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Supplement of

Behavior of KCl sorbent traps and KCl trapping solutions used for atmospheric mercury speciation: stability and specificity

Jan Gačnik et al.

Correspondence to: Milena Horvat (milena.horvat@ijs.si)

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Table S1: Chemicals used in the presented work

Description	Purity / type	Producer
65 % nitric acid	For analysis	Supelco, Darmstadt, Germany
30 % hydrochloric acid	Suprapur	Merck, Darmstadt, Germany
47 % hydrobromic acid	For analysis	Merck, Darmstadt, Germany
Tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$)	For analysis, max. 0.000001 % Hg	Merck, Darmstadt, Germany
Gold (III) chloride hydrate ($HAuCl_4 \cdot xH_2O$)	99.995 % trace metal basis	Merck, Darmstadt, Germany
Elemental mercury	99.9999 % Suprapur	Merck, Darmstadt, Germany
Sodium tetrapropylborate	/	Merck, Darmstadt, Germany
Acetic acid	Puriss.	Merck, Darmstadt, Germany
Ammonium acetate	LiChropur	Merck, Darmstadt, Germany
2,2,4-trimethylpentane	For HPLC, ≥99 %	Merck, Darmstadt, Germany
Silica gel	Technical grade 40, 6-14 mesh	merck, Darmstadt, Germany
Anhydrous sodium sulfate	≥99.99 % trace metal basis	Merck, Darmstadt, Germany
NIST SRM 3133: Mercury (Hg) Standard Solution	/	NIST, Gaithersburg, MD, USA
^{196}Hg enriched elemental Hg	51.58 % ^{196}Hg	Isoflex, San Francisco, CA, USA
Type I purified water	Electrical resistivity 18.2 MΩ cm	Merck, Darmstadt, Germany

Table S2: Instruments used in the presented work

Description	Model	Producer
High-purity germanium (HPGe) coaxial-type detector	Model 7229P	Canberra Industries Inc., Meriden, CT, USA
High-purity germanium (HPGe) well-type detector	Model GCW6023/S	Canberra Industries Inc., Meriden, CT, USA
Cold vapor atomic absorption spectrometer	Model Hg-201 Semi-Automated Mercury Analyzer	Sanso Seisakusho Co., Ltd., Tokyo, Japan
Liquid evaporative generator for oxidized mercury	/	Optoseven Ltd. & VTT Ltd., Espoo, Finland
Amalgamation-atomic fluorescence spectrometer	Model PSA 10.525 Sir Galahad	P S Analytical, Orpington, UK
Temperature-controlled bath	Model R2	Grant Instruments Ltd., Cambridge, UK
Bell Jar elemental Hg calibrator	Model PSA 10.555	P S Analytical, Orpington, UK
Cavkit elemental Hg vapor generator	Model PSA 10.536	P S Analytical, Orpington, UK
Capillary gas chromatography atomic fluorescence spectrometry	Model PSA 10.725 with Agilent J&W, DB1, 15 m 0.53 mm ID, film thickness 1.50 µm	P S Analytical, Orpington, UK

Equation S1 was applied for calculation of both A_0 (activity at reference time) of the sample and A_0 of the standard. The recoveries were calculated using Equation S2.

Equation S1

$$A_{0,sample} = \frac{A_{sample} * \frac{\ln 2}{t_{1/2}}}{e^{-\left(\frac{t_{passed} * \ln 2}{t_{1/2}}\right)} * \left[1 - e^{-\left(\frac{t_{measurement} * \ln 2}{t_{1/2}}\right)}\right]}$$

Equation S2

$$R = \frac{A_{0,sample}}{A_{0,std.}} * \frac{m_{Hg,std.}}{m_{Hg,sample}} * 100$$

Where:

$A_{0,\ sample}$ is the sample activity at reference time t=0 [Bq],
$A_{0,\ std}$ is the standard activity at reference time t=0 [Bq],
A_{sample} is the sample activity at the time of measurement [Bq],
$t_{1/2}$ is the half-life of ^{197}Hg [s],
t_{passed} is the time passed since reference time t=0 till the start of measurement [s],
$t_{measurement}$ is the time passed during the measurement [s],
R is the recovery [%],
$m_{Hg,std.}$ is the mass of Hg used for standard [pg],
$m_{Hg\ sample}$ is the mass of Hg used for sample, assuming 100 % recovery [pg].

The dimensionless Henry's law constant can be calculated according to Equation S3.

Equation S3

$$k_{H'} = \frac{[Hg_{gas}]}{[Hg_{solution}]}$$

Where:
$k_{H'}$ is the dimensionless Henry's law constant,
$[Hg_{gas}]$ is the concentration of mercury in gas phase,
$[Hg_{solution}]$ is the concentration of mercury in liquid phase.

The true gas flow in the extractor stripping vessel, $\overline{Q_{(g)}}$ was calculated using Equation S4.

Equation S4

$$\overline{Q_{(g)}} = Q^{o}_{(g)} \times \frac{T \times p_0}{(\bar{p} - p_w) \times T_0}$$

Where:
T is the absolute temperature of the sample in the extractor,
$Q°_{(g)}$ is the dry standard flow rate from the mass flow controller at reference conditions T_0 (293.15 K) and p_0 (1013.2 mbar),
$\bar{p}$ is the pressure of the headspace in the vessel,
p_w is the saturated vapor pressure of the KCl at temperature of the vessel.

Henry's law describes the relationship between the partial pressure of a gas and the amount of that gas species dissolved into a liquid phase. The ratio of the two is constant for a given system (temperature, gas species and liquid phase composition). For low gas-phase concentrations, the gas to liquid concentration ratio (in matrix independent units) can be used (Equation S3), with the constant of proportionality, $k_{H'}$, called the dimensionless Henry's law constant (HLC).(Saxholm et al., 2020)

Assuming equilibrium between elemental Hg in the aqueous and gas phases and considering Henry's law, the differential equation (Equation S5) can be applied, which describes the rate of decrease of Hg^0 dissolved in the aqueous phase as it is stripped out into the flowing gas.

Equation S5

$$\frac{dC_{aq}}{dt} = -\frac{\overline{Q_{(g)}} \times k_{H'} \times C_{aq}}{V_{solv}}$$

Where:
C_{aq} is the Hg concentration in the solvent,
V_{solv} is the volume of solvent in the extractor.

Solving Equation S5 gives Equation S6.

Equation S6

$$\frac{C_{aq}}{C_0} = \mathrm{e}^{-\frac{\overline{Q_{(g)}} \times t \times k_{H'}}{V_{solv}}}$$

Equation S6 can be expressed as Equation S7 and Equation S8

Equation S7

$$C_{aq} = C_0 \times \mathrm{e}^{-\alpha}$$

Where:

Equation S8

$$\alpha = \frac{\overline{Q_{(g)}} \times t \times k_{H'}}{V_{solv}} = \frac{V_{(g)} \times k_{H'}}{V_{solv}}$$

The amount of Hg collected during every extraction depends on the volume of gas and the volume of solution. During each successive extraction (n = 1, 2, 3 …) of the same period the concentration of mercury in solution can be calculated using Equation S9.

Equation S9

$$C_{aq}(n) = C_0 \times \mathrm{e}^{-n*\alpha}$$

The mass of mercury collected from the gas phase, $m_{Hg}(n)$, during extraction n is the difference between the mass of Hg in solution after the extraction (n - 1) and the mass of Hg in solution after extraction n, which can be expressed as Equation S10.

Equation S10

$$m_{Hg}(n) = V_{solv} \times C_{aq}(n-1) - V_{aq} \times C_{aq}(n)$$

Equation S10 can also be expressed as Equation S11.

Equation S11

$$m_{Hg}(n) = V_{solv} \times C_0 \times (\mathrm{e}^{\alpha} - 1) - \mathrm{e}^{-n\times\alpha}$$

The natural logarithm of Equation S11 is expressed in Equation S12.

Equation S12

$$ln\left(m_{Hg}(n)\right) = -(n \times \alpha) + ln\left(V_{solv} \times C_0 \times (\mathrm{e}^{\alpha} - 1)\right)$$

Therefore, a graph of $\ln\left(m_{Hg}(n)\right)$ against n has a slope of $-\alpha$ and an intercept of $\ln\left(V_{solv} \times C_0 \times (\mathrm{e}^{\alpha} - 1)\right)$. If both V_{solv} and $V_{(g)}$ are known, the dimensionless HLC can be calculated from α using Equation S8.

Table S3 shows the temperature program that was used for determination of oxidized Hg in KCl trapping solutions by gas chromatography with atomic fluorescence detection (GC-AFS).

Table S3: GC-AFS temperature program.

Stage	Start temperature [°C]	Ramp [°C min^{-1}]	End temperature [°C]	Hold [min]
1	30	/	30	2
2	30	20	80	0
3	80	50	120	1
4	120	100	280	4

Table S4: Results of the stability test for the $^{197}Hg^{2+}$ (radiotracer) spike on KCl crystal. Low concentrations were loaded with less than 1 ng Hg per time period and high concentrations were loaded with more than 50 ng of Hg per time period. Low air flow experiments were performed with 100 mL min^{-1} air flow while high air flow experiments were performed with 400 mL min^{-1} flow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
$HgCl_2$	High	High	Average loss (%)	0.92	0.67	0.57	0.61	×
			SD (%)	0.52	0.46	0.14	0.23	×
			RSD	56.7	68.6	24.0	37.9	×
		Low	Average loss (%)	2.43	0.21	0.03	0.12	0.03
			SD (%)	1.45	0.26	0.03	0.10	0.03
			RSD	59.8	126	115	86.6	88.4
	Low	High	Average loss (%)	2.01	0.80	1.04	1.00	0.69
			SD (%)	1.25	1.07	1.50	1.70	1.04
			RSD	62.1	133	143	169	152
$HgBr_2$	High	High	Average loss (%)	0.04	0.01	0.02	0.02	0.00
			SD (%)	0.05	0.03	0.02	0.02	0.00
			RSD	104	199	100	118	0.00
		Low	Average loss (%)	0.02	0.09	0.04	0.00	×
			SD (%)	0.03	0.03	0.06	0.00	×
			RSD	173	31.9	173	509	×
	Low	High	Average loss (%)	0.95	0.17	0.03	0.13	0.00
			SD (%)	0.76	0.17	0.05	0.21	0.00
			RSD	80.1	103	173	154	173

Table S5. Results of the stability test for the calibrator loading of $^{197}Hg^{2+}$ (radiotracer) on KCl crystal. Low concentrations were loaded with less than 1 ng Hg per time period and high concentrations were loaded with more than 50 ng of Hg per time period. Low air flow experiments were performed with 100 mL min^{-1} air flow while high air flow experiments were performed with 400 mL min^{-1} flow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
$HgCl_2$	High	High	Average loss (%)	0.27	0.01	0.01	0.02	×
			SD (%)	0.27	0.00	0.01	0.02	×
			RSD	101	41.9	141	141	×
		Low	Average loss (%)	0.03	0.01	0.01	0.01	×
			SD (%)	0.02	0.01	0.02	0.01	×
			RSD	72.1	94.6	165	72.9	×
	Low	High	Average loss (%)	2.37	1.50	0.33	0.02	×
			SD (%)	0.61	1.06	0.56	0.02	×
			RSD	25.7	70.7	173	97.0	×
$HgBr_2$	High	High	Average loss (%)	0.04	0.01	0.01	0.01	×
			SD (%)	0.02	0.01	0.00	0.01	×
			RSD	41.7	70.3	18.9	43.7	×
		Low	Average loss (%)	0.03	0.02	0.02	0.02	×
			SD (%)	0.02	0.02	0.02	0.02	×
			RSD	78.2	103	85.1	82.2	×
	Low	High	Average loss (%)	1.86	0.19	0.10	0.18	×
			SD (%)	0.95	0.33	0.17	0.26	×
			RSD	51.4	173	173	147	×

Table S6. Results of the stability test for the $^{197}Hg^{2+}$ (radiotracer) spike on quartz wool impregnated with KCl. Low concentrations were loaded with less than 1 ng Hg per time period and high concentrations were loaded with more than 50 ng of Hg per time period. Low air flow experiments were performed with 100 mL min^{-1} air flow while high air flow experiments were performed with 400 mL min^{-1} flow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
$HgCl_2$	High	High	Average loss (%)	0.55	0.21	0.19	0.14	0.10
			SD (%)	0.22	0.09	0.18	0.10	0.09
			RSD	40.4	40.0	96.4	75.8	93.9
		Low	Average loss (%)	0.31	0.18	0.22	0.12	0.08
			SD (%)	0.17	0.13	0.28	0.08	0.10
			RSD	53.1	76.5	127	71.6	115
	Low	High	Average loss (%)	1.36	0.17	0.09	0.02	0.12
			SD (%)	0.47	0.27	0.10	0.04	0.05
			RSD	34.8	164	109	173	40.2
$HgBr_2$	High	High	Average loss (%)	0.21	0.07	0.03	0.02	0.02
			SD (%)	0.06	0.03	0.01	0.02	0.02
			RSD	31.2	47.8	44.7	122	121
		Low	Average loss (%)	0.23	0.18	0.03	0.02	0.01
			SD (%)	0.18	0.12	0.04	0.02	0.01
			RSD	77.1	68.6	131	90.5	86.9
	Low	High	Average loss (%)	1.59	0.32	0.25	0.11	0.08
			SD (%)	1.21	0.35	0.22	0.08	0.06
			RSD	76.1	107	87.3	74.6	75.1

Table S7. Results of the stability test for the calibrator loading of $^{197}Hg^{2+}$ (radiotracer) on quartz wool impregnated with KCl. Low concentrations were loaded with less than 1 ng Hg per time period and high concentrations were loaded with more than 50 ng of Hg per time period. Low air flow experiments were performed with 100 mL min^{-1} air flow while high air flow experiments were performed with 400 mL min^{-1} flow

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
$HgCl_2$	High	High	Average loss (%)	0.57	0.11	0.11	0.10	×
			SD (%)	0.07	0.11	0.13	0.04	×
			RSD	12.5	95.8	122	41.7	×
		Low	Average loss (%)	0.17	0.12	0.05	0.03	×
			SD (%)	0.15	0.11	0.07	0.03	×
			RSD	86.0	89.3	135	96.5	×
	Low	High	Average loss (%)	3.15	0.00	0.18	0.56	×
			SD (%)	0.67	0.00	0.32	0.72	×
			RSD	21.3	0.00	173	130	×
$HgBr_2$	High	High	Average loss (%)	0.12	0.00	0.02	0.01	×
			SD (%)	0.05	0.01	0.01	0.01	×
			RSD	46.0	173	70.9	104	×
		Low	Average loss (%)	0.30	0.03	0.05	0.02	×
			SD (%)	0.22	0.04	0.03	0.02	×
			RSD	74.8	140	59.7	120	×
	Low	High	Average loss (%)	2.38	0.15	0.15	0.17	×
			SD (%)	1.60	0.13	0.26	0.22	×
			RSD	67.2	86.6	173	129	×