

Development of fast sampling and high recovery extraction method for stable isotope measurement of gaseous mercury in the air

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## Abstract

Techniques for fast large-volume sampling of total gaseous mercury (TGM) in the air and extracting the TGM with 5 mL acid solution were developed for stable mercury isotope ratio measurements. A Big gold coated sand Trap (BAuT), a 45 mm i.d. × 300 mm length quartz tube containing 131 times more gold coated silica than a conventional gold trap has, was used for the collection of a large amount of TGM from the air. The collected TGM was then extracted by 5 mL reversed aqua regia in a 2L Tedlar bag, and the extract was analyzed by a cold-vapor generator coupled with a multi collector inductively coupled plasma mass spectrometer for the isotopic compositions. The sampling tests of BAuT showed 99.9% or higher collection efficiency during the sampling time of 1 - 24 h under the flow rate of 20 - 100 L min<sup>-1</sup>. Recovery tests of the bag extraction using 100 ng of NIST SRM 8610 exhibited nearly 100% of recovery yields and agreement of the measured five stable mercury isotope ratios with the reference values within 2  $\sigma$  of uncertainty when using the trapping solution of 40% reversed aqua regia with the extraction time of a day. The overall methodology tested in the pilot field and laboratory studies demonstrated the successful analysis, promising highly precise stable mercury isotopic data with the time resolution less than a day. Part of the procedure can be automated, ideal for unmanned sampling at a remote site.

## 1. Introduction

Mercury is a notorious pollutant triggering serious adverse health effects (WHO, 2003). This metal element has a very unique characteristic that it can evaporate under the room temperature and pressure. Because of this nature, mercury spreads globally and, thus, is ubiquitous in the natural environment. In August 2017 the international regulation on the use and trade of the man-made mercury started under the name of Minamata Convention on Mercury to lower the mercury level in the natural environment. However, it is known that there are also natural sources of mercury, such

as volcanic activities (e.g., Zambardi *et al.*, 2009), evasion from the ocean surface (e.g., Gill and Fitzgerald, 1987; Mason, 1992; Gardfeldt *et al.*, 2003), forest (e.g., Demers *et al.*, 2013), permafrost (e.g., Schuster *et al.*, 2017), and etc. Because of the complex emission sources, sinking processes, and uncertain source contributions, the effectiveness of the Minamata Convention on Mercury is a challenging issue (Kwon *et al.* 2020). To gain insight into the complex mixing state highly precise measurements of stable mercury isotopes at natural abundances by a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) has been catching attention.

Mercury naturally has seven stable isotopes,  $^{196}\text{Hg}$ ,  $^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$ , and  $^{204}\text{Hg}$ , the relative natural abundances (relative to the sum of all isotope abundances) of which are 0.155%, 10.04%, 16.94%, 23.14%, 13.17%, 29.73%, and 6.83%, respectively (Blum and Bergquist, 2007). A MC-ICP-MS allows simultaneous high precision measurements of those stable mercury isotope ratios ( $\delta\text{Hg}$ ) in four to six significant figures. As trading off, the analysis requires ng order of mercury at least. To date some field studies for  $\delta\text{Hg}$  of atmospheric TGM have been reported (Gratz *et al.*, 2010; Demers *et al.*, 2013; Yamakawa *et al.*, 2019; Fu *et al.*, 2016), but with their methods a sampling duration was a few days to weeks. Improving the sampling technique, faster sampling for the  $\delta\text{Hg}$  analysis, will better understand the atmospheric transport and processing of TGM in the air, and this is a challenging issue in the atmospheric  $\delta\text{Hg}$  research.

There is another challenging issue in the sample preparation step: How 5 ng or higher amount of mercury in the gaseous state is oxidized and trapped in a small amount of solution for the isotope analysis. While the conventional quantitative mercury analysis is done by the combination of trapping TGM by a gold trap, converting the TGM to gaseous elemental mercury (GEM) by heating, and flushing the GEM into an atomic absorption or fluorescence spectrometer, the current  $\delta\text{Hg}$  analysis is done by a constant injection of a liquid sample containing mercury ions into a cold-vapor generator (CV) coupled with MC-ICP-MS to gain sufficient and stable signal strengths of GEM during the sequence of measurement. The latter method requires oxidation of gaseous mercury and enclose of oxidized mercury into a solution. To date a dynamic oxidation method (bubbling GEM in an acid solution) has been used to capture GEM generated from the TGM samples (Gratz *et al.*, 2010; Demers *et al.*, 2013; Fu *et al.*, 2014; Yamakawa *et al.*, 2017), but this method may not result in high recovery yields for a large amount of GEM because of the short contacting time with the acid solution. High recovery yield is a key for the stable isotope analysis because it would minimize artificial and unfavored isotope fractionations that are more or less accompanied with any physical and chemical

processes.

In this paper we report novel offline techniques to collect sufficient amount of GEM within a reasonable amount of time (24 h or less) and to oxidize and effectively capture the collected mercury by 5mL of acid solution for the  $\delta\text{Hg}$  measurements.

## 2. Methodology

The analytical procedures include sampling TGM in the air using a big gold trap, extracting the trapped TGM by 5mL of acid solution, and measuring  $\delta\text{Hg}$  by CV (HGX-200, Teledyne CETAC Technol., NE, U.S.A.) coupled with MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific GmbH, Bremen, Germany) under the method averaging out 50 measurements in a sample run and bracketed by SRM 3133 (NIST, MD, U.S.A.) measurements for the conversion of the isotope ratios relative to the isotope ratios of SRM 3133. Artificial isotopic fractionation occurring at the ICP was corrected by measuring the isotope ratio of standard thallium (SRM 997, NIST, MD, U.S.A.), which was simultaneously injected to the HGX-200 using an aerosol generator (Aridus II, Teledyne CETAC Technol., NE, U.S.A.). Only the novel sampling and extraction techniques are described in detail in the following sections.

### 2.1. Sampling TGM and pre-concentration

TGM in the air was collected using Big gold coated sand Trap (BAuT). BAuT is a customary made 50 mm o.d  $\times$  45 mm i.d. $\times$ 300 mm long quartz tube that a 45 mm o.d.  $\times$ 5 mm thickness fritted quartz plate was fused in the middle (COSMOS VID, Fukuoka, Japan). On the plate approximately 10.5 g of quartz sand coated with vaporized gold (Nippon Instruments Corp., Osaka, Japan) was placed and approximately 0.1 g of quartz wool was stuffed on the top. Compared to a commercially available conventional gold coated trap (a 4 mm i.d. $\times$ 160 mm long quartz tube with 0.08g of the gold coated silica sand, capable of capturing 70  $\mu\text{g}$  of gaseous mercury and supplied by the Nippon Instruments Corp., Osaka, Japan), the mouth of BAuT is approximately 11 times wider and the amount of the gold coated sand is approximately 131 times more contained. Because of the large mouth BAuT theoretically accepts large flow of air for TGM sampling. For instance, the flow rates of BAuT that gives the same linear velocities as those given by the conventional gold coated sand trap sampling under the typical flow rates of 0.5 and 1.0 L min<sup>-1</sup>, corresponding to 39.8 m min<sup>-1</sup> and 79.6 m min<sup>-1</sup> of linear velocity, are 63.3 L min<sup>-1</sup> and 126.6 L min<sup>-1</sup>, respectively. To the best of our knowledge, the reported techniques for TGM sampling from the ambient air use the flow rates of 2 - 20 L min<sup>-1</sup> (an iodine or chlorine impregnated carbon trap, Fu *et al.*, 2014), 14.4 L min<sup>-1</sup>

(1.8 L min<sup>-1</sup> × 8 gold traps, Gratz et al., 2010; Demers et al., 2011), and 16 L min<sup>-1</sup> (1 L min<sup>-1</sup> × 16 gold traps, Yamakawa *et al.*, 2019) with the sampling duration of 15 – 20 days, 2 - 3 days, and 3 days, respectively. Given the same collection efficiencies for all these sampling methods, the sampling speed by BAuT is theoretically 3 to 9 folds of magnitude faster than the reported methods. Additional advantage of BAuT is the use of single trap, making the following pre-concentration procedure simple.

TGM sampling by BAuT was tested by outdoor, indoor, experimental air sampling under a variety of flow rates, from 20 to 100 L min<sup>-1</sup> with a float flow meter (RK230, KOFLOC, Kyoto, Japan) and diaphragm pumps (N860FTE, KNF, Freiburg, Germany and DOA-P501-DB, GAST MFG Corp., MI, U.S.A.). For the outdoor sampling the air was filtered through a 47 mm o.d. Teflon coated glass fiber filter (Pallflex Emfab 47 mm, Pall Corp., NY, U.S.A.) set on a polycarbonate open face filter holder (NL-O-01, NILU, Kjeller, Norway) in order to remove airborne particulate matter. All connections used were a half inch or 3/8 inch o.d. PFA tubing (Tombo 9003-PFA, Nichias, Co., Tokyo, Japan), together with PFA connectors (Swagelok, U.S.A.) and/or PTFE connectors (Flowell 30 series, Flowell Corp., Yokohama, Japan). Indoor air sampling was performed in the same manner, but without the particulate filter. Collection efficiency of BAuT was evaluated by conducting the breakthrough tests for the limited number of samples: Air was drawn through the two BAuTs connected in series (double BAuT sampling) and the quantity of TGM in the backup and front BAuTs was compared. In this test the TGM captured by BAuTs was pre-concentrated in the manner described below. The pre-concentrated TGM in the backup BAuT was then quantified by cold-vapor atomic fluorescence spectrometer (WA-5F, Nippon Instruments Corp., Osaka, Japan), and the pre-concentrated TGM in the front BAuT was extracted in the manner described in the sub-section 2.2, and then quantified by CV-MC-ICP-MS using the signal strength for <sup>201</sup>Hg. The determined GEM masses in the backup BAuT were compared with the GEM masses found in the front BAuT for the determination of the collection efficiencies.

After the sampling, TGM collected by BAuT was pre-concentrated to a conventional small gold trap for the efficient transfer in the following extraction procedure. At this step BAuT was heated to 873 K for 1 h under 0.5 L min<sup>-1</sup> flow of zero air, which was prepared from the compressed room air (super oil free BEBICON 0.4LE-8SB, Hitachi Industrial Equipment Systems Co., Ltd., Tokyo, Japan) through a drier stuffed with silica gel (Kanto Chemical Co. Inc., Tokyo, Japan) and a mercury trap stuffed with activated charcoal (Hokuetsu MA-HG, Ajinomoto Fine Techno, Co., Yokohama, Japan) and was supplied via a mass flow controller unit (SEC-E40 and PE-D20, HORIBA

STEC, Kyoto, Japan). The background of zero air was  $0.03 \text{ pg L}^{-1}$  or less. A hand-made heating system used for heating BAuT was built using nichrome wire (1.0 mm o.d., Sunko Corp. Kyoto, Japan), quartz wool (quartz wool, grade B, GL Science, Tokyo, Japan), and glass tape (insulating glass tape, Komeri, Niigata, Japan). Approximately 35V of electricity was applied to the nichrome wire to heat BAuT via a variable transformer (RAS-10, Tokyo Rikosha, Co. Ltd., Saitama, Japan). The temperature was kept constant using a temperature controller (TR-KN, AS ONE Corp., Osaka, Japan).

## 2.2. Plastic bag extraction of TGM

The pre-concentrated TGM in the conventional trap was extracted by 5 mL trapping solution in a plastic bag. The pre-concentrated TGM from the BAuT was heated to 973K using another hand-made heating system built for the conventional trap under the  $0.5 \text{ L min}^{-1}$  flow of the zero air for four minutes so that the pre-concentrated TGM was reduced to GEM and then flushed into a 2L Tedler bag through the attached PTFE stopcock (AS ONE Corp., Osaka, Japan). For the efficient transfer of GEM during the limited time of four minutes the zero gas started being flown as soon as the temperature reached to 573K. Prior to the transfer,  $5 \pm 0.01 \text{ mL}$  of reversed aqua regia (RAR), a 2:1 (v/v) mixture of nitric and hydrochloric acids (PMA grade, Kanto Chemical Co. Inc., Tokyo, Japan) with ultra-pure water (Milli-Q Direct 3, Merck KGaA, Darmstadt, Germany), was pipetted (Research plus 1000, Eppendorf AG, Hamburg, Germany) into the bag. A variety of RAR concentrations were tested. After the transfer of GEM the stopcock was closed and the plastic bag was shaken for 3 min and left for 6 to 24 h. During the extraction period the bag was shaken 3 more times, each of which was for 1 min. The plastic bag was also weighed at the start and the end of the extraction using an electronic balancer (ML4002T, Mettler-Toledo GmbH, Greifensee, Switzerland) to check any leak during the extraction.

As trapping solution, a stronger acid oxidizes metals more quickly in general. Thus, the use of stronger acid for the trapping solution must have advantage. Contrarily, strong acid interferes the production of GEM in the CV because produced GEM by reduction of  $\text{Hg}^{2+}$  with  $\text{Sn}^{2+}$  is oxidized back to  $\text{Hg}^{2+}$  during the transfer through the CV to the MC-ICP-MS. To find the upper limit of RAR concentration we checked the sensitivity dependence of the  $^{201}\text{Hg}$  signal strength on the RAR concentration that SRM 3133 was dissolved in.

## 2.3. Testing the overall methodology

The methodology was tested by sampling outdoor, indoor, and experimental air. Two

types of outdoor air sampling were conducted: normal air sampling from the window of our laboratory and sampling plumes from open field burning. The Aso open field burning (Noyaki) takes place annually in the season between March and April and it burns approximately 161 km<sup>2</sup> of the natural grass field and stock farms for the purpose of the sustainable healthy nature in this region. TGM from the plumes was sampled by BAuT from the window of the vehicle. The air was drawn by a diaphragm pump described earlier, the electricity of which was supplied by UPS (SURTA1500XLJ, American Power Conservation, U.S.A.). Sampling flow rate and duration were 75 L min<sup>-1</sup> and between 1 and 6 h, respectively. Indoor air was also sampled in our laboratories, with the flow rate and sampling duration of 75 - 100 L min<sup>-1</sup> and between 6 and 24 h, respectively. Sampling GEM from the gas mixture in the indoor photochemical reactor was also tested. The experimental condition was the similar to that reported by Irei et al. (2006 and 2011). Briefly, in this pilot laboratory experiment 200 ng of GEM produced from the SRM 8610 (NIST, MD, U.S.A.), oxidant precursors, and dried zero air were introduced into a 1.5 m<sup>3</sup> photochemical reactor, which was made of PFA sheet. 366 nm UV light (UV lamp 4, CAMAG, Muttenez, Switzerland) was switched on and off to initiate and stop the photochemical reactions with OH radicals, and residual GEM was sampled by BAuT through a KCl coated 8-channel annular denuder (URG-2000-30CF, URG Co., NC, U.S.A.), which removed oxidized mercury. The pre-concentration and extraction procedures for these samples are exactly the same as those referred earlier.

### 3. Results and Discussion

#### 3.1. Collection efficiency of BAuT

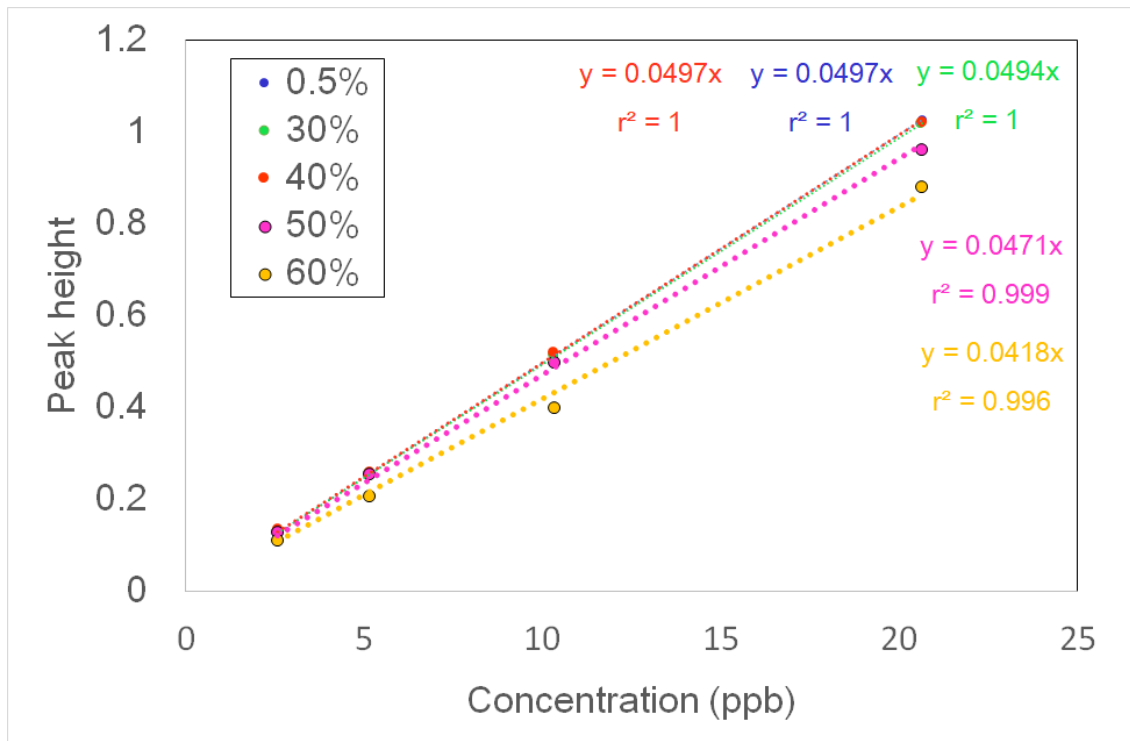
The breakthrough tests performed by the double BAuT sampling showed only 7 to 115 pg of GEM passed the front BAuT then was captured by the backup BAuT during the 1.3 to 24 h sampling under the flow rate of 20 to 100 L min<sup>-1</sup> (Table 1). Note that the sampling flow rate for the outdoor sampling could not be increased because the pressure loss at the PFA tubing between the filter and front BAuT. Compared to the quantity of TGM trapped at the front BAuT, which will be shown and discussed in the sub-section 3.4, the breakthrough TGM at the front BAuT was very small and the calculated collection efficiency of the front BAuT was 99.9%. The results are theoretically reasonable and satisfy our demand for the fast and large volume sampling to achieve the collection of a GEM sample from the air within a day or less.

**Table 1. Results of TGM breakthrough**

Sample	Sampling duration	Flow rate	Total volume	Hg in backup	Collection efficiency
	h	L min <sup>-1</sup>	m <sup>3</sup>	pg	%
Laboratory air	6	100	36	7	99.99
Clean room air	24	100	144	115	99.86
Reactor air	1.3	20	1.5	74.8	99.93

### 3.2. Recovery test of the plastic bag extraction

The dependence check of <sup>201</sup>Hg signal strength on the RAR concentration demonstrate that the slopes of the external calibrations made by SRM 8610 in the 0.5 to 40% of RAR were identical, 0.049 V ppb<sup>-1</sup>, while the slope was lowered with higher concentration of RAR when the higher concentration of RAR than 40% was used (Fig. 1). This indicates that evolved GEM from the sample solution started being oxidized back to the solution during the transfer through the CV apparatus when the concentration of RAR higher than 40% was used as the base solution. Thus, we used the RAR concentration lower than 40% in the following recovery tests.



**Fig. 1. Dependence of external calibrations of CV-MC-ICP-MS (<sup>201</sup>Hg signal height) on a variety of reversed aqua regia concentration.**

Collected volume of the trapping solutions from the plastic bags was more than 4.8 mL out of 5 mL, corresponding to 96% (Table 2). Such high collection efficiency of the pipetted solution was achieved due to the hydrophobicity of Tedler material, polyvinyl fluoride: the material makes the trapping solution collectable small liquid beads.

It should be noted that small differences in the weights of the plastic bag between the start and end of the extraction were observed, and the differences seemed to be associated with the extraction time. The weight differences were converted to the volume differences using the estimated densities of the RAR mixtures (Table 2). Because the plastic bag was fully expanded even at the end of the extraction, we suspect that the loss was likely due to the slow permeation of water molecules through the Tedler membrane. Such phenomenon has been known to occur through the similar material (*e.g.*, Nafion), thus, used in the drying material. For the calculation of the recovery yields, the correction of this volume loss was made.

Concentrations of mercury in the trapping solution were measured by CV-MC-ICP-MS using the external calibration referred earlier, and the recovery yields were calculated based on those concentrations, the volume of the trapping solution (5 mL), and 103 ng of GEM introduced into the plastic bag (Table 2). The average  $\pm$  standard deviation of the blank extracts ( $n = 12$ ) was  $55 \pm 61 \text{ pg g}^{-1}$ , and all the recovery yields determined were blank corrected. The recovery yields exhibited that the use of the 20%, 30%, and 40% v/v RAR gave the same recovery yields of 100% when the GEM was exposed to the solution for 24 h. Although it is not shown here the use of 5% RAR required 7 days to achieve more than 90% of the recovery yields. The results here exhibited that the recovery yields did not change significantly as the extraction time decreased down to 6 h, but those were prone to fluctuate as the extraction time was 3 h only.



**Table 2. Summary of plastic bag extraction test using NIST SRM 8610<sup>†</sup>**

Solution	n	Spiked Hg	Extraction time	Collected volume	Lost volume	Concentration	Recovery yield
		ng	h	mL	mL	ng mL <sup>-1</sup>	%
40% RAR	6	103 ± 2	24	4.86 ± 0.02	0.12 ± 0.05	21.4 ± 0.9	102 ± 5
30% RAR	4	103 ± 2	24	4.83 ± 0.02	0.12 ± 0.01	21.0 ± 0.4	100 ± 2
20% RAR	3	103 ± 2	24	4.5 ± 0.2	0.16 ± 0.01	21.8 ± 0.6	103 ± 3
40% RAR	3	103 ± 2	12	4.83 ± 0.04	0.09 ± 0.03	20.3 ± 0.4	97 ± 2
30% RAR	3	103 ± 2	12	4.83 ± 0.02	0.12 ± 0.01	20.76 ± 0.08	99.1 ± 0.5
40% RAR	3	103 ± 2	6	4.92 ± 0.07	0.07 ± 0.03	20.1 ± 0.3	97 ± 2
30% RAR	3	103 ± 2	6	4.89 ± 0.02	0.03 ± 0.01	20.6 ± 0.3	99 ± 2
20% RAR	2	103 ± 2	6	4.83	0.04	19 ± 1	92 ± 6
40% RAR	3	103 ± 2	3	4.99 ± 0.01	0.07 ± 0.02	18 ± 2	87 ± 11
30% RAR	2	103 ± 2	3	4.83 ± 0.04	0.08 ± 0.01	20 ± 1	96 ± 5

<sup>†</sup>The values shown are the average ± standard deviation.

### 3.3. Stable Hg isotope measurement

Results of stable mercury isotope measurements of the trapping solution from the recovery tests showed that overall the difference from the reference value was in the range from -0.03 to 0.02 ‰ for  $\delta^{199}\text{Hg}$ , -0.04 to 0.11 ‰ for  $\delta^{200}\text{Hg}$ , -0.06 to 0.18 ‰ for  $\delta^{201}\text{Hg}$ , -0.07 to 0.23 ‰ for  $\delta^{202}\text{Hg}$ , and -0.12 to 0.33 ‰ for  $\delta^{204}\text{Hg}$  (Table 3). The measured isotope ratios agreed with the reference values within the two times of the standard deviations, but the accuracy and precision were slightly poorer for the samples with 3 h extraction time than those for other samples. Thus, we concluded that there was no significant artificial isotopic fractionation during the extraction procedure with the extraction time longer between 6 and 24 h.

**Table 3. Summary of isotope measurements of plastic bag extraction test<sup>†</sup>**

Sample	n	Extraction time	$\delta^{199}\text{Hg}$	$\delta^{200}\text{Hg}$	$\delta^{201}\text{Hg}$	$\delta^{202}\text{Hg}$	$\delta^{204}\text{Hg}$
		h	‰				
SRM 8610			$-0.17 \pm 0.01$	$-0.27 \pm 0.01$	$-0.46 \pm 0.02$	$-0.56 \pm 0.03$	$-0.82 \pm 0.07$
40% RAR	6	24	$-0.19 \pm 0.05$	$-0.30 \pm 0.06$	$-0.51 \pm 0.06$	$-0.62 \pm 0.09$	$-0.91 \pm 0.07$
30% RAR	4	24	$-0.20 \pm 0.01$	$-0.30 \pm 0.03$	$-0.52 \pm 0.02$	$-0.63 \pm 0.04$	$-0.92 \pm 0.05$
20% RAR	3	24	$-0.10 \pm 0.02$	$-0.18 \pm 0.03$	$-0.40 \pm 0.03$	$-0.45 \pm 0.06$	$-0.67 \pm 0.06$
40% RAR	3	12	$-0.19 \pm 0.05$	$-0.29 \pm 0.05$	$-0.48 \pm 0.09$	$-0.59 \pm 0.08$	$-0.94 \pm 0.15$
30% RAR	3	12	$-0.20 \pm 0.01$	$-0.31 \pm 0.03$	$-0.52 \pm 0.03$	$-0.62 \pm 0.05$	$-0.92 \pm 0.06$
40% RAR	3	6	$-0.11 \pm 0.03$	$-0.18 \pm 0.02$	$-0.36 \pm 0.06$	$-0.44 \pm 0.03$	$-0.67 \pm 0.03$
30% RAR	3	6	$-0.19 \pm 0.05$	$-0.27 \pm 0.05$	$-0.44 \pm 0.08$	$-0.55 \pm 0.06$	$-0.87 \pm 0.08$
20% RAR	2	6	$-0.15 \pm 0.01$	$-0.19 \pm 0.05$	$-0.28 \pm 0.09$	$-0.33 \pm 0.14$	$-0.49 \pm 0.34$
40% RAR	3	3	$-0.15 \pm 0.01$	$-0.21 \pm 0.03$	$-0.38 \pm 0.04$	$-0.46 \pm 0.08$	$-0.69 \pm 0.21$
30% RAR	2	3	$-0.15 \pm 0.05$	$-0.24 \pm 0.09$	$-0.44 \pm 0.17$	$-0.50 \pm 0.20$	$-0.74 \pm 0.30$

<sup>†</sup>The values shown are the average  $\pm$  standard deviation.

### 3.4. Results of the overall methodology test

Using the optimized methodology TGM samples were collected from the plumes of the Noyaki in the Aso area and analyzed for  $\delta\text{Hg}$  (Table 4). TGM samples in the plume free air (denoted as the background air) were also collected in the Aso area when the field burning was absent. The measurement results showed that the concentrations of TGM during the Noyaki were higher than  $1 \text{ ng m}^{-3}$ , while in the background air was constant ( $0.7$  and  $0.8 \text{ ng m}^{-3}$ ), indicating that the elevation of TGM concentrations was likely due to Noyaki. Note that the elevated TGM concentrations during the Noyaki are mixtures of TGM from the plumes and in the background air. Since the TGM in the background air was constant during this pilot study, we averaged the concentrations and isotopic compositions of TGM in the background air to calculate the  $\delta\text{Hg}$  of TGM emitted from the Noyaki using the mass balance for the isotope ratios (Irei *et al.*, 2006, Irei *et al.*, 2018). Except  $\delta^{204}\text{Hg}$  in the sample collected April 6, estimated  $\delta\text{Hg}$  showed lighter isotopic compositions than those in the background air (Table 5). Such light isotopic compositions may be associated with the isotopic fractionations occurring in the evaporation process at the field burning, but the evidence is weak and further study is needed for solid conclusion.

**Table 4. Results of overall analytical tests on the open field burning (Noyaki), outdoor, indoor, and experimental air samples.**

Sample	Flow rate L min <sup>-1</sup>	Sampling duration h	Air volume m <sup>3</sup>	Conc. of extract <sup>†</sup> ng g <sup>-1</sup>	Conc. in the air <sup>‡</sup> ng m <sup>-3</sup>	$\delta^{199}\text{Hg}$	$\delta^{200}\text{Hg}$	$\delta^{201}\text{Hg}$	$\delta^{202}\text{Hg}$	$\delta^{204}\text{Hg}$
						‰				
Noyaki 1, March 24	75	0.9	4.2	3.1	3.7	-0.58	-0.58	-1.01	-0.93	-1.40
Noyaki, April 6	78	0.8	3.5	1.0	1.4	-0.98	-0.48	-0.92	-0.96	2.43
Background air March 31	54	2.1	6.7	1.1	0.8	-0.05	0.44	0.35	1.06	1.30
Background air May 23	80	4.2	20.1	3.0	0.7	-0.02	0.13	-0.06	0.16	0.49
the average of the background					0.8	-0.04	0.28	0.14	0.61	0.89
Outdoor air	75	22.3	100.2	17.6	0.9	-0.12	0.08	0.01	0.29	0.48
Laboratory air	100	6.0	36.0	23.2	3.2	-0.12	-0.11	-0.22	-0.12	-0.16
Clean room air	100	24.0	144.0	17.0	0.6	-0.23	-0.20	-0.45	-0.40	-0.59
Reactor GEM	20	1.3	1.5	22.5	74.6	8.72	-1.90	4.74	-0.67	9.13

**Table 5. Background corrected stable mercury isotopic compositions of TGM from the open field burning (Noyaki).**

	$\delta^{199}\text{Hg}$	$\delta^{200}\text{Hg}$	$\delta^{201}\text{Hg}$	$\delta^{202}\text{Hg}$	$\delta^{204}\text{Hg}$
	‰				
Noyaki 1, March 24	-0.734	-0.816	-1.325	-1.354	-2.031
Noyaki, April 6	-2.175	-1.447	-2.269	-2.946	4.370

The analysis of TGM samples from the outdoor and indoor (the laboratory and clean room) air showed the sufficient collection of GEM (85 – 116 ng) and the successful analysis of their  $\delta\text{Hg}$  values (Table 4). The  $\delta\text{Hg}$  values of the outdoor air varied from -0.12 ‰ to 0.48 ‰, while those of the laboratory and clean room air varied from -0.11 ‰ to -0.22 ‰ and from -0.20 ‰ to -0.59 ‰, respectively. The slightly lighter  $\delta\text{Hg}$  values of the clean room air than those of the laboratory air may attribute to the isotope fractionation occurring at mercury absorbent.

The  $\delta\text{Hg}$  of residual GEM collected after the photochemical reaction with OH radical, the major sinking pathway of atmospheric GEM, exhibited large isotope fractionations from the reference values, ranging from -1.63 ‰ to 9.96 ‰ as the extent of Hg reaction estimated from the extract concentration was 44% (Table 4). Except  $\delta^{204}\text{Hg}$ , the mass dependent and independent fractionation (MDF and MIF) were observed on odd and even mass numbers of GEM, respectively. The unusual isotope fractionation of mercury found in the precipitation of Peterborough, Canada (Chen *et al.*, 2012), the heavier  $^{199}\text{Hg}$  composition with the lighter  $^{202}\text{Hg}$  composition, is likely explained by this process. However, this is only one sample analysis and thorough evaluations on the isotope fractionations relevant to the atmospheric oxidations are needed.

#### 4. Summary and future application

We developed a fast and large volume sampling method of TGM in the air and its extraction method using static extraction technique. The sampling tests demonstrated 99.9% collection efficiency of TGM by BAuT under the flow rate of 20 - 100 L min<sup>-1</sup>

over the sampling duration of 1.3 - 24 h. The recovery tests of the plastic bag extraction using 100 ng of GEM prepared from NIST SRM 8610 showed almost 100% of the recoveries of when the extraction time was 24 h and the 20 – 40% RAR were used in the extractions. Those techniques were used in the pilot studies of the source characterization of open field burning, the ambient air TGM analysis, and laboratory experiments of atmospheric oxidation. The method successfully determined the stable mercury isotope ratios of TGM or GEM in the air.

The developed technique can be used for other field studies. The technique from the large volume sampling to the pre-concentration can be simply automated, thus, can be applied to a long-term monitoring study for stable mercury isotope measurements at remote sites.

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