Supplementary Information (SI) for Journal of Analytical Atomic Spectrometry.

Supplementary Materials

Automated Online SPE–ICP-MS for Ultra-Trace Determination of Mercury in Freshwaters

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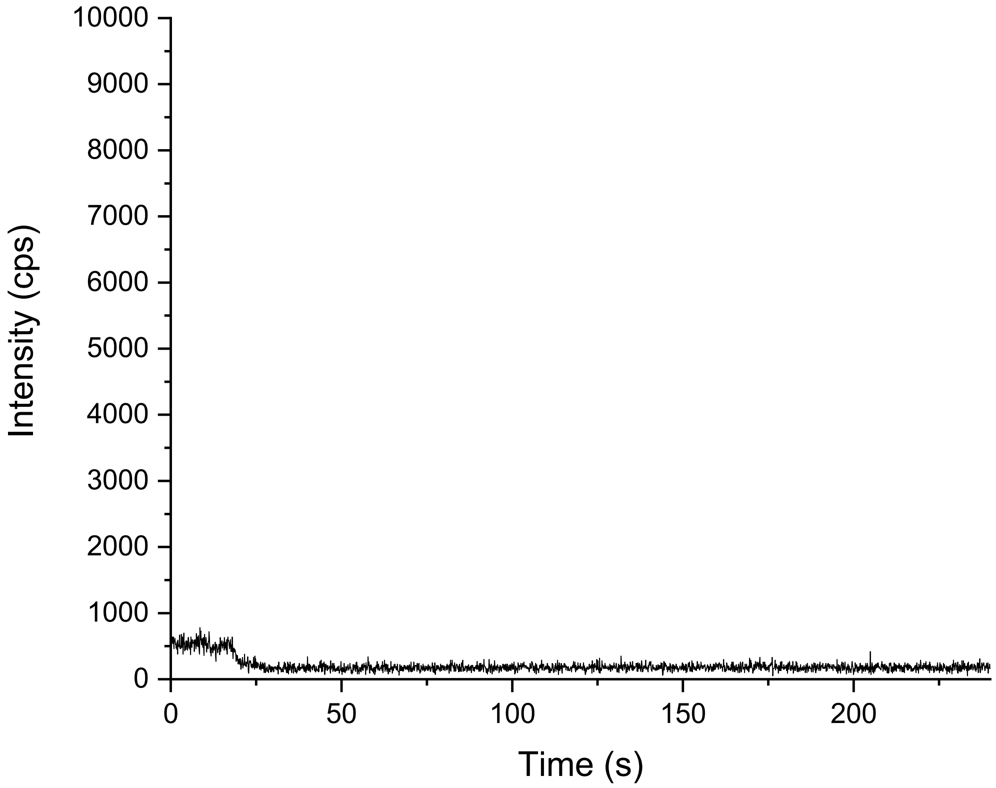

Figure S1. Signal profile recorded during the accumulation step. A 5 mM thiourea (TU) solution spiked with 1 µg/kg of both Hg(II) and MeHg was fed through the column. The graph illustrates the trend of the analytical signal as a function of the accumulation time.

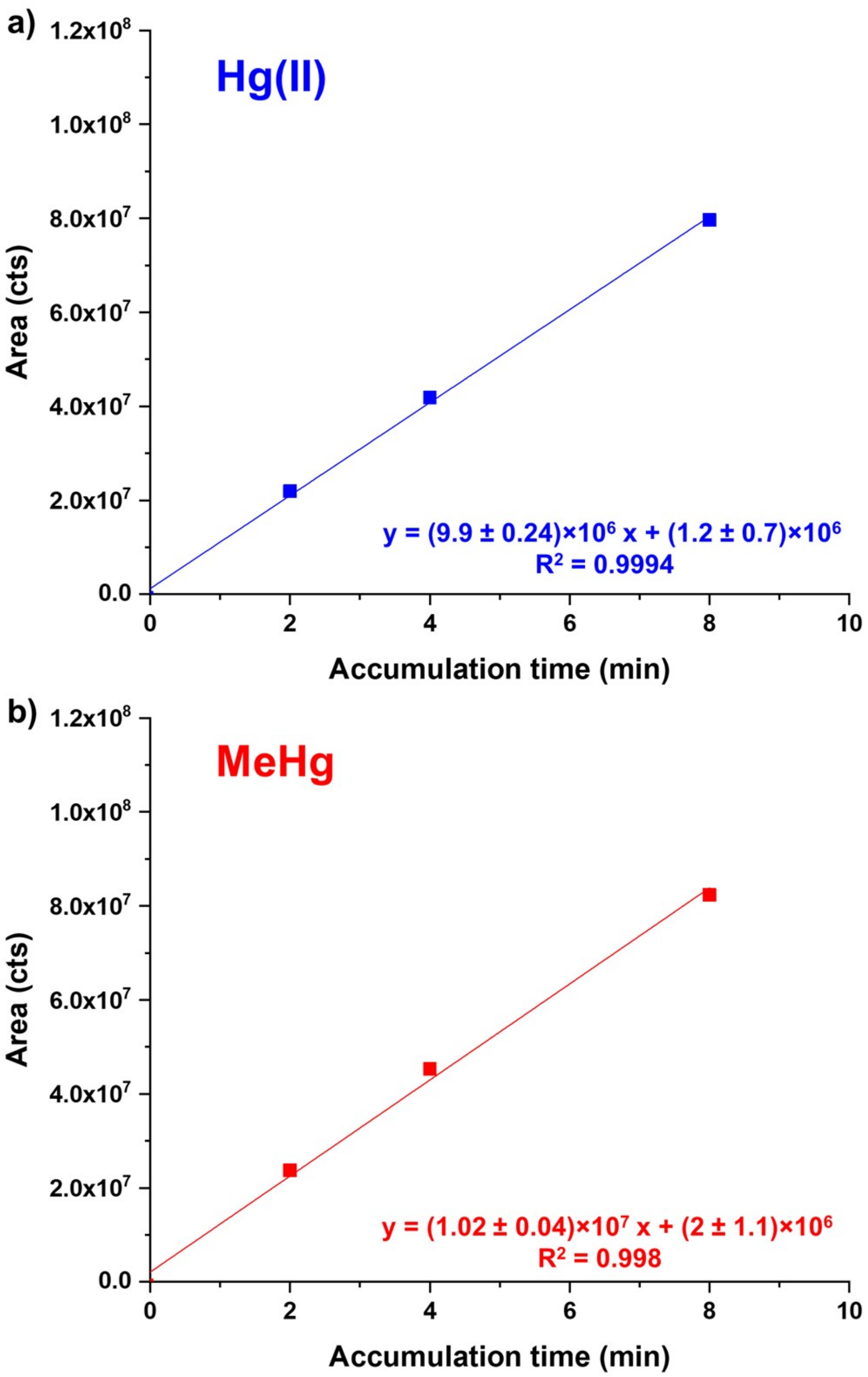

Figure S2. Effect of the accumulation time on Hg(II) (a) and MeHg (b) integrated peak areas.

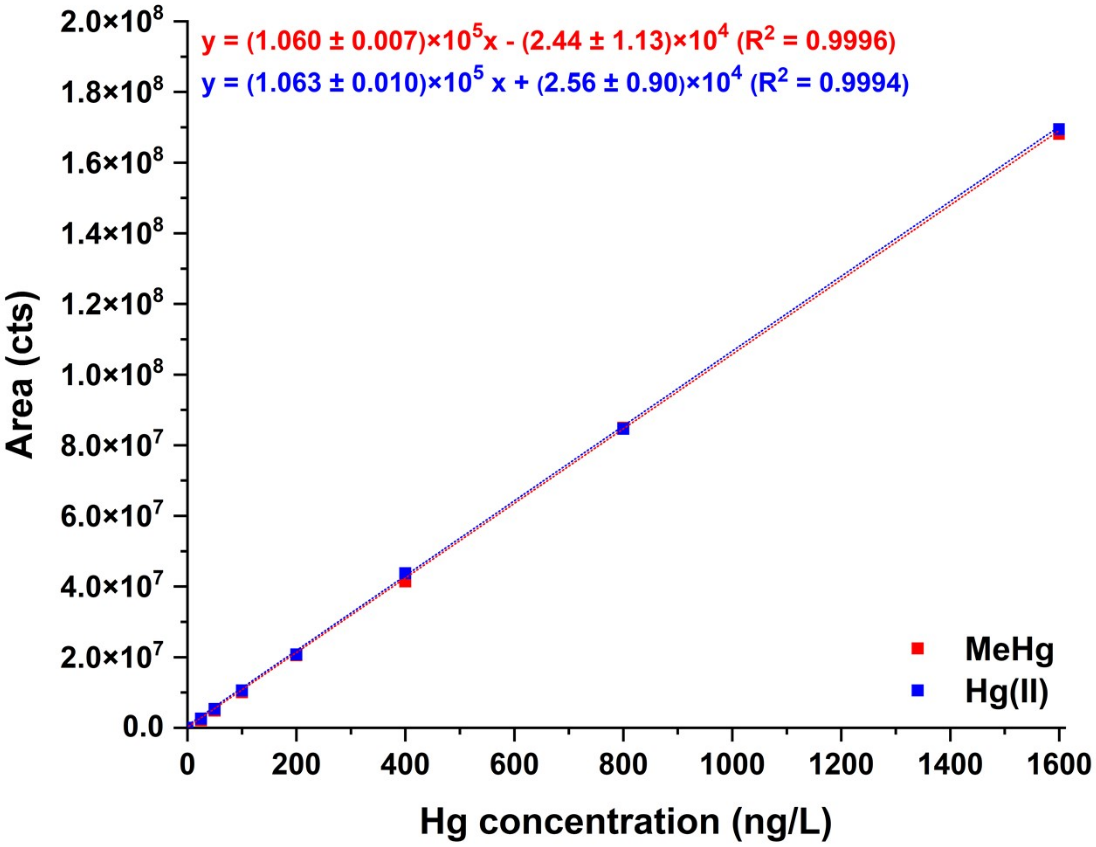

Figure S3. Calibration curves for Hg(II) (blue) and MeHg (red) showing peak area versus Hg concentration (ng/L). The accumulation time was set at 4 minutes.

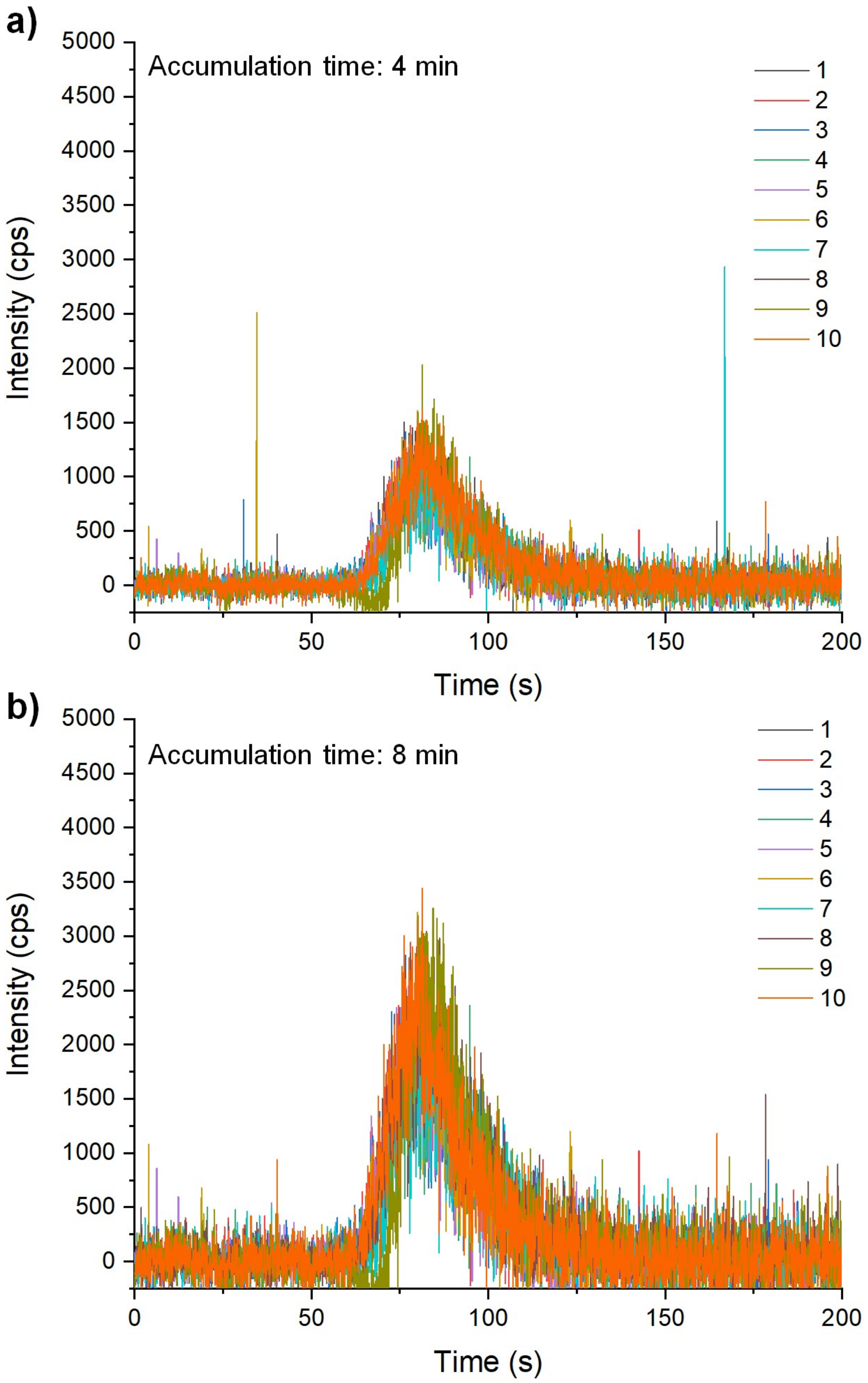

Figure S4. Analytical signals (after baseline subtraction) of the ten replicates of a 5 ng/kg Hg(II) standard solution for the determination of the limit of detection (LOD). a) Signals obtained with an accumulation time of 4 minutes. b) Signals obtained with an accumulation time of 8 minutes.

Table S1. Chemical composition of the mineral water samples (MW1, MW2, MW3) analyzed in this work.

Parameter	MW1	MW2	MW3
Conductivity (µS/cm)	52	15	173.3
Fixed residue (mg/L)	34.9	14.4	123.6
pH	7	6.9	7.4
Ca^{2+} (mg/L)	10.8	1.0	37.0
Na^{+} (mg/L)	0.58	0.90	1.1
Mg^{2+} (mg/L)	0.39	0.37	6.7
K^{+} (mg/L)	0.45	0.10	0.52
HCO_3^{-} (mg/L)	32.3	4.9	138
SO_4^{2-} (mg/L)	1.5	n.d.	3.2
Cl^{-} (mg/L)	0.55	n.d.	1.1
NO_3^{-} (mg/L)	1	1.6	1.4

Table S2. Optimized online SPE-ICP-MS working parameters.

Parameter	Value
RF Power	1550 W
Nebulizer gas flow	1.06 L/min
Auxiliary gas flow	0.80 L/min
Cooling gas flow	13.99 L/min
Dwell time	100 ms
Monitored m/z Channels	^{202}Hg
Step 1: Sample uptake and Accumulation of Hg Species	
Sample solution composition	TU 5 mM, HCl 500 mM
Sample flow rate	1.7 mL/min
Duration (min)	2-8
Step 2: Elution Hg Species	
Eluent composition	HCl 1 M
Sample flow rate	1.7 mL/min
Duration (min)	3

Table S3. Results of spike-recovery experiments for total Hg determination. Reported concentrations correspond to the mean of three replicates (n = 3), with uncertainties expressed as 95% confidence intervals calculated using the coverage factor t(0.95, 2 df) = 4.303. Expected concentrations and the associated recovery percentages are also shown.

Hg(II) spiked (ng/L)	MeHg spiked (ng/L)	Total Hg spiked (ng/L)	Total Hg measured (ng/L)	Recovery (%)
10	10	20	21 ± 2	105 ± 10
30	30	60	62 ± 2	103 ± 3
50	50	100	96 ± 4	96 ± 4
10	40	60	63 ± 3	105 ± 5

50	10	60	65 ± 5	108 ± 8

Table S4. Comparison of analytical performance for total mercury determination using different instrumental approaches, applied to water samples.

Analytical method	**LOD (ng/L)**	**Linearity Range (ng/L)**	**References**
CV-ICP-MS	0.8	1.9-50	1
FI-CV-AAS with ionic liquid extraction	2.3	10-2’500	2
ICP-MS	7.9	50-5’000	3
TDA-AAS	350	350-130’000	3
Offline SPE-ICP-MS	0.05 (MeHg) 0.08 (iHg)	10-500	4
Online SPE-HPLC-ICP-MS (Not fully automated)	0.001 (Hg(II)) 0.002 (MeHg) 0.002 (EtHg)	0.1-100	5
Online SPE-HPLC-ICP-MS	0.78 (iHg) 0.63 (MeHg) 0.49 (EtHg)	5-500	6
Online SPE-HPLC-ICP-MS	17 (MeHg) 15 (iHg)	Up to 100’000	7
Online SPE-HPLC-ICP-MS (Not fully automated)	0.005 (iHg) 0.006 (MeHg) 0.009 (EtHg)	0.05-50	8

Offline SPE-ICP-MS	0.52	2-5000	[9]
Online SPE-ICP-MS	0.93	Up to 1’600	This work

CV-ICP-MS = Cold Vapor Inductively Coupled Plasma Mass Spectrometry, FI-CV-AAS = Flow Injection Cold Vapor Atomic Absorption Spectrometry, TDA-AAS = Thermal Decomposition Atomic Absorption Spectrometry.

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