A Novel Method for Stable Isotope Measurement of Gaseous Elemental Mercury

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1. Objective: This project is to develop the fast large-volume sampling and efficient extraction method of total gaseous mercury (TGM) for stable mercury isotope analysis by cold-vapor generator multicollector ICP-MS. Developed techniques will be used for source characterization, ambient measurements, and laboratory studies of TGM.

2. Methodology

2.1. Big gold (Au)-coated sand Trap (BAuT)
A BAuT was developed from a conventional mercury trap (CMT) (Fig. 1). Due to the large mouth and amount of trapping material a BAuT theoretically samples gas 127 times faster than a CMT does. Captured TGM by a BAuT was subject to the pre-concentration to a CMT. Collection efficiency of BAuT was evaluated by sampling TGM using double BAuTs connected in series (Fig. 2) and comparing TGM in the backup BAuT with TGM in the front BAuT.
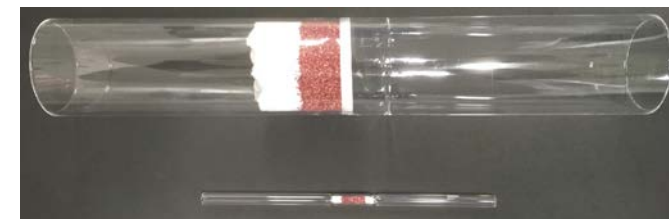

Fig. 1. BAuT (above) and conventional gold trap (below).

2.2. Plastic bag extraction
Efficient conversion of hundred ng order of gaseous mercury to the stable Hg^{2+} state in solution, required for the isotope analysis, is challenging. A novel static extraction method of TGM, enclosing TGM flushed from a CMT with 5 mL reversed aqua resia (RAR) extracting solution in a 2 L Tedler bag, was developed (Fig. 3). Extraction tests were carried out by flushing 100 ng elemental Hg gas (GEM) prepared from NIST SRM 8610 solution into the Tedler bag, in which 5mL of RAR was pipetted in advance.

Fig. 3. Plastic bag extraction.
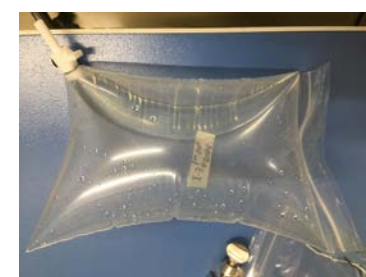
Fig. 2. Double BAuT Sampling.

2.3. Method test
The techniques were tested in the source characterization studies of the open field burning in March-April, 2019 (Fig. 4) and the laboratory experiments for the evaluation of isotope fractionation accompanied by the reaction with OH radical, the typical atmospheric oxidation (Fig. 5).

Fig. 4. Open field burning in Aso, Japan.

Fig. 5. Photooxidation experiment.

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3. Results and Discussion

3.1. Collection efficiency estimated by double BAuT sampling
Under the 20 - 100 LPM flow rate and the 1.3 - 24 h sampling duration, the TGM captured at the backup BAuT was only 7 to 115 pg (Table 1). The comparison with the TGM in the front BAuT indicated the 99.86 - 99.99% of TGM was collected in the front BAuT.

Table 1. Results of sampling breakthrough test

Sample	Sampling duration	Flow rate	Total volume	Hg in backup BAuT	Collection efficiency of front BAuT
	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

3.2. Plastic bag extraction test
Recovery tests of 103 ng GEM with variety of extraction time and RAR concentration exhibited that use of 20-40% RAR with the 24 h extraction time gave the best recovery yields (approximately 100%) and acceptable accuracy in isotope ratios, $\Delta\delta$Hg (Table 2).

Table 2. Results of plastic bag extraction test[†].

Solution	n	Spiked Hg	Extraction time	Concentration	Recovery yield	$\Delta\delta^{199}$Hg[‡]	$\Delta\delta^{200}$Hg[‡]	$\Delta\delta^{201}$Hg[‡]	$\Delta\delta^{202}$Hg[‡]	$\Delta\delta^{204}$Hg[‡]
		ng	h	ng mL^{-1}	%	‰				
40% RAR	6	103 ± 2	24	21.4 ± 0.9	102 ± 5	-0.02 ± 0.02	-0.03 ± 0.03	-0.05 ± 0.03	-0.06 ± 0.05	-0.09 ± 0.08
30% RAR	4	103 ± 2	24	21.0 ± 0.4	100 ± 2	-0.03 ± 0.01	-0.03 ± 0.02	-0.06 ± 0.02	-0.07 ± 0.04	-0.10 ± 0.08
20% RAR	3	103 ± 2	24	21.8 ± 0.6	103 ± 3	0.07 ± 0.02	0.09 ± 0.02	0.06 ± 0.02	0.11 ± 0.04	0.15 ± 0.08
40% RAR	3	103 ± 2	12	20.3 ± 0.4	97 ± 2	-0.02 ± 0.03	-0.02 ± 0.03	-0.02 ± 0.06	-0.03 ± 0.05	-0.12 ± 0.11
30% RAR	3	103 ± 2	12	20.76 ± 0.08	99.1 ± 0.5	-0.03 ± 0.01	-0.04 ± 0.02	-0.06 ± 0.03	-0.06 ± 0.04	-0.10 ± 0.08
40% RAR	3	103 ± 2	6	20.1 ± 0.3	97 ± 2	0.06 ± 0.02	0.09 ± 0.01	0.10 ± 0.04	0.12 ± 0.04	0.15 ± 0.07
30% RAR	3	103 ± 2	6	20.6 ± 0.3	99 ± 2	-0.02 ± 0.03	0.00 ± 0.03	0.02 ± 0.05	0.01 ± 0.05	-0.05 ± 0.08
20% RAR	2	103 ± 2	6	19 ± 1	92 ± 6	0.02 ± 0.01	0.08 ± 0.04	0.18 ± 0.07	0.23 ± 0.10	0.33 ± 0.25
40% RAR	3	103 ± 2	3	18 ± 2	87 ± 11	0.02 ± 0.01	0.06 ± 0.02	0.08 ± 0.03	0.10 ± 0.05	0.13 ± 0.14
30% RAR	2	103 ± 2	3	20 ± 1	96 ± 5	0.02 ± 0.04	0.03 ± 0.07	0.02 ± 0.12	0.06 ± 0.14	0.08 ± 0.23

[†]The values shown are average ±standard deviation for spiked Hg, collected volume, concentration, and recovery yield and average ±standard error for isotope ratios. [‡]Difference from the reference isotope ratios (measured – reference) of SRM 8610.

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3.3. Method test Field studies demonstrated successful sampling of detectable amount of TGM from for the open field burning during the short sampling period less than an hour (Table 3), which was limited by out of battery used for the power supply of a sampling pump. Compared to the TGM concentration in the background air, the concentration level of TGM increased, indicating the evasion of mercury by this event. Laboratory studies also demonstrated successful sampling of mercury from the 1 m³ reactor, promising the application of BAuT for the evaluation of isotope fractionations accompanied by the atmospheric oxidation.

Table 3. Results of method test

Sample	Flow rate	Sampling duration	Air volume	Conc. of extract[†]	Conc. In the air[‡]	$\delta^{199}Hg$	$\delta^{200}Hg$	$\delta^{201}Hg$	$\delta^{202}Hg$	$\delta^{204}Hg$
	L min⁻¹	h	m³	ng g⁻¹	ng m⁻³			‰		
Aso, March 24	75	0.9	4.2	3.1	3.7	-0.58	-0.58	-1.01	-0.93	-1.40
Aso, April 6	78	0.8	3.5	1.0	1.4	-1.14	-0.69	-1.25	-1.39	1.19
Aso background air, March 31	54	2.1	6.7	1.1	0.8	-0.05	0.44	0.35	1.06	1.30
Aso 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 air					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

4. Summary Results here demonstrated successful development of the fast large-volume sampling and highly efficient extraction method for stable isotope analysis of gaseous Hg in the air. The method will be applied to source, field, and laboratory studies for stable mercury isotope analysis.