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A modified introduction device and a preconcentration method were developed to enhance the sensitivity of the Hg isotopic analysis method.

Fig. 1 Schematic of the introduction device (A) and the preconcentration method (B)
Isotopic composition analysis of dissolved mercury in seawater with purge & trap preconcentration and a modified Hg introduction device for MC-ICP-MS

Haiying Lin, Dongxing Yuan, Bingyan Lu, Shuyuan Huang, Lumin Sun, Fan Zhang and Yaqin Gao

This study aimed to solve the common problems in Hg isotope analysis of water samples at low concentration. The isotope composition of dissolved Hg in seawater is reported for the first time. A modified device for introducing Hg into a multi-collector inductively coupled plasma mass spectrometer and a preconcentration method for the preconcentration of dissolved Hg were developed to enhance the sensitivity of the isotopic composition analysis method. The modified cold-vapor generator was used to transfer dissolved Hg\(^{2+}\) from matrix into gaseous Hg\(^{0}\). The purge & trap method was developed and employed to preconcentrate dissolved Hg in water samples. Keeping other parameters the same, the Hg signal generated with the modified Hg introduction device was twice as much as the commercial one (HGX 200). In the measurement of NIST SRM 3133, the external precision for \(\delta^{202}\text{Hg}\) was 0.06‰ (2SD, n=310), and the \(\delta^{202}\text{Hg}\) value of the UM-Almadén in-house secondary standard was -0.57±0.10‰ (2SD, n=49), indicating that the modified device was stable and reliable. Factors influencing the efficiency of the purge & trap method, e.g., concentration of KMnO\(_4\) in the trapping solution, flow rate of the purge gas and purge time, were optimized. With ultrapure water (blank) and seawater (matrix) spiked with NIST SRM 3133 at Hg concentrations of 5.00-35.50 ng/L and 10.00-35.50 ng/L, the \(\delta^{202}\text{Hg}\) value of the blank spike and matrix spike was 0.0±0.04‰ (2SD, n=19) and -0.02±0.04‰ (2SD, n=12), respectively. The results indicated that the purge & trap method was free from matrix interference. The results of this practical application showed good stability and reproducibility of the proposed methods.

Keywords: purge & trap, preconcentration, mercury isotope, cold-vapor generator, seawater, MC-ICP-MS.

Introduction

Mercury (Hg) is a toxic metal of global concern \(^1\). Hg is released to the environment through both natural and anthropogenic pathways. Once being emitted to the atmosphere, gaseous elemental Hg\(^{0}\) can be transformed to reactive bivalent and particulate Hg species which can be deposited into aquatic reservoirs via dry and wet deposition.\(^2\) Hg exists in the ocean mainly in inorganic forms such as dissolved Hg (Hg\(^{0}\); Hg\(^{2+}\)) and particulate Hg\(^{2+}\). Dissolved Hg may either return to the atmosphere through air-sea exchange \(^3\), or attach onto particulates and thus remain in seawater.

The isotopic tracing technique is an effective method in the research of Hg pollution. Using the technique, researchers have studied the source, pathway and fate of Hg in the environment, including its transport, transformation and sink. Fractionations of Hg isotopes \(\text{Hg}^{199}, \text{Hg}^{200}, \text{Hg}^{201}, \text{Hg}^{202}\) and \(\text{Hg}^{208}\) have been induced with some natural processes, e.g., photo-reduction \(^4\), volatilization or evaporation \(^5, 6\), and biological processes \(^7, 8\). Previous studies report very large variations in both mass dependent fractionation (MDF) and mass independent fractionation (MIF) in solid samples, such as coals/soils \(^9\), sediments \(^10, 11\), rocks \(^12\), hydrothermal ores \(^13\), biological samples \(^14-16\), atmospheric precipitation \(^17\). The study of Hg fractionation in water samples was increased in recent years. Wang et. al. investigate the Hg fractionation of photoreduction in natural water \(^18\) and volatilization of Hg\(^0\) from solution into gas phase \(^6\), observing that MDF and MIF result from the preferential photoreduction and volatilization of light or odd isotopes. Sherman et. al. \(^19\) prove that the Hg in Arctic snow is fractionated by the re-emission of Hg\(^0\) and sunlight-induced reactions. The MIF of even isotope \(\text{Hg}^{200}\) Hg is found in rain and snow samples \(^20\). However, no Hg isotope data of seawater have been reported due to the complicated matrix. Hence, the MDF and MIF of Hg isotopes in seawater remain unknown.

A multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) is usually used to accurately analyse isotopes with a mass of 7-238. With the development of MC-ICP-MS, there is increasing interest in applying the Hg isotope tracing technique to understand the sources and behaviour of Hg in the environment. The commercial cold-vapor generator (CVG; HGX 200, CETAC, U.S.) is a commonly used sample introduction device to transfer dissolved
Hg\textsuperscript{2+} to gaseous Hg\textsuperscript{0} \cite{21, 22, 23}, within which the special U-shaped gas-liquid separator (GLS) has a large dead volume. A large amount of carrier gas (6-8 L/min) is needed in the device. Therefore, Hg\textsuperscript{0} concentration is diluted by the carrier gas, which decreases signal intensity.

The concentration of Hg in waters is usually as low as ng/L \cite{24, 25, 26}. On the other hand, for better precision and accuracy, the isotopic analysis method needs Hg concentration in the prepared samples (samples ready for instrumental analysis) at ng/mL level \cite{16, 17, 18, 19, 20}. Preconcentration is one of the ways to reach higher concentration.

Until now, two methods have been successfully performed in preconcentrating Hg in water samples. The gas-liquid separation and trap method \cite{17, 19, 20, 25} method employs a GLS to separate Hg\textsuperscript{0} from the samples, and then trap Hg\textsuperscript{0} in KMnO\textsubscript{4} solution. Alternatively, AG 1 × 4 ion-exchange resin \cite{26} is used to directly pre-concentrating Hg from lake water and roof stream water. Although the two methods have resulted in quantitative yields and been applied to analyse Hg isotopes in natural waters, they suffer some disadvantages. For instance, the gas-liquid separation method consumes much more reagent during the reduction process, and it usually takes much time for treating litters of water at the introduction rate of 0.8 mL/min \cite{17}. Even more, the enrichment factor is limited with the gas-liquid separation method. The preconcentration process with the ion-exchange resin has to be carried out in a clean room to avoid the possible contamination. Neither of the methods has been applied in seawater samples.

A refined two-stage gold amalgamation preconcentration technique \cite{22, 23} has been applied for the determination of Hg in seawater at sub-ng/L with recovery higher than 95%. It takes 30 min for purge Hg from 500 mL seawater \cite{27}. The Au column used in the method for absorbing gaseous Hg\textsuperscript{0} is easily purified with less contamination. 204\textsuperscript{Hg} is significant isobaric interfered with 204\textsuperscript{Pb}; the commonly used procedure to eliminate isobaric interferences is the mathematical correction following an appropriately designed algorithm \cite{28, 30}. With gold amalgamation preconcentration technique, Hg can be completely separated from Pb, thus precisely determination of 204\textsuperscript{Hg} composition without correction can be achieved. Since the sample state is required to be liquid before introduction to the MC-ICP-MS, Hg preconcentrated on the Au column has to be transferred into solution. KMnO\textsubscript{4} solution is commonly used \cite{17, 20, 25} for oxidizing and trapping Hg\textsuperscript{0}.

Purge & trap method is practical and free from seawater with high salt matrix. For the measurement of dissolved Hg isotope composition in seawater, a modified CVG Hg introduction device and a purge & trap preconcentration method with gold amalgamation and KMnO\textsubscript{4} solution trapping were developed in this study. Application of the method to the analysis of dissolved Hg isotopic composition in seawater was carried out.

**Materials and methods**

**Instrumentation and measurement**

The Hg isotope analysis system can be divided into two parts, the introduction device and the analysis/detection instrument. As shown in Fig. 1, the introduction device included a modified CVG for Hg introduction and a desolvating nebulizer (DSN-100, Nu Instruments, Great Britain) for thallium (Tl) introduction. MC-ICP-MS (Nu Plasma HR, Nu Instruments, Great Britain) was employed as the analysis/detection instrument. The modified CVG was made out of a self-designed quartz tube, in which Hg standard or sample solutions were adequately mixed with tin chloride (SnCl\textsubscript{2}) in a tee junction (t1) and pumped into the GLS from the top. The Hg\textsuperscript{0} in the mix solution was blown off with a counter-flow argon (Ar) gas at flow rate of 80-100 mL/min from the bottom of the GLS. After removing moisture in the carrier gas with a 0.45 μm PTFE filter, Hg\textsuperscript{0} was mixed with Tl aerosol and injected into the ICP. Two peristaltic pumps (Baoding Longer Precision Pump Co., China) were used to introduce standard/sample and reagents, and to remove waste from the GLS.

The DSN-100 was employed for the Tl introduction. Seven Faraday cups of the MC-ICP-MS were used to detect Hg and Tl isotope; in which, L6, L5, L4, L3, L2, L1, Ax and H1 were set for 198\textsuperscript{Hg}, 197\textsuperscript{Hg}, 200\textsuperscript{Hg}, 201\textsuperscript{Hg}, 202\textsuperscript{Hg}, 203\textsuperscript{Tl} and 205\textsuperscript{Tl}. The concentration of 198\textsuperscript{Hg} was too low to be detected; the isotope was not used in the measurement.

The uptake rate of the Hg standard, sample and reagents was adjusted to 0.75 mL/min, and that of the Tl standard was 0.10 mL/min. Between standard and sample, the CVG and DSN-100 were rinsed with 3% (v/v) HNO\textsubscript{3} solution for 7 min until the signal intensity returned to the background level, typically between 10-30 mV.

A cold vapor atomic fluorescence spectrophotometer (Rayleigh Analytical Instrument Corp., China) was used for the analysis of total Hg \cite{29}.

**Reagents and solutions**

All reagents were prepared in ultrapure water (18.00 MΩ·cm) from a water purification system (Millipore, USA). HCl, HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} (Merck, Germany) of GR grade were used for vessel cleaning and reagent preparation. A 0.13 mol/L SnCl\textsubscript{2}·2H\textsubscript{2}O (Xilong Chemical Co., China) solution was prepared in 1.20 mol/L HCl. The SnCl\textsubscript{2}·2H\textsubscript{2}O solution is usually taken as the standard carrier, which is usually used to determine trace Hg concentrations in seawater. Two types of reference solutions of Hg standard were obtained from National Research Council Canada.

**Fig. 1 Schematic of the introduction device**

(CVG: cold-vapor generator, GLS: gas-liquid separator, DSN-100: desolvating nebulizer, MC-ICP-MS: multi-collector inductively coupled plasma mass spectrometer. P1: P2: pump 1, pump 2, t1, t2, tee 1, tee 2.)
solution was purged prior to use with Hg-free Ar gas overnight to remove Hg. Bromine monochloride (BrCl) solution was made by dissolving 5.40 g of potassium bromide (Xilong Chemical Co. China) in 0.50 L of HCl with stirring for approximately 1 h in a fume hood, then slowly adding 7.60 g potassium bromate (Xilong Chemical Co. China) with stirring for another hour. The KMnO₄ (Alfa Aesar, UK) solutions of 1.00-5.00 mmol/L were prepared in 0.50 mol/L H₂SO₄. The Hg (NIST SRM 3133) and Tl (NIST SRM 997) standard solutions were purchased from the National Institute of Standards and Technology, USA, their certified compositions were reported in earlier researches. The U-M-Almadén in-house secondary standard was kindly provided by Dr. Blum of the University of Michigan.

Sample collection and preparation

Seawater samples were collected from a coal-fired power plant located near Xiamen western sea area, Fujian. The plant is equipped with a seawater flue gas desulfurization system. Five sampling sites were selected, including the inlet pool of fresh seawater (S1), the outlet of the desulfurization tower (S2), inside the aeration pool (S3, S4) and the outlet of waste seawater (S5). Sampling and sample preparation were performed following the US EPA (1996) method. 5-10 L seawater was collected and filtered through a 0.45 µm aceta cellulose membrane. The filtrate was stabilized in 0.5% (v/v) BrCl (US EPA, 1631).

Purge & trap preconcentration

The dissolved Hg in spike samples and seawater samples was preconcentrated with a purge & trap method. After the treatment, the Hg concentration in the trapping solution could be up to 3.00 ng/mL. The arrangement of the purge & trap method is schematically illustrated in Fig. 2. In Fig. 2a, within a 2 L purge bottle, the Hg⁰ was purged with Ar gas at a flow rate of 300-400 mL/min, and then consequently trapped onto a series of Au columns (Au-1, Au-2, Au-3) containing gold-coated glass beads (Brooks Rand Lab, USA). A drying column filled with soda lime was inserted before the Au columns to protect the gold trap from moisture. As shown in Fig. 2b, the Au columns were then transferred to a thermal desorption device (D), and desorption was performed at 500 °C for several seconds to release Hg⁰ in each column. The carrier gas at a flow rate of 20 mL/min sent the released Hg⁰ to the trapping solution containing KMnO₄. Another Au column (Au-4) was placed at the outlet of the trapping bottle to trap Hg⁰ residues, which could verify if Hg⁰ was efficiently trapped in the KMnO₄ solution. Teflon tubing was used as transfer lines in the purge & trap system.

Data Analysis

Instrumental mass bias was monitored and corrected using the internal correction method and the standard-sample bracketing method. Exponential mass fractionation law was applied as the internal correction method assuming a reference ⁰⁰°⁰°Tl concentration of 2.38714 for Tl internal standard. The Tl to Hg signal ratio was adjusted to 0.80-1.00. The results of Hg isotopic measurements can be expressed as δ-values, which represent the MDF of isotopes:

δ³⁴Hg(‰) = \left[ \frac{\left( \frac{Hg}{Tl} \right)_{\text{sample}}}{\left( \frac{Hg}{Tl} \right)_{\text{standard}}} \right] \times 1000 \quad (1)

where ³⁴Hg is ¹⁹⁸Hg, ²⁰⁰Hg, ²⁰¹Hg and ²⁰²Hg. The MIF of Hg isotopes was expressed as Δ³⁴Hg values, which can be calculated using the following equation:

Δ³⁴Hg = δ³⁴Hg - (δ²⁰²Hg × β) \quad (2)

where the fractionation factor β is 0.2520, 0.5024 and 0.7520 for ¹⁹⁸Hg, ²⁰⁰Hg and ²⁰¹Hg.

Results and discussion

Optimization of parameters for isotope measurement

Gas-liquid separators

The design of the modified CVG was focused on improving the Hg signal and simplifying the device. As a core part of the CVG, the GLS was designed to be tube-shape with a cylindrical chamber of 10 mm i.d. and 250-400 mm height. Diagrams of four home-made GLSs and the commercial one are shown in Fig. 3. In the four homemade GLSs, the main outlets at the top and in the bottom were the outlet of the carrier gas and waste, respectively. The side inlets near
the top and near the bottom were the inlet of mix solution and carrier gas, respectively. The height of the GLS and the flow way of the carrier gas were different among the four GLSs. The height of GLS-1 and GLS-2 was 400 mm, GLS-3 was 300 mm, and GLS-4 was 250 mm. The carrier gas flowed horizontally into GLS-1. There was a 45° angle between the bottom side inlet and the cylindrical chamber for GLS-2, GLS-3 and GLS-4. The commercial GLS is U-shaped and embedded with a frosted glass post, and the carrier gas flows horizontally into it.

Fig. 3 Diagram of four GLS designs (GLS-1, GLS-2, GLS-3, GLS-4) and the commercial GLS.22,36

The gas-liquid separation efficiency of the GLSs was the ratio of the amount of Hg$^{2+}$ purged out by the carrier gas to initial amount of Hg in the standard. When the mixed solutions of SnCl$_2$ and Hg standard were continuously pumped into the GLS, Hg$^{2+}$ reduced from Hg$^{0}$ was purged and carried out by Ar gas. An Au blank column was installed on the top outlet of the GLS to trap Hg$^{0}$ for 20 s. And then the amount of Hg$^{0}$ on the Au column was quantitatively analysed and considered as the amount of Hg$^{0}$ purged out by the carrier gas. As the initial amount of Hg in the standard solution was known, the separation efficiency of the GLS could be calculated. The measured efficiencies of the four GLSs were 101.1±4.8% (SD, n=12), which corresponded to the previous studies.34,35

The Hg concentration of 3.00 ng/mL, 100 integration cycles and 5 s per cycle were chosen as the condition in the comparison test of the $^{202}$Hg signal and standard error of $^{202}$Hg with the four modified GLSs. The $^{202}$Hg signal was 2.86±0.05 V for GLS-1, 2.88±0.02 V for GLS-2, 2.87±0.02 V for GLS-3, and 2.84±0.04 V for GLS-4 (SD, n=3). No significant statistical differences were identified among the four GLSs. However, the relatively strong and steady signal found in GLS-2 and GLS-3. The main reason could be that the angle between the gas inlet and the cylindrical chamber greatly improved the turbulent flow of the carrier gas, resulting in efficient purge of Hg$^{0}$ from the mixed solution. The $^{202}$Hg values of GLS-2 (0.01±0.03‰, 2SD, n=3) and GLS-3 (-0.01±0.03‰, 2SD, n=3) were close to each other, but the larger dead volume in the higher cylindrical chamber of GLS-2 was inconvenient to use compared to GLS-3. Therefore, GLS-3 was considered to be the best one to use among the four.

Compared with the commercial GLS, there were three major advantages in the modified GLSs. First, the dead volume was reduced, and the chamber could be washed more easily. Second, the carrier gas flowed from the bottom side inlet to the top of the GLS in an opposite direction to the mix solution, which provided turbulent flow of the carrier gas for rapid and efficient gas-liquid separation. Third, the modified introduction device consumed less carrier gas than the commercial one. The $^{202}$Hg signal with a modified introduction device was 2.84-2.88 V at the Hg concentration of 3 ng/mL, while that with the commercial one was 0.60-1.32 V.11,36 V stands for volts, the unit of the $^{202}$Hg signal given by the MC-ICP-MS. The Hg signal with a modified introduction device was twice that of the commercial one, showing a significant improvement in sensitivity for Hg isotopic analysis.

Data acquisition time

Data acquisition time was one of the key parameters in order to achieve good internal precision. 100 integration cycles were adopted in a single block using an Hg standard with concentration of 3.00 ng/mL. The internal precision was expressed as the standard error of data collected in a single block. By varying the integration time from 2 to 10 s per cycle, the total acquisition time was in the range 200 s to 17 min. As shown in Fig. 4a, an obvious improvement in the internal precision of $^{202}$Hg was found when the integration time per cycle was longer than 6 s. Thus 6 s was chosen as the integration time to obtain an internal precision of better than 0.04‰, and the total acquisition time was 10 min. A sample volume of 9.0 mL was needed for a single measurement.

Mercury concentration in samples

The mercury concentration in prepared samples was another factor affecting the internal precision. When the Hg concentration increased from 0.50 to 7.00 ng/mL, the internal precision of each measurement increased from 0.06 to 0.03‰ (Fig. 4b). A $^{202}$Hg signal of approximately 2.80 V was achieved with the Hg concentration at 3 ng/mL, and the internal precision was better than 0.04‰, which was considered to be good enough for the analysis. Higher concentrations did not significantly improve internal precision, but increased the rinsing time and the risk of carry over between samples. Consequently, the Hg concentration of 3 ng/mL was required for isotopic measurement to obtain designed accuracy and reproducibility, the concentration was lower than the earlier researches.10,11,17,22,36.
Flow rate of the purge gas

A flow rate of the purge gas ranging from 100 to 600 mL/min was optimized with the Hg concentration of 15 ng/L. If the gas flow rate was too low, Hg was hard to be purged from the solution. On the other hand, if the flow rate was too high, it could be more difficult for Hg\(^{2+}\) to be absorbed on the Au columns (Fig. 2a, Au-1, Au-2, Au-3), and the Hg\(^{2+}\) could escape to the air. Fig. 5a shows the recoveries at different purge flow rates within 95.0-105.0% with a gas flow rate ranging from 100 to 600 mL/min. Compared with those with flow rates of 100-200 mL/min, the air bubbles from the purge were fine and abundant in the solution with the rate of 300-400 mL/min, which showed better results. On the other hand, the flow rate of 500-600 mL/min was too high. Therefore, 300 mL/min was employed as the gas flow rate for purge to obtain better reproducibility represented as SD, and finer air bubbles.

Purge time

The Hg concentration of 15 ng/L and a gas flow rate of 300 mL/min were chosen to study the influence of purge time on Hg recovery. As shown in Fig. 5b, the recovery greatly increased with purge time from 0 to 50 min, and then it slowly reached a plateau at about 103.0% after 60 min purge. Hence, 75 min was selected as the purge time.

Optimization of parameters of the preconcentration system

Concentration of KMnO\(_4\) solution

The concentration of KMnO\(_4\) (1.00-5.00 mmol/L) in the trapping solution was tested for trapping a certain mass of Hg. The Hg recoveries with different KMnO\(_4\) concentrations were in the range of 99.6-102.8% with Hg addition of 75 ng. These recoveries were comparable with a previous study\(^\text{17}\), where 25, 40 and 250 ng Hg are spiked into 1 L sample, respectively, and sample recoveries are 74.0-97.0%. It was proved that the concentrations of KMnO\(_4\) ranged from 1.00 to 5.00 mmol/L were all suitable for trapping Hg\(^{2+}\). Among them, solution of 2.00 mmol/L was chosen as the trapping solution due to its good recovery and SD. The Hg isotopic composition in 2.00 mmol/L KMnO\(_4\) was 0.02±0.04‰ (2SD, n=3) for δ\(^{202}\)Hg, which was acceptable.

Blank spike and matrix spike

In order to study the effect of a different matrix on the purge & trap method, ultrapure water and seawater collected from a coal-fired plant were selected to be the matrices for blank spike and matrix spike, respectively. Based on the concentration of the discharged waste seawater, the seawater samples were spiked with NIST SRM 3133 at a different Hg mass of 20, 30, 50, 75 ng. The Hg recoveries
of the spike samples were within 95.0-105.0%, which proved that the spiked Hg was efficiently trapped in the KMnO₄ solution. The δ²⁰²Hg values of the trapping solution after preconcentration are shown in Fig. 6. The δ²⁰²Hg values were 0.00±0.04‰ (2SD, n=19) for the blank spike and -0.02±0.04‰ (2SD, n=12) for the matrix spike. After preconcentration, δ²⁰²Hg variation in the trapping solution was very small compared with the composition of NIST SRM 3133. In general, the modified device and proposed preconcentration method were reliable, and precise, and could be used to analyse the Hg isotopic composition of real samples.

Fig. 6 δ²⁰²Hg variation of the spike samples

Preconcentration of Hg from seawater

As previously mentioned, a sample of 9.0 mL 3 ng/mL was required for the isotopic measurement. Once the Hg concentration of seawater sample was less than 3 ng/mL, the preconcentration should be processed. The total Hg concentration of the seawater discharged from the coal-fired power plant was ranged between 5-100 ng/L 39, and the dissolved Hg concentration was less than 70 ng/L, thus 0.5-10.0 L seawater samples was needed for the preconcentration. Table 1 lists the Hg recoveries and isotopic composition. The recovery was defined as the amount of Hg in the trapping solution to that of the seawater sample. The Hg recoveries from the seawater samples were within 95.0-104.0%.

Slightly negative MDF was observed (δ²⁰²Hg = -0.23‰ to -0.02‰) in the seawater samples except for S2 (δ²⁰²Hg = 0.12±0.04‰, 2SD, n=3). The δ²⁰²Hg values were different from that of Arctic snow 39 and lake water 28. The Hg isotopic composition of seawater differed greatly from that of fresh waters. The δ²⁰²Hg value of S2 located at the outlet of the desulfurization tower was positive, which was different from that of the fresh seawater S1 (-0.10±0.06‰, 2SD, n=3), the result indicated that the heavier Hg isotopes were enriched in the seawater in the desulfurization tower. The physical and chemical process 40, including evaporation, diffusion, redox and adsorption of Hg in the tower, could be the reason for the enrichment of heavier isotopes. As the heaviest isotope, the variation range of δ²⁰⁸Hg value was the largest, from -0.76‰ to 0.36‰. The change of δ²⁰⁸Hg value from fresh seawater to the desulfurization seawater was also positive, providing a useful and potential tracing parameter for Hg. The data of isotopic signature of dissolved Hg would be very helpful to explain the mechanism of sea-air exchange and deposition of Hg.

The seawater samples displayed significant MIF of odd isotope (Δ²⁰⁹Hg = -0.09‰ to -0.16‰, Δ²⁰⁵Hg = -0.11‰ to -0.22‰), the reason might be photo-reduction 4, 36 volatilization 6 and other natural processes 39. No MIF of δ²⁰⁵Hg was found in the seawater samples.

Table 1 Hg isotope compositions in seawater samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolved total Hg (ng/mL)</th>
<th>Δ²⁰⁹Hg</th>
<th>Δ²⁰⁵Hg</th>
<th>Δ²⁰²Hg</th>
<th>Recovery (%), 2SD</th>
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</thead>
<tbody>
<tr>
<td>SI (n=3)</td>
<td>20.54</td>
<td>-0.14±0.06</td>
<td>-0.03±0.04</td>
<td>-0.15±0.02</td>
<td>98.4±3.4</td>
</tr>
<tr>
<td>S2 (n=3)</td>
<td>54.07</td>
<td>-0.11±0.06</td>
<td>-0.05±0.04</td>
<td>-0.12±0.04</td>
<td>99.7±2.5</td>
</tr>
<tr>
<td>S3 (n=3)</td>
<td>49.68</td>
<td>-0.20±0.06</td>
<td>-0.32±0.04</td>
<td>-0.23±0.04</td>
<td>97.5±2.1</td>
</tr>
<tr>
<td>S4 (n=3)</td>
<td>100.8±3.5</td>
<td>-0.14±0.06</td>
<td>-0.25±0.04</td>
<td>-0.26±0.04</td>
<td>98.5±3.5</td>
</tr>
<tr>
<td>S5 (n=3)</td>
<td>3.66</td>
<td>-0.02±0.06</td>
<td>-0.05±0.04</td>
<td>-0.10±0.04</td>
<td>98.8±3.0</td>
</tr>
</tbody>
</table>

Hg isotopic analytical uncertainties are 2 times standard deviations (2 SD). n: number of samples.
Conclusions

The modified introduction device and preconcentration method for the determination of dissolved Hg isotopic composition of seawater were developed in the present study. The relevant parameters were optimized to achieve the best performance, and the precision and accuracy indicated the proposed method was stable and reliable. The proposed method was applied to study the MDF and MIF in desulfurized seawater samples. The Hg isotope composition of the waste seawater at the outlet of the desulfurization tower showed a different isotope compared with other seawater samples, which could be caused by evaporation, diffusion, redox and adsorption of Hg in the tower. The isotopic signature of dissolved Hg could provide useful information for explanation of mechanism of sea-air exchange and deposition of Hg.

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Notes and references