	0.11	0.04	−0.22	−0.45	0.686
Power ($^{203}Tl/^{205}Tl$)	0.152 97 ± 42	9.997 ± 13	16.892 ± 12	23.1152 ± 84	13.1887 ± 57	29.811 ± 18	6.8434 ± 77	
Df (%)	−0.31	0.29	0.11	0.08	0.06	−0.17	−0.31	0.572
Exponential ($^{203}Tl/^{205}Tl$)	0.152 97 ± 42	9.997 ± 13	16.892 ± 11	23.1152 ± 84	13.1887 ± 57	29.814 ± 18	6.8434 ± 77	
Df (%)	−0.31	0.29	0.11	0.08	0.06	−0.17	−0.31	0.572
Exponential ($^{191}Ir/^{193}Ir$)	0.155 08 ± 32	10.0739 ± 22	16.9724 ± 56	23.1575 ± 89	13.1741 ± 51	29.6912 ± 79	6.7759 ± 58	
Df (%)	1.07	1.06	0.59	0.27	−0.05	−0.58	−1.30	2.17
Exponential ($^{190}Os/^{192}Os$)	0.154 64 ± 27	10.0578 ± 35	16.9555 ± 52	23.1487 ± 77	13.1771 ± 51	29.7163 ± 73	6.7899 ± 28	
Df (%)	0.78	0.90	0.49	0.23	−0.03	−0.49	−1.09	1.78
Russell ($^{203}Tl/^{205}Tl$)	0.152 90 ± 42	9.995 ± 13	16.890 ± 11	23.1148 ± 84	13.1893 ± 58	29.814 ± 18	6.8443 ± 77	
Df (%)	−0.35	0.27	0.10	0.08	0.06	−0.16	−0.30	0.577
Russell ($^{191}Ir/^{193}Ir$)	0.155 08 ± 34	10.0745 ± 19	16.9731 ± 50	23.1580 ± 86	13.1740 ± 50	29.6901 ± 73	6.7752 ± 52	
Df (%)	1.07	1.07	0.59	0.27	−0.05	−0.58	−1.31	2.18
Russell ($^{190}Os/^{192}Os$)	0.154 68 ± 28	10.0593 ± 38	16.9572 ± 50	23.1497 ± 75	13.1769 ± 51	29.7139 ± 72	6.7883 ± 24	
Df (%)	0.81	0.92	0.50	0.23	−0.03	−0.50	−1.12	1.81

$^{191}Ir/^{193}Ir$ and $^{190}Os/^{192}Os$, were tested for mass bias correction efficacy as they are second and third best candidates in terms of a mass match to the Hg isotopes. Only the exponential law was tested for Ir and Os internal standards. As is shown in Table 2, much larger Df values were obtained when attempting to use these internal references for mass bias correction, suggesting that Tl is better for this purpose.

Mass bias correction based on the Russell correction model

Results for Hg isotope abundances obtained using Tl, Os and Ir as internal mass bias correction reference standards based on the Russell approach are also summarized in Table 2. Since the Russell correction model depends on the absolute masses of the isotopes comprising the ratio (eqn. 4), it should provide better mass bias correction when compared with the use of power and exponential laws, as already reported by others.[21] Consistent with this, a slight decrease in the Df of several isotope ratio abundances was obtained using this approach for mass bias correction when Tl was selected as the internal reference. No significant decreases in the Df values of the Hg isotope abundances were obtained using the Russell equation for mass bias correction when Os and Ir were selected as internal reference standards compared with those obtained using the power or exponential law models. With the Russell correction model, the Tl internal reference standard continued to generate the best estimate of mass bias for Hg ratios compared with the other internal standards studied here.

Mass bias correction using the CAIS model

At least two isotope ratios derived from the isotopes of one or more internal reference elements are required to apply eqn. 6 of the CAIS model for mass bias correction. In addition to selecting internal references having mass numbers close to that of the analyte, ΔM should be the same for all the measured isotope ratios for the internal references and the analyte. Thus, Hg isotope ratios were divided into two groups in order to optimise mass bias correction: group 1 ($\Delta M = 1$) includes $^{199}Hg/^{200}Hg$ and $^{200}Hg/^{201}Hg$; and group 2 ($\Delta M = 2$) includes $^{196}Hg/^{198}Hg$, $^{198}Hg/^{200}Hg$, $^{200}Hg/^{202}Hg$ and $^{202}Hg/^{204}Hg$. To satisfy the above requirements for use of the CAIS model, internal reference isotope ratios of $^{188}Os/^{190}Os$, $^{190}Os/^{192}Os$, $^{191}Ir/^{193}Ir$ and $^{203}Tl/^{205}Tl$ were chosen for group 2 ($\Delta M = 2$) to calculate mass bias based on eqn. 6. Since there are no available elements whose isotopic compositions are invariant in nature, having one mass unit difference in the mass number range 200–210, the equation $R^{true}/R^{obs} = 1 + \Delta M\varepsilon$, suggested by Al-Ammar and Barnes[24] in the original CAIS model, was used to calculate ratios of m/z at 191/192 using $^{191}Ir/^{193}Ir$ and 203/204 using $^{203}Tl/^{205}Tl$ to generate additional points for eqn. 6, along with ratios of $^{188}Os/^{189}Os$ and $^{189}Os/^{190}Os$ to calculate mass bias for group 1 isotopes ($\Delta M = 1$).

The mass bias corrected $^{196}Hg/^{200}Hg$ ratio was obtained using the mass bias corrected $^{196}Hg/^{198}Hg$ ratio multiplied by the mass bias corrected $^{198}Hg/^{200}Hg$ ratio. Similarly, mass bias corrected $^{201}Hg/^{200}Hg$ and $^{202}Hg/^{200}Hg$ ratios were obtained from the reciprocals of the mass bias corrected $^{200}Hg/^{201}Hg$ and $^{200}Hg/^{202}Hg$ ratios, respectively. The mass bias corrected $^{204}Hg/^{200}Hg$ ratio was obtained using eqn. 10:

$$R^{204/200} = \frac{1}{R^{200/202} \cdot R^{202/204}} \quad (10)$$

where $R^{200/202}$ and $R^{202/204}$ are the mass bias corrected Hg isotope ratios. Hg isotope abundances, calculated from ratios of $^{196}Hg/^{200}Hg$, $^{198}Hg/^{200}Hg$, $^{199}Hg/^{200}Hg$, $^{201}Hg/^{200}Hg$, $^{202}Hg/^{200}Hg$ and $^{204}Hg/^{200}Hg$, are reported in Table 3. Clearly, absolute values of Df for these data obtained using the CAIS model are larger than those obtained with the power, exponential or Russell models based on Tl as the internal standard.

It was noted in preliminary studies that the mass bias correction factor for $^{191}Ir/^{193}Ir$ based on R^{true}/R^{obs} falls slightly out of the series trend of those comprising $^{188}Os/^{189}Os$, $^{189}Os/^{190}Os$, $^{188}Os/^{190}Os$, $^{190}Os/^{192}Os$, $^{191}Ir/^{193}Ir$ and $^{203}Tl/^{205}Tl$. Mercury isotope abundances were therefore recalculated using only Os and Tl as internal standards with the CAIS model. The square root of the sum of the squares of Df of Hg abundances decreased slightly under this condition. Overall, data show that the CAIS model for mass bias correction of Hg isotope ratio measurements results in the largest square root of the sum of the squares of Df in Hg abundances as compared to the power, exponential and Russell models, contrary to the improvements reported by Al-Ammar and Barnes[24] for Ga, Br and Re ratio measurements.

Mass bias correction based on the polynomial model

A polynomial model for mass bias correction was proposed by Ingle *et al.*[21] and is based on a second order polynomial instrument response function. A recent study by Quétel *et al.*[26] has shown that a similar instrument response curve exists for the Element2. To account for sample matrix effects, the use of internal standardisation to determine the constants a and b in eqns. 7 and 8b was recommended by Ingle *et al.*[21] in their study. Because at least two isotope ratios derived from internal reference elements are required to apply eqns. 7 and 8b, Os, Ir and Tl were chosen to test this model and ratios of $^{188}Os/^{189}Os$, $^{189}Os/^{190}Os$ $^{188}Os/^{190}Os$, $^{190}Os/^{192}Os$, $^{191}Ir/^{193}Ir$ and $^{203}Tl/^{205}Tl$ were used to calculate values of a and b. The "Solver" function in Microsoft Excel was initially tested to find optimum a and b values that minimise the sum of the squared differences between E^{obs} calculated from the above measured isotope ratios (eqn. 8a) and that predicted by the response model of eqn. 8b.[21] Unfortunately, it was found that Solver could not isolate unique optima for these parameters from a given set of data; different values were generated if different initial values for a and b were used. This may arise because E^{obs} predicted from the model may be insensitive to the absolute values of the

Table 3 Hg isotope abundances arising from a natural abundance Hg standard solution obtained using CAIS and polynomial mass bias correction models (presented as mean with one standard deviation on the last two digits of the number; $n = 10$)

Internal standards	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg	$\sqrt{\sum Df^2}$
IUPAC	0.153 44 ± 19	9.968 ± 13	16.873 ± 17	23.096 ± 26	13.181 ± 13	29.863 ± 33	6.865 ± 7	
CAIS (Os, Ir and Tl)	0.153 71 ± 35	10.0186 ± 91	16.9115 ± 86	23.1211 ± 80	13.1824 ± 53	29.781 ± 14	6.8321 ± 58	
Df (%)	0.18	0.51	0.23	0.11	0.01	−0.27	−0.48	0.811
CAIS (Os and Tl)	0.153 58 ± 37	10.014 ± 10	16.905 ± 10	23.1192 ± 81	13.1846 ± 55	29.788 ± 15	6.8355 ± 65	
Df (%)	0.09	0.46	0.19	0.10	0.03	−0.25	−0.43	0.719
Polynomial model (Os, Ir and Tl)	0.153 28 ± 43	9.998 ± 13	16.887 ± 14	23.104 ± 11	13.1845 ± 52	29.816 ± 23	6.857 ± 11	
Df (%)	−0.10	0.30	0.08	0.04	0.03	−0.16	−0.11	0.387
Polynomial model (Os and Tl)	0.153 45 ± 36	10.0076 ± 97	16.8985 ± 98	23.1132 ± 98	13.1840 ± 54	29.799 ± 16	6.8443 ± 74	
Df (%)	0.01	0.40	0.15	0.07	0.02	−0.21	−0.30	0.569

a and b coefficients since their values are generally very small for the second order polynomial function used.

To solve this problem, a different optimisation approach was used, based on regression analysis to generate correct a and b values. By rearranging eqn. 8b, eqn. 11 can be obtained.

$$E^{obs} = a(m_2^2 - m_1^2 - m_1^2 E^{obs}) + b(m_2 - m_1 - m_1 E^{obs}) \quad (11)$$

Making the following substitutions: $z = E^{obs}$, $x = m_2^2 - m_1^2 - m_1^2 E^{obs}$ and $y = m_2 - m_1 - m_1 E^{obs}$ the following equation arises:

$$z = ax + by \quad (12)$$

For a set of measured ratios of $^{188}Os/^{189}Os$, $^{189}Os/^{190}Os$, $^{188}Os/^{190}Os$, $^{190}Os/^{192}Os$, $^{191}Ir/^{193}Ir$ and $^{203}Tl/^{205}Tl$, *x*, *y* and *z* values can be calculated. By applying the "Regression" function in Microsoft Excel to the calculated *x*, *y* and *z* data set (treat *z* values as "Input y range", both *x* and *y* values for "Input x range" and check "Constant is zero"), a and b values can be obtained from the coefficients generated for the two variables, *x* and *y*. Typical values of 0.000 031 4 and −0.012 05 were obtained for a and b, respectively: indeed very small values. Measured Hg isotope ratios were subsequently corrected for mass bias using eqn. 7 and results based on this model are reported in Table 3. Clearly, as shown in Table 3, absolute values of Df for Hg isotope abundances obtained with this polynomial model using Os, Ir and Tl are smaller than those obtained with any of the other five models.

For comparison, Hg isotopic abundances were also recalculated with only Os and Tl as internal standards using the polynomial model. Better precisions (smaller standard deviations) in 10 measured Hg isotope abundances were obtained, while slightly larger Df values were generated. A value of 0.569 for the square root of the sum of the squares of Df for Hg isotope abundances was obtained using the polynomial model with Os and Tl internal standards, still slightly better than those obtained with the power, exponential and Russell models using Tl as the internal standard. Among the six models, a smallest value of 0.387 for the square root of the sum of the squares of Df for Hg isotope abundances was obtained using the polynomial model with Os, Ir and Tl as the internal standards. These observations suggest that the polynomial model provides the best estimation of mass bias correction for Hg isotope ratio measurements based on current IUPAC values.

In recent studies by Evans *et al.*[27] and Klaue *et al.*,[28] all seven isotopes of Hg were measured in Almaden cinnabar using different MC-ICP-MS instruments. For comparison purposes, Hg isotope abundances were calculated based on their reported mass bias corrected ratios and results are summarized in Table 4. Clearly, Hg isotope abundances measured using the same Almaden cinnabar apparently vary significantly when using different MC-ICP-MS instruments. This suggests that corrections implemented by these authors for mass bias correction are inconsistent. Although modern MC-ICP-MS instrumentation can attain a precision of 0.001% for Hg isotope ratio measurement, any inaccuracy in a mass bias correction will still degrade the accuracy of this result.[25] As expected, precisions in Hg isotope abundances measured using the single collector SF-ICP-MS Element2 in this study are 10-fold inferior to those reported using MC-ICP-MS instruments.

Conclusion

Six mass bias correction models having different internal standards produced significantly different results for Hg isotope abundances, highlighting that proper mass bias correction is of paramount importance in achieving accurate isotope ratio results. No significant difference was observed in the Df values of Hg isotope abundances obtained using a power law, an exponential law or Russell equation models with Tl as an internal standard. Surprisingly, the CAIS model for mass bias correction of Hg isotope ratio measurements resulted in the largest square root of the sum of the squares of Df in Hg abundances with the Element2. This may largely be due to not having suitable and sufficient internal standard isotope pairs available over the Hg isotope mass range, or the instrument response function used for quadrupole ICP-MS to derive the CAIS model may not reflect the true response function for the Element2. In order to have proper correction of mass bias for ratio measurements, different mass bias correction models may be preferable for different instrumentation.

As demonstrated in recent studies,[25,27,28] although the precision required in Hg ratio measurements can be achieved with MC-ICP-MS instruments to differentiate natural variations in Hg isotope ratios among different cinnabar ores, the accuracy of such results cannot be validated due to the lack of a precisely certified Hg isotopic abundance standard. Such a Hg certified reference material (CRM) having precise isotopic composition is urgently needed to validate methodologies for absolute Hg ratio measurements and to enable comparison of results obtained by different research teams. For this reason,

Table 4 Hg isotope abundances determined in cinnabar and a natural abundance Hg standard solution obtained using different instruments (presented as mean with one standard deviation on the last two digits of the number), as reported in recent literature

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg	$\sqrt{\sum Df^2}$
IUPAC	0.153 44 ± 19	9.968 ± 13	16.873 ± 17	23.096 ± 26	13.181 ± 13	29.863 ± 33	6.865 ± 7	
Plasma 54[28] (cinnabar)	0.154 103 ± 10	10.034 56 ± 32	16.936 45 ± 48	23.136 33 ± 86	13.170 19 ± 38	29.749 69 ± 32	6.818 628 ± 73	
Df (%)	0.43	0.67	0.38	0.17	−0.08	−0.38	−0.68	1.19
Axiom[27] (cinnabar)	0.154 723 ± 14	10.064 41 ± 29	16.966 06 ± 38	23.152 01 ± 15	13.167 78 ± 12	29.697 30 ± 15	6.797 711 ± 34	
Df (%)	0.84	0.97	0.55	0.24	−0.10	−0.55	−0.98	1.81
Isoprobe[27] (cinnabar)	0.157 936 5 ± 75	10.038 34 ± 39	16.935 79 ± 378	23.137 26 ± 33	13.173 28 ± 17	29.743 23 ± 19	6.814 173 ± 43	
Df (%)	2.93	0.71	0.37	0.18	−0.06	−0.40	−0.74	3.16
Nu Plasma[27] (cinnabar)	0.143 625 ± 24	10.044 81 ± 42	16.946 53 ± 53	23.143 51 ± 51	13.173 04 ± 21	29.735 97 ± 25	6.812 512 ± 58	
Df (%)	−6.40	0.77	0.44	0.21	−0.06	−0.43	−0.76	6.52
Element2 (Hg std. this study; $n = 10$)	0.153 28 ± 43	9.998 ± 13	16.887 ± 14	23.104 ± 11	13.1845 ± 52	29.816 ± 23	6.857 ± 11	
Df (%)	−0.10	0.30	0.08	0.04	0.03	−0.16	−0.11	0.387

[a]Uncertainties reported for cinnabar are internal precision calculated from data in ref. 27.

the accuracy of the Hg isotopic abundances measured in this study cannot be claimed at this point.

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