Supplement of

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

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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

$$A_{0,sample} = \frac{A_{sample} * \lambda}{e^{-(\lambda * t_{passed})} * [1 - e^{-(\lambda * t_{measurement})}]}$$

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],

λ is the decay constant: $\ln(2)/t_{1/2}$ [s^{-1}],

$t_{1/2}$ 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].

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

31 **Equation S3**

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

32 Where:

33 $k_{H'}$ is the dimensionless Henry's law constant,

34 $[Hg_{gas}]$ is the concentration of mercury in gas phase,

35 $[Hg_{solution}]$ is the concentration of mercury in liquid phase.

36

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

38 **Equation S4**

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

39 Where:

40 T is the absolute temperature of the sample in the extractor,

41 $Q_{(g)}^\circ$ is the dry standard flow rate from the mass flow controller at reference conditions T_0 (293.15 K) and p_0

42 (1013.2 mbar),

43 $\bar{p}$ is the pressure of the headspace in the vessel,

44 p_w is the saturated vapor pressure of the KCl at temperature of the vessel.

45   Henry's law describes the relationship between the partial pressure of a gas and the amount of that gas

46 species dissolved into a liquid phase. The ratio of the two is constant for a given system (temperature, gas

47 species and liquid phase composition). For low gas-phase concentrations, the gas to liquid concentration ratio

48 (in matrix independent units) can be used (Equation S3), with the constant of proportionality, $k_{H'}$, called the

49 dimensionless Henry's law constant (HLC).

50   Assuming equilibrium between elemental Hg in the aqueous and gas phases and considering Henry's law,

51 the differential equation (Equation S5) can be applied, which describes the rate of decrease of Hg^0 dissolved in

52 the aqueous phase as it is stripped out into the flowing gas.

53 **Equation S5**

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

54 Where:

55 C_{aq} is the Hg concentration in the solvent,

56 V_{solv} is the volume of solvent in the extractor.

57 Solving Equation S5 gives Equation S6.

58 **Equation S6**

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

59 Equation S6 can be expressed as Equation S7 and Equation S8

60 **Equation S7**

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

61 Where:

62 **Equation S8**

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

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

66 **Equation S9**

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

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

70 **Equation S10**

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

71 Equation S10 can also be expressed as Equation S11.

72 **Equation S11**

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

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

74 **Equation S12**

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

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

77 Table S1 shows the temperature program that was used for determination of oxidized Hg in KCl trapping
78 solutions by gas chromatography with atomic fluorescence detection (GC-AFS).

79 **Table S1: 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

80

Table S2: 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 S3. 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 S4. 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 S5. 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	×