Application of enriched stable ^{196}Hg isotope for monitoring the stability of total mercury in water samples

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A Perkin-Elmer ELAN® DRC II inductively coupled plasma mass spectrometer (ICP-MS) equipped with Elemental Scientific (ESI) MP² hydrideICP Hydride Generation System and SC-2 DX autosampler, controlled by ELAN software version 3.4, was used for the mercury measurements. The Cold Vapor (CV) unit consisted of a 4-channel peristaltic pump and a gas/liquid separator. The CV unit was connected directly to the neck of the cyclonic spray chamber, made of quartz and cooled by ESI Peltier cooling system (PC³).

The instrumental parameters are shown in Tables 1 – 3. They were mainly chosen according to the results of earlier validation studies and manufacturer's recommendations. The sample introduction system is described in Figure 1.

Table 1 ICP-MS spectrometer settings used for the cold vapour ICP-MS measurements.

Parameter	Setting
RF power (W)	1250
Nebuliser gas (Ar) flow (L min ⁻¹)	0.35
Make-up gas (Ar) flow (L min ⁻¹)	1.09-1.14
Dwell time (ms)	100
Number of sweeps	50
Number of replicates	3
Total integration time (s)	15

Table 2 MP² hydrideICP Hydride Generation System program used for the CV-ICP-MS measurements.

Step	Time (s)	ELAN pump speed (rpm)	MP ² pump speed (rpm)
Sample flush + Delay	95	-8.0	40
Analysis	15	-8.0	40
Rinse	60	-8.0	40

Table 3 MP² hydrideICP and ELAN DRC II pump tubings with their colour codes and inner diameter (i.d.)

Solution	ELAN pump	MP ² pump
Rinse solution via nebuliser	black/black (0.76 mm i.d.)	
Waste from spray chamber	red/red (1.14 mm i.d.)	
Sample		black/black (0.76 mm i.d.)
SnCl ₂		2 x orange/green (0.38 mm i.d.)
Waste from gas/liquid separator		yellow/blue (1.52 mm i.d.)

Figure 1. Set-up of sample introduction system for the measurement of total mercury by CV-ICP-MS

For stability study, a natural water with a low total Hg mass concentration (ca. 10 ng/L, sample code N2) was collected from River Vanjoki. Typical matrix parameters of this river water are presented in Table 4. As there was no certified reference material available for ^{196}Hg , the synthetic control samples (5 and 50 ng/L) were prepared at each time of measurement by diluting working solutions 2 and 3. Results of the control samples and reagent blank samples measured during stability study period are presented in Table 5.

Table 4 Typical matrix parameters and their concentrations analysed in River Vanjoki in 2013

Analyte	BOD ₇	Colour	Cond.	NH ₄	NO ₂ +NO ₃	N _{tot}	O ₂	pH	PO ₄	P _{tot}	SS	Turbidity
Unit	mg/L	mg Pt/L	mS/m	μg/L	μg/L	μg/L	mg/L	-	μg/L	μg/L	mg/L	FNU
Average concentration	1.3	95	8	25	600	1300	11	7.2	4.5	32	12	11
Range	0.8 – 3.5	70 – 120	6 – 11	6 – 100	450 – 800	550 – 3500	7.5 – 13.5	6.8 – 7.4	1 – 6	15 – 120	1 – 60	2 – 55

BOD₇ = Biological Oxygen Demand, 7 days incubation time, Cond. = Electrical conductivity, NH₄ = Ammonium nitrogen, NO₂+NO₃ = Sum of nitrite and nitrate nitrogen, N_{tot} = Total nitrogen, O₂ = Dissolved oxygen, PO₄ = Dissolved orthophosphate phosphorus, P_{tot} = Total phosphorus, SS = Suspended Solids with glass fiber filter Whatman GF/C, TIC = Total Inorganic Carbon, TOC = Total Organic Carbon

Table 5 Results of control samples and reagent blank samples measured during stability study period

Date	^{196}Hg 50 ng/l	^{202}Hg 5 ng/l	^{202}Hg 50 ng/l	Reagent blank ^{196}Hg ng/l	Calibration blank ^{196}Hg cps	Calibration standard 50 ng/l ^{196}Hg cps
24.9.2013	47.98		48.90	0.0019	0.92	4113.10
24.9.2013	47.93		51.41	-0.0011		
24.9.2013	48.72		49.74	-0.0020		
24.9.2013	49.00		50.12	0.0000		
24.9.2013			49.30			
24.9.2013			50.45			
25.9.2013	49.16		51.92	-0.0030	1.17	4257.19
25.9.2013	48.73		49.30	-0.0040		
25.9.2013	50.30		48.59	0.0000		
25.9.2013	48.98		48.23			
27.9.2013	50.05		52.15	0.0352	2.83	4649.34
27.9.2013	50.05		49.16	0.0187		
27.9.2013	48.65		52.36	0.0121		
27.9.2013	49.86		49.32	0.0005		
27.9.2013	48.23					
27.9.2013	48.14					
27.9.2013	50.30					

27.9.2013	49.55					
27.9.2013	48.64					
27.9.2013	49.84					
4.10.2013	50.32			-0.0005	9.33	4580.30
4.10.2013	51.17			0.0086		
4.10.2013	49.55			0.0123		
4.10.2013	50.45			0.0004		
4.10.2013	51.94			-0.0171		
4.10.2013	48.19			0.0105		
4.10.2013	50.68					
4.10.2013	49.91					
4.10.2013	49.20					
18.10.2013	49.75	5.16	50.20	0.0019	9.17	4362.59
18.10.2013	46.88	4.90	50.11	0.0000		
18.10.2013	50.88		46.12	-0.0201		
18.10.2013	50.00		49.02	-0.0345		
18.10.2013	46.39					
18.10.2013	48.08					
18.10.2013	50.95					
18.10.2013	50.11					
21.10.2013	47.74			0.1388	2.83	3995.36
21.10.2013	52.23			0.0898		
21.10.2013				0.0929		
25.10.2013	48.10			0.1175	1.25	3653.52
25.10.2013	50.18			0.0924		
25.10.2013	51.27			0.0434		
25.10.2013	52.33			0.0319		
25.10.2013	49.86					
25.10.2013	50.11					
25.10.2013	49.67					
25.10.2013	50.45					
5.11.2013	46.88			0.0039	1.67	3206.72
5.11.2013	51.48			-0.0065		
5.11.2013	50.48			-0.0026		
5.11.2013	49.89			0.0000		
5.11.2013	52.61					
19.11.2013	51.88			0.1552	19.67	3859.46
19.11.2013	52.02			0.1432		
19.11.2013	53.96			0.1291		
19.11.2013	52.37			0.0369		
19.11.2013	49.05					
19.11.2013	48.54					
19.11.2013	46.51					
19.11.2013	49.67					
19.11.2013	52.52					
19.11.2013	50.00					
19.11.2013	50.98					
19.11.2013	51.55					
16.1.2014	50.30			0.0000	0.83	3208.88
16.1.2014	49.82			-0.0039		
16.1.2014	49.72			0.0078		
16.1.2014	50.02			0.0026		
16.1.2014	46.27					
16.1.2014	46.61					
16.1.2014	49.64					
16.1.2014	50.11					
16.1.2014	49.18					
16.1.2014	50.46					
16.1.2014	49.80					
Average	49.77		49.80	0.027		
Standard deviation	1.58		1.53	0.050		
Relative standard deviation	3.2 %		3.0 %			