

Comparison of two pretreatment methods for mercury stable isotope analysis in Antarctic moss

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Abstract Mercury (Hg) stable isotope analysis can provide new insight for understanding the biogeochemistry and sources of Hg in the polar regions. To completely extract the low contents of Hg in polar samples and to avoid isotopic fractionation during the sample preparation stage, an effective and reliable pretreatment method is needed. In this work, two different pretreatment methods were compared for measuring Hg stable isotopes in Antarctic moss samples. One method was acid digestion ($\text{HNO}_3 : \text{H}_2\text{O}_2 = 5 : 3$, v/v) and the second was a combustion-trapping treatment with a trapping solution ($\text{HNO}_3 : \text{HCl} = 2 : 1$, v/v). There were no significant differences in the analytical results obtained with the two methods. The overall mean values and uncertainties of total Hg (THg) and the isotopic compositions of Hg in the referenced materials were all in good agreement with the certified and reported values, indicating that both methods were accurate and applicable. Acid digestion is highly efficient, while the combustion-trapping method can be used to treat samples with low Hg content. The proposed methods were successfully used to determine the Hg isotopic compositions in moss samples collected from the Antarctic.

Keywords mercury stable isotope, pretreatment, acid digestion, combustion-trapping treatment

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1 Introduction

As a global pollutant, mercury (Hg) can deposit in the polar regions via long range transport. Hg has been detected in various samples collected from the Antarctic such as sea ice (Nerentorp Mastromonaco et al., 2016), soils (De Andrade et al., 2012; Zvěřina et al., 2017), guano (Nie et al., 2012), and biological tissues (Zvěřina et al., 2014; Wintle et al., 2015; Becker et al., 2016; Cipro et al., 2017). Because Hg can be released from both natural and anthropogenic sources, it is difficult to identify the sources of Hg in the polar regions using concentration-based observations.

Hg stable isotope analysis provides a novel approach for Hg source tracing. It is potentially possible to distinguish Hg isotope compositions between natural and anthropogenic sources and among different anthropogenic sources, such as coal combustion (Yin et al., 2014) and volcanic emissions (Zambardi et al., 2009). Currently, both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) signatures of Hg stable isotopes have been observed in natural samples (Bergquist et al., 2007; Bergquist et al., 2009; Chen et al., 2012), and this can provide new insight for understanding the biogeochemistry of Hg in the environment. Zheng et al. (2015) studied the historical cycling of Hg in the Ross Sea by measuring Hg stable isotopes in ornithogenic deposits. Yin et al. (2015) used Hg isotopic compositions to identify the sources and

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processes of Hg in sediments. In addition, Lepak et al. (2015) established an isotopic mixing model to calculate Hg sources in the Great Lakes. Thus, Hg isotopic compositions can be used to identify both the potential sources and the fates of Hg.

However, Hg stable isotope analysis is more difficult than total Hg (THg) determination because the isotopic fractionations are very small and can also occur during the sample pretreatment (Sun et al., 2013a). Thus, a sensitive and accurate analytical method with a high-recovery pretreatment is needed, especially for polar samples in which Hg levels are generally low ($<100 \text{ ng}\cdot\text{g}^{-1}$). Multi-collector inductively coupled plasma mass spectrometry (MC-ICP/MS) is a widely used instrument that can be used for sensitive detection of small differences in Hg isotopic compositions (Yin et al., 2010). The precision within a single measurement (internal precision) of an isotopic ratio using MC-ICP/MS is $<0.1\%$ (1RSD), which indicates the applicability of MC-ICP/MS in sensitive isotopic fractionation measurements. To completely and effectively extract Hg in specific samples and to avoid isotopic fractionation during sample pretreatment, various pretreatment methods have been used. For wet pretreatment methods, a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (Estrade et al., 2010; Yin et al., 2013), sulfonitric acid (Carignan et al., 2009), and a mixture of $\text{HNO}_3/\text{H}_2\text{O}_2$ (Meng et al., 2014) have been recommended for pretreating samples with elevated Hg concentrations. Modified digestion methods using Anton Paar Asher or an Anton Paar microwave oven (Estrade et al., 2010) have also been used to pretreat samples with relatively low Hg concentrations ($<100 \text{ ng}\cdot\text{g}^{-1}$). In addition, a double-stage tube furnace system was developed for determination of samples with very low Hg concentrations (Sun et al., 2013b). However, an applicable method for pretreating Antarctic moss samples has not yet been reported.

The aim of this work was to establish an effective and accurate pretreatment method for measuring Hg stable isotopes in Antarctic moss samples. To this end, acid digestion and combustion-trapping treatment methods, which can be used to pretreat samples containing various Hg concentrations, were investigated in detail for THg concentration and Hg stable isotope analysis. The advantages and disadvantages of the two pretreatment methods are discussed. The proposed methods were successfully applied for determination of Hg isotopic compositions in the referenced materials and in moss samples collected from the Antarctic. These methods can be used to further study the biogeochemistry and sources of Hg in the polar regions.

2 Experimental

2.1 Materials and reagents

Ultrapure grade HNO_3 , H_2O_2 , and HCl were used in the

experiments. For the combustion-trapping procedure, highly purified O_2 ($>99.99\%$) was used as the carrier gas and the combustion gas. During isotopic analysis, a 3% (w/v) stannous chloride (SnCl_2 , 98%, Sigma-Aldrich) solution dissolved in 10% (v/v) HCl, was used for online reduction, and 3% HNO_3 (v/v) was used as the rinsing solution. The Hg standard solutions SRM 3133 and SRM 997 were purchased from the National Institute of Standards and Technology (NIST, USA) and were used for standard solutions and for an online mass bias correction. The Teflon beakers used in this experiment were immersed in 5% HNO_3 for 24 h and triple rinsed with ultrapure water. Brown borosilicate glass bottles were pre-cleaned at 550°C for 0.5 h. Ultrapure water was produced using a Milli-Q system (Millipore Billerica, MA).

2.2 Hg pretreatment methods

Two pretreatment methods were selected for this work: acid digestion and combustion-trapping. For the acid digestion method (Figure 1), about 0.5–1.0 g of ground moss samples were digested using a mixed solution ($\text{HNO}_3 : \text{H}_2\text{O}_2 = 5 : 3$, v/v, 8 mL) in 70 mL Teflon beakers on a conventional hot plate (120°C , 3 h) (Gundogdu et al., 2007). Twenty minutes of pre-digestion, including sonication and shaking (Estrade et al., 2010), was executed in case overpressure was caused by the fierce reaction during heating (Figure 1). After digestion, the solution was filtered through a plastic syringe interfaced filter ($0.45 \mu\text{m}$, Millipore, mixed ester of cellulose nitrate and cellulose acetate) and transferred into brown borosilicate glass bottles. The analytical blanks for the pre-digestion procedure were $<20 \text{ pg}\cdot\text{mL}^{-1}$, which is lower than 1% of the Hg in the sample.

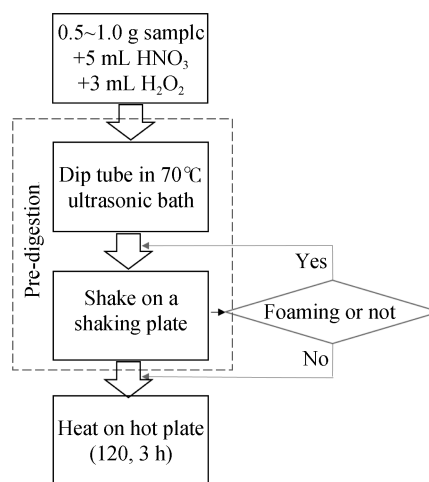


Figure 1 Flow chart of the acid digestion method.

The combustion-trapping method (Figure 2) was based on that reported by Sun et al. (2013a, 2013b) with some modification. 1.0 g of ground moss samples was decomposed in a double-stage tube furnace (Thermo Scientific, USA). A quartz tube with 26 mm outer diameter (OD), 22 mm inner diameter (ID), and 1m in length was

installed in a combustion furnace and a decomposition furnace. The combustion furnace was heated from room temperature to 1000°C within 4 h, the heating process was divided into 3 steps. First, heat furnace from room temperature to 100°C within half an hour; then, heat furnace from 100°C to 650°C within 3 h; finally, heat combustion furnace from 650°C to 1000°C within 30 min. For sufficient oxidization, the decomposition furnace was programmed to remain 1000°C. The temperature setting was shown in Table 1. An inner tube (20 mm OD, 17 mm ID and 10 cm in length), containing a powdered moss sample and capped

with quartz wool (pre-cleaned at 550°C), was placed inside the quartz tube in the combustion furnace. Gold-trap purified O₂ was fed into the combustion furnace at a constant flow rate (25 mL·min⁻¹). Approximately 5 mL of a 40% (v/v) acid mixture of HNO₃ and HCl (2 : 1, v/v) was put in a bubbler installed at the outlet of the quartz tube and was used as the oxidizing trapping solution for the emitted Hg vapor. After 4 h of heating a sample, the trapping solution was transferred to a brown borosilicate glass bottles. The analytical blanks for the pre-digestion procedure were <19 pg·mL⁻¹, which is lower than 1% of the Hg in the sample.

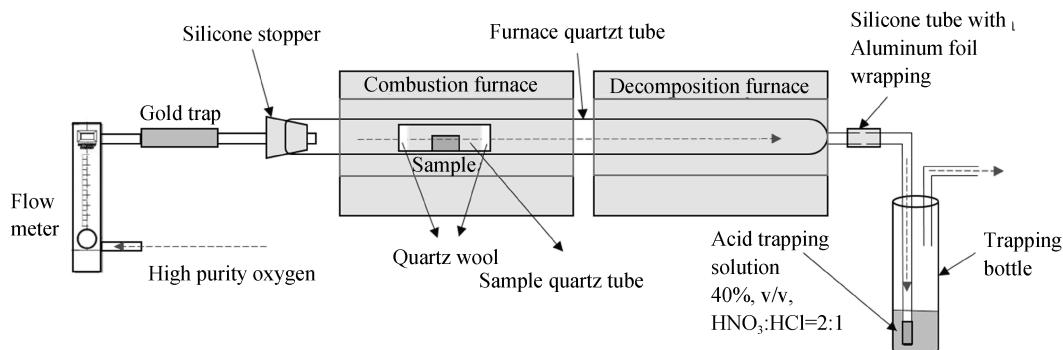


Figure 2 Diagram for the combustion method.

Table 1 Operation program of the double-stage tube furnaces

	Temperature/°C	Time/min
Combustion furnace	100	30
	650	180
	1000	30
Decomposition furnace	1000	240

All solutions were stored at 4°C before subsequent analysis. The concentration of THg in each solution was determined using a MERX Automatic Mercury System (Brooks Rand Instruments, USA) following EPA Method 1631. Using ultrapure water, each solution was then diluted to a Hg concentration of 2 µg·L⁻¹ for isotopic analysis.

2.3 Hg isotope analysis

Hg stable isotope analysis (Yin et al., 2010) was performed using MC-ICP/MS (Nu Plasma II, Nu Instruments, UK). A continuous cold vapor generation (CVG) system (HGX-200, CETAC, USA) was adopted for online reduction of Hg²⁺ to Hg⁰ using a SnCl₂ solution (3%, w/v). The flow rate for sample introduction (1.0 mL·min⁻¹) was controlled using a peristaltic pump (Minipuls 3, Gilson, USA).

Instrumental mass bias was corrected using the standard-sample bracketing (SSB) method and a simultaneously introduced Tl solution. The NIST SRM 3133 Hg standard and the UM-Almadén standard (Bergquist et al., 2007) were used to optimize the instrumental parameters and to guarantee the accuracy of

the Hg isotopic measurements. Between subsequent samples, a washout time of 10 min was used to ensure that the blank levels were <1% of the preceding sample or of the bracketed standard signals. To calibrate the instrumental mass bias during isotopic analysis, NIST SRM 997 (Tl standard solution, 20 µg·L⁻¹ in 3% HCl) was used as an internal standard simultaneously introduced into the HGX-200 by a Desolvation Nebulizer System (DSN-100, Nu Instruments, UK), which can produce a dry aerosol from a liquid standard (Chen et al., 2010; Day et al., 2012; Yin et al., 2015). The Hg isotopic composition was reported using delta notation (δ) in units of parts per million referenced to the bracketed NIST SRM 3133 Hg standard using the following formula:

$$\delta^{xxx}\text{Hg} = \left[\frac{(\text{xxxHg}/^{198}\text{Hg})_{\text{Sample}}}{(\text{xxxHg}/^{198}\text{Hg})_{\text{SRM 3133}}} - 1 \right] \times 1000 \quad (1)$$

where $(\text{xxxHg}/^{198}\text{Hg})_{\text{Sample}}$ means the ratio of each isotope (¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg and ²⁰²Hg) to ¹⁹⁸Hg in the sample, and $(\text{xxxHg}/^{198}\text{Hg})_{\text{SRM3133}}$ represents the average ratio of the NIST SRM 3133 standards bracketing that sample. The MIF is defined as the difference between the measured $\delta^{xxx}\text{Hg}$ and the theoretically predicted $\delta^{xxx}\text{Hg}$ value, which is reported using the capital delta notation ($\Delta^{xxx}\text{Hg}$, in parts per million, ‰) using the following formula (Bergquist et al., 2009):

$$\Delta^{xxx}\text{Hg} \approx \delta^{xxx}\text{Hg} - (\delta^{202}\text{Hg} \times \beta) \quad (2)$$

The values of β vary for the different isotopes. For ¹⁹⁹Hg, ²⁰⁰Hg and ²⁰¹Hg, the β values (Bergquist et al., 2009) are 0.252, 0.502 and 0.752, respectively.

The internal precision of the isotope ratio measurements was lower than 0.1‰ (1 RSD). The external

precision (the uncertainty of the repeated measurement of the same sample) of the repeated isotopic measurement of NIST SRM 3133 was $<0.06\text{‰}$ ($n=21$, 2σ). The values of $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ measured in UM-Almadén were $-0.61\text{‰}\pm 0.02\text{‰}$, $-0.03\text{‰}\pm 0.03\text{‰}$ and $-0.06\text{‰}\pm 0.05\text{‰}$ ($n=6$, 2σ), respectively, and these are comparable to the reported values (Bergquist et al., 2007; Estrade et al., 2010).

3 Results and discussion

3.1 Recoveries of THg

The ranges of the MDF in the natural samples are over 10‰ for $\delta^{202}\text{Hg}$ (Blum et al., 2014). Physical (volatilization (Zheng et al., 2007) and evaporation/condensation (Estrade et al., 2009)), chemical (oxidation/reduction (Yang et al., 2009; Gratz et al., 2010)), and biological (methylation/ demethylation (Kritee et al.,

2007; Kritee et al., 2009)) processes can lead to the MDF of Hg isotopes. Therefore, the recovery of a pretreatment method is critical. In this study, two certified reference materials (CRMs), GBW 10052 (green tea, The National Centre Research for Methods, China) and BCR482 (epiphytic lichen, Institute for Reference Materials and Measurements, European Commission), were analyzed and treated using the same procedures as the moss samples. As seen in Table 2, the recoveries of the acid digestion method were $106\text{‰}\pm 3.1\%$ for GBW 10052 and $99\text{‰}\pm 2.2\%$ for BCR 482, and the recoveries of the combustion-trapping pretreatment were $99\text{‰}\pm 4.5\%$ for GBW 10052 and $98\text{‰}\pm 1.7\%$ for BCR 482. The determined concentrations of THg in both of the two CRMs are in good agreement with the certified values, suggesting that the two pretreatment methods are applicable for further Hg stable isotope analysis.

Table 2 Analytical results of THg in CRMs

CRMs	Certified THg/(ng·g ⁻¹)	Recovery (1σ)	
		Acid digestion	Combustion-trapping
GBW 10052	8.1±1.5	106%±3.1% (n=3)	99%±4.5% (n=4)
BCR 482	480±20	99%±2.2% (n=11)	98%±1.7% (n=6)

1σ: the uncertainty of the repeated measurement of the same sample.

3.2 Hg isotopic measurement

To further validate the two pretreatment methods, the Hg isotopic compositions in BCR 482 were analyzed. As seen in Table 3, the determined isotopic compositions of Hg are comparable with published data (Estrade et al., 2010), and

there was no significant difference between the two pretreatment methods ($P>0.05$, T -test). This proved that no significant isotopic fractionation was induced during the two pretreatment procedures. Therefore, both of the two pretreatment methods are accurate and suitable for THg and Hg isotopic measurements.

Table 3 Hg isotopic compositions in BCR 482

	<i>n</i>	$\delta^{202}\text{Hg}$ (2σ)/‰	$\Delta^{199}\text{Hg}$ (2σ)/‰	$\Delta^{200}\text{Hg}$ (2σ)/‰	$\Delta^{201}\text{Hg}$ (2σ)/‰
Estrade et al. (2010)	28	-1.53±0.24	-0.62±0.11	0.07±0.08	-0.62±0.08
Yu et al. (2016)	7	-1.67±0.16	-0.57±0.10	0.06±0.08	-0.58±0.09
Acid digestion	11	-1.58±0.12	-0.64±0.06	0.06±0.06	-0.65±0.08
Combustion trapping	6	-1.55±0.09	-0.62±0.03	0.08±0.05	-0.63±0.06

2σ: twice uncertainty of the repeated measurement of the same sample.

3.3 Application for Hg isotope analysis in moss samples

The proposed methods were used for determination of Hg isotopic compositions in 3 moss samples from the Antarctic. The mosses were collected from King George Island and Ardley Island during December 2009 and January 2010. All of the samples were sealed in clean plastic bags and kept at -20°C until analysis. The details regarding the sampling procedure were presented elsewhere (Wang et al., 2012).

The determined THg and Hg isotopic compositions in the moss samples are shown in Table 4. The concentrations

of THg in the 3 moss samples ranged from 59 to 89 ng·g⁻¹, and these results were comparable with the results reported in previous studies (Bubach et al., 2016; Wojtuń et al., 2013). Significant negative $\delta^{202}\text{Hg}$ (acid digestion method: $-0.32\text{‰}\sim -0.40\text{‰}$; combustion-trapping treatment: $-0.31\text{‰}\sim -0.36\text{‰}$) and $\Delta^{199}\text{Hg}$ (acid digestion method: $-0.07\text{‰}\sim -0.17\text{‰}$; combustion-trapping treatment: $-0.01\text{‰}\sim -0.17\text{‰}$) were observed in all of the samples, and these can be used for further study of the biogeochemistry and sources of Hg in the Antarctic region. Comparing the two pretreatment methods, there were no significant differences between the analytical results of THg and the Hg isotopic compositions in the 3 samples.

Table 4 Analytical results of Antarctic moss samples($n=3$)

	Acid digest					Combustion-trapping				
	THg (1σ) / ($\text{ng}\cdot\text{g}^{-1}$)	$\delta^{202}\text{Hg}$ (2σ)/‰	$\Delta^{199}\text{Hg}$ (2σ)/‰	$\Delta^{200}\text{Hg}$ (2σ)/‰	$\Delta^{201}\text{Hg}$ (2σ)/‰	THg (1σ) / ($\text{ng}\cdot\text{g}^{-1}$)	$\delta^{202}\text{Hg}$ (2σ)/‰	$\Delta^{199}\text{Hg}$ (2σ)/‰	$\Delta^{200}\text{Hg}$ (2σ)/‰	$\Delta^{201}\text{Hg}$ (2σ)/‰
Moss 1	88±6.5	-0.39±0.11	-0.15±0.08	-0.06±0.01	-0.11±0.05	89±3.2	-0.33±0.12	-0.15±0.06	-0.03±0.01	-0.08±0.03
Moss 2	59±3.1	-0.40±0.12	-0.17±0.06	-0.02±0.01	-0.09±0.03	62±2.5	-0.36±0.11	-0.17±0.02	-0.02±0.02	-0.08±0.01
Moss 3	61±3.5	-0.32±0.02	-0.07±0.02	0.02±0.02	-0.08±0.01	60±4.5	-0.31±0.01	-0.01±0.06	0.02±0.01	-0.10±0.03

1 σ : the uncertainty of the repeated measurement of the same sample.

2 σ : twice uncertainty of the repeated measurement of the same sample.

While both of the pretreatment methods are accurate and applicable, there are advantages and disadvantages associated with each of the two pretreatment methods. Acid digestion is a classic protocol for extracting Hg from solid samples (e.g., biological tissue, soil and sediment), and is efficient and applicable for Hg stable isotope analysis. However, the matrix may influence the reduction of Hg in CVG when the acid concentration is higher than 20% (Sun et al., 2013b). An ion-exchange column purification method (Chen et al., 2010) can be used for eliminating matrix interferences. In addition, if the Hg is in acid-resistant and insoluble matrix components (e.g., rocks and coal), the recovery will be incomplete (Liang et al., 2003; Sun et al., 2013) and isotopic fractionation may occur (Sun et al., 2013).

For the combustion-trapping method, a considerable amount of sample can be combusted to satisfy the requirement for Hg isotopic analysis, and this is especially important when the Hg contents in the samples are extremely low. The matrix effect can be minimized because most of the sample components are volatilized as gases or are retained in combustion residuals and because the prepared trapping solution is uniform and stable. Moreover, no extra reagent or pre-concentration procedure is necessary with the combustion-trapping method. Therefore, it is a valid strategy for pretreating samples with low concentrations of Hg. However, a treatment time of 4 h is needed for treating one sample, and this is a relatively low efficiency compared to the acid digestion method used in this study.

4 Conclusions

Two pretreatment methods were compared for the determination of THg and Hg isotopic compositions in moss samples collected from the Antarctic region. The overall mean values and uncertainties of THg and the Hg isotopic compositions in the CRMs were all in good agreement with the certified and reported values, indicating that the two pretreatment methods are accurate and applicable. Although no significant differences were found between the two methods, the acid digestion method has the advantage of high efficiency while the combustion-trapping method can be used to pretreat samples with relatively low contents of Hg. The proposed methods can be used for

further study of the biogeochemistry and sources of Hg in the polar regions.

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