An optimized protocol of high precision measurement of Hg isotopic compositions in samples with low concentrations of Hg using MC-ICP-MS

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Abstract

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) enables the precise determination of mercury (Hg) isotopic compositions in different types of samples. However, isotopic measurements in samples with low Hg concentrations and small sample mass remain a challenge. In this study, we developed an optimized protocol for high precision Hg isotopic determination using the modified cone arrangement (X skimmer cone + jet cone) with Neptune Plus MC-ICP-MS. Through modification of the HGX-200 continuous-flow cold-vapor generation system, and careful optimization of the instrument gas flows, we obtained steady and high signal sensitivity for Hg (^{202}Hg: 1.78 V per ng mL^{-1}). Our method allowed the precise determination of low Hg solutions (0.10 ng mL^{-1}), which is the lowest according to the literature. Only 0.70 ng Hg in samples was required according to our new analytical method, which enables the direct measurement of low Hg in samples (down to 5 ng g^{-1}), after direct acid digestion treatment. Using our method, the Hg isotopic compositions of four igneous rock standard reference materials (BCR-2, BHVO-2, GSP-2, GSR-2)

were reported for the first time. The standard reference materials showed large variations of δ^{202}Hg (-1.24 ~ -2.47‰), indicating that mass dependent fractionation (MDF) of Hg isotopes occurred during magmatic processes.

1. Introduction

With the development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), stable isotopes of Hg have been successfully used as tracers to understand the geochemical cycling of Hg in the environment. [1-3] Mercury has seven natural stable isotopes (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg and ^{204}Hg), which undergo both mass dependent fractionation (MDF, mostly reported as δ^{202}Hg) and mass independent fractionation (MIF, mainly reported as Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg) during various physical, chemical, and biological processes[1,2]. Natural samples from Earth's reservoirs have shown large variations of >10‰ in both δ^{202}Hg and Δ^{199}Hg values, which are attributed to the isotope fractionation processes.[2] Combining the MDF and MIF signatures of Hg, Hg isotopes can provide multi-dimensional information to identify the sources and biogeochemical pathways of Hg in various sample medium.

For Hg isotopic composition analysis, the commercial HGX-200 continuous-flow cold-vapor generation system (CETAC Technologies, USA) has been conventionally used for sample introduction to MC-ICP-MS. [4-6] This introduction approach consists of continuously reducing of Hg in solutions by $SnCl_2$ and generating Hg(0) vapor, which gives low matrix effect, and steady and continuous Hg signals. Such technique requires substantial amounts of Hg, but tends to greatly improve external precisions of the measurements. For samples with high Hg concentrations (i.e., ≥ 25 ng g^{-1}), the samples

can be acid digested with perfect Hg recoveries (>90%), and diluted to proper Hg concentrations (0.5-5 ng mL^{-1}) and acid concentrations (<20%, v/v), and directly measured using MC-ICP-MS. The results showed small uncertainties of 0.10‰ (2SD) and 0.05‰ (2SD) for $\delta^{202}Hg$ and $\Delta^{199}Hg$, respectively. [5-8] At least 5-10 mL of solution is normally required for Hg isotope analysis. [5-8]

For samples with low concentrations of Hg (< 25 ng g^{-1}), such as igneous and metamorphic rocks, however, the isotopic composition determination is challenging using the conventional method. Even with 100% recovery, the dilution of acid concentrations to < 20% would cause low Hg concentrations (i.e., < 0.5 ng mL^{-1}) that are difficult for Hg isotope analysis. To solve the problem, gold trapping,[9] activated carbon trapping,[10] $KMnO_4$+H_2SO_4 trapping[11-16] and chromatographic pre-concentration[17] have been developed to pre-concentrate Hg to proper levels (≥ 0.5 ng mL^{-1} Hg). Although these pre-concentration techniques enabled the isotopic analysis of low Hg samples, it is noteworthy that pre-concentration suffers from tedious procedures, which are not only time consuming and chemical use, but also pose risks for Hg isotope fractionation due to Hg loss (or contamination) in the processes. More importantly, for precious samples with limited masses, such as meteorite and aerosol samples, the measurement of Hg isotopic composition is not possible by acid digestion and pre-concentration methods due to the limited mass of Hg in samples.

An alternative way of measuring samples with low concentrations of Hg and limited sample sizes is to directly improve the Hg sensitivity in instrument. The uncertainty of Hg isotope ratio decreases when the Hg signal intensity is increased, therefore the improvement of Hg sensitivity will enable the precise measurement of low Hg solutions.

The new generation Neptune Plus MC-ICP-MS (Thermo Electron Corp, Bremen, Germany), which has combined modified skimmer and sample cone geometries with enhanced interface pumping configuration, has largely enhanced the ion sampling efficiency and overall signal sensitivity. It is worthy to note that the signal sensitivity of Hg is also dependent on the types of introduction systems and the gas flow rates. In a recent study, the use of modified cones combined with an adapted cold-vapor generator resulted in higher Hg sensitivity than the traditional methods, which enabled the precise measurement of low Hg in solutions (0.3 ng mL^{-1}).[18]

In the present study, we modified the continuous-flow cold-vapor generation system based on the HGX-200 system. Through careful optimization of the instrument gas flows, we achieved much higher signal sensitivity of 1.78 V per ng mL^{-1} Hg for ^{202}Hg. With this signal sensitivity, high precision measurement of much lower Hg solutions (0.10 ng mL^{-1}) was achieved. Our method enabled the direct measurement of low Hg samples (low to 5 ng g^{-1}), after the direct acid digestion treatment. Using our developed method, the Hg isotope compositions of four igneous rock reference materials were measured and reported for the first time. In addition, it has always been a conundrum about how to optimize the Hg isotope signals because it has rarely been clearly described in pervious publications. Based on our experiments, visualized correlations were obtained between the Hg signal intensity and the gas flows. The present study, therefore, deciphers this procedure by presenting a digital guide between the Hg signal intensity and the gas flow rates.

2. Experimental methods

2.1 Reagents

Hg (NIST SRM 3133) and Tl (NIST SRM 997) standard solutions were purchased from the National Institute of Standards and Technology (NIST, U.S. Department of Commerce). The UM-Almadén secondary Hg standard solution, produced by University of Michigan, USA, was provided by Professor Dongxing Yuan from Xiamen University, China. Ultra-pure acids (HCl and HNO_3) were used to prepare the standard solutions and digest the samples. $SnCl_2$ (3%, w/w) was prepared in 10% (v/v) HCl. 18.2 MΩ cm water (ELGA LabWater) was used for the preparation of reagents and solutions.

2.2 Digestion of the standard reference materials

NIST SRM 2711a (Montana II Soil) and four igneous rock standard reference materials (SRMs), including BCR-2 (basalt), BHVO-2 (basalt), GSP-2 (granodiorite) and GSR-2 (andesite) were digested for Hg isotopic composition analysis. Briefly, approximate 0.4 g of each SRM were digested using 4 mL of aqua regia (HCl/HNO_3 = 3, v/v) in a water bath (95 °C) for 2 hours, following the method reported previously.[19-21] Acid blanks were prepared for each test. The blanks of Hg for acids were lower than <20 pg mL^{-1}. The relative standard deviation of sample duplicates was within 10% of the measured values.

2.3 Instrumental setting

Mercury isotope measurements were conducted on a Neptune Plus MC-ICP-MS housed at the University Research Facility in Chemical and Environmental Analysis (UCEA) in the Hong Kong Polytechnic University. The instrument was equipped with the HGX-200 system and an Aridus II Desolvating Nebulizer System (CETAC Technologies, USA) for Hg and Tl introduction, respectively. $SnCl_2$ was continually pumped along

with Hg(II) solutions and allowed to mix prior to be introduced into the HGX-200 system, producing gaseous elemental Hg(0). In the chamber of HGX-200, the Hg(0) was mixed with the dry Tl aerosol generated by the Aridus II desolvating nebulizer before being introduced into the plasma (Fig. 1a). A computer-controlled Perimax Spetec peristaltic pump (Spetec GmbH, Germany) and a PFA-50 nebulizer were used for uptake Hg and Tl solutions, with the uptake rates of about 0.63 mL min^{-1} and 0.05 mL min^{-1}, respectively.

As shown in Figure 1b-1, the “additional gas 2”, which is used for delivering Tl aerosols from the Aridus II desolvating nebulizer, was originally connected to left side of HGX-200. The “sample gas”, which is for delivering Hg(0) vapor, was originally connected to the right side of HGX-200. We found that such connection generated fluctuate Hg signals. The fluctuated Hg signals may be explained by the fact that the “additional gas 2” usually had much higher flow rates than the “sample gas” (Table 1). The higher flow rates of “additional gas 2” caused relatively higher pressure in the chamber, which tends to suppress the pass of “sample gas” through the chamber. In this circumstance, the “sample gas” accumulated and the pressure increased below the chamber. When the accumulated pressure surpassed the pressure in the chamber, the “sample gas” quickly breaks through the chamber. Then the accumulation continued below the chamber until another break through, which caused the fluctuated Hg signal. To solve the problem, the Teflon filter originally located in the middle of chamber was removed (note that many studies did not use filter in their Hg introduction system), and the tubing of “additional gas 2” was extended below the chamber (Fig. 1b-2). After these changes, the “additional gas 2” mixed well with "sample gas" before entering the chamber, and therefore giving stable Hg signals.

2.4 Mercury isotope determination

The NIST SRM 997 Tl standard ($^{205}Tl/^{203}Tl$=2.38714) was used as an internal standard for simultaneous instrument mass bias correction of Hg. The nine faraday cups L4, L3, L2, L1, C, H1, H2, H3 and H4 were used to monitor the ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{203}Tl, ^{204}Hg, ^{205}Tl and ^{206}Pb isotopes, respectively. The nickel X skimmer cone combined with the jet cone was employed in the tests. Hg and Tl concentrations in solutions were monitored using ^{202}Hg and ^{205}Tl signal intensities. The signal intensity of ^{202}Hg was approximately 10 mV for 10% (v/v) acid blanks. Isobaric interference of ^{204}Pb to ^{204}Hg was evaluated by measuring the signal intensity of ^{206}Pb, which was $<10^{-4}$ V during the analytical session, suggesting limited interference of ^{204}Pb to ^{204}Hg.

The gains of the amplifier associated with each Faraday collector were calibrated for efficiency on a daily basis. Instrumental parameters (e.g., gas flows, torch settings, and lens system) were tuned to guarantee steady signals, high intensities and good peak shapes. Data were acquired using 2.097 seconds per cycle, similar to previous studies.[5,18] ASX-112FR Flowing Rinse Micro Autosampler (CETAC Technologies) was employed for every test. Between samples, the autosampler was rinsed using 3% (v/v) HNO_3 for 3.5 minutes until Hg signal intensity returned to the background level. Following the protocol by Blum and Bergquist,[6] the 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 equation (1):

$$\delta^{xxx}Hg\ (‰) = [(^{xxx}Hg/^{198}Hg_{sample})/(^{xxx}Hg/^{198}Hg_{NIST3133})-1] \times 1000 \qquad (1)$$

where xxx value is 199, 200, 201, 202 and 204 amu. Hg-MIF is reported in Δ notation ($\Delta^{xxx}Hg$, deviation from mass dependency in units of permil, ‰) and is the difference

between the measured $\Delta^{xxx}Hg$ and the theoretically predicted $\Delta^{xxx}Hg$ value following equations (2-5):

$$\Delta^{199}Hg \approx \delta^{199}Hg - \delta^{202}Hg \times 0.2520 \quad (2)$$

$$\Delta^{200}Hg \approx \delta^{200}Hg - \delta^{202}Hg \times 0.5024 \quad (3)$$

$$\Delta^{201}Hg \approx \delta^{201}Hg - \delta^{202}Hg \times 0.7520 \quad (4)$$

$$\Delta^{204}Hg \approx \delta^{204}Hg - \delta^{202}Hg \times 1.4930 \quad (5)$$

3. Results and Discussion

3.1 Effects of "additional gas 2" and "sample gas" flow rates on signal intensities

Four gas flows, i.e., Ar sweep gas and N_2 addition gas of the Aridus II Desolvating Nebulizer System, and "additional gas 2" and "sample gas" of HGX-200 were involved in our method (Fig. 1a). The flow rates of Ar sweep gas and N_2 addition gas were controlled by on-board rotameters, and the flow rates of "additional gas 2" and "sample gas" were controlled by computer. NIST SRM 3133 (1 ng mL^{-1} Hg in 10% HCl) and NIST SRM 997 (50 ng mL^{-1} Tl in 3% HNO_3) standard solutions were employed during the test. Based on the initial flow rates of 1.0 L min^{-1} and 0.3 L min^{-1} for "additional gas 2" and "sample gas", respectively, the torch position, source lens, zoom optics of MC-ICP-MS, and the Ar sweep gas and N_2 addition gas of the Aridus II Desolvating Nebulizer System, were tuned for a maximum ^{202}Hg signal intensity. These optimal parameters, as summarized in Table 1, remained unchanged in the later tests.

To test the effects of "additional gas 2" and "sample gas" flow rates on signal intensities, "additional gas 2" was firstly set to 0 L min^{-1}, and "sample gas" was adjusted to achieve the maximum ^{202}Hg signal intensity, and the signal intensities of Hg and Tl were

recorded. Then the “additional gas 2” was increased to 0.1 L min^{-1}, and the "sample gas" was tuned to reach the maximum ^{202}Hg signal intensity again, and the Hg and Tl signal intensities were also recorded. The above processes were repeated with an incremental of 0.1 L min^{-1} for the “additional gas 2” until it reached to the maximum (2 L min^{-1}), which enabled us to build curves (Fig. 2 and 3) to fully understand the effects of “additional gas 2” and "sample gas" flow rates on signal intensities, as shown in Table S1.

A negatively linear correlation in flow rates was observed between “additional gas 2” and "sample gas" (Fig. 2). Since the “additional gas 2” usually had much higher flow rates than the “sample gas” (Table 1), it indicates that to achieve the highest signal intensity of Hg, high flow rates of “additional gas 2” and low flow rates of “sample gas” were required in the analysis. More interestingly, a positively linear correlation between the flow rate of “additional gas 2” and ^{202}Hg signal intensity (Fig. 3a), and a negatively linear correlation between the flow rate of “sample gas” and ^{202}Hg signal intensity (Fig. 3b), were observed. These correlations may be explained by the fact that high flow rates of "sample gas", which delivers Hg(0) vapor, tend to dilute Hg signals. Although high flow rates of “additional gas 2” also dilute Hg signal, however, the “additional gas 2” carries Tl aerosols. We hypothesize that the Tl aerosols may adsorb a substantial amount of Hg(0) vapor, which helps to improve the Hg signal intensity. Our hypothesis can be supported by the Hg signal intensity dropped rapidly when the Aridus II Desolvating Nebulizer System introduced air instead of Tl aerosols.

The change of the flow rates of “additional gas 2” and "sample gas" also affected Tl signal intensities. As shown in Figure 3c, the signal intensity of ^{205}Tl signal was close

to zero when the flow rates of "additional gas 2" ranged from 0 to 0.4 L min^{-1}, indicating that limited Tl was delivered with low "additional gas 2" flow rates. As "additional gas 2" increased to >0.4 L min^{-1}, ^{205}Tl signals emerged, and their intensities increased until the flow rate of "additional gas 2" reached to 1.0 L min^{-1} (Fig. 3c). This indicated that the increase of "additional gas 2" flow rate in certain ranges (0.4-1.0 L min^{-1}) was able to increase the delivering of Tl. As the flow rate of "additional gas 2" increased further (1.0-2.0 L min^{-1}), ^{205}Tl signal intensities decreased gradually (Fig. 3c). This indicated that high flow rates of "additional gas 2" (1.0-2.0 L min^{-1}) tended to dilute the Tl signal intensities. The flow rates of "sample gas" showed a mirror image to that of "additional gas 2" (Fig. 3d), which can be explained by the inverse correlation between the two gases (Fig. 2)

^{202}Hg showed consistently linear increase (Fig. 3a) while ^{205}Tl showed a parabolic curve as the "additional gas 2" flow rates increased (Fig. 3c). It can be seen that with the "additional gas 2" flow rate of 1.7 L min^{-1}, ^{202}Hg and ^{205}Tl had comparable signal intensities. Therefore, 1.7 L min^{-1} was chosen as the optimized "additional gas 2" flow rate in our method. With this flow rate, the ^{202}Hg signal sensitivity of 1.78 V per ng mL^{-1} can be reached when tuning the "sample gas" flow rate to 0.181 L min^{-1}. The high Hg sensitivity (^{202}Hg: 1.78 V per ng mL^{-1}) at low "sample gas" flow rate may be explained by the removal of the Teflon filter from our introduction system. Mercury has a relatively high ionization potential. Decreasing sample gas flow would permit greater time in plasma for ionization. The remove of the Teflon filter from our introduction system and using the "additional gas 2" created a dilution gas, which could decrease the high gas flow to the plasma, and therefore permitted more efficient ionization of Hg.

3.2 Mercury isotopic determination of low Hg solutions

Based on optimized instrumental conditions (Table 1) and gas flows ("additional gas 2" = 1.7 L min^{-1}; "sample gas" = 0.181 L min^{-1}), UM-Almadén secondary Hg standard solution was diluted to 1.0, 0.7, 0.5, 0.4, 0.3, 0.2, 0.1 ng mL^{-1} in 10% HCl (v/v) for Hg isotope analysis, using the SSB approach. The bracketed NIST SRM 3133 Hg solutions were diluted to have same Hg concentrations and acid matrices with the UM-Almadén standard. For a certain Hg concentration, replicate measurements (n = 7) were performed. Georg and Newman demonstrated that the use of X skimmer cone with the Neptune Plus MC-ICP-MS may cause the formation of Hg hydrides, which results in an artificial change in $^{205}Tl/^{203}Tl$ and mass bias during Hg isotope analysis.[7] However, a recent study by Yin et al.[18] proved that Hg hydride formation is less important when the Hg isotope measurements are conducted with high Tl concentrations (20-50 ng mL^{-1} Tl). In our study, NIST SRM 997 (50 ng mL^{-1} Tl in 3% HNO_3) standard solution was used throughout the analysis.

For both UM-Almadén and NIST SRM 3133 solutions, Hg isotopic ratios (i.e. $^{199}Hg/^{198}$, $^{200}Hg/^{198}$, $^{201}Hg/^{198}$, $^{202}Hg/^{198}Hg$) increased with the increase of Hg concentrations (Fig. S1), and the uncertainties of Hg isotopic ratios increased with the decrease of Hg concentrations (Fig. 4). Similar patterns have been observed by a previous study.[18] As shown in Table 2 and Fig. 4, when transformed to δ and Δ values, UM-Almadén solutions of 0.3, 0.4, 0.5, 0.7 and 1.0 ng mL^{-1} showed consistent Hg isotopic composition with previous results,[6] indicating no anomalous mass bias. However, UM-Almadén solutions of 0.1 ng mL^{-1} gave more scattered Hg isotopic composition than previous results, and UM-Almadén solutions of 0.2 ng mL^{-1} showed consistent Hg isotopic composition but with larger standard deviations. It is noteworthy that the above

tests were all performed using 3 blocks, 60 cycles per block and 2.097 seconds per cycle. Since each block gave stable and consistent isotopic compositions, we hypothesized that the detection limit can be pushed even lower, by increasing the sample uptake rate, and by decreasing the integration time. Our results showed that the Hg signal intensities can be nearly doubled by increasing the sample uptake rates from 0.63 to 1.26 mL min^{-1}. Only one block (60 cycles, 2.097 seconds per cycle) was used to test the isotopic composition of 0.1 and 0.2 ng mL^{-1} Hg solutions, with the sample uptake rate of 1.26 mL min^{-1} and 60 seconds of sample introduction time to guarantee stable Hg signal intensities, together with the simultaneous introduction of 50 ng mL^{-1} Tl. As shown in Table 2, 0.1 and 0.2 ng mL^{-1} Hg solution then gave comparable results with previous studies.[6] An additional quality control measure was used for the isotopic analysis of NIST SRM 2711a, which was diluted to 0.1 ng mL^{-1} Hg. As shown in Table 3, the results obtained during the multiple measurement sessions were in good agreement with previously published results.[22,23] In this regard, the detection limit of our current system can be confidently set at 0.10 ng mL^{-1}, which, to our knowledge, is the ultimate low value in the available publications.

The 0.3, 0.4, 0.5, 0.7 and 1.0 ng mL^{-1} tests were performed using 3 blocks, 60 cycles per block, and 2.097 seconds per cycle, with a total integration time of 380 seconds, plus 90 seconds of sample introduction to guarantee stable Hg signal intensities. The sample uptake was about 0.63 mL min^{-1}, in other words, at least 5.0 mL solution was required to accomplish each test. Similarly, for the 0.1 and 0.2 ng mL^{-1} tests, it required 4.0 mL solution. Since the sample probe of the autosampler cannot reach to the very bottom of the tube, it actually requires 7 mL solution. In fact, the volume of our autosampler tube was 7 mL.

Considering 7.0 mL of solution was necessary in our method, to obtain a confident Hg isotope data, at least 0.7 ng Hg (0.10 ng mL^{-1} × 7.0 mL) is required. This was much lower than previous studies that at least 3-20 ng of Hg were used.[18] Considering the acid concentration within each sample should be below 20%, for 7.0 mL diluted solution, the acid should be no more than 1.4 mL, which corresponds to the maximum of 0.14 g of sample used for digestion. In other words, our method can allow the direct measurement of Hg isotopic composition of low Hg samples (5 ng g^{-1} = 0.7 ng/0.14 g), using the acid digestion approach. Combined with the available pre-concentration methods,[10-17] the amount of samples and chemicals may be further saved. For example, for very low concentration (< 5 ng g^{-1}) samples, the analysis needs to pre-concentrate the samples to get 0.70 ng Hg. This is extremely helpful for the measurement of precious samples (e.g., meteorites and aerosol samples) both with low sample size and low Hg concentrations.

3.3 Igneous rock reference materials

Igneous rocks are one of the natural materials with low concentration of Hg.[24] Four igneous rock SRMs, named BCR-2 (basalt), BHVO-2 (basalt), GSP-2 (granodiorite) and GSR-2 (andesite), were digested and tested for Hg isotopic compositions. The Hg concentration of the SRMs ranged from 6.0 to 22.2 ng g^{-1}, according to the ^{202}Hg signal intensities (Table 4). The Hg concentrations of the SRMs are within the range of previous results.[25] The SRMs were analyzed repeatedly over separate analytical sessions on different days, with Hg concentration in the digests of 0.12 to 0.44 ng mL^{-1} (Table 4). For solutions with Hg > 0.20 ng mL^{-1}, the isotopic compositions were measured using 3 blocks, 60 cycles per block, and 2.097 seconds per cycle, with the

sample uptake rate of 0.63 min^{-1}. For solutions with Hg concentration ≤ 0.20 ng mL^{-1}, the isotopic composition were measured using 1 blocks, 60 cycles per block, and 2.097 seconds per cycle, with the sample uptake rate of 1.26 min^{-1}. UM-Almaden was analyzed right after each SRM. The Hg concentrations and acid matrices of NIST SRM 3133 were matched to the bracketed samples.

As shown in Table 4, the long-term reproducibility of the SRMs was comparable to that of the UM-Almadén secondary solutions. The SRMs showed large variations in $\delta^{202}Hg$ (-1.24 to -2.47‰) but little variation in $\Delta^{199}Hg$ (0.01 to 0.11‰), indicating MDF rather than MIF of Hg isotopes occurred during magmatic processes. Our results about the granodiorite (GSP-2) and andesite (GSR-2) SRMs were similar to that reported for with volcanic rocks of the Clear Lake Volcanic Field, USA ($\delta^{202}Hg$: -1.20‰ to -0.25‰; $\Delta^{199}Hg$~0)[25], but the basalt SRMs (BCR-2, BHVO-2) showed much lower $\delta^{202}Hg$ values, indicating the isotopic composition in igneous rocks are largely variable, with mafic rocks of lower $\delta^{202}Hg$, and felsic rocks of higher $\delta^{202}Hg$.

4 Conclusions

Through a modified HGX-200 continuous-flow cold-vapor generation system, and careful optimizations of the instrument gas flows, we obtained steady and high signal sensitivity for Hg, and achieved a detection limit of 0.10 ng mL^{-1} for the high precision Hg isotope determination. Only 0.70 ng Hg in samples is required using our new method, which enables the direct measurement of low Hg samples (low to 5 ng g^{-1}), after direct acid digestion treatment. Using the developed method, the Hg isotopic compositions of four igneous rock SRMs (BCR-2, BHVO-2, GSP-2, GSR-2) were reported for the first time. The SRMs showed large variations of $\delta^{202}Hg$, indicating

MDF occurred during magmatic processes.

Author Contributions

Hongyan Geng and Runsheng Yin contributed equally to this work.

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Table 1 Operating parameters for Hg isotope analysis

MC-ICP-MS	
Cool gas (Ar)	16.00 L min^{-1}
Auxiliary gas (Ar)	0.8 L min^{-1}
Sample gas (Ar)	0.181 L min^{-1}
Additional gas 2 (Ar)	1.7 L min^{-1}
X-Pos	-3.76 mm
Y-Pos	-1.76 mm
Z-Pos	-3.43 mm
RF power	1200 W
Extraction	-1610 V
Focus	-502 V
X-Defl	6.49 V
Y-Defl	-0.73 V
Shape	208 V
Rot Quad 1	6.07 V
Source Offset	1.00 V
Focus Quad	10 V
Dispersion Quad	0 V
Aridus II	
Nebulizer	PFA-50
Sweep gas (Ar)	3.31 L min^{-1}
Addition gas (N_2)	0 L min^{-1}

Table 2 Hg isotope composition of UM-Almadén. The tests for 0.1 and 0.2 ng mL^{-1} solutions were performed with the sample uptake rate of 1.26 mL min^{-1}, and using 1 block, 60 cycles per block and 2.097 seconds per cycle. The tests for other solutions were performed with the sample uptake rate of 0.63 mL min^{-1}, and using 3 blocks, 60 cycles per block and 2.097 seconds per cycle.

Hg concentration (ng mL^{-1})	$\delta^{199}Hg$ (‰)	$\delta^{200}Hg$ (‰)	$\delta^{201}Hg$ (‰)	$\delta^{202}Hg$ (‰)	$\Delta^{199}Hg$ (‰)	$\Delta^{200}Hg$ (‰)	$\Delta^{201}Hg$ (‰)
0.1	-0.20	-0.37	-0.42	-0.54	-0.07	-0.10	-0.01
	-0.16	-0.31	-0.42	-0.55	-0.02	-0.03	0.00
	-0.10	-0.19	-0.26	-0.48	0.02	0.05	0.11
	-0.13	-0.22	-0.33	-0.52	0.00	0.04	0.06
	-0.05	-0.23	-0.39	-0.47	0.07	0.00	-0.03
	-0.11	-0.25	-0.35	-0.48	0.01	-0.01	0.01
	-0.11	-0.25	-0.40	-0.53	0.03	0.02	0.00
	-0.11	-0.26	-0.47	-0.61	0.05	0.05	-0.01
Average	-0.12	-0.26	-0.38	-0.52	0.01	0.00	0.01
SD	0.04	0.06	0.07	0.05	0.04	0.05	0.05
0.2	-0.10	-0.24	-0.33	-0.50	0.00	0.00	0.00
	-0.11	-0.25	-0.39	-0.50	0.01	0.00	-0.02
	-0.13	-0.19	-0.33	-0.47	-0.01	0.05	0.03
	-0.14	-0.31	-0.38	-0.49	-0.01	-0.06	-0.01
	-0.12	-0.25	-0.38	-0.51	0.01	0.01	0.00
	-0.16	-0.31	-0.42	-0.55	-0.02	-0.03	0.00
	-0.04	-0.25	-0.34	-0.50	0.08	0.00	0.04
	-0.16	-0.31	-0.42	-0.55	-0.02	-0.03	0.00
Average	-0.12	-0.26	-0.37	-0.51	0.01	-0.01	0.00
SD	0.04	0.04	0.04	0.03	0.03	0.03	0.02
0.3	-0.11	-0.27	-0.49	-0.46	-0.03	-0.02	0.03
	-0.12	-0.30	-0.45	-0.48	0.02	0.01	0.03
	-0.10	-0.24	-0.33	-0.49	0.02	0.01	0.03
	-0.13	-0.24	-0.35	-0.47	-0.01	0.00	0.00
	-0.16	-0.31	-0.42	-0.55	-0.02	-0.03	0.00
	-0.07	-0.23	-0.46	-0.55	0.07	0.05	-0.05
	-0.09	-0.28	-0.39	-0.56	0.05	-0.01	0.03
	-0.17	-0.25	-0.39	-0.48	-0.05	-0.01	-0.03
Average	-0.12	-0.26	-0.41	-0.51	0.01	0.00	0.01
SD	0.03	0.03	0.05	0.04	0.04	0.02	0.03
0.4	-0.10	-0.19	-0.28	-0.48	0.02	0.05	0.08
	-0.14	-0.26	-0.34	-0.48	-0.02	-0.02	0.02
	-0.15	-0.29	-0.35	-0.47	-0.03	-0.05	0.01
	-0.12	-0.23	-0.33	-0.48	0.00	0.01	0.03
	-0.14	-0.30	-0.42	-0.58	0.00	-0.01	0.01
	-0.19	-0.27	-0.43	-0.52	-0.06	0.00	-0.04
	-0.12	-0.24	-0.41	-0.50	0.00	0.02	-0.03
	-0.15	-0.26	-0.45	-0.52	-0.02	0.00	-0.06
Average	-0.14	-0.25	-0.38	-0.50	-0.01	0.00	0.00
SD	0.03	0.03	0.06	0.03	0.03	0.03	0.04
0.5	-0.14	-0.25	-0.40	-0.52	-0.01	0.01	-0.01
	-0.13	-0.25	-0.40	-0.50	-0.01	0.00	-0.02

	-0.14	-0.26	-0.42	-0.55	0.00	0.02	-0.01
	-0.13	-0.29	-0.45	-0.58	0.01	0.00	-0.01
	-0.13	-0.25	-0.41	-0.50	-0.01	0.00	-0.03
	-0.12	-0.26	-0.43	-0.49	0.01	-0.02	-0.06
	-0.15	-0.28	-0.37	-0.47	-0.04	-0.04	-0.02
	-0.13	-0.27	-0.35	-0.49	0.00	-0.02	0.02
Average	-0.13	-0.26	-0.40	-0.51	0.00	-0.01	-0.02
SD	0.01	0.02	0.03	0.04	0.01	0.02	0.02
0.7	-0.12	-0.25	-0.38	-0.51	0.01	0.01	0.00
	-0.11	-0.25	-0.40	-0.53	0.03	0.02	0.00
	-0.15	-0.28	-0.46	-0.55	-0.02	0.00	-0.05
	-0.18	-0.26	-0.44	-0.57	-0.03	0.02	-0.01
	-0.11	-0.25	-0.35	-0.48	0.01	-0.01	0.01
	-0.11	-0.23	-0.43	-0.54	0.03	0.04	-0.03
	-0.12	-0.25	-0.38	-0.51	0.01	0.01	0.00
	-0.11	-0.25	-0.40	-0.53	0.03	0.02	0.00
Average	-0.12	-0.25	-0.41	-0.53	0.01	0.01	-0.01
SD	0.03	0.01	0.03	0.03	0.02	0.01	0.02
1	-0.12	-0.28	-0.43	-0.56	0.02	0.01	-0.01
	-0.11	-0.25	-0.41	-0.56	0.03	0.03	0.01
	-0.12	-0.24	-0.40	-0.53	0.02	0.03	0.00
	-0.11	-0.24	-0.42	-0.54	0.03	0.03	-0.01
	-0.14	-0.28	-0.45	-0.51	-0.01	-0.03	-0.06
	-0.14	-0.24	-0.41	-0.54	0.00	0.03	-0.01
	-0.11	-0.25	-0.39	-0.50	0.02	0.01	-0.01
	-0.08	-0.24	-0.45	-0.51	0.05	0.02	-0.07
Average	-0.11	-0.25	-0.42	-0.53	0.02	0.02	-0.02
SD	0.02	0.02	0.02	0.02	0.02	0.02	0.03

Table 3 Hg isotope composition of 0.1 ng mL^{-1} SRM NIST 2711a (Montana II soil). The tests were performed with the sample uptake rate of 1.26 mL min^{-1}, and using 1 block, 60 cycles per block and 2.097 seconds per cycle.

	$\delta^{199}Hg$ (‰)	$\delta^{200}Hg$ (‰)	$\delta^{201}Hg$ (‰)	$\delta^{202}Hg$ (‰)	$\Delta^{199}Hg$ (‰)	$\Delta^{200}Hg$ (‰)	$\Delta^{201}Hg$ (‰)
	-0.22	-0.03	-0.25	-0.09	-0.19	0.01	-0.18
	-0.23	-0.07	-0.26	-0.08	-0.21	-0.03	-0.20
	-0.24	-0.10	-0.26	-0.11	-0.21	-0.04	-0.17
	-0.22	-0.06	-0.26	-0.08	-0.20	-0.02	-0.20
	-0.28	-0.08	-0.26	-0.12	-0.25	-0.02	-0.17
	-0.23	-0.06	-0.26	-0.14	-0.19	0.01	-0.15
	-0.28	-0.08	-0.27	-0.07	-0.26	-0.04	-0.22
	-0.23	-0.04	-0.22	-0.07	-0.21	0.00	-0.17
Average	-0.24	-0.07	-0.25	-0.10	-0.22	-0.02	-0.18
SD	0.02	0.02	0.01	0.03	0.02	0.02	0.02

Table 4 Hg isotope compositions of the igneous rock SRMs

SRM	N	Hg ($ng\ g^{-1}$)	Hg ($ng\ mL^{-1}$)	$\delta^{199}Hg$ (‰)	SD (‰)	$\delta^{200}Hg$ (‰)	SD (‰)	$\delta^{201}Hg$ (‰)	SD (‰)	$\delta^{202}Hg$ (‰)	SD (‰)	$\Delta^{199}Hg$ (‰)	SD (‰)	$\Delta^{200}Hg$ (‰)	SD (‰)	$\Delta^{201}Hg$ (‰)	SD (‰)
BCR-2	5	6.8	0.14	-0.52	0.07	-1.04	0.04	-1.56	0.04	-2.08	0.04	0.00	0.07	0.01	0.04	0.00	0.07
BHVO-2	5	6.0	0.12	-0.65	0.05	-1.24	0.06	-1.84	0.04	-2.44	0.05	-0.03	0.04	-0.01	0.06	0.00	0.03
GSP-2	5	22.2	0.44	-0.29	0.08	-0.59	0.12	-0.88	0.11	-1.20	0.11	0.01	0.07	0.02	0.07	0.02	0.06
GSR-2	5	11.5	0.23	-0.26	0.06	-0.69	0.12	-1.09	0.19	-1.47	0.13	0.11	0.03	0.05	0.07	0.02	0.12

Figure Captions

Fig. 1 (a) Sketch of the sample introduction system. Figure (b-1) shows the original setting of the tubing of "additional gas2", which produces fluctuate Hg signals. Figure (b-2) shows the modified setting, where the tubing is extended below and give stable Hg signals.

Fig. 2 Relationship between the flow rates of "additional gas 2" and "sample gas".

Fig. 3 Gas flows vs ^{202}Hg intensity and ^{205}Tl intensity.

Fig. 4 Hg isotopic composition of UM-Almadén with different Hg concentrations. The tests for 0.1 and 0.2 ng mL^{-1} solutions were performed with the sample uptake rate of 1.26 mL min^{-1}, and using 1 block, 60 cycles per block and 2.097 seconds per cycle. The tests for other solutions were performed with the sample uptake rate of 0.63 mL min^{-1}, and using 3 blocks, 60 cycles per block and 2.097 seconds per cycle. The red diamond shows the average of the eight analyses for each concentration and the bar represents the error of the replicate analyses.

Figure 1

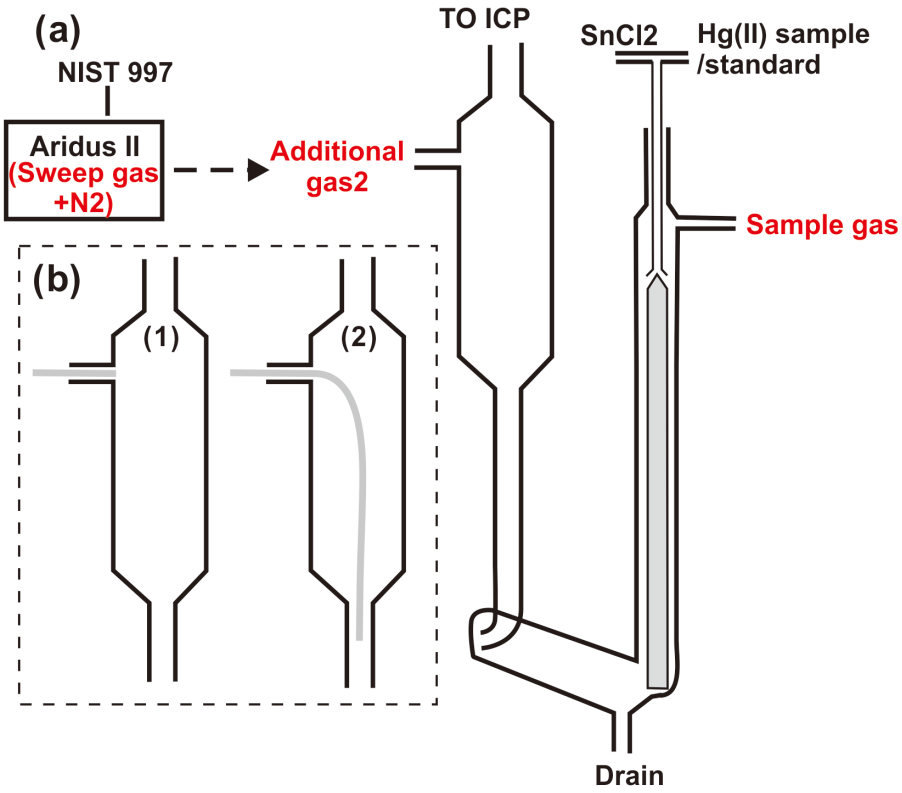

(a)
NIST 997
Aridus II
(Sweep gas
+N2)
Additional
gas2
TO ICP
SnCl2
Hg(II) sample
/standard
Sample gas
(b)
(1)
(2)
Drain

Figure 2

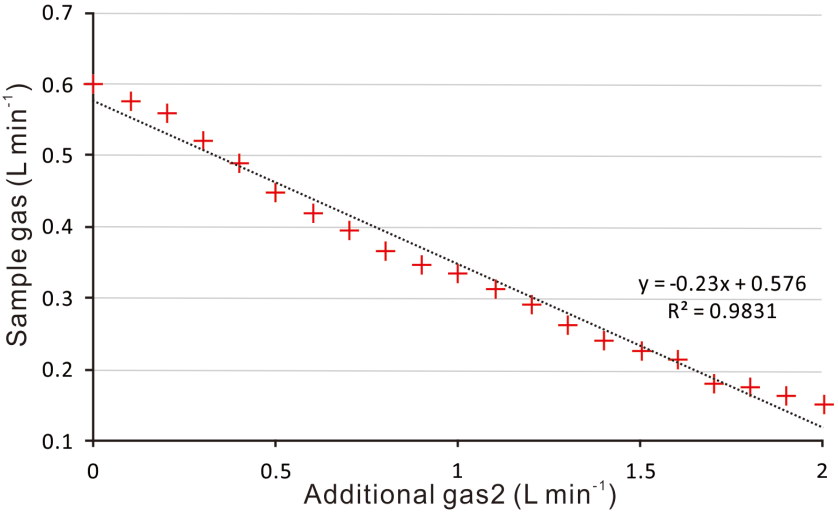

0.7
0.6
0.5
0.4
0.3
0.2
0.1
Sample gas (L min-1)
0
0.5
1
1.5
2
Additional gas2 (L min-1)
y = -0.23x + 0.576
R² = 0.9831

Figure 3

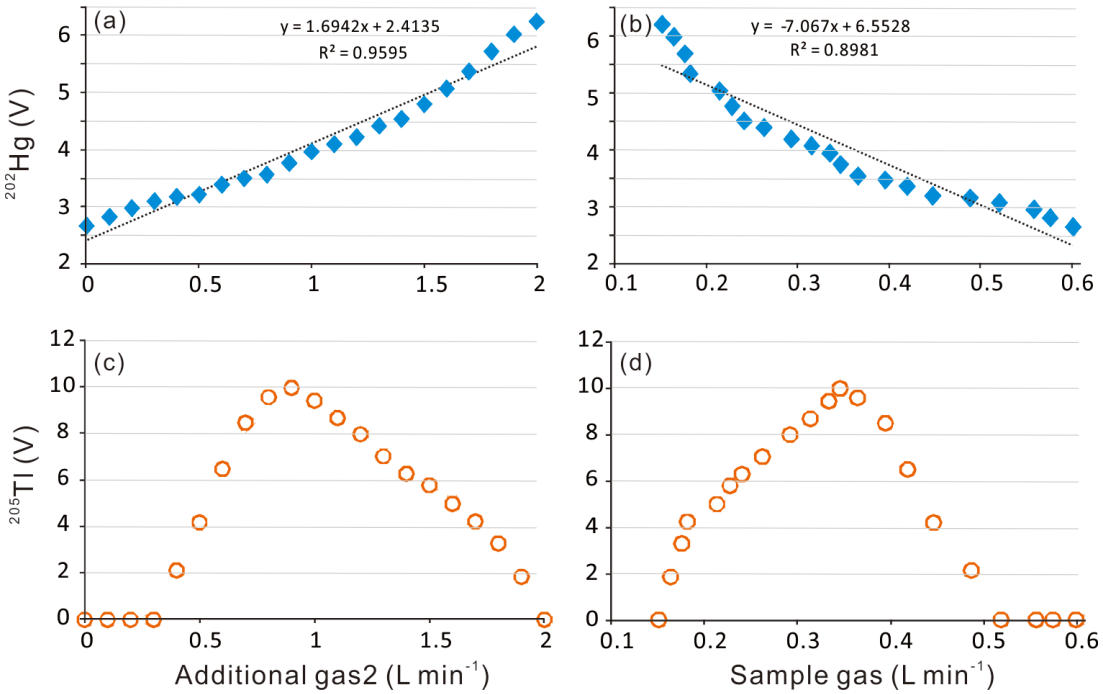
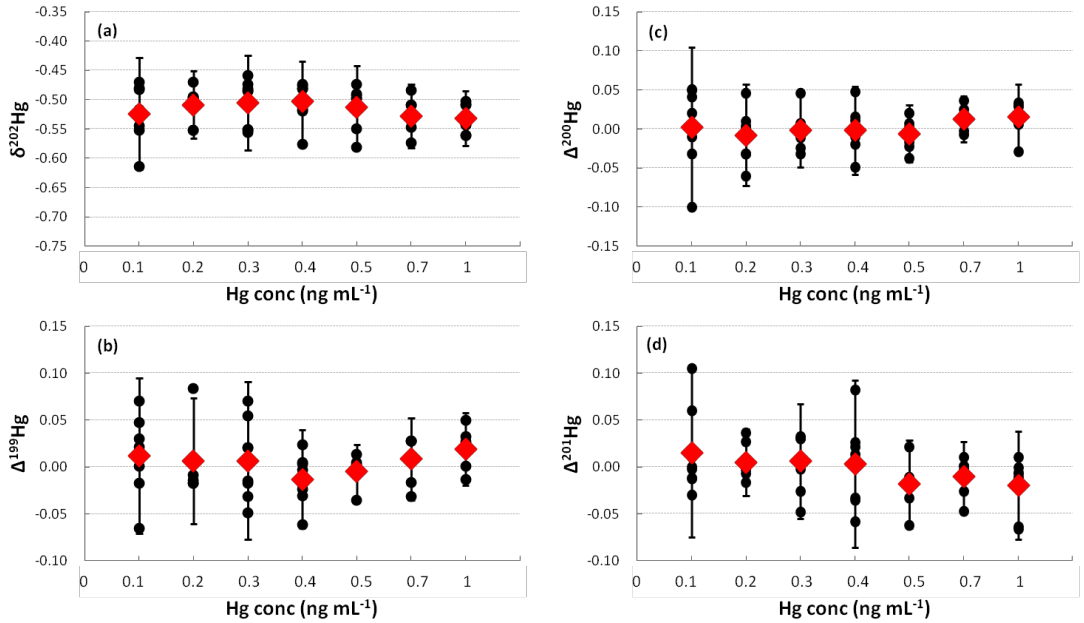

(a)
y = 1.6942x + 2.4135
R² = 0.9595
(b)
y = -7.067x + 6.5528
R² = 0.8981
(c)
(d)
^{202}Hg (V)
^{205}Tl (V)
Additional gas2 (L min^{-1})
Sample gas (L min^{-1})

Figure 4


(a)
δ202Hg
-0.35
-0.40
-0.45
-0.50
-0.55
-0.60
-0.65
-0.70
-0.75
0 0.1 0.2 0.3 0.4 0.5 0.7 1
Hg conc (ng mL-1)
(c)
Δ200Hg
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
0 0.1 0.2 0.3 0.4 0.5 0.7 1
Hg conc (ng mL-1)
(b)
Δ199Hg
0.15
0.10
0.05
0.00
-0.05
-0.10
0 0.1 0.2 0.3 0.4 0.5 0.7 1
Hg conc (ng mL-1)
(d)
Δ201Hg
0.15
0.10
0.05
0.00
-0.05
-0.10
0 0.1 0.2 0.3 0.4 0.5 0.7 1
Hg conc (ng mL-1)