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Effects of Mercury and Thallium Concentrations on High Precision Determination of Mercury Isotope Composition by Neptune Plus Multiple Collector Inductively Coupled Plasma Mass Spectrometry

Runsheng Yin[a, b, *], David P. Krabbenhoft[c], Bridget A. Bergquist[d], Wang Zheng[e], Ryan F. Lepak[b], James P. Hurley[b, f, *]

[a]State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

[b]Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI, 53706, USA

[c]U.S. Geological Survey, Mercury Research Laboratory, Middleton, WI, 53562, USA

[d]University of Toronto, Department of Earth Sciences, 22 Russell Street, Toronto, Ontario M5S 3B1,Canada

[e]Arizona State University, School of Earth and Space Exploration, Tempe, AZ 85287, USA

[f]Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI, 53706, USA

*contact author: Runsheng Yin (yinrunsheng2002@163.com) and James P. Hurley (jphurley@wisc.edu)

Abstract

Thallium (Tl) has been widely used as an internal standard for mass bias correction during high precision mercury (Hg) isotope ratio measurements using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, a recent study by Georg and Newman[1] indicated the potential for Hg hydrides formation (HgH_x, x=1, 2) during Hg isotope measurements using the X skimmer cone with the Neptune Plus MC-ICP-MS. Mercury hydride formation could result in an artificial change in $^{205}Tl/^{203}Tl$. Due to this observation, the applicability of using Tl as an internal standard for instrumental mass bias correction during high precision Hg isotope measurements has been questioned. In this study, using an adapted gas/liquid phase separator for Hg introduction and NIST SRM 997 Tl standard for mass bias correction, mercury isotope measurements were performed by the Neptune Plus MC-ICP-MS. While we confirm Georg and Newman's[1] observations, we show that Hg hydride formation is less important when Hg isotope measurements are conducted with high Tl and low Hg concentrations. With careful sample-standard bracketing (with Hg concentration matching within 10%), we demonstrate that measuring 20 to 50 ng mL^{-1} of Tl and 0.5 to 3.0 ng mL^{-1} of Hg, high precision Hg isotope ratio measurements are achievable. We caution researchers using other Hg inlet systems to recognize the importance of Hg and Tl concentrations, and encourage optimization of these values during their Hg isotope measurements.

1. Introduction

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has enabled simultaneous determination of Hg's seven natural stable isotopes (196, 198, 199, 200, 201, 202 and 204)[1-9]. Both mass dependent fractionation (MDF, reported as δ values) and mass independent fractionation (MIF, reported as Δ values) have been observed during a variety of chemical, physical, and biological processes. Large variations of $\delta^{202}Hg$ (~10‰), $\Delta^{199}Hg$ (~10‰) and $\Delta^{200}Hg$ (~1‰) have been reported in environmental samples[10-12]. Mercury

stable isotopes have been successfully used as tracers to understand the sources and fates of Hg in the environment[10-12].

Mercury isotope measurements have been performed by two commercial MC-ICP-MS systems, Nu-Plasma[3, 7] and Thermo Finnigan Neptune[1-2, 4-5, 8-9]. To enhance the ion sampling efficiency and overall sensitivity, the new generation Neptune Plus MC-ICP-MS have combined modified skimmer and sample cone geometries with enhanced interface pumping configuration[13]. Compared to the H cone geometry, the X skimmer cone has been shown to result in a seven-fold increase in sensitivity for Tl, and a 10-20% increase in sensitivity for Hg[1]. Thus, the sample quantity needed for isotope ratio measurements can be significantly reduced. However, concern has been recently raised by the observation of Hg hydride formation (HgH_x) when using the high-sensitivity X skimmer cones with a Neptune MC-ICP-MS equipped with the Plus upgrade[1]. Hg hydride formation has shown to result in increased ^{203}Tl beam intensities. Due to close isotopic mass to Hg, Tl has been widely used as an internal standard for instrumental mass bias correction of Hg isotopes[1-9], using the Russell equation to determine the instrumental mass bias factor (β):

$$\beta = \ln[(^{205}Tl/^{203}Tl_{true})/(^{205}Tl/^{203}Tl_{measured})]/\ln(m^{205}/m^{203}) \qquad (1)$$

where $^{205}Tl/^{203}Tl_{true}$ and $^{205}Tl/^{203}Tl_{measured}$ is the true (mass bias corrected) ratio (2.38714) and the measured ratio of $^{205}Tl/^{203}Tl$ for NIST SRM 997 Tl standard, respectively; and m^{205} and m^{203} are the masses of ^{205}Tl and ^{203}Tl, respectively. The estimated β is applied to the mass bias correction of Hg isotopic ratios (equation 2):

$$^{xxx}Hg/^{198}Hg_{true} = {}^{xxx}Hg/^{198}Hg_{measured} \times (m^{xxx}/m^{198})^{\beta} \qquad (2)$$

where $^{xxx}Hg/^{198}Hg_{true}$ and $^{xxx}Hg/^{198}Hg_{measured}$ is the true and measured ratio of $^{xxx}Hg/^{198}Hg$, respectively; m^{xxx} and m^{198} are the masses of ^{xxx}Hg and ^{198}Hg, respectively; and xxx are 199-204 amu. According to Georg and Newman[1], the increase of ^{203}Tl beam intensity due to Hg hydride formation could result in decreased $^{205}Tl/^{203}Tl_{measured}$, which would unavoidably cause artificial effect of the β (according to equation 1) and Hg isotope ratios (according to equation 2). As a result, mercury hydride formation has raised significant concerns not only to users of Neptune Plus MC-ICP-MS, but also to others using Tl for mass bias correction for Hg isotope measurements[1].

In order to confirm whether the concerns of Hg hydride formation were directly applicable to our analyses, we performed a series of independent tests based on well known Hg standard solutions. It is worth noting that measurements by Georg and Newman[1] were mainly based on high Hg concentrations (e.g., 5, 10 and 25 ng mL^{-1}). To our knowledge, most Hg isotope data reported to date were mainly measured at low Hg concentrations (0.5 to 5 ng mL^{-1})[1-9]. Theoretically, effects of Hg hydride formation may be reduced by measuring low Hg concentrations. To test this speculation, we performed Hg isotope analysis at much lower Hg concentrations (0.3 to 3.0 ng mL^{-1}). We acknowledge the potential for discrepancies between the Georg and Newman[1] and our own system due to inlet system differences. The Cetac HGX-200 cold vapor system was used by Georg and Newman[1] and others[1-2, 4-5, 8-9], however we used a adapted gas-liquid phase separator (Figure 1) which initially developed at University of Toronto, Department of Earth Sciences laboratory. Our study, however, was designed to investigate the potential for artifact formation using conditions typical of our laboratory's protocol for geological and environmental samples.

2. Experimental methods

2.1 Instrumentation and mercury isotope determination

Mercury isotopic measurements were conducted on a Neptune Plus MC-ICP-MS housed at the University of Wisconsin-Madison's State Laboratory of Hygiene. The instrument was equipped with the gas-liquid phase separator (Figure 1) and an Apex-Q nebulizer (Elemental Scientific Inc., USA) for Hg and Tl introduction, respectively. Briefly, stannous chloride ($SnCl_2$) was continually pumped along with Hg(II) solutions and allowed to mix prior to being introduced to a frosted glass phase separator, producing gaseous elemental Hg(0). The Hg(0) was then mixed with the dry Tl aerosol generated by the Apex-Q nebulizer before being introduced into the plasma. The Apex-Q nebulizer (free flow-mode) and the glass phase separator were flushed with the "sample" gas (Ar) and "additional" gas (Ar) of the MC-ICP-MS, respectively. NIST SRM 997 Tl standard ($^{205}Tl/^{203}Tl = 2.38714$) was used as an internal standard for simultaneous instrumental mass bias correction of Hg. Seven of the nine faraday cups were used to monitor the ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{203}Tl and ^{205}Tl

isotopes, respectively (Table 1). The nickel X skimmer cone was combined with a jet cone. Hg and Tl concentrations in solutions were monitored by ^{201}Hg and ^{203}Tl signals. The signals for ^{201}Hg and ^{203}Tl were 0.6×10^{-2} and 0.2×10^{-2} V for acid blanks, respectively. Isobaric interferences of ^{196}Pt, ^{198}Pt and ^{204}Pb were evaluated by measuring the peak intensities of ^{194}Pt and ^{206}Pb, and no signals above background were observed (< 10^{-4} V).

Gains of the amplifier associated with each Faraday collector were calibrated for efficiency on a daily basis. Instrumental parameters (e.g., Ar gas flows, torch settings, and lens system) were tuned for a maximum ion intensity of Hg and Tl in standard solutions (Table 2). Data was acquired using 3 blocks each of 60 cycles, 2.097 seconds per cycle. An initial uptake of sample solution for 3 min ensured stable signals before isotope analyses were initiated. Between samples, the glass phase separator was rinsed using 3% (v/v) HNO_3 for 6 minutes until the signal intensity returned to background level. A sample-standard bracketing (SSB) approach was used to compare relative per mil (‰) deviation (using the δ notation) of all our measurements to NIST SRM 3133, according to Blum and Bergquist[3]:

$$\delta^{xxx}\mathrm{Hg}(‰) = \{(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg}_{sample})/(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg}_{\mathrm{NIST\ SRM\ 3133}})-1\}\times1000 \qquad (3)$$

were xxx are 199, 200, 201 and 202 amu. Hg-MIF is reported in Δ notation (Δ^{xxx}Hg, deviation from mass dependency in units of permil, ‰) and is the difference between the measured Δ^{xxx}Hg and the theoretically predicted Δ^{xxx}Hg value following equations by Blum and Bergquist[3]:

$$\Delta^{199}\mathrm{Hg} \approx \delta^{199}\mathrm{Hg} - \delta^{202}\mathrm{Hg}\times0.2520 \qquad (4)$$

$$\Delta^{200}\mathrm{Hg} \approx \delta^{200}\mathrm{Hg} - \delta^{202}\mathrm{Hg}\times0.5024 \qquad (5)$$

$$\Delta^{201}\mathrm{Hg} \approx \delta^{201}\mathrm{Hg} - \delta^{202}\mathrm{Hg}\times0.7520 \qquad (6)$$

2.2 Reagents.

$SnCl_2$ (3%, w/w) was prepared in 10% (v/v) HCl. In sections 2.3 and 2.4, all Hg solutions were prepared by 3% HCl. We observed that using HCl is necessary to prevent the volatilization of Hg from acidic solutions, whereas using 3%HNO_3 is insufficient. In section 2.5, acid mixtures (HCl, HNO_3 and H_2SO_4) were used to prepare the different standard reference materials (SRMs). All acids used in this study were of ultrapure grades (certified ACS Plus, Fisher Scientific), and 18.2 MΩ·cm water (ELGA LabWater) was used for the preparation of reagents and solutions.

2.3 Measurements of varied Hg concentrations with consistent Tl concentrations.

Four sequences were conducted to evaluate the effect of Hg concentration on Hg isotope ratios. We prepared four different NIST SRM 997 standard solutions with variable Tl concentrations (2, 20, 30 and 50 ng mL^{-1}). For each sequence, the concentration of Tl was held constant, whereas we measured UM-Almadén secondary standard Hg solutions containing 0.3, 0.5, 0.8, 1.2, 1.7, 2.3 to 3.0 ng mL^{-1} of Hg. The bracketed NIST SRM 3133 Hg solutions were diluted to have same Hg concentrations of the UM-Almadén standard. With the SSB approach, replicate measurements of UM-Almadén (n=4) and NIST SRM 3133 (n=5) of each specific Hg concentration were measured, which enabled measurement reproducibility (n=4).

2.4 Measurements of varied Tl concentrations with consistent Hg concentrations.

Two sequences were performed to evaluate the effect of Tl concentrations on Hg isotope ratios. We prepared two different NIST SRM 3133 Hg solutions with Hg concentrations of 0.5 and 1.0 ng mL^{-1}. The concentrations of NIST SRM 3133 was held constant during each sequence, however, instrumental mass bias correction were performed by measuring NIST SRM 997 with variable Tl concentrations (1, 2, 3, 4, 7, 15, 20, 30, 40, 50, 60,100 ng mL^{-1}). Replicate measurements (n=4) for a specific Tl concentration were conducted.

2.4 Measurements of standard reference materials.

For biological SRMs such as TORT-2 (Lobster), DORM-2 (Fish protein), DORM-3 (Fish protein) and DOLT-2 (dogfish liver), about 0.2 g of each SRM was weighed and digested at 95 °C for 3 h with a 4 mL acid mixture (HNO_3:H_2SO_4= 7:3, v/v) following method by Pfeil and Stalvey[15]. BrCl (200 µL) was later added to each sample and kept for 12 h to allow the conversion of Hg to Hg(II). Hydroxylamine (400 µL) was added to the biological solutions prior to Hg isotope measurements. For other SRMs such as NIST SRM 2711 (Montana Soil II) and MESS-1 (marine sediment), about 0.2 g of ground sample was digested (95 °C, 1 hour) in a 2 mL aqua regia (HCl:HNO_3 = 3:1, v:v) according to Yin et al.[16]. For each SRM, triplicate digests were prepared (n=3).

On basis of the certified total Hg concentrations for SRMs, about 5 and 10 ng Hg were taken up and diluted to 0.5 and 1.0 ng mL^{-1} of Hg, respectively. The acid solutions used for dilution of biological SRMs were 10% HNO_3:H_2SO_4 mixture (7:3, v/v), whereas that used

for other SRMs are 10% $HCl:HNO_3$ (3:1, v/v). UM-Almadén and NIST SRM 3133 solutions containing 0.5 and 1.0 ng mL^{-1} of Hg were also prepared by 10% $HNO_3:H_2SO_4$ mixture (7:3, v/v) and 10% $HCl:HNO_3$ (3:1, v/v) acid mixtures. During analysis, Hg concentrations and acid matrices of the NIST SRM 3133 solutions were matched to the bracketed samples. THg concentrations in the digest solutions were measured by the ^{201}Hg intensities, which showed that the recoveries of Hg for the SRMs were 94 to 109%.

2.5 Reporting uncertainties.

For isotope ratios of Hg and Tl, uncertainties were reported using the theoretical statistical errors (SE) of all cycles, which was automatically calculated by online data acquisition software of the instrument. For δ and Δ values of UM-Almadén, uncertainties were reported using the standard deviation (SD) of repeated measurements of the same solution; for δ and Δ values of SRMs, uncertainties were reported using the SD values of the duplicate sample digests.

3. Results and discussion

3.1 Hg and Tl sensitivities during Hg isotope analysis.

Sample uptake rates for Hg and Tl solutions in this study were about 0.65 and 0.05 mL min^{-1}, respectively. Intensities of Hg and Tl showed linear correlations with Hg and Tl concentrations as shown in Figure S1 of Supplemental Information (SI). The sensitivity of ^{201}Hg (~0.56 V per ng mL^{-1} Hg) of our study is higher than previous studies[1-2, 4-5, 8-9]. Sensitivity differences can be caused by a variety of factors, such as the type of cones and the operating conditions of individual instrument, and the inlet system used for Hg introduction[1-2, 4-5, 8-9, 14, 17].

3.2 Effects of Hg and Tl concentrations on Tl isotope ratios.

Our data confirm that varied Tl and Hg concentrations have a large effect on $^{205}Tl/^{203}Tl_{measured}$ ratios (Figure 2A-C). When Tl concentration was held constant, increased Hg concentration resulted in decreased $^{205}Tl/^{203}Tl_{measured}$ (Figure 2A). When measuring Hg standards with similar Hg concentrations, the increase of Tl concentration resulted in increased $^{205}Tl/^{203}Tl_{measured}$, but such an increase was smaller at higher Tl concentration (Figure 2B). The increase of $^{205}Tl/^{203}Tl_{measured}$ was small at higher Tl/Hg ratios (Figure 2C).

These results are consistent with the observation by Georg and Newman[1], which showed that the formation of Hg hydride could result in increased ^{203}Tl intensities and decreased ^{205}Tl/^{203}Tl, when using Neptune Plus MC-ICP-MS with an X skimmer cone. By measuring 0.3 to 3.0 ng mL^{-1} of Hg and without Tl introduction (only 3% HNO_3) by the Apex-Q, we monitored the ^{203}Tl and ^{205}Tl intensities to evaluate the rate of Hg hydride formation. All our measurements showed increased ^{203}Tl intensities but no increase for ^{205}Tl (Figure 3). This is consistent with previous prediction that Hg hydride is mainly formed in HgH_2^+ rather than HgH^+ species[1]. A positive linear correlation was observed between ^{201}Hg and ^{203}Tl intensities, which indicated a rate of ~0.07% for HgH_2^+ formation in our study (Figure 3) and was comparable to that reported by Georg and Newman (0.1%)[1].

According to equation 1, artificial changes of ^{205}Tl/^{203}Tl$_{measured}$ due to Hg hydride formation should cause the shift of β values. Our results showed that when Tl concentrations were held constant, increased Hg concentrations resulted in the increase of β (Figure 2D). When measuring Hg standards with similar Hg concentrations, an increase in Tl concentration caused negative shift of β, but the shift was small at high Tl concentration (Figure 2E). For instance, measurements of high Tl solutions (20 to 50 ng mL^{-1}) resulted in small shifts of <0.3 for β (Figure 2E), whereas measuring low Tl solutions (2 ng mL^{-1}) resulted in a large shift of β of ~1 (Figure 2D). The shift of β was much smaller at high Tl/Hg ratios (Figure 2F).

3.3 Effects of Hg and Tl concentrations to Hg isotopic ratios.

The mass-bias corrected ^{xxx}Hg/^{198}Hg$_{true}$ ratios (e.g. ^{199}Hg/^{198}Hg$_{true}$, ^{200}Hg/^{198}Hg$_{true}$, ^{201}Hg/^{198}Hg$_{true}$ and ^{202}Hg/^{198}Hg$_{true}$) are summarized in Table S1 (SI) and Figure 4. The mean ratios for NIST SRM 3133 measurements (Table S1, SI) are in the range of previous results[3, 4, 9, 18]. The uncertainties of ^{xxx}Hg/^{198}Hg$_{true}$ ratios are of the same magnitude with those reported by Blum and Bergquist[3], and Ridley and Stetson[18], but smaller than those reported by Berni et al.[9]. The larger uncertainties reported by Berni et al.[9] are representative of a very much longer period of time, accounting for variability within several measurement sessions (480 measurements). Yang and Sturgeon[4] also reported larger uncertainties of the ^{xxx}Hg/^{198}Hg$_{true}$ ratios, but their uncertainties were estimated as random error propagation, and uncertainty from ^{205}Tl/^{203}Tl ratio was included in their reported Hg ratios. According to

equation 2, artificial shifts of β could unavoidably cause changes in mass-bias corrected Hg isotope ratios. In our study, positive linear correlations between Hg concentrations and $^{xxx}Hg/^{198}Hg_{true}$ ratios (e.g. $^{199}Hg/^{198}Hg_{true}$, $^{200}Hg/^{198}Hg_{true}$, $^{201}Hg/^{198}Hg_{true}$ and $^{202}Hg/^{198}Hg_{true}$) were observed (Figure 4). When Tl concentration was constant, the rates of increase for mass-bias corrected Hg isotope ratios were similar for UM-Almadén and NIST SRM 3133. The slopes between $^{xxx}Hg/^{198}Hg_{true}$ and Hg concentrations were much higher at lower Tl concentrations (Figure 4), consistent with the observation that lower Tl concentrations tend to result in more artificial shift of β (Figures 2D and 2E). This observation confirms that measuring lower Hg and higher Tl solution is necessary for Hg isotope measurements, and that concentrations of Hg between samples and standards must be carefully matched, is necessary for Hg isotope measurements.

3.4 Optimization of Hg and Tl concentrations for Hg isotope measurement.

Changes in Hg and Tl concentrations also affect the SE values of $^{xxx}Hg/^{198}Hg_{true}$ ratios (Figure 5). Using low Tl standard of 2 ng ml^{-1}, the SE of $^{xxx}Hg/^{198}Hg_{true}$ ratios is much higher than high Tl standards (20, 30, and 50 ng mL^{-1}). The high SE of $^{xxx}Hg/^{198}Hg_{true}$ ratios using low Tl standard (2 ng ml^{-1}) could be explained by the fact that the precision of $^{205}Tl/^{203}Tl_{measured}$ is compromised at lower Tl concentrations (Figure 6B). Using higher Tl standards (20, 30, and 50 ng mL^{-1}), the SE of $^{xxx}Hg/^{198}Hg_{true}$ ratios decreased as Hg concentration increased (Figure 5), similar to previous observations by Foucher and Hintelmann[2]. The SE of $^{202}Hg/^{198}Hg_{true}$ decreased from 0.00008 to 0.00004 as Hg concentrations increased from 0.3 to 3.0 ng mL^{-1}, which is only equivalent 0.02‰ to 0.03‰ changes for $\delta^{202}Hg$. No significant decreases of the SE for $^{xxx}Hg/^{198}Hg_{true}$ were observed when Hg concentrations were above 0.5 ng mL^{-1}, whereas increasing Hg concentrations would (1) increase the rinsing time and the risk of carry over between samples; and (2) increase the sample quantities for measurements. We suggest that Hg concentrations of 0.5 to 1.0 ng mL^{-1} should be the best compromise between obtainable precision, rinsing time and analyte consumption.

Varied Tl concentrations (1, 2, 3, 4, 7, 15, 20, 30, 40, 50, 60,100 ng mL^{-1}) were measured to evaluate the optimum concentrations of Tl when measurements were performed at specific Hg concentrations of 0.5 and 1.0 ng mL^{-1}. We observed that the $^{205}Tl/^{203}Tl_{measured}$

increased exponentially with the increase of Tl concentrations, whereas the SE of $^{205}Tl/^{203}Tl_{measured}$ and β decreased (Figure 6). As shown in Figure S2, the SE of $^{xxx}Hg/^{198}Hg_{true}$ is positive correlated with the SE of $^{205}Tl/^{203}Tl_{measured}$. Hg isotope ratios and their SE values decreased significantly with the increase of Tl concentrations until the Tl concentrations were beyond 20 ng mL^{-1}(Figure 7). For our instrument therefore, we suggest at least 20 ng mL^{-1} of Tl should be used during high precision Hg isotope measurement.

3.5 Importance to match Hg concentrations between Hg solutions and NIST SRM 3133.

The SSB approach is a common practice to correct for mass bias of Hg isotope measurement with the assumption that samples and bracketing standards are subjected to similar mass bias[3]. However, our results showed that mass bias is in fact, concentration dependent (Figure 4), so the SSB requires concentration match between sample and standard. We evaluated the effect of mismatch in Hg concentrations between UM-Almadén and NIST SRM 3133 [termed as $THg_{UM\text{-}Almadén}/THg_{NIST\ SRM\ 3133}$ - 1 (%)] on Hg isotopic compositions. Mean Hg isotope ratios of UM-Almadén and NIST SRM 3133 with the same Hg concentrations were calculated, then mean Hg isotope ratio of UM-Almadén with a certain Hg concentration were bracketed by that of NIST SRM 3133 with other Hg concentrations. As shown in Figure 8, the isotopic composition of Hg for concentrations matched within 10% agreed with published values[3], whereas the THg mismatched results show large deviations in both $\delta^{202}Hg$ values and Δ values (Figure 8). It appears as though bracketing with higher NIST SRM 3133 concentration results in more negative $\delta^{202}Hg$, whereas bracketing with lower NIST SRM 3133 concentration results in $\delta^{202}Hg$ that is larger than the reported number. This can be explained by positive linear correlations between Hg concentrations and measured $^{202}Hg/^{198}Hg$ (Figure 4). The calculated values for UM-Almadén (Figure 8) highlight the importance of concentration matching while using the SSB method.

The δ and Δ values of UM-Almadén, based on Hg concentration matched NIST SRM 3133, were estimated (Table S2, SI). With the exception of the analysis using a 2 ng mL^{-1} Tl internal standard, all analysis showed consistent δ and Δ values that is in well agreement with previous results[3]. Our results suggest that high precision measurements of Hg isotopes should be performed based on higher Tl internal standards. Typically, for low Hg solutions

(0.3 to 3.0 ng mL^{-1}) measured in our study, results of δ and Δ values were consistent for internal standards containing ≥20 ng $mL^{-1}$of Tl. Theoretically, accurate Hg isotope measurements for high Hg solutions may be also achieved by increasing the concentrations of Tl for mass bias correction. However, this is not necessary considering that higher Hg and Tl concentrations will result in larger rinsing time and analyte consumption. In previous studies from our laboratory, most measurements are based on 0.5 to 1 ng mL^{-1} Hg and 20 ng mL^{-1} Tl solutions. A minimum of at least 4 to 8 ng of Hg per measurement (an initial uptake of 3 min for signal stabilization plus ~7 min of acquisition, sample solution uptake: 0.65 mL min^{-1}) is required to reach precise determination of δ^{202}Hg (within ±0.10‰, 2sd).

3.6 Mercury isotope composition of standard reference materials.

As mentioned in Section 2.5, SRMs were measured to test the potential isotope bias during measurements of different environmental matrices. All tests were performed with low Hg solutions containing 0.5 and 1.0 ng mL^{-1} of Hg, and high internal standard containing 20 ng mL^{-1} of Tl. Based on well-matched THg concentrations and acid matrices between samples and the bracketed NIST SRM 3133, the measured Hg isotope composition and uncertainties for SRMs (Table S3, SI) were in agreement with previous studies[6, 16, 19-22].

4. Conclusion

While our study agrees with the results by Georg and Newman[1], that measuring Hg isotopes by Neptune Plus MC-ICP-MS with high sensitivity X skimmer cones may result in interference to ^{205}Tl/^{203}Tl ratio and inaccurate mass bias determination due to Hg hydride formation. We confirm these interferences can be minimized when higher Tl (20 to 50 ng mL^{-1}) and lower Hg (0.5 to 3 ng mL^{-1}) concentrations are introduced. Based on careful optimization of Tl and Hg concentrations, combined with carefully matched Hg concentration between samples and bracketing standards, we demonstrated that accurate Hg isotopic measurements can be achieved. We acknowledge that our measurements were performed using an adapted inlet system, which may not directly apply to other introduction systems such as the Cetac HGX-200. Therefore, we advise other Neptune users perform internal optimization steps to minimize potential for matrix effects when measuring Hg isotopes.

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Figure captions

Figure 1 Hg gas phase separator for Hg isotope measurements in this study.

Figure 2 Correlations between $^{205}Tl/^{203}Tl_{measured}$ and Tl concentrations (A), Hg concentrations (B) and Hg/Tl ratios (C); Correlations between mass-bias correction factor (β) and Tl concentrations (D), Hg concentrations (E) and Hg/Tl ratios (F).

Figure 3 Correlation between ^{201}Hg and Tl (^{203}Tl: black circles; ^{205}Tl: blue circles) beam intensities. Measurements were conducted by introducing 0.3 to 3.0 ng mL^{-1} of Hg without of Tl.

Figure 4 Correlations between $^{xxx}Hg/^{198}Hg_{true}$ ratios and Hg concentrations over varied Tl concentrations. Red circles represent UM-Almadén; blue circles represent NIST SRM 3133.

Figure 5 Relationship between the standard error of $^{xxx}Hg/^{198}Hg_{true}$ ratios and Hg concentration over varied Tl concentrations. Red circles represent UM-Almadén; blue circles represent NIST SRM 3133.

Figure 6 Variations of $^{205}Tl/^{203}Tl_{measured}$ (A), standard error of $^{205}Tl/^{203}Tl_{measured}$ (B), and mass-bias correction factor β (C) over varied Tl concentrations. Dark circles represent that measurements were based on NIST SRM 3133 of 0.5 ng mL^{-1} Hg; tubular diamonds represent that measurements were based on NIST-3133 of 1.0 ng mL^{-1} Hg;

Figure 7 Variations of $^{xxx}Hg/^{198}Hg_{true}$ ratios and standard errors (SE) over varied Tl concentrations.Dark circles represent that measurements were based on NIST SRM 3133 of 0.5 ng mL^{-1} Hg; tubular diamonds represent that measurements were based on NIST SRM 3133 of 1.0 ng mL^{-1} Hg;

Figure 8 Relationship of Hg isotopic compositions ($\delta^{202}Hg$, $\Delta^{199}Hg$ and $\Delta^{200}Hg$) to relative Hg concentration differences between UM-Almadén and NIST SRM 3133 over varied Tl concentrations. Row 2 is an expansion of row 1. Row 3 is a more detailed expansion of row 2. (Blue circles: 3 ng mL^{-1} Tl; brown circles: 20 ng mL^{-1} Tl; green circles: 30 ng mL^{-1} Tl; red circles: 50 ng mL^{-1} Tl).

Figure 1

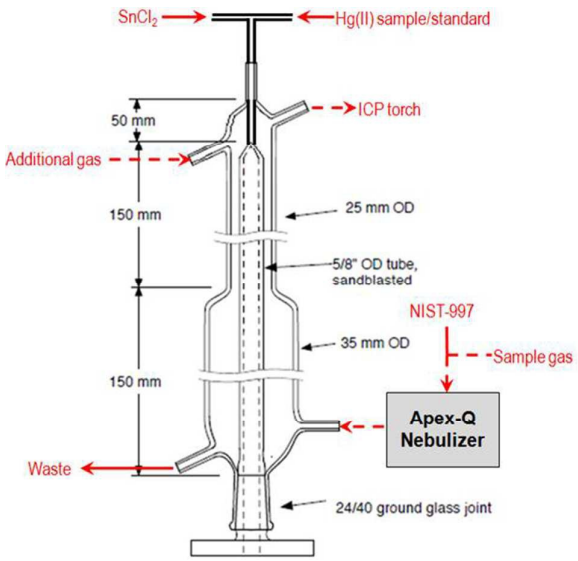


Figure 2

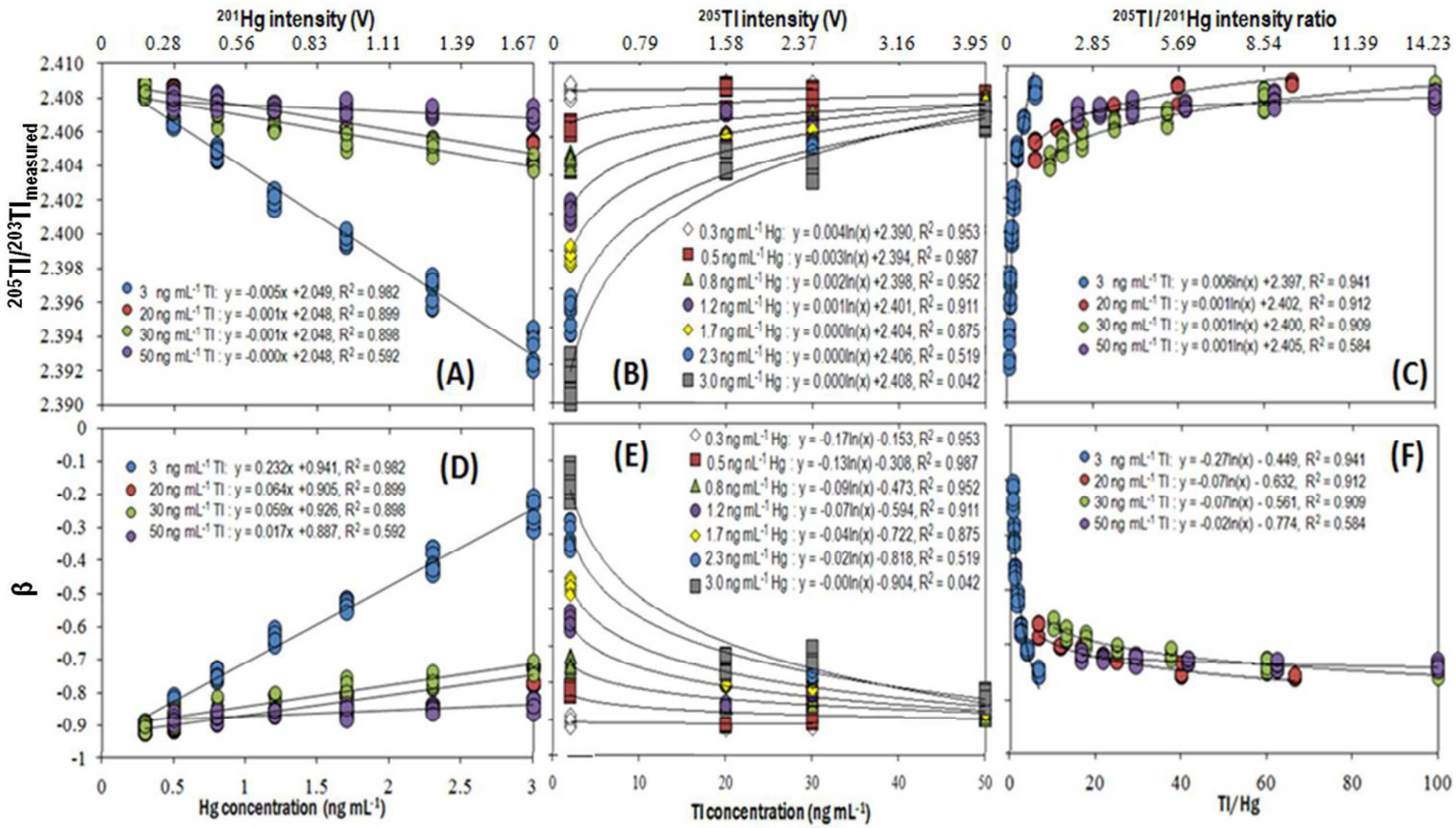


Figure 3

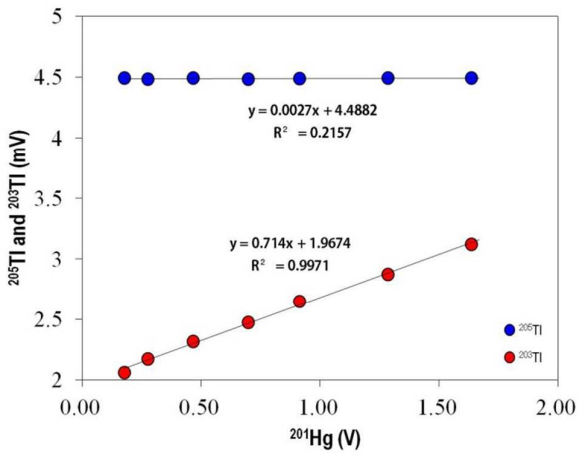


Figure 4

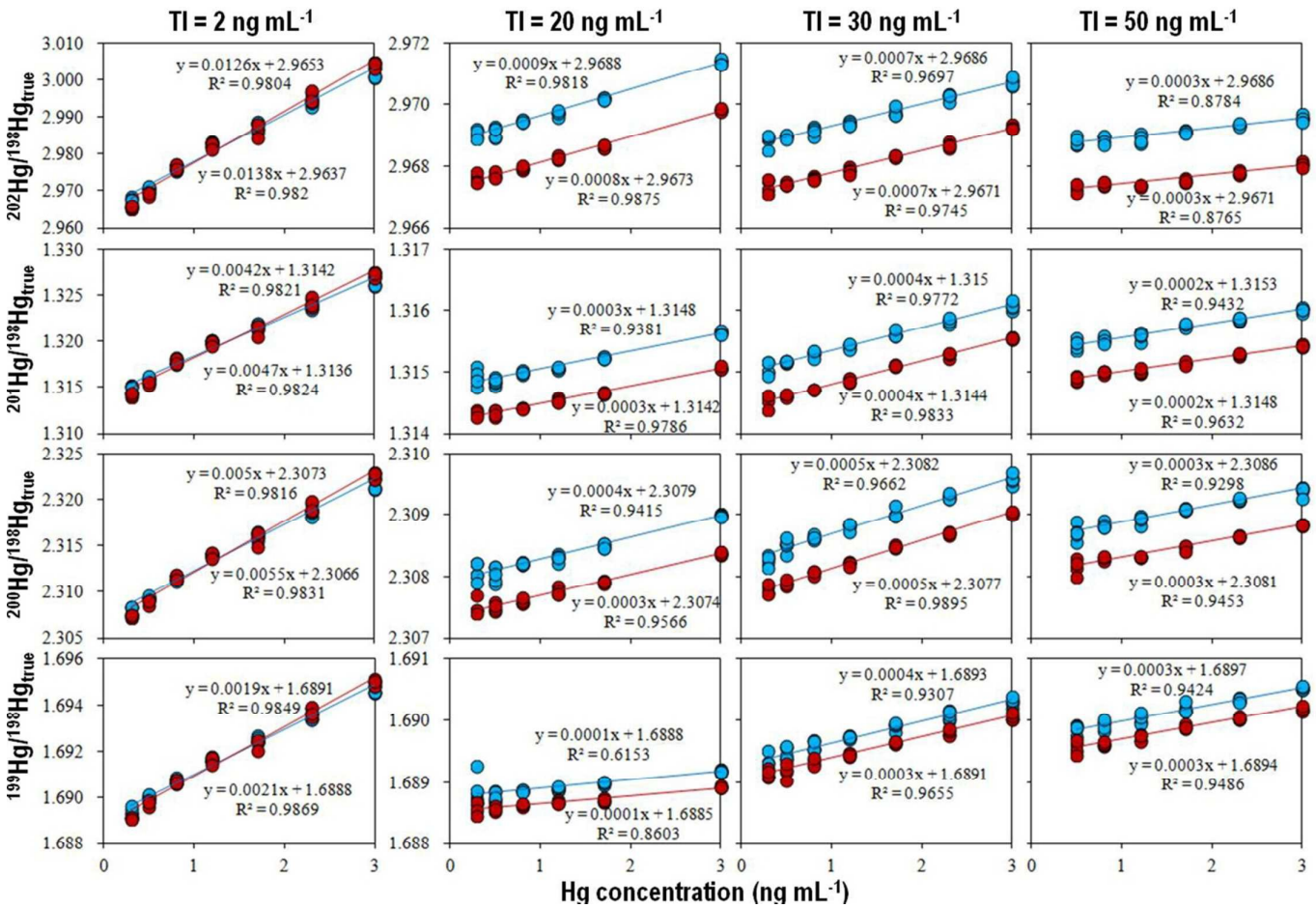


Figure 5

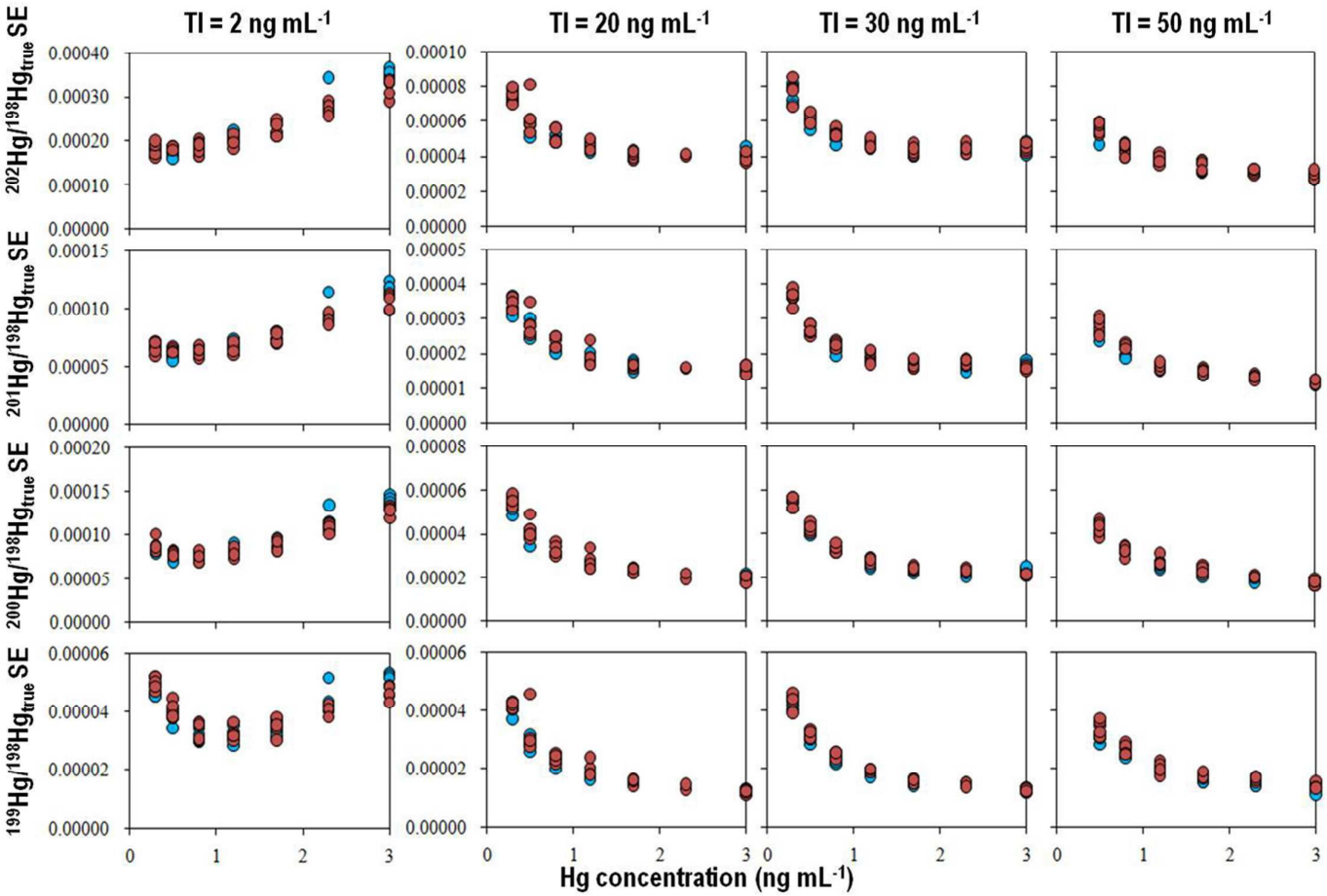


Figure 6

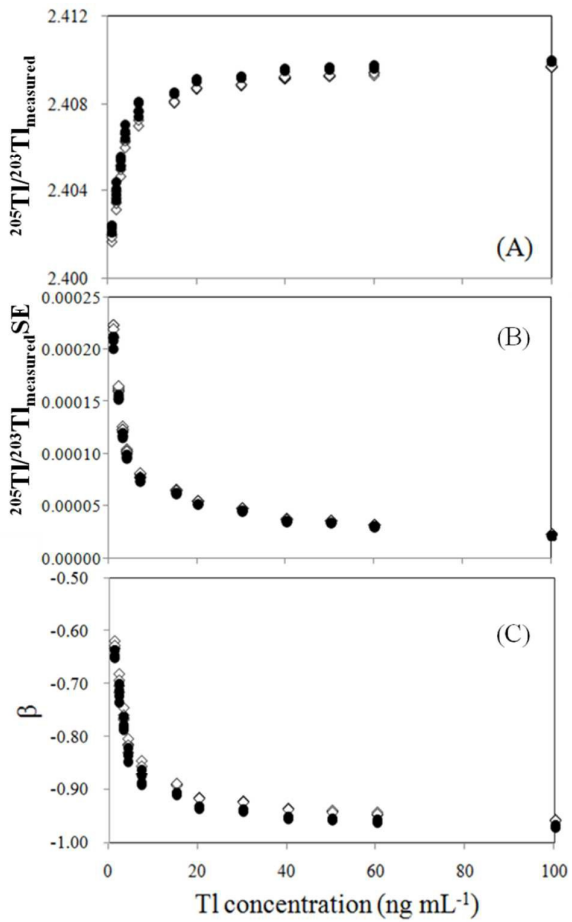


Figure 7

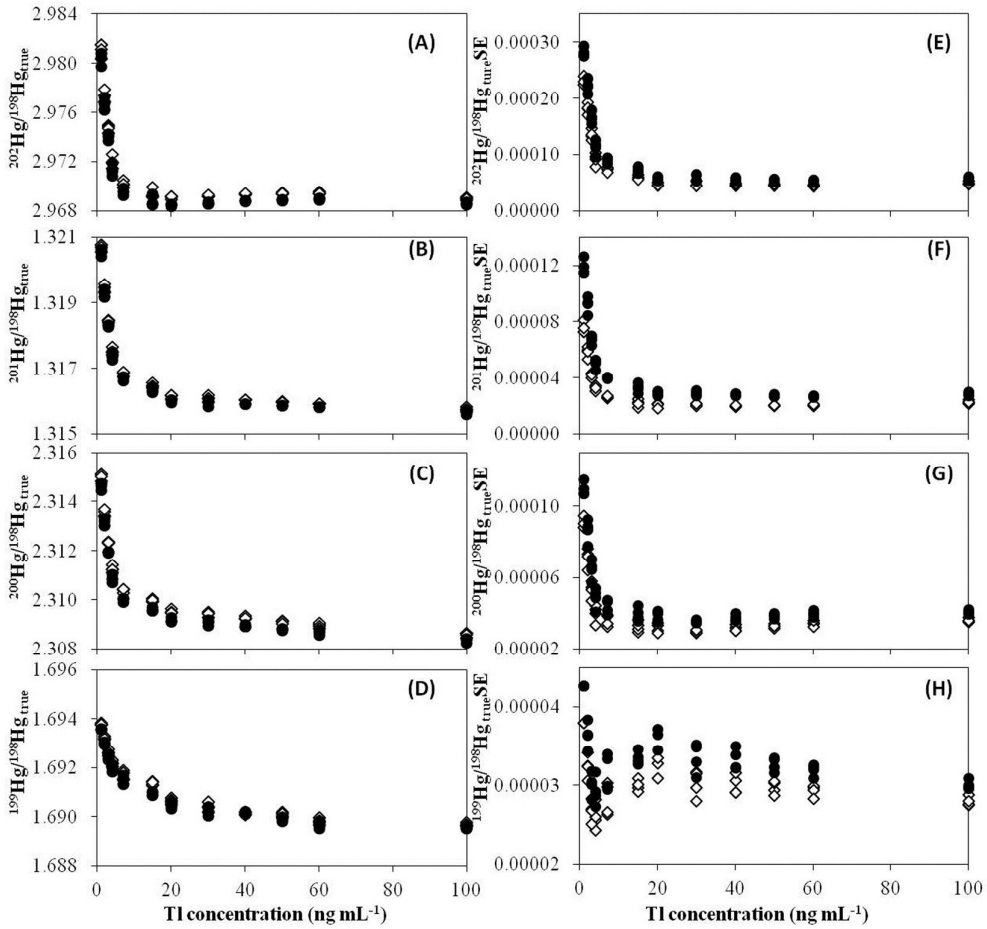


Figure 8

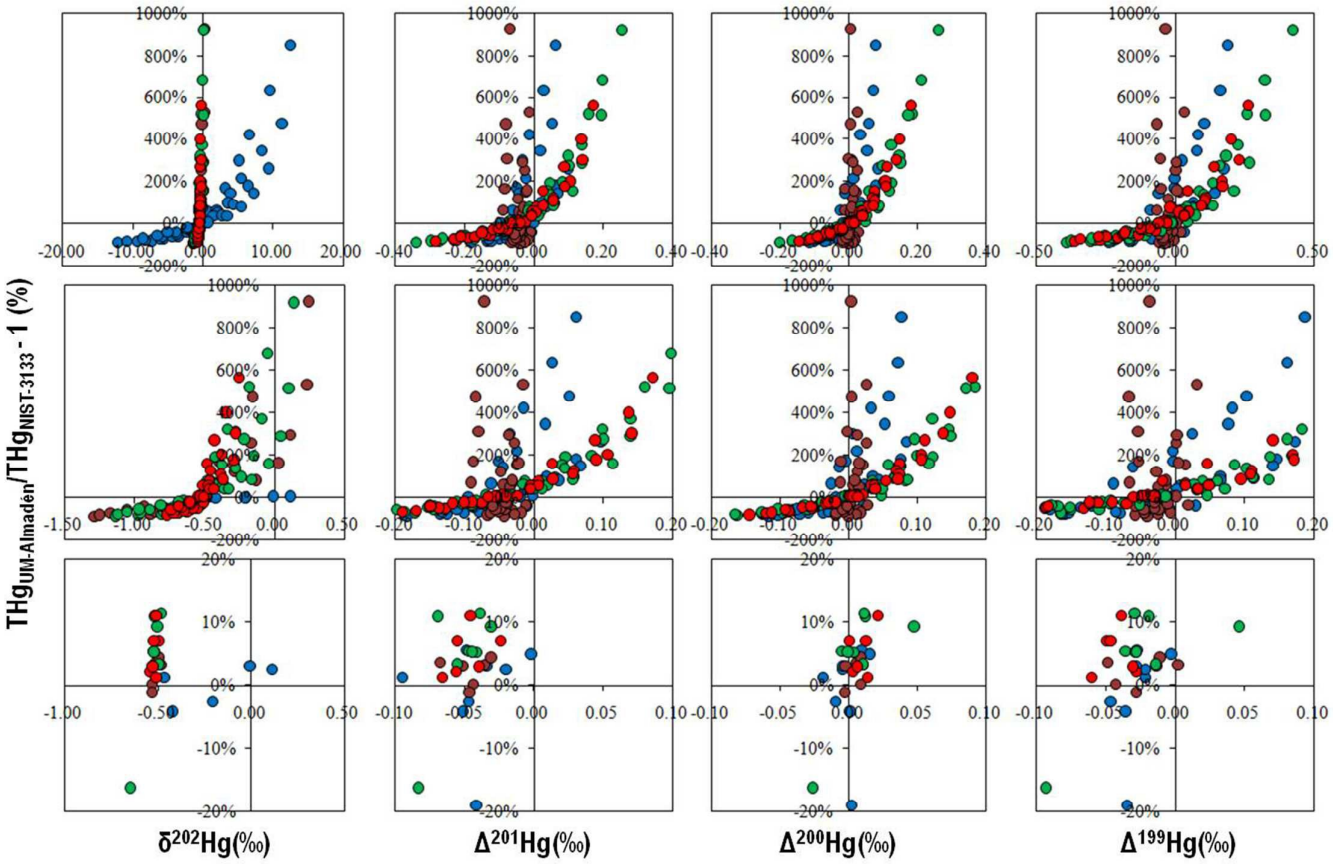
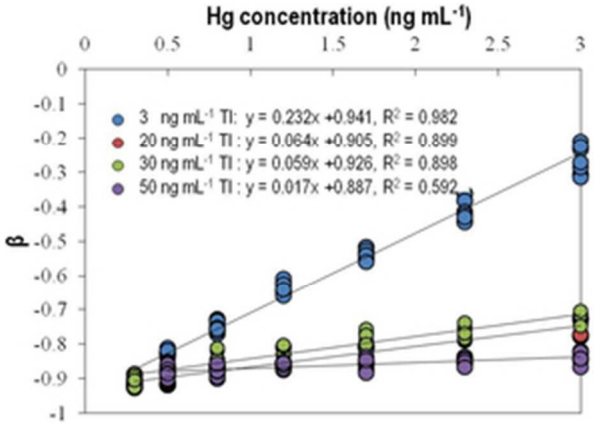


Table 1 Faraday cups configuration for Hg isotope ratio measurements

Cups	L4	L3	L2	L1	C	H1	H2	H3	H4
isotopes		^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{203}Tl	^{205}Tl	

Table 2 Operating parameters during Hg isotope analysis

MC-ICP-MS Plasma parameters	
Sample gas	0.82–0.84 L min^{-1}
Additional gas	0.23–0.25 L min^{-1}
Cool gas	16.0 L min^{-1}
Auxiliary gas	0.80 L min^{-1}
RF power	1400 W
Apex-Q	
Heater temperature	100°C
Chiller temperature	2°C
Nebulizer	PFA-50
Tl solution uptake rate	0.05 mL min^{-1}
Peristaltic pump	
Hg solution uptake rate	0.65 mL min^{-1}



24x17mm (300 x 300 DPI)