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An improved dual-stage protocol to pre-concentrate mercury from airborne particles for precise isotopic measurement

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Abstract: Hg isotopic signature may provide insight into tracking the sources and pathways of both airborne particulate matter (PM) and particle-bound Hg (PHg) in the atmosphere. However, separating and concentrating trace level of PHg and accurately analyzing its isotope ratios remain technical challenge. Here, we optimized a combustion-trapping dual-stage protocol specifically for the pre-concentration of Hg from PM sample collected on quartz fiber membrane (QFM) for high-precision Hg isotopic analysis. The protocol was validated by testing synthetic samples of varying concentrations and trapping solutions of different volumes, and by comparison with two conventional methods (acid digestion and column purification). Using the dual-stage protocol, individual sample containing up to 570 ng of Hg can be combusted at programmed temperatures in a Hg-free O_2 stream, and the volatilized gaseous Hg was trapped in a 5-ml acid (4 M HNO_3 and 1.3 M HCl) mixture. The method results in relatively lower procedural blank and quantitative recovery (99±6%, 2SD, *n*=90). Long-term measurements of three certified reference materials (CRM021, CRM024, and GBW07405) with complex matrices using the optimized protocol gave identical Hg isotopic ratios of both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF), in agreement with the results obtained from the standard addition method. The protocol was applied to two $PM_{2.5}$ samples collected on a 20.3×12.5 cm QFM. The result showed evident variations of both MDF and MIF, highlighting the importance of studying Hg isotopic compositions in PM of variable environments in order to fully understand the behaviors of Hg and its isotopes in the atmosphere.

Keywords: Combustion-trapping protocol; Hg isotopes; Recovery; Standard addition method; Quartz fiber membrane; Airborne particles

1. Introduction

Because of its fugitive nature, mercury (Hg) is an important air pollutant of major environmental significance.[1] Hg is mainly present in three forms in the atmosphere including gaseous elemental mercury (Hg^0, GEM), divalent reactive gaseous mercury (Hg^{2+}, RGM), and particle-bound mercury (PHg),[2] the latter is defined as the mercury associate with airborne particulate matter (PM) and is often collected on quartz fiber membrane (QFM).[3, 4] The airborne PHg is of particular interest because its concentration levels and its isotopic signatures may be indicative of the sources of both Hg and PM and the geochemical processes that Hg has undergone.

Accurate analysis of isotope compositions for PHg has remained technically challenged due largely to its extremely low concentrations. In general, typical outdoor air contains PHg at 1-100 pg/m^3 levels,[5-8] but higher level (up to 1,000 pg/m^3) can be found in heavily contaminated industrial areas and for major cities in China.[9-12] Even with current state-of-art isotopic analysis instrument (i.e., multi-collector inductively coupled plasma mass spectrometry, MC-ICP-MS), hundreds to thousands of cubic meters of air should be sampled in order to obtain a mass of >10 ng Hg for a single accurate isotopic analysis[13, 14] and a high-volume sampler (i.e. 300 and 500 L/min) is needed to collect PM on QFM. Unlike the normal environmental and geological solid samples, the collected PM particles are not readily separated from the QFM matrix, which maybe hamper accurate Hg isotope analysis. Thus, the QFM matrix, which sometime far outweighs PM, has to be included in the analysis of PHg. Therefore, appropriate pre-concentration is a major prerequisite for the study of PHg.

Acid digestion and chromatographic column purification are two conventional methods of sample preparation for isotopic analysis of trace metals including Hg in environmental and geological solid matrices.[15-20] While they have advantage of rapidly processing large number of samples, these protocols require complete digestion of solid matrix and certainly are not best suited for extracting PHg from PM samples deposited on QFM matrix, because an extraordinarily large volume of acids is needed to digest both PM samples and the fluffy QFM matrix. The high procedural Hg blanks resulting from the excessive acids can cause large uncertainty in determination of Hg isotopic compositions on MC-ICP-MS using cold vapor (CV) generation system. Even though anion-exchange column system can be employed after wet acid digestion to purify Hg from the matrix,[13, 21] we are unaware of any chromatographic method dedicated to accurate measurements of Hg isotopic compositions in airborne particles.

An alternative protocol using thermal decomposition and acid trapping of Hg was recently proposed for separation and purification of Hg from powered geological samples (sediments, coal, organic soils and vegetation).[22-25] It is known that different Hg species such as Hg^0, $HgCl_2$, HgS and HgO in airborne PM[26] can be converted to Hg^0 at approximately 700°C.[27] Indeed, such a thermal decomposition method has long been used for quantifying Hg in geological samples,[28] and has been modified in several studies for pre-concentration of Hg from geologic samples for isotopic analysis,[22-25, 29] Rolison et al. used thermal decomposition method to pre-concentrate Hg from QFM matrix for investigating species-specific atmospheric Hg isotope compositions,[30] while others employed a dual tube furnace protocol.[22, 29, 31] According to these studies, the dual-stage protocol employed two tube furnaces connected in series and a carrier gas (Ar, O_2, or air) for purging Hg from the combustion chamber into the acid trap. The drawback of using this protocol was that it often requires long time (up to 6 hrs) to complete the entire procedure. Sun et al.[29] developed a double-stage protocol in which O_2 was used as the carrier gas and diluted HNO_3/HCl (v/v=2:1) mixtures as the trap, that reduces considerably the process time to 3.5 hrs. However, they reported the Hg recovering efficiency ranged from 80 to 120% for a large sample set,[29] which, although acceptable, apparently requires further improvement. This may limit its direct application to airborne particles. Though the dual-stage protocol reported in previous studies appears very promising for PHg study, further improvement is needed to enhance the recovery efficiency and reproducibility, and provide the QA-QC details for accurate measurements of Hg isotopes in airborne particles.

In this study, we optimized the combustion-trapping dual-stage protocol for accurate analysis of Hg isotope compositions in PM samples collected on QFM. The overarching goal was to lower the procedural Hg blanks, improve recovering efficiency and reduce the Hg mass needed for accurate isotopic analysis. The protocol was validated by testing synthetic samples of variable Hg concentrations and by comparison with two conventional methods. Long-term (6 months) measurements of reference materials using this protocol gave identical Hg isotopic ratios to the standard addition method. The result indicated that our modified combustion-trapping dual-stage protocol, that was characterized by lower baseline Hg concentration, higher recovery efficiency and better Hg isotope reproducibility, could be used to pre-concentrate Hg from PM samples collected on QFM for accurate measurements of Hg isotope compositions.

2. Experimental methods

2.1. Materials, reagents and standards

Milli-Q water (18.2 MΩ) was used for preparation of all aqueous solutions in ultra-clean room. Concentrated HCl and HNO_3 (Sinopharm Chemical Reagent Co., Ltd, China) were double-distilled and used for preparing all the solutions and reagents including the aqua regia and the acid trapping solution (2:4:9 ratio of 10 M HCl, 15 M HNO_3 and Milli-Q water). 0.2 M BrCl solution was made by mixing the concentrated HCl with pre-heated (250°C, 12 hrs) KBr and $KBrO_3$ (>99%, ACS reagent, Aldrich, USA) powders. Two $SnCl_2$ solutions at 0.2 and 0.03 g/mL were prepared by dissolving the solid in 1 M HCl and were used for on-line reduction of Hg for concentration (cold vapor atomic fluorescence spectroscopy, CVAFS) and isotope (MC-ICP-MS) analysis, respectively. A 0.2 g/mL NH_2OH•HCl solution was prepared for BrCl neutralization. The reductants were bubbled for 6 hrs with Hg-free N_2 to remove trace levels of Hg vapor. All the solutions prepared were used only in 7 days.QFM (8×5 inch, Millipore, USA) were heated for 3 hrs in a muffle furnace at 550°C before use. Borosilicate glass bottles, impingers, and sample quartz tubes were acid-cleaned by soaking in 20% HNO_3 solution for 24 hrs followed by rinsing three times with Milli-Q water, then baked for 4 hrs in a muffle furnace at 460°C. Teflon materials including bottles and fittings were cleaned similarly and air dried for 24 hrs in a laminar fume hood.

The NIST SRM 997 Thallium (20 ng/mL Tl in 3% HNO_3) was used for mass bias correction and the international Hg standard NIST SRM 3133 was employed as the isotopic standard. UM-Almaden and Fluka Hg (provided by Dr Wiederhold)[32] were used as the reference material for isotopic analysis and a laboratory Hg standard solution (National Center for Standard Materials, Beijing, China) was used as a control standard for concentration measurement. Three certified soil reference materials, Trace Metals-Sandy Loam 1 (CRM024) and 3 (CRM021) (Sigma Aldrich, USA) and Yellow-Red Soil GBW07405 (National Center for Standard Materials, Beijing, China) with certified Hg concentrations of 0.71±0.11, 4.7±0.3 and 0.29±0.03 ng/mg, respectively, were sieved through acid-cleaned mesh (<125 μm) and used for method development. The use of soil CRMs are technically appropriate, since soils have also complex matrix and are an important component of atmospheric particulate matter, as demonstrated by previous studies.[33-35]

2.2. Hg pre-concentration on dual-stage assembly

Fig. 1 schematically illustrates the combustion-trapping dual-stage assembly for pre-concentration of Hg from PM samples. The main components and the architecture of the assembly were adopted from Sun et al.[29] The system consisted of a furnace quartz tube (25 mm OD, 22 mm ID, 1.0 m length) placed in two combustion tube furnaces (Lindberg/Blue M Mini-Mite, Thermo Ltd., USA). The first combustion furnace was set to rapidly raise temperature from ambient to 950°C, followed by a second decomposition furnace for maintaining constant temperature at 1,000°C. An O_2 purification system with a sand-coated gold trap (Brooks Rand Labs, USA) and an acid trapping system were separately connected to the end caps of the quartz tube. The O_2 gas was controlled by a flow meter (Cole Parmer, USA) at 5-50 mL/min with accuracy of 2% and fed into the furnace quartz tube using a thick-walled PFA tube inserted into a silicone stopper. Three adiabatic sets were used at the outlets of the two furnaces for maintaining relatively constant temperatures around the quartz tubes. The acid trapping device consisted of a 25-ml borosilicate glass impinger and an elbow-shaped custom-made fritted glass tube (porosity # 40-100 μm). Thin-walled PFA tubing (7 mm OD, 6 mm ID) was used to connect the outlet of the furnace quartz tube to impinger elbow. The tubing was replaced before each sample treatment. The entire furnace tube-impinger connection, including the Teflon tubing, was wrapped by aluminum foil (pre-cleaned at 450°C for 3 hrs) to keep the temperature and to avoid condensation of water and other volatile compounds.

FIGURE 1

During each run, a clean QFM, folded in half and rolled into a cylinder, then loaded with known mass of CRMs or NIST 3133, was placed into a 10-cm length sample quartz tube (20 mm OD and 18 mm ID). The tube was capped with quartz wool (pre-cleaned at 500°C) at both ends to avoid particle release during sample combustion, and then inserted into the furnace quartz tube situated within the combustion furnace. The samples were step-combusted in the dual-stage system with the steps of 12 min to ramp the ambient temperature to 200°C, then 90 min from 200°C to 600°C, and 23 min from 600 to 950°C. The combustion furnace was held at 950°C for 30 min, and then cooled down from 950 to 25°C in about 60 min. The combustion products were carried by Hg-free O_2 gas into the trapping solution. After a combustion-trapping procedure, the acid-trapping solution was transferred to a 40-mL pre-cleaned (at 500°C for 4 hrs) borosilicate glass bottle. The trapping system was rinsed with Milli-Q water, and the rinsates were combined into acid-trapping solution too. An aliquot of 50 μL of 0.2 M BrCl was added to the trapping solution to convert possible elemental mercury to Hg^{2+}. The final Hg^{2+} solution was stored at 4°C before subsequent concentration and Hg isotopic analysis.

2.3. Acid digestion and chromatographic pre-concentration

To independently evaluate the combustion-acid trapping dual-stage protocol, we used conventional acid digestion and chromatographic pre-concentration methods for analyzing the same reference soil materials (CRM021, CRM024 and GBW07405). In brief, powdered samples were weighed and digested with 2 mL of aqua regia at 95°C for 2 hrs. After cooled down to ambient temperature, the digested samples were treated with 0.2 M BrCl (5% v/v) for at least 12 hrs to remove residue organic matter. The contents were then transferred to pre-cleaned polyethylene centrifuge vials and centrifuged at 4000 rpm (about 4000 G) for 15 min to separate solid residue from solution. The supernatant of each centrifuge vial was transferred to a pre-cleaned vial followed by 5-fold dilution with Milli-Q water. The final solution was divided to two portions: one was stored at 4°C and the other was further purified using anion-exchange chromatographic column (described below). Both portions were analyzed for Hg concentrations and Hg isotope ratios.

The anion-exchange chromatographic method was used to extract Hg from the acid digestion solution. The column and the detailed procedure were modified from previous studies.[13, 21] In brief, a borosilicate glass column (volume 1.5 mL, I.D. 0.7 cm, L. 4 cm) with a polypropylene reservoir (volume 7.5 mL, I.D. 1.7 cm, L. 3.5 cm) was filled with approximate 0.5 mL of strong basic anion-exchange resin AG1-X4 (200-400 mesh, Bio-Rad). After cleaned with 10 mL 0.05% L-cysteine (Aldrich, USA) in 4 M HNO_3, 10 mL of 4 M HNO_3, and 20 mL Milli-Q water, the resin was converted to chloride form with 6 mL of 2 M HCl. The second portion of aqua regia digestion solution was adjusted to a mixture of 2 M HCl and 1 M HNO_3 and was directly introduced into the column. After rinsing with 10 mL of 1 M HCl, Hg was eluted with 10 mL of 0.5 M HNO_3+ 0.05% L-cysteine. The Hg elution was digested with 0.2 M BrCl (5%) for at least 12 hrs to remove L-cysteine. The solution was then stored at 4°C before subsequent Hg concentration and Hg isotopic determinations. The recovery efficiency of Hg was assessed for each sample by comparing the loaded Hg mass with that of Hg elution and Hg concentrations for the aliquots taken before and after Hg elution and was about 100±5% (2 standard deviation, 2SD, *n*=7).

2.4. Hg concentration and isotopic measurements

CVAFS (Tekran 2500, Tekran® Instruments Corporation, CA) was used to measure Hg concentrations. The results were used to calculate Hg recovery efficiency of the dual-stage protocol and to assess the procedural Hg blanks. The analytical procedures used in this study were similar to a previous work.[36] In brief, all aqueous solution samples were first added 0.1% NH_2OH•HCl to react with excessive BrCl and then mixed with $SnCl_2$ solution to reduce Hg^{2+} to the Hg^0 form, which was purged from the solution using an Hg-free N_2 stream and collected on a gold-coated bead trap. Quantification of Hg was accomplished using a CVAFS analyzer.

Hg isotopic ratios were determined with a CV-MC-ICP-MS (Nu Instruments Ltd., UK) in Xiamen University (Xiamen, China). The analytical procedures used in this study were similar to the published work.[37] In brief, a home-made continuous flow cold-vapor Hg generation system was coupled with a Desolvating Nebulizer System (DSN-100, Nu Instruments Ltd., UK) for Hg and Tl introduction, respectively. The Faraday cups were positioned to simultaneously collect five Hg isotopes and two Tl isotopes including ^{205}Tl (H1), ^{203}Tl (L1), ^{202}Hg (L2), ^{201}Hg (L3), ^{200}Hg (L4), ^{199}Hg (L5), and ^{198}Hg (L6). The instrumental baseline was measured by de-focusing before each sample and standard. A single measurement consisted of 100 integrations of 4.2 s in 5 blocks of 20 cycles. After measurement, an 8-min washout time was applied to ensure that the blank level was <1% of the preceding sample or standard Hg signals. The sample was introduced at 0.75 mL/min, which typically gave an instrumental sensitivity of 1.5 V on ^{202}Hg for 2 ng/mL Hg solutions. Both the internal standard method and the standard-sample bracketing technique were used to correct for instrumental mass bias.[38] The concentrations of samples were diluted to about 2.0±0.4 ng/mL for matching the concentration (2.0 ng/mL) of bracketing standards within 20%.

Hg isotopic composition is reported in delta notation (δ) in units of per mil referenced to the bracketed NIST 3133 Hg standard,[39] which is expressed as:

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

where xxx= 199, 200, 201, and 202. Any isotope composition that does not follow the theoretical mass-dependent fractionation (MDF) is considered as an isotope anomaly caused by mass-independent fractionation (MIF). MIF values are indicated by “capital delta (Δ)” notation (in per mil) and predicted from δ^{202}Hg using the MDF law:[39]

$$\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - \beta_{xxx} \times \delta^{202}\text{Hg}$$

where the mass-dependent scaling factor β_{xxx} is 0.252 for ^{199}Hg, 0.502 for ^{200}Hg, 0.752 for ^{201}Hg and 1.493 for ^{204}Hg, respectively.

3. Results and discussion

3.1. Uncertainty of instrumental analysis

Analysis on both CVAFS and CV-MC-ICPMS may introduce significant drifting from real values that should be corrected. For quantification of Hg concentration measurements, NIST 3133 with various Hg mass (0.05, 0.10, 0.20, 0.40 ng), were analyzed once every six samples. The lab Hg standard was measured 56 times during ten analytical sessions between Mar and Sep 2014, and the average Hg concentration was 7.46 with a precision of ±0.41 ng/mL (2SD, *n*=56). The final uncertainty of Hg concentrations for all fractions derived from either the dual-stage protocol or the aqua regia digestion and column purification procedures was estimated to be within 6% (2SD).

During the analysis period, the typical long-term precision of NIST 3133 Hg isotopic ratios (e.g., ^{202}Hg/^{198}Hg) was <0.09‰ (2SD, *n*=90). Repeated analysis gave average values of −0.54±0.10‰, −0.02±0.04‰ and −0.04±0.04‰ for δ^{202}Hg, Δ^{199}Hg and Δ^{201}Hg of UM-Almaden Hg (2SD, *n*=21), and of −1.22±0.16‰, 0.06±0.09‰ and 0.03±0.10‰ for those of Fluka Hg (2SD, *n*=13), respectively. All these values are consistent with the published results.[13, 14, 32, 39-44] The 2SD of the isotopic compositions of the UM-Almaden were considered as the analytical uncertainty for the isotopic compositions of samples. When the uncertainty of the replicate isotopic measurements of one sample was larger than the 2SD of the UM-Almaden, the uncertainty was applied to the sample.[39]

3.2. Optimization of combustion-trapping assembly and operating conditions

Maintaining very low and stable concentration of Hg in the method blanks was crucial for analysis of Hg isotope ratios. The preliminary tests using the original combustion-trapping assembly of Sun et al. (2013)[29] showed that the procedure blank was about 0.91±1.7 ng (2SD, *n*=10), comparable with that (0.60±1.2 ng, 2SD, *n*=10) reported in their study.[29] Apparently, this blank was very high compared to the total Hg mass (10-20 ng) of samples. Our further investigation of Hg blank for single part of the assembly showed that the silicone tube used for connecting the outlet of the furnace tube to impinger had strong affinity for Hg. The higher procedural Hg blank was thus likely derived from the silicone connector. Since the high blank may cause large uncertainty on the analysis of Hg isotope ratios in $PM_{2.5}$ particles, were placed the silicone connector with a PFA tube, outside of which was wrapped with aluminum foil. Moreover, in order to eliminate possible cross contamination, the PFA tube was also changed before each run. Another major modification made on the assembly was to use three adiabatic sets for insulating the quartz tube outside of the furnaces in an effort to maintain a relatively constant temperature throughout the quartz tube, which eliminated possible condensation of Hg on the internal wall of the quartz tube due to temperature differences.

Using the above modification of the assembly, the procedure blank, which contained Hg from the whole dual-stage system with a blank QFM, was considerably reduced and was consistently <0.21 ng (mean value of 0.10±0.10 ng, 2SD, *n*=20). These values were insignificant low (<2%) when compared to the lowest total Hg mass (10 ng) trapped in 10 mL diluted solution for a single isotopic analysis. However, some procedure blanks obtained right after treatment of the samples having total Hg exceeding 500 ng also had higher Hg background. Excessive cleaning-up of the system was needed before start of next treatment. The low procedure blank indicated that the Hg introduced to the assembly for pre-concentration was efficiently flushed out.

In this study, the blanks of reagents such as 0.2 M BrCl and acid-trapping solution were also monitored to access the main source of Hg in the sample preparation procedure. In general, Hg concentrations in 0.2 M BrCl and acid-trapping solutions were consistently

<0.0026 ng/mL (mean values of 0.0018±0.0010 ng/mL and 0.0013±0.0006 ng/mL, 2SD, *n*=8, respectively). As a result, the main Hg in blanks maybe derived from the residue inside the quartz tube, the air entered during sample loading, and the air exposed during transfer of trapping solution. To further reduce the background levels of Hg, excessive clean-up of the residue after each sample treatment is suggested and the ultra-clean room including advanced purification of air may be helpful.

Except for the above modifications on the combustion-trapping assembly, multiple tests were carried out to reduce the volume of the trapping solution and fix the appropriate O_2 flux and temperature ramp rate. To find the minimal volume of the acid trapping solution, different Hg amounts (25, 100, 200 and 500 ng) of the CRM021 were processed in full runs and each quantity run was duplicated, and trapped into 5, 10, 15, or 20 mL of acid trapping solutions, resulting in 32 CRM021 loaded samples. During these tests, a second impinger was also connected in series to monitor possible breakthrough of Hg vapor from the first trapping impinger. The results showed no breakthrough at all in all the tests. Meanwhile, the combusted residues of the standards were collected after each run, and subsequent analysis showed that these residues contained negligible Hg, indicating that the mercury in the solid powders were completely volatilized and quantitatively trapped. The Hg recovery efficiency for these tests ranged from 92 to 104% with average values of 99±4% (2SD, *n*=8), 100±4% (*n*=8), 101±7% (*n*=8) and 101±7% (*n*=8) respectively for the acid-trapping solutions of 5, 10, 15 and 20 mL. The volume of the acid trapping solution doesn't display statistically significant correlation with the recovery efficiencies. Thus, 5 mL of acid solution is enough and efficient for trapping at least 500 ng Hg thermally released from solid samples and is selected for all further experiments.

O_2 flow rate and temperature ramp rate are also important for determining the efficiency and the speed of Hg extraction from solid matrix. According to Lopez-Anton et al.,[27] Hg^0 is produced predominantly between 200 to 600°C. In this study we performed two sets of tests: the first was run at varying temperature ramp rates of 2.5, 3.3, 4.4 and 6.7°C/min between 200 to 600°C and a fixed O_2 flow rate of 20 mL/min, and the second was done at varying O_2 flow rates of 10, 20, 30, and 40 mL/min but a fixed temperature ramp rate of 4.4°C/min between 200 to 600°C. Each individual run was duplicated and the mass of CRM021 was fixed at 20 mg. The results showed that the recoveries ranged from 96 to 104% (average of 100±7%, 2SD, *n*= 8) for tests with different temperature ramp rates, and the quantitative yield ranged from 95 to 102% for O_2 flow rate experiments, with an average of 99±3% (2SD, *n*=8). This indicated no statistically significant difference in Hg recovery efficiencies for the CRM021 under a wide range of operating conditions, suggesting that the Hg in CRM021 was completely volatilized and quantitatively trapped. For the purpose of shorter processing time and higher trapping efficiency, we selected O_2 flow rate of 20 mL/min and temperature ramp rate of 4.4°C/min as optimal conditions for treatment of airborne particle samples.

3.3. Hg recoveries and reproducibility of isotopic measurements

A series of experiments were done using our optimized combustion-acid trapping protocol to pre-concentrate Hg from standard-spiked samples and reference materials. Since pre-cleaned QFMs were used for particle collection, one set of samples consisted of QFMs spiked with known volume of aqueous standard (NIST 3133) equivalent to total Hg mass of 10, 20, 50, 100 or 200 ng were measured. The recoveries of the spiked Hg varied from 91 to

102% with an average value of 98±6% (2SD, *n*=15). Another set of samples had QFMs loaded with known mass of CRM021 (5.3 to 121 mg, equal to certified Hg mass of 25 to 570 ng), CRM024 (15.9 to 285 mg, equal to certified Hg mass of 11 to 200 ng) and GBW07405 (39.8 to 1460 mg, equal to certified Hg mass of 12 to 420 ng). The measured average concentrations of Hg were 4.68±0.26 ng/mg (2SD, *n*=31), 0.697±0.051 ng/mg (2SD, *n*=24), and 0.284±0.016 ng/mg (2SD, *n*=11) for CRM021, CRM024 and GBW07405, which were favorably comparable to their certified values of 4.7±0.3, 0.71±0.11 and 0.29±0.03 ng/mg, respectively. As shown in Fig. 2a, the recovery efficiencies against the certified Hg concentrations varied from 91 to 104% with an average value of 99±6% (2SD, *n*=90) for the tests with three reference soil materials. In this study, the previous method developed by Sun was also used for investigating the recovery efficiency with the same CRMs samples. As shown in Fig. 2b, our optimized method resulted in relatively better recovery for Hg in variable solid samples compared to the previous dual-stage protocol.[29]

FIGURE 2

Isotopic measurements of Hg thermally released from standard-spike materials showed δ^{202}Hg value of−0.10 to 0.04‰ (average −0.04±0.12‰, 2SD, *n*=4) and Δ^{199}Hg of −0.04 to 0.04‰ (average −0.01±0.04‰, 2SD, *n*=4) relative to the initial NIST 3133 Hg (Table 1). This suggests that no isotopic fractionation occurs during our improved dual-stage protocol. For the three reference soil samples, the average δ^{202}Hg values were −1.36±0.07‰ (2SD, *n*=10), −1.40±0.09‰ (2SD, *n*=9) and −1.81±0.15‰ (2SD, *n*=5) for CRM021, CRM024 and GBW07405, respectively. As shown in Table 1, δ^{202}Hg values determined over 6 months for each of the three CRMs fell in very narrow ranges with very small standard deviations

(<0.13‰), indicating that the optimized dual-stage protocol was reliable over a relatively long time period. Interestingly, significant negative Δ^{199}Hg of −0.31±0.02‰ was determined for GBW07405 (Table 1). Since this is the first report of Hg isotope ratios for the reference soil material, a further investigation using the standard addition method was carried out to compare and confirm our determination.

TABLE 1

3.4. Validation by the standard addition method

The standard addition method was employed to evaluate the Hg recovery and to control the quality of Hg isotope analysis in this study. This method is commonly used in previous studies to quantify the accuracy and precision of stable isotope compositions for samples having complex matrices, which are often significantly different from the matrix of standard materials.[45] Following the method, solid samples were doped with various mass of standard of known isotope ratio. The mixtures obtained had known proportions of standard in each sample fraction, and the isotope ratios of the mixtures should correlate linearly with the proportions of standard (also of sample). In this study, we used GBW07405 as the target solid sample and NIST 3133 as the doped isotope standard. A total of nine samples were prepared by spiking the target samples with NIST3133 at three different Hg mass ratios, each level having triplicates. After combustion-trapping procedure, these nine samples were determined for Hg concentrations and isotope ratios. Fig. 3 shows that the average value of the isotope ratios obtained for each sample-standard mixture were linearly correlated with the mass fraction of the spiked standard (NIST 3133) within 95% confidential level. The intercept on y-axis of the linear correlation represents Hg isotope value of the sample and this data should have little or no interference from the sample matrices. Fig. 3a shows an error-weighted linear fit (R^2=0.995) to the data of δ^{202}Hg with an intercept of −1.91±0.22‰, the corresponding δ^{202}Hg value for GBW07405. Fig. 3b and 3c demonstrates linear fits for Δ^{199}Hg and Δ^{201}Hg too with R^2 values of 0.977 and 0.898, respectively. The corresponding Δ^{199}Hg and Δ^{201}Hg values when extrapolated the linear relationships in Fig. 3b and 3c were respectively −0.34±0.02‰ and −0.31±0.05‰ for GBW07405. These data were consistent with the data listed in Table 2, confirming our determination using the optimized dual-stage protocol. These results also indicated that the QFM matrix had no interference on the isotope analysis of Hg in powder or particulate matters deposited on the filter. The optimized dual-stage protocol could thus be used for routine pre-concentration of Hg from airborne particles.

FIGURE 3

TABLE2

3.5. Comparison with acid digestion and chromatographic pre-concentration methods

As shown in Table 3, the results obtained with both the aqua regia digestion procedure and the aqua regia digestion-column purification procedure had no statistical difference. Taking CRM021 as an example, the average δ^{202}Hg and Δ^{199}Hg values obtained with the acid digestion procedure were −1.24±0.07‰ (2SD, *n*=4) and −0.03±0.02‰ (2SD, *n*=4), respectively, and the average δ^{202}Hg and Δ^{199}Hg values obtained with the acid digestion-column purification procedure were −1.27±0.13‰ (2SD, *n*=4) and 0.01±0.04‰ (2SD, *n*=4), respectively.

TABLE 3

For further comparison, we used a built-in statistical analysis on Origin Pro (version 8) with the option of nonparametric analysis with K independent samples to evaluate the isotope data obtained independently using our improved dual-stage protocol and the two classic procedures. The results of such an exercise indicated that each dataset for a given reference material obtained with the three different procedures had no statistically significant difference at the 95% confidence level. It indicated that our improved combustion-trapping dual-stage protocol is efficient and accurate for pre-concentration of Hg from powered solids. Although both methods of aqua regia digestion and the aqua regia digestion-column purification work well with the powder solid references, the dual-stage protocol is more suitable for the sample low in Hg level needed large volume, such as particular particle sample collected on QFM.

3.6. Application to $PM_{2.5}$ samples

The improved and validated combustion-trapping dual-stage protocol was used to treat two ambient $PM_{2.5}$ samples for Hg concentration and isotope ratio analysis. The sampling site was located within the campus of Institute of Geochemistry, Chinese Academy of Sciences (Guiyang, China). These two samples were collected on a 20.3×12.5 cm (8×5 inch) QFM over 7 days at air flow rate of 300 L/min during a haze episode in March 2014 ($PM_{2.5}$-1), and clear days in June 2014 ($PM_{2.5}$-2), with an aluminum alloy $PM_{2.5}$ sampler (Guangzhou Mingye Huanbao Technology Company, China). The air volume was thus of about 2592 and 3024 $m^3$for these two samples, respectively. Meanwhile, a field blank was also collected with sample and exposed to ambient conditions only for the length of time (<15 min) required to set up the routine PM samples. It reflected possible contamination during setting up the sampling of PM and sorption of Hg from atmosphere during the sampling procedure. During pre-concentration with the dual-stage protocol, three unequal portions of the QFM filter of $PM_{2.5}$-1 (apportioned with a pre-cleaned polyethylene scissor), half of the QFM filter of $PM_{2.5}$-2 and the field blank were processed as individual samples, and the trapping solutions were analyzed for the Hg concentrations and Hg isotope ratios following the procedures described above. The three unequal portions of filters of $PM_{2.5}$-1 were used for two purposes: 1) testing the repeatability of the protocol, and 2) investigating if the Hg isotope composition of the real PM sample with low Hg amount was effected by the blank Hg (from the background or system).

The Hg analysis showed that the field blank had total Hg (0.35 ng) less than <5% of the Hg in the PM samples, and that $PM_{2.5}$-1 and $PM_{2.5}$-2 had the PHg of 101 and 13 pg/m^3, respectively, indicating higher PHg in the air of the haze episode compared to clear days.

The Hg isotope compositions obtained for the two $PM_{2.5}$ samples are listed in Table 4 and a composition with the data for other rain and atmospheric particulate samples was given in Fig. S1 (see Supplemental Material).[14, 23, 30, 46, 47] The samples $PM_{2.5}$-1 had a δ^{202}Hg value of −1.71±0.09‰ (2SD, *n*=3) and a significantly positive MIF Δ^{199}Hg value of 0.21±0.05‰ (2SD, *n*=3), and it was no systematic difference of Hg isotope compositions among these three portions, this indicates the limited effect of residual Hg (from the background or system) on Hg isotope measurements and, again confirms the validation of our protocol for analyzing Hg isotopic ratios in real PM sample. Interestingly, the sample $PM_{2.5}$-2 displayed a higher δ^{202}Hg value of −1.13‰ and a lower Δ^{199}Hg value of 0.16‰. Both samples did not display measurable mass-independent fractionation of even-numbered Hg isotopes. PHg of airborne particles showed thus evident δ^{202}Hg and Δ^{199}Hg variations with respect to the climatic conditions. The δ^{202}Hg and Δ^{199}Hg values in our airborne particles were relatively lower than those (δ^{202}Hg value of −1.05±0.15‰ to −0.14±0.17‰ (2SD) and Δ^{199}Hg value of 0.12±0.13‰ to 0.48±0.04‰ (2SD), respectively) found in atmospheric PHg of a special coastal environment.[30] Interestingly, the precipitation samples collected from the same site displayed larger variation of δ^{202}Hg (from −4.27‰ to −0.44‰, mean of −1.11‰) and higher Δ^{199}Hg values (from 0.19‰ to 1.16‰, mean of 0.62‰).[46] Therefore, specific Hg may thus display different isotopic compositions in the atmosphere. Our study demonstrates that further study is needed to systematically investigate Hg isotopes in airborne particles of variable environments, for example, research on Hg isotope systematic in Chinese urban aerosols would provide useful information about the sources and pathways of both Hg and PM, given the fact that China has experienced deteriorated air pollution due to rapid industrialization in recent decades.

TABLE 4

4. Conclusions

In this study, we optimized the dual-stage protocol that allows for specifically pre-concentrating Hg from PM samples for high-precision isotopic analysis. The modification can significantly reduce procedural Hg blank (0.10±0.10 ng, *n*=20) and thus guarantee good Hg recovery (average 99±6%, *n*=90) and high precision of Hg isotope analysis. Using our optimized protocol, up to 570 ng Hg thermally released from solid samples could be efficiently trapped in a 5-mL acid solution within 3.5-hr. Long-term isotopic analysis of Hg in reference soil materials gave relatively constant results within 95% confidential level, attesting the reproducibility of measured isotope ratios. The determined isotope values for Hg in reference solid materials using our protocol were further validated by standard addition method. The fact that three pre-concentration processes gave identical results suggests our optimized protocol as a complementary method that could be used, together with the conventional acid digestion and column purification methods, to separate Hg from various solid samples for isotopic analysis. Our study highlights the importance of studying Hg isotopic compositions in airborne particles of variable environments in order to fully understand the behaviors of Hg and its isotopes in the atmosphere.

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Table 1 Mercury stable isotope ratios of the certified reference materials measured in different experiment sessions using the dual stage protocol. NIST 3133 is standard solution. CRM021, CRM024 and GBW07405 are three solid reference materials.

Sample	Hg (ng)	Recovery (%)	δ^{199}Hg (‰)	δ^{200}Hg (‰)	δ^{201}Hg (‰)	δ^{202}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)
NIST3133									
1	10.0	99	-0.01	-0.09	-0.02	-0.10	0.02	-0.04	0.06
2	40.0	102	-0.02	-0.03	-0.07	-0.05	-0.01	-0.01	-0.03
3	50.0	99	-0.03	0.01	-0.03	0.04	-0.04	-0.01	-0.06
4	100	100	-0.02	-0.05	-0.05	-0.06	0.00	-0.02	-0.01
Average		100	-0.02	-0.04	-0.04	-0.04	-0.01	-0.02	-0.01
2SD		3	0.01	0.08	0.04	0.12	0.04	0.03	0.10
CRM021									
1	91.5	99	-0.34	-0.61	-0.99	-1.32	-0.01	0.05	-0.00
2	93.0	100	-0.33	-0.65	-1.02	-1.31	0.00	0.01	-0.03
3	101	100	-0.36	-0.66	-1.05	-1.33	-0.02	0.01	-0.05
4	104	100	-0.36	-0.67	-1.10	-1.36	-0.02	0.01	-0.08
5	105	99	-0.35	-0.66	-1.06	-1.33	-0.01	0.00	-0.06
6	104	97	-0.39	-0.70	-1.08	-1.37	-0.05	-0.01	-0.06
7	103	93	-0.41	-0.72	-1.12	-1.42	-0.05	-0.01	-0.05
8	102	98	-0.36	-0.67	-1.06	-1.38	-0.01	0.02	-0.03
9	572	100	-0.41	-0.69	-1.15	-1.39	-0.06	0.00	-0.11
10	566	101	-0.35	-0.67	-1.11	-1.36	0.00	0.01	-0.09
Average		99	-0.37	-0.67	-1.08	-1.36	-0.02	0.01	-0.06
2SD		4	0.06	0.06	0.09	0.07	0.04	0.03	0.06
CRM024									
1	47.2	97	-0.32	-0.69	-1.03	-1.39	0.03	0.00	0.01
2	35.8	97	-0.30	-0.69	-0.99	-1.37	0.05	-0.00	0.04
3	201	95	-0.32	-0.69	-1.04	-1.38	0.02	0.00	0.01
4	108	91	-0.32	-0.71	-1.03	-1.41	0.04	0.00	0.04
5	108	102	-0.32	-0.67	-1.02	-1.34	0.02	0.01	-0.01
6	108	98	-0.33	-0.71	-1.09	-1.42	0.03	0.00	-0.02
7	108	99	-0.35	-0.73	-1.12	-1.46	0.02	0.00	-0.03
8	109	97	-0.34	-0.71	-1.09	-1.45	0.02	0.02	-0.00
9	109	99	-0.33	-0.66	-1.04	-1.33	0.01	0.01	-0.04
Average		97	-0.33	-0.70	-1.05	-1.40	0.03	0.01	0.00
2SD		6	0.03	0.04	0.08	0.09	0.02	0.01	0.05
GBW07405									
1	24.1	97	-0.76	-0.87	-1.59	-1.72	-0.32	-0.01	-0.29
2	11.0	94	-0.76	-0.90	-1.62	-1.83	-0.29	0.02	-0.24
3	50.7	98	-0.75	-0.86	-1.61	-1.74	-0.31	0.01	-0.30
4	22.6	100	-0.79	-0.94	-1.66	-1.86	-0.32	0.00	-0.26
5	22.5	101	-0.80	-0.94	-1.69	-1.89	-0.32	0.01	-0.27
Average		98	-0.77	-0.90	-1.63	-1.81	-0.31	0.01	-0.27
2SD		5	0.04	0.07	0.08	0.15	0.02	0.02	0.05

Table 2 Mercury stable isotope ratios measured using the dual stage protocol from the standard addition method.

Sample		Fraction of standard	Recovery (%)	δ^{199}Hg (‰)	δ^{200}Hg (‰)	δ^{201}Hg (‰)	δ^{202}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)
GBW07405										
n= 5	Average	0	98	-0.77	-0.90	-1.63	-1.81	-0.31	0.01	-0.27
	2SD		5	0.04	0.07	0.08	0.15	0.02	0.02	0.05
GBW07405+NIST3133										
n= 3	Average	0.22	100	-0.65	-0.77	-1.39	-1.53	-0.26	0.00	-0.24
	2SD		5	0.03	0.04	0.05	0.06	0.02	0.01	0.01
n= 3	Average	0.46	100	-0.47	-0.56	-1.02	-1.09	-0.20	-0.01	-0.20
	2SD		5	0.03	0.03	0.04	0.05	0.02	0.01	0.00
n= 3	Average	0.69	99	-0.27	-0.33	-0.58	-0.65	-0.11	-0.01	-0.09
	2SD		4	0.03	0.04	0.05	0.05	0.02	0.01	0.01
NIST3133										
n= 4	Average	1	100	-0.02	-0.04	-0.04	-0.04	-0.01	-0.02	-0.01
	2SD		3	0.01	0.08	0.04	0.12	0.04	0.03	0.10

Table 3 Mercury stable isotope ratios obtained using dual stage protocol, aqua regia digestion and aqua regia digestion-column purification procedure.

Method/Sample			Recovery (%)	δ^{199}Hg (‰)	δ^{200}Hg (‰)	δ^{201}Hg (‰)	δ^{202}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)
CRM021										
Dual stage	*n*=10	Average	99	-0.37	-0.67	-1.08	-1.36	-0.02	0.01	-0.06
		2SD	4	0.06	0.06	0.09	0.07	0.04	0.03	0.06
Aqua regia	*n*= 4	Average	100	-0.35	-0.63	-1.00	-1.24	-0.03	-0.01	-0.07
		2SD	6	0.03	0.03	0.07	0.07	0.02	0.02	0.02
Column chemistry	*n*= 4	Average	102	-0.31	-0.62	-0.96	-1.27	0.01	0.02	-0.01
		2SD	3	0.03	0.06	0.08	0.13	0.04	0.02	0.05
CRM024										
Dual stage	*n*= 9	Average	97	-0.33	-0.70	-1.05	-1.40	0.03	0.01	0.00
		2SD	6	0.03	0.04	0.08	0.09	0.02	0.01	0.05
Aqua regia	*n*= 3	Average	101	-0.32	-0.61	-0.95	-1.27	0.00	0.03	0.01
		2SD	4	0.07	0.02	0.05	0.12	0.09	0.04	0.07
Column chemistry	*n*= 3	Average	100	-0.20	-0.60	-0.86	-1.28	0.12	0.05	0.11
		2SD	4	0.09	0.07	0.16	0.13	0.07	0.03	0.06

Table 4 Mercury stable isotope ratios of two $PM_{2.5}$ samples. P1-3 are three fractions of the same $PM_{2.5}$-1 that were treated as individual sample. $PM_{2.5}$-2 was measured only one time.

Sample	Total-Hg (ng)	δ^{199}Hg (‰)	δ^{200}Hg (‰)	δ^{201}Hg (‰)	δ^{202}Hg (‰)	δ^{204}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)	Δ^{204}Hg (‰)
$PM_{2.5}$-1										
P1	46.8	-0.26	-0.86	-1.20	-1.75	-2.68	0.18	0.02	0.12	-0.07
P2	60.0	-0.21	-0.82	-1.15	-1.71	-2.56	0.22	0.04	0.13	-0.01
P3	32.8	-0.20	-0.80	-1.11	-1.66	-2.53	0.22	0.04	0.14	-0.05
	Average	-0.22	-0.83	-1.15	-1.71	-2.59	0.21	0.03	0.13	-0.04
	2SD	0.06	0.06	0.09	0.09	0.16	0.05	0.02	0.02	0.07
$PM_{2.5}$-2										
	18.9	-0.13	-0.48	-0.78	-1.13	-1.66	0.16	0.09	0.07	0.02

Fig. 1 Schematic diagram of the combustion-trapping assembly. The dashed arrow indicates the gas flow direction. Thin-walled (0.5 mm) PFA tubing is used for connecting the outlet of furnace quartz tube to the impinger elbow. Three adiabatic sets are used for maintaining constant temperatures.

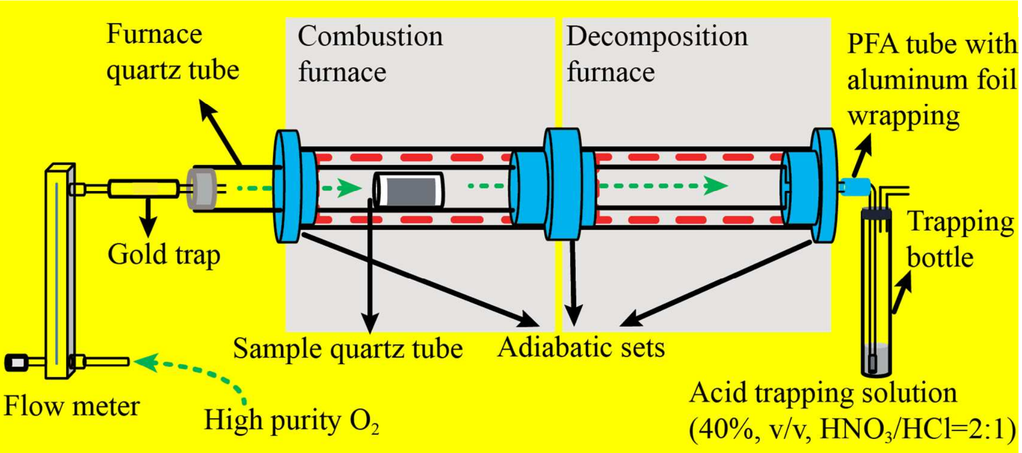


Fig. 2 a) Hg recoveries of 90 tests on various dosages of reference materials using our optimized combustion-trapping protocol. The solid and two dashed horizontal lines are the average value and the 2 standard deviations, respectively. b) the comparison of Hg recoveries obtained using the previous method reported in Sun et al. (2013) and the optimized protocol in this study. A normal curve (to the right) and a boxplot (to the left) represent the distribution of data points. The horizontal lines at the bottom, middle, and top of each boxplot are the lower quartile (below which 25% lowest values are found), median, and upper quartile (above which 25% highest values are found), respectively.

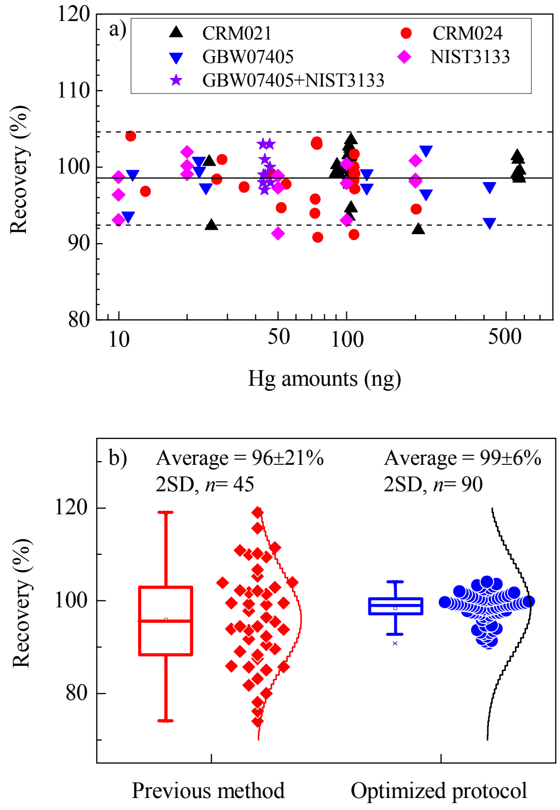
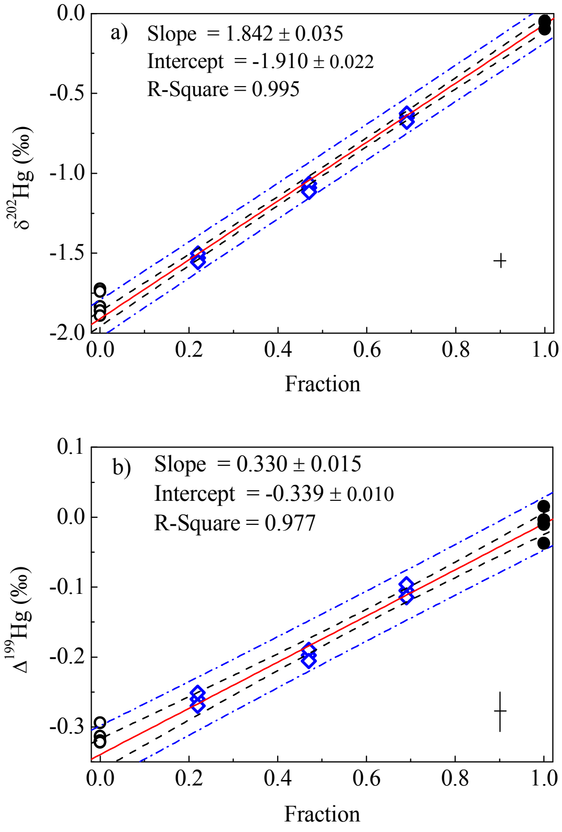
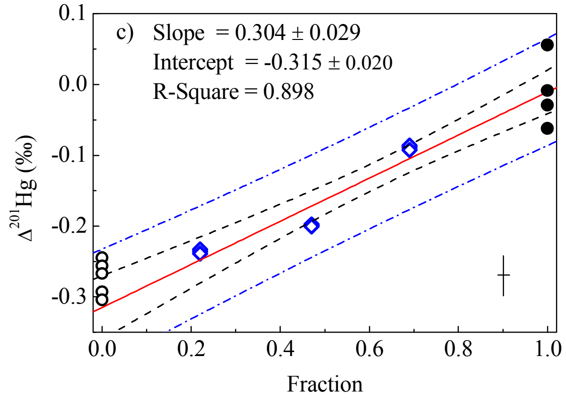


Fig. 3 Standard addition method for validation of isotopic analysis using our optimized protocol. Measurements of Hg in mixtures of reference soil GBW07405 with various proportions of NIST 3133 define linear arrays for isotope ratios δ^{202}Hg (a), Δ^{199}Hg (b) and Δ^{201}Hg (c) as a function of standard fraction. The linear fits were obtained by an error weighted regression, excluding the pure standard points (black points) and sample points (hollow circles). The error envelopes on the fit are at the 95% confidence levels. The blank dashed line and blue dash-dotted line are the 95% confidence levels of upper and low confidence limit and prediction limit, respectively.




c) Slope = 0.304 ± 0.029
Intercept = -0.315 ± 0.020
R-Square = 0.898
Δ^{201}Hg (‰)
Fraction
0.1
0.0
-0.1
-0.2
-0.3
0.0
0.2
0.4
0.6
0.8
1.0