Supplementary Material

Stability and selectivity of pre-concentration methods for gaseous oxidized mercury in the air

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Table S1. Mass balance for plasma oxidation of $^{197}Hg^{0}$ to $^{197}Hg^{II}$ performed on different denuders. Plasma GOM refers to $^{197}Hg^{II}$ retained on denuders, generated by the NTP oxidation method whereas breakthrough refers to unoxidized $^{197}Hg^{0}$ collected on Au trap. Mass balance is given as sum of both NTP generated Hg^{II} and breakthrough.

	Plasma GOM (%)	Breakthrough (%)	Mass balance (%)
Denuder A	96.1	3.8	99.9
	94.0	7.4	101.5
	92.3	8.2	100.5
Denuder B	86.8	9.2	96.0
	89.6	11.6	101.1
	89.7	11.2	100.9
Denuder C	86.2	11.3	97.5
	89.3	11.9	101.2
	93.1	8.1	101.2

Table S2. Plasma oxidation of Hg^{0} to Hg^{II} performed on CEMs for the production of HgO, $HgCl_2$, and $HgBr_2$. Overall mass balances for NTP-Hg^{II} loading are represented here, as the sum of Hg^{II} recovered from CEMs by digestion, residual leftover in CEMs post-digestion, Hg^{II} recovered from the inner Teflon walls of the filter pack (FP), and breakthrough collected on the Au trap during loading.

Hg^{II} species	CEM digestate (%)	CEM residual (%)	Retained on FP (%)	Breakthrough (%)	Mass balance (%)
HgO	89.6	6.5	5.8	2.9	104.8
	79.0	6.8	4.8	3.5	94.2
	78.4	3.0	8.8	7.3	97.5
	86.2	2.6	5.1	4.5	98.4
	80.4	3.9	8.2	4.9	97.4
$HgCl_2$	85.9	3.7	8.3	0.0	97.9
	88.7	3.7	4.0	0.2	96.6
	91.0	5.4	0.8	0.0	97.2
	84.6	5.8	7.6	0.0	98.0

	86.0	7.1	3.0	0.5	96.6
	84.5	7.5	2.2	0.0	94.2
$HgBr_2$	82.5	5.7	7.8	0.4	96.4
	83.6	5.6	7.4	0.3	96.9
	82.6	4.7	7.4	0.3	95.0
	86.6	6.2	1.1	0.7	94.6
	68.8	5.5	17.9	0.8	93.0
	87.3	6.3	4.6	0.8	99.0

Table S3. Hg^{II} sample losses from freshly prepared denuders when exposed to various airflows. Mass balances are presented as the sum of $^{197}Hg^{II}$ losses quantified at each exposure period (4 × 0.5 hours), based on the initially loaded $^{197}Hg^{II}$ on the denuders, and the $^{197}Hg^{II}$ finally recovered from the denuders at the end of the exposure period through thermal decomposition, referred to as the 'Measured' fraction.

Denuders	Loss at 0.5 hrs (%)	Loss at 1.0 hrs (%)	Loss at 1.5 hrs (%)	Loss at 2.0 hrs (%)	Measured fraction (%)	Mass balance (%)
N_2 flow						
	10.3	n.d	1.6	n.d	90.1	102.0
A	16.8	n.d	n.d	n.d	82.6	99.4
	3.7	0.2	n.d	n.d	96.4	100.2
	10.0	1.6	n.d	0.4	90.7	102.7
B	4.3	n.d	1.9	n.d	93.8	100.0
	2.1	n.d	n.d	n.d	94.2	96.3
	6.1	n.d	n.d	n.d	97.6	103.7
C	4.1	n.d	0.6	n.d	95.2	99.8
	0.1	0.4	n.d	n.d	98.7	99.3
Ambient air - dark						
	15.6	12.2	9.6	13.9	47.3	98.6
A	8.4	8.3	n.d	2.1	79.8	98.7
	4.1	4.1	4.6	8.7	77.9	99.3
	19.1	20.3	10.9	11.2	39.5	100.9
B	8.7	7.8	2.1	3.2	81.0	102.9
	4.4	4.7	6.0	9.3	77.3	101.7
	16.0	14.0	17.6	11.2	41.9	100.7
C	14.0	5.4	n.d	2.3	78.1	99.8
	6.5	6.8	8.9	3.2	72.3	97.7
Ambient air - light						
	4.2	7.1	3.8	8.1	76.8	100.0
A	3.2	0.5	5.7	6.0	85.3	100.8
	7.9	3.0	2.7	6.1	80.0	99.7
	7.1	7.4	7.5	8.1	74.4	104.4
B	4.6	2.1	4.8	3.0	86.3	100.8
	3.1	3.5	4.3	2.0	89.8	102.5
	4.3	12.3	11.6	5.5	69.1	102.8
C	2.1	5.3	7.9	2.2	81.0	98.5
	5.7	5.2	7.4	7.0	77.2	102.5

*n.d. means “not detectable”

Table S4. Cumulative Hg^{II} losses from reused denuders (previously subjected to several heating cycles), collected on Au-traps, after a 2-hour exposure to various airflows. Experiments were conducted without mass balance (leftover Hg^{II} on denuders after the exposure period was not measured).

Exp. no.	Ambient air (% losses – 2 hrs)	N_2 flow (% losses – 2 hrs)
1	32.4	11.9

2	41.8	12.0
3	32.6	6.1
4	54.3	16.8
5	79.4	6.2
6	66.9	4.7
7	53.1	3.8
8	59.1	2.1
9	33.6	0.5
10	29.4	2.6
11	77.3	
12	49.1	
13	79.7	
14	35.6	
15	71.0	
16	63.8	
17	37.0	
18	16.7	
19	42.7	
20	63.5	

S5. Description of microwave digestion for CEMs

A set of three CEM membranes loaded with $^{197}Hg^{II}$ were precisely weighed (0.3g each) using a high-precision balance. The weighed membranes were individually transferred to pre-cleaned digestion vessels. The digestion process began with a sequential addition of concentrated acids: 4 mL HNO3 (65% Suprapur), followed by 1 mL HCl (37% Suprapur), allowing sufficient reaction time between each addition. After a 30-minute reaction period at room temperature, the vessels were securely sealed and placed in the Milestone ETHOS 1 Advanced Microwave Digestion System. The digestion program consisted of four stages: a 20-minute ramp period to reach 200°C, 15 minutes of digestion at 200°C, a 5-minute hold time, and a 30-minute cooling period before vessel opening. Following digestion, the samples were quantitatively transferred to 15-mL conical vials and diluted to a final volume of 15 mL using high-purity MQ water (water with a resistivity of 18.2 MΩcm, purified in a Millipore Elix® Essential 5 UV Milli-Q system). From this, 8 mL aliquot was transferred into glass vial immediately for measurements in the well-type gamma detector.

Table S6. Recovery of Hg^{II} residuals from CEMs previously subjected to BrCl digestion, by microwave digestion method.

$HgBr_2$ loaded on CEM (10ng)			
% recovery of initially loaded Hg^{II}	CEM A	CEM B	CEM C
Ambient air exposure losses in 72 hrs	5.2	5.6	4.8
CEM digestate – BrCl digestion	84.8	85.5	88.4
CEM residuals – post BrCl digestion	**3.3**	**4.2**	**4.5**
Filter pack acid wash	4.9	3.4	2.6
Mass balance	98.2	98.7	100.2
Total recovery from CEM alone (before microwave digestion)	**96.2**	**95.3**	**95.2**
Residuals recovered from CEM by microwave digestion	**4.1**	**4.6**	**4.4**
Total recovery from CEM alone (after microwave digestion)	**100.8**	**100.4**	**100.0**