

Supplementary Materials for the manuscript entitled: Development of A Fast Sampling and High Recovery Extraction Method for Stable Isotope Measurement of Gaseous Mercury

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This Supplementary Materials contain: 4 Pages, 1 Figures 2, Tables 2, sub-sections (S1 and S2).

S1. Dependence of signal sensitivity on inversed aqua regia concentration

For the trapping solution used in the plastic bag extraction, a stronger acid should oxidize mercury more quickly, thus must have advantage. Contrarily, strong acid interferes the measurements by the CV-MC-ICP-MS because the GEM generated in the CV will be oxidized back by contacting with the strong acid during the transfer. Therefore, we evaluated the sensitivity dependence of the CV-MC-ICP-MS measurements on inversed aqua regia concentration to find the upper limit of inversed aqua regia concentration. In this test, 2.5, 5, 10, and 20 ng g⁻¹ SRM 3133 solutions were prepared in 0.5, 30, 40, 50, and 60% (v/v) inversed aqua regia, then the slopes of quantitative calibrations (signal height for ²⁰¹Hg versus concentration) were compared.

The test demonstrated that the slopes of the quantitative calibrations made for ²⁰¹Hg by SRM 8610 diluted in the 0.5 to 40% of inversed aqua regia were identical, 0.084 V min. g ng⁻¹ mL⁻¹, while the slopes were lower when the concentrations of inversed aqua regia were higher than 40% (Figure S1). This indicates that gaseous elemental mercury generated from the sample solution was oxidized back to the solution during the transfer through the CV when the concentration of inversed aqua regia was higher than 40%. Based on these results, we used the inversed aqua regia concentration lower than 40% in the following recovery tests.

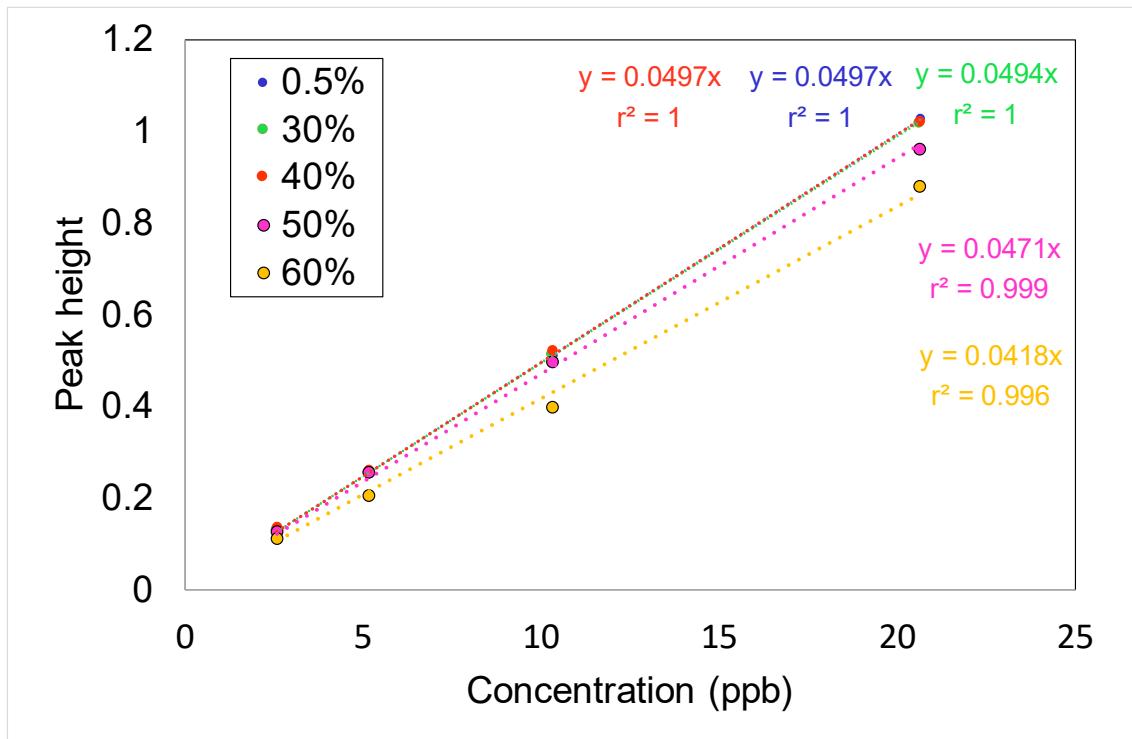


Figure S1. Dependence of quantitative calibrations of CV-MC-ICP-MS (^{201}Hg signal height) on a variety of inversed aqua regia concentration (0.5-60%).

Table S1. Weather and BAuT sampling information during the methodology tests.

Date	Time	Weather Information				Location	Sampling Information		
		Location	Sky	Temp/°C	RH/%		Sampling Duration/h	Flow Date/L min ⁻¹	Total Volume/m ³
2019/3/24	9:00–15:00	Kumamoto city [†]	sunny	12 ± 2	40 ± 8	Aso	0.9	75	4.2
2019/3/31	12:00–15:00	Kumamoto city [†]	sunny	12.1 ± 0.3	41 ± 1	Aso	2.1	54	6.7
2019/4/6	9:00–11:00	Kumamoto city [†]	sunny	17 ± 3	63 ± 12	Aso	0.8	78	3.5
2019/2/20	11:00–16:00	Kumamoto city [†]	sunny	27 ± 1	37 ± 5	Aso	4.2	80	20.1
2019/3/26–27	20:00–19:08	Ushibuka [‡]	sunny	15 ± 3	73 ± 17	Minamata	22.3	75	100.2
2020/2/15	10:00–17:00	Ushibuka [‡]	cloudy	18 ± 1	82 ± 4	Laboratory	6.0	100	36.0
2020/2/20–21	15:00–16:00	Clean room [§]	n.a.	22	55	Clean room	24.0	100	144.0

*The data were obtained from the weather archive of the Japan Meteorological Agency (https://www.data.jma.go.jp/obd/stats/etrn/index.php?prec_no=86&block_no=&year=2020&month=6&day=7&view=). [†]The weather monitoring station nearest to the Aso region. [‡]The weather monitoring station nearest to the National Institute for Minamata Disease. [§]Temperature and relative humidity were controlled.

S2. Loss of trapping solution during the plastic bag extraction

The results of the mass measurements demonstrated that the collected volume of the trapping solutions from the plastic bags was more than 4.8 mL out of 5 mL, corresponding to more than 96% of the trapping solution pipetted (Table S2). 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 the collectable small liquid beads. As discussed in the sub-chapter 3.2 of the main text, the solution also successfully captured nearly 100% of GEM in the plastic bag, resulting the sufficient sample concentration for the isotope analysis, higher than 10 ng g⁻¹ (Table S2).

Even though the trapping solutions were highly yielded, there were small differences in the weights of the plastic bag between the start and end of the extraction. The differences were associated with the extraction time. The weight differences were converted to the volume differences using the estimated densities of the inversed aqua regia mixtures. We suspect that the loss was not a leakage, but likely due to the slow permeation of water molecules through the Tedler membrane because the plastic bag was fully expanded even at the end of the extraction. Such phenomenon is molecular size selective and 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 described in the main text, the correction for this volume loss was made.

Table S2. The volume and mercury concentration of trapping solution yielded from the plastic bag extraction test.

Solution	n	Collected Volume/mL	Lost Volume/mL	Concentration/ng mL ⁻¹
40% RAR	6	4.86 ± 0.01	0.12 ± 0.02	21.4 ± 0.4
30% RAR	4	4.83 ± 0.01	0.12 ± 0.00	21.0 ± 0.2

40% RAR	3	4.5 ± 0.12	0.16 ± 0.01	21.8 ± 0.4
40% RAR	3	4.83 ± 0.02	0.09 ± 0.02	20.3 ± 0.2
30% RAR	3	4.83 ± 0.01	0.12 ± 0.00	20.76 ± 0.05
40% RAR	3	4.92 ± 0.04	0.07 ± 0.02	20.1 ± 0.2
30% RAR	3	4.89 ± 0.01	0.03 ± 0.00	20.6 ± 0.2
20% RAR	2	4.83	0.04	18.9 ± 0.7
40% RAR	3	4.99 ± 0.01	0.07 ± 0.01	18 ± 1
30% RAR	2	4.83 ± 0.03	0.08 ± 0.01	20.0 ± 0.7