

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

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Abstract

10 Techniques for fast large-volume sampling of total gaseous mercury (TGM) in the air 11 and extracting the TGM with 5 mL acid solution were developed for stable mercury 12 isotope ratio measurements. A Big gold coated sand Trap (BAuT), a 45 mm i.d. × 300 13 mm length quartz tube containing 131 times more gold coated silica than a conventional 14 gold trap has, was used for the collection of a large amount of TGM from the air. The 15 collected TGM was then extracted by 5 mL reversed aqua regia in a 2L Tedler bag, and 16 the extract was analyzed by a cold-vapor generator coupled with a multi collector 17 inductively coupled plasma mass spectrometer for the isotopic compositions. The 18 sampling tests of BAuT showed 99.9% or higher collection efficiency during the 19 sampling time of 1-24 h under the flow rate of 20-100 L min⁻¹. Recovery tests of the 20 bag extraction using 100 ng of NIST SRM 8610 exhibited nearly 100% of recovery 21 yields and agreement of the measured five stable mercury isotope ratios with the 22 reference values within 2 % of uncertainty when using the trapping solution of 40% 23 reversed aqua regia with the extraction time of a day. The overall methodology tested in 24 the pilot field and laboratory studies demonstrated the successful analysis, promising 25 highly precise stable mercury isotopic data with the time resolution less than a day. Part 26 of the procedure can be automated, ideal for unmanned sampling at a remote site.

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13 isotope ratio measurements. A Big gold coated sand Trap (BAuT), a 45 mm i.d. × 300
14 mm length quartz tube containing 131 times more gold coated silica than a conventional
15 gold trap has, was used for the collection of a large amount of TGM from the air. The
16 collected TGM was then extracted by 5 mL reversed aqua regia in a 2L Tedler bag, and
17 the extract was analyzed by a cold-vapor generator coupled with a multi collector
18 inductively coupled plasma mass spectrometer for the isotopic compositions. The
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20 sampling time of 1 - 24 h under the flow rate of 20 - 100 L min⁻¹. Recovery tests of the
21 bag extraction using 100 ng of NIST SRM 8610 exhibited nearly 100% of recovery
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23 reference values within 2 σ of uncertainty when using the trapping solution of 40%
24 reversed aqua regia with the extraction time of a day. The overall methodology tested in
25 the pilot field and laboratory studies demonstrated the successful analysis, promising
26 highly precise stable mercury isotopic data with the time resolution less than a day. Part
27 of the procedure can be automated, ideal for unmanned sampling at a remote site.

28
29 1. Introduction

30 Mercury is a notorious pollutant triggering serious adverse health effects (WHO,
31 2003). This metal element has a very unique characteristic that it can evaporate under
32 the room temperature and pressure. Because of this nature, mercury spreads globally
33 and, thus, is ubiquitous in the natural environment. In August 2017 the international
34 regulation on the use and trade of the man-made mercury started under the name of
35 Minamata Convention on Mercury to lower the mercury level in the natural
36 environment. However, it is known that there are also natural sources of mercury, such

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

45 Mercury naturally has seven stable isotopes, ^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg ,
46 and ^{204}Hg , the relative natural abundances (relative to the sum of all isotope
47 abundances) of which are 0.155%, 10.04%, 16.94%, 23.14%, 13.17%, 29.73%, and
48 6.83%, respectively (Blum and Bergquist, 2007). A MC-ICP-MS allows simultaneous
49 high precision measurements of those stable mercury isotope ratios (δHg) in four to six
50 significant figures. As trading off, the analysis requires ng order of mercury at least. To
51 date some field studies for δHg of atmospheric TGM have been reported (Gratz *et al.*,
52 2010; Demers *et al.*, 2013; Yamakawa *et al.*, 2019; Fu *et al.*, 2016), but with their
53 methods a sampling duration was a few days to weeks. Improving the sampling
54 technique, faster sampling for the δHg analysis, will better understand the atmospheric
55 transport and processing of TGM in the air, and this is a challenging issue in the
56 atmospheric δHg research.

57 There is another challenging issue in the sample preparation step: How 5 ng or higher
58 amount of mercury in the gaseous state is oxidized and trapped in a small amount of
59 solution for the isotope analysis. While the conventional quantitative mercury analysis
60 is done by the combination of trapping TGM by a gold trap, converting the TGM to
61 gaseous elemental mercury (GEM) by heating, and flushing the GEM into an atomic
62 absorption or fluorescence spectrometer, the current δHg analysis is done by a constant
63 injection of a liquid sample containing mercury ions into a cold-vapor generator (CV)
64 coupled with MC-ICP-MS to gain sufficient and stable signal strengths of GEM during
65 the sequence of measurement. The latter method requires oxidation of gaseous mercury
66 and enclose of oxidized mercury into a solution. To date a dynamic oxidation method
67 (bubbling GEM in an acid solution) has been used to capture GEM generated from the
68 TGM samples (Gratz *et al.*, 2010; Demers *et al.*, 2013; Fu *et al.*, 2014; Yamakawa *et al.*,
69 2017), but this method may not result in high recovery yields for a large amount of
70 GEM because of the short contacting time with the acid solution. High recovery yield is
71 a key for the stable isotope analysis because it would minimize artificial and unfavored
72 isotope fractionations that are more or less accompanied with any physical and chemical

73 processes.

74 In this paper we report novel offline techniques to collect sufficient amount of GEM
75 within a reasonable amount of time (24 h or less) and to oxidize and effectively capture
76 the collected mercury by 5mL of acid solution for the δHg measurements.

77

78 2. Methodology

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

90

91 2.1. Sampling TGM and pre-concentration

92 TGM in the air was collected using Big gold coated sand Trap (BAuT). BAuT is a
93 customary made 50 mm o.d \times 45 mm i.d. \times 300 mm long quartz tube that a 45 mm o.d.
94 \times 5 mm thickness fritted quartz plate was fused in the middle (COSMOS VID, Fukuoka,
95 Japan). On the plate approximately 10.5 g of quartz sand coated with vaporized gold
96 (Nippon Instruments Corp., Osaka, Japan) was placed and approximately 0.1 g of quartz
97 wool was stuffed on the top. Compared to a commercially available conventional gold
98 coated trap (a 4 mm i.d. \times 160 mm long quartz tube with 0.08g of the gold coated silica
99 sand, capable of capturing 70 μg of gaseous mercury and supplied by the Nippon
100 Instruments Corp., Osaka, Japan), the mouth of BAuT is approximately 11 times wider
101 and the amount of the gold coated sand is approximately 131 times more contained.
102 Because of the large mouth BAuT theoretically accepts large flow of air for TGM
103 sampling. For instance, the flow rates of BAuT that gives the same linear velocities as
104 those given by the conventional gold coated sand trap sampling under the typical flow
105 rates of 0.5 and 1.0 L min^{-1} , corresponding to 39.8 m min^{-1} and 79.6 m min^{-1} of linear
106 velocity, are 63.3 L min^{-1} and 126.6 L min^{-1} , respectively. To the best of our knowledge,
107 the reported techniques for TGM sampling from the ambient air use the flow rates of 2 -
108 20 L min^{-1} (an iodine or chlorine impregnated carbon trap, Fu *et al.*, 2014), 14.4 L min^{-1}

109 (1.8 L min⁻¹ × 8 gold traps, Gratz et al., 2010; Demers et al., 2011), and 16 L min⁻¹ (1 L
110 min⁻¹ × 16 gold traps, Yamakawa *et al.*, 2019) with the sampling duration of 15 – 20
111 days, 2 - 3 days, and 3 days, respectively. Given the same collection efficiencies for all
112 these sampling methods, the sampling speed by BAuT is theoretically 3 to 9 folds of
113 magnitude faster than the reported methods. Additional advantage of BAuT is the use of
114 single trap, making the following pre-concentration procedure simple.

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

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

145 STEC, Kyoto, Japan). The background of zero air was 0.03 pg L^{-1} or less. A hand-made
146 heating system used for heating BAuT was built using nichrome wire (1.0 mm o.d.,
147 Sunko Corp. Kyoto, Japan), quartz wool (quartz wool, grade B, GL Science, Tokyo,
148 Japan), and glass tape (insulating glass tape, Komeri, Niigata, Japan). Approximately
149 35V of electricity was applied to the nichrome wire to heat BAuT via a variable
150 transformer (RAS-10, Tokyo Rikosha, Co. Ltd., Saitama, Japan). The temperature was
151 kept constant using a temperature controller (TR-KN, AS ONE Corp., Osaka, Japan).

152

153 2.2. Plastic bag extraction of TGM

154 The pre-concentrated TGM in the conventional trap was extracted by 5 mL trapping
155 solution in a plastic bag. The pre-concentrated TGM from the BAuT was heated to
156 973K using another hand-made heating system built for the conventional trap under the
157 0.5 L min^{-1} flow of the zero air for four minutes so that the pre-concentrated TGM was
158 reduced to GEM and then flushed into a 2L Tedler bag through the attached PTFE
159 stopcock (AS ONE Corp., Osaka, Japan). For the efficient transfer of GEM during the
160 limited time of four minutes the zero gas started being flown as soon as the temperature
161 reached to 573K. Prior to the transfer, $5 \pm 0.01 \text{ mL}$ of reversed aqua regia (RAR), a 2:1
162 (v/v) mixture of nitric and hydrochloric acids (PMA grade, Kanto Chemical Co. Inc.,
163 Tokyo, Japan) with ultra-pure water (Milli-Q Direct 3, Merck KGaA, Darmstadt,
164 Germany), was pipetted (Research plus 1000, Eppendorf AG, Hamburg, Germany) into
165 the bag. A variety of RAR concentrations were tested. After the transfer of GEM the
166 stopcock was closed and the plastic bag was shaken for 3 min and left for 6 to 24 h.
167 During the extraction period the bag was shaken 3 more times, each of which was for 1
168 min. The plastic bag was also weighed at the start and the end of the extraction using an
169 electronic balancer (ML4002T, Mettler-Toledo GmbH, Greifensee, Switzerland) to
170 check any leak during the extraction.

171 As trapping solution, a stronger acid oxidizes metals more quickly in general. Thus,
172 the use of stronger acid for the trapping solution must have advantage. Contrarily,
173 strong acid interferes the production of GEM in the CV because produced GEM by
174 reduction of Hg^{2+} with Sn^{2+} is oxidized back to Hg^{2+} during the transfer through the CV
175 to the MC-ICP-MS. To find the upper limit of RAR concentration we checked the
176 sensitivity dependence of the ^{201}Hg signal strength on the RAR concentration that SRM
177 3133 was dissolved in.

178

179 2.3. Testing the overall methodology

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

181 types of outdoor air sampling were conducted: normal air sampling from the window of
182 our laboratory and sampling plumes from open field burning. The Aso open field
183 burning (Noyaki) takes place annually in the season between March and April and it
184 burns approximately 161 km² of the natural grass field and stock farms for the purpose
185 of the sustainable healthy nature in this region. TGM from the plumes was sampled by
186 BAuT from the window of the vehicle. The air was drawn by a diaphragm pump
187 described earlier, the electricity of which was supplied by UPS (SURTA1500XLJ,
188 American Power Conservation, U.S.A.). Sampling flow rate and duration were 75 L
189 min⁻¹ and between 1 and 6 h, respectively. Indoor air was also sampled in our
190 laboratories, with the flow rate and sampling duration of 75 - 100 L min⁻¹ and between 6
191 and 24 h, respectively. Sampling GEM from the gas mixture in the indoor
192 photochemical reactor was also tested. The experimental condition was the similar to
193 that reported by Irei et al. (2006 and 2011). Briefly, in this pilot laboratory experiment
194 200 ng of GEM produced from the SRM 8610 (NIST, MD, U.S.A.), oxidant precursors,
195 and dried zero air were introduced into a 1.5 m³ photochemical reactor, which was made
196 of PFA sheet. 366 nm UV light (UV lamp 4, CAMAG, Muttenz, Switzerland) was
197 switched on and off to initiate and stop the photochemical reactions with OH radicals,
198 and residual GEM was sampled by BAuT through a KCl coated 8-channel annular
199 denuder (URG-2000-30CF, URG Co., NC, U.S.A.), which removed oxidized mercury.
200 The pre-concentration and extraction procedures for these samples are exactly the same
201 as those referred earlier.

202

203 3. Results and Discussion

204 3.1. Collection efficiency of BAuT

205 The breakthrough tests performed by the double BAuT sampling showed only 7 to
206 115 pg of GEM passed the front BAuT then was captured by the backup BAuT during
207 the 1.3 to 24 h sampling under the flow rate of 20 to 100 L min⁻¹ (Table 1). Note that the
208 sampling flow rate for the outdoor sampling could not be increased because the pressure
209 loss at the PFA tubing between the filter and front BAuT. Compared to the quantity of
210 TGM trapped at the front BAuT, which will be shown and discussed in the sub-section
211 3.4, the breakthrough TGM at the front BAuT was very small and the calculated
212 collection efficiency of the front BAuT was 99.9%. The results are theoretically
213 reasonable and satisfy our demand for the fast and large volume sampling to achieve the
214 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 ⁻¹ | m ³ | 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 |

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216

217 3.2. Recovery test of the plastic bag extraction

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

226

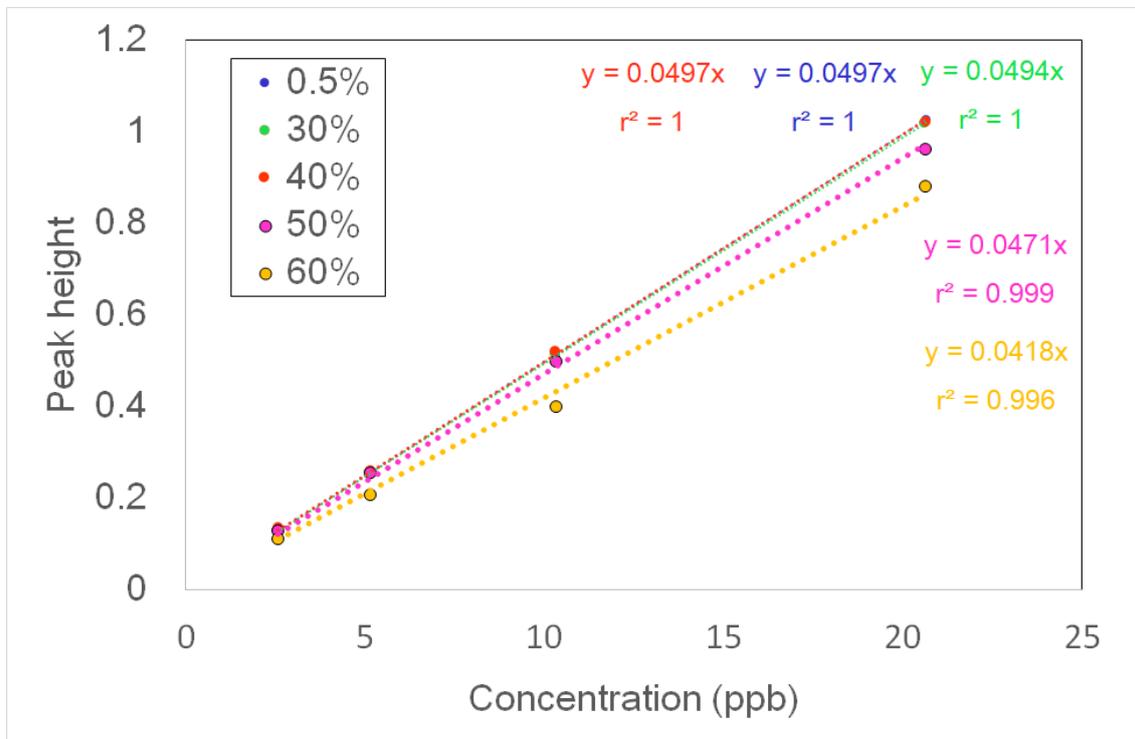


Fig. 1. Dependence of external calibrations of CV-MC-ICP-MS (²⁰¹Hg signal height) on a variety of reversed aqua regia concentration.

227

228

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

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

243 Concentrations of mercury in the trapping solution were measured by CV-MC-ICP-MS
244 using the external calibration referred earlier, and the recovery yields were calculated
245 based on those concentrations, the volume of the trapping solution (5 mL), and 103 ng
246 of GEM introduced into the plastic bag (Table 2). The average \pm standard deviation of
247 the blank extracts ($n = 12$) was $55 \pm 61 \text{ pg g}^{-1}$, and all the recovery yields determined
248 were blank corrected. The recovery yields exhibited that the use of the 20%, 30%, and
249 40% v/v RAR gave the same recovery yields of 100% when the GEM was exposed to
250 the solution for 24 h. Although it is not shown here the use of 5% RAR required 7 days
251 to achieve more than 90% of the recovery yields. The results here exhibited that the
252 recovery yields did not change significantly as the extraction time decreased down to 6
253 h, but those were prone to fluctuate as the extraction time was 3 h only.

254

Table 2. Summary of plastic bag extraction test using NIST SRM 8610[†]

| Solution | n | Spiked Hg ng | Extraction time h | Collected volume mL | Lost volume mL | Concentration ng mL ⁻¹ | Recovery yield % |
|----------|---|-----------------|----------------------|------------------------|-------------------|--------------------------------------|---------------------|
| 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 |

[†]The values shown are the average ± standard deviation.

255

256

257 3.3. Stable Hg isotope measurement

258 Results of stable mercury isotope measurements of the trapping solution from the
259 recovery tests showed that overall the difference from the reference value was in the
260 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
261 $\delta^{201}\text{Hg}$, -0.07 to 0.23 ‰ for $\delta^{202}\text{Hg}$, and -0.12 to 0.33 ‰ for $\delta^{204}\text{Hg}$ (Table 3). The
262 measured isotope ratios agreed with the reference values within the two times of the
263 standard deviations, but the accuracy and precision were slightly poorer for the samples
264 with 3 h extraction time than those for other samples. Thus, we concluded that there was
265 no significant artificial isotopic fractionation during the extraction procedure with the
266 extraction time longer between 6 and 24 h.

267

Table 3. Summary of isotope measurements of plastic bag extraction test[†]

| 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 ± 0.01 | -0.27 ± 0.01 | -0.46 ± 0.02 | -0.56 ± 0.03 | -0.82 ± 0.07 |
| 40% RAR | 6 | 24 | -0.19 ± 0.05 | -0.30 ± 0.06 | -0.51 ± 0.06 | -0.62 ± 0.09 | -0.91 ± 0.07 |
| 30% RAR | 4 | 24 | -0.20 ± 0.01 | -0.30 ± 0.03 | -0.52 ± 0.02 | -0.63 ± 0.04 | -0.92 ± 0.05 |
| 20% RAR | 3 | 24 | -0.10 ± 0.02 | -0.18 ± 0.03 | -0.40 ± 0.03 | -0.45 ± 0.06 | -0.67 ± 0.06 |
| 40% RAR | 3 | 12 | -0.19 ± 0.05 | -0.29 ± 0.05 | -0.48 ± 0.09 | -0.59 ± 0.08 | -0.94 ± 0.15 |
| 30% RAR | 3 | 12 | -0.20 ± 0.01 | -0.31 ± 0.03 | -0.52 ± 0.03 | -0.62 ± 0.05 | -0.92 ± 0.06 |
| 40% RAR | 3 | 6 | -0.11 ± 0.03 | -0.18 ± 0.02 | -0.36 ± 0.06 | -0.44 ± 0.03 | -0.67 ± 0.03 |
| 30% RAR | 3 | 6 | -0.19 ± 0.05 | -0.27 ± 0.05 | -0.44 ± 0.08 | -0.55 ± 0.06 | -0.87 ± 0.08 |
| 20% RAR | 2 | 6 | -0.15 ± 0.01 | -0.19 ± 0.05 | -0.28 ± 0.09 | -0.33 ± 0.14 | -0.49 ± 0.34 |
| 40% RAR | 3 | 3 | -0.15 ± 0.01 | -0.21 ± 0.03 | -0.38 ± 0.04 | -0.46 ± 0.08 | -0.69 ± 0.21 |
| 30% RAR | 2 | 3 | -0.15 ± 0.05 | -0.24 ± 0.09 | -0.44 ± 0.17 | -0.50 ± 0.20 | -0.74 ± 0.30 |

[†]The values shown are the average \pm standard deviation.

268

269

270 3.4. Results of the overall methodology test

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

287

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

| Sample | Flow rate | Sampling duration | Air volume | Conc. of extract [†] | Conc. in the air [‡] | $\delta^{199}\text{Hg}$ | $\delta^{200}\text{Hg}$ | $\delta^{201}\text{Hg}$ | $\delta^{202}\text{Hg}$ | $\delta^{204}\text{Hg}$ |
|-------------------------------|---------------------|-------------------|------------|-------------------------------|-------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| | L min ⁻¹ | | | | | | | | | |
| 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 |

290

291

292 **Table 5. Background corrected stable mercury isotopic compositions of TGM from**
 293 **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 |

294

295

296 The analysis of TGM samples from the outdoor and indoor (the laboratory and clean
 297 room) air showed the sufficient collection of GEM (85 – 116 ng) and the successful
 298 analysis of their δHg values (Table 4). The δHg values of the outdoor air varied from
 299 -0.12 ‰ to 0.48 ‰, while those of the laboratory and clean room air varied from
 300 -0.11 ‰ to -0.22 ‰ and from -0.20 ‰ to -0.59 ‰, respectively. The slightly lighter δHg
 301 values of the clean room air than those of the laboratory air may attribute to the isotope
 302 fractionation occurring at mercury absorbent.

303 The δHg of residual GEM collected after the photochemical reaction with OH radical,
 304 the major sinking pathway of atmospheric GEM, exhibited large isotope fractionations
 305 from the reference values, ranging from -1.63 ‰ to 9.96 ‰ as the extent of Hg reaction
 306 estimated from the extract concentration was 44% (Table 4). Except $\delta^{204}\text{Hg}$, the mass
 307 dependent and independent fractionation (MDF and MIF) were observed on odd and
 308 even mass numbers of GEM, respectively. The unusual isotope fractionation of mercury
 309 found in the precipitation of Peterborough, Canada (Chen *et al.*, 2012), the heavier
 310 ^{199}Hg composition with the lighter ^{202}Hg composition, is likely explained by this
 311 process. However, this is only one sample analysis and thorough evaluations on the
 312 isotope fractionations relevant to the atmospheric oxidations are needed.

313

314 4. Summary and future application

315 We developed a fast and large volume sampling method of TGM in the air and its
 316 extraction method using static extraction technique. The sampling tests demonstrated
 317 99.9% collection efficiency of TGM by BAuT under the flow rate of 20 - 100 L min⁻¹

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

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

329

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