Supporting Information

Title:

A new DGT technique for measuring inorganic arsenic and selenium (IV) using a titanium dioxide-based adsorbent (Metsorb™)

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Details on the speciation of inorganic arsenic and selenium by Strong Anion Exchange – Solid Phase Extraction.

SAX-SPE for inorganic arsenic speciation

Inorganic arsenic species were determined using a modification of the method of Le *et al.*[1] The pH of the sample or standard was adjusted to within pH 7-8 using dilute HNO_3 (Baseline; Seastar, Canada) or NaOH and a portion was retained for total arsenic analyses. 10 mL of sample was passed through a SAX-SPE cartridge (Supelco, USA) at a flow rate of approximately 2 mL min^{-1} using a tube adapter and 20 mL syringe. The first eluent contained As^{III} only, as it is uncharged at this pH and not retained on the anion exchange resin. As^{V} is quantitatively retained on the cartridge and was eluted with 5 mL of 2.0 mol L^{-1} HNO_3 (Baseline; Seastar, Canada). This is in contrast to Le and co-workers[1] who eluted As^{V} with 1.0 mol L^{-1} HCl. Both eluents and the original solution were analysed by ICP-MS.

SAX-SPE for inorganic selenium speciation

Inorganic selenium species were determined using a modification of the method of Gomez-Ariza *et al.*[2] The solution pH was adjusted to between pH 7-8, and a portion retained for total selenium analyses. 10 mL of sample was passed through a SAX-SPE cartridge at a flow rate of approximately 2 mL min^{-1} using a tube adapter and 20 mL syringe. The first eluent contained no selenium as at pH 7-8 both inorganic species are anions and quantitatively retained on the cartridge, however, this fraction was retained and analysed for confirmation. Selenite was eluted with 5 mL of 1.0 mol L^{-1} formic acid

followed by selenate with 5 mL of 2.0 mol L^{-1} HNO_3. Both of these eluents were retained for ICP-MS analysis. Formic acid increased the ionisation efficiency of selenium with ICP-MS analysis and so matrix matched quality control standards were prepared to account for this.

Table S-1. The effect of pH and ionic strength on the accumulation of inorganic arsenic and selenium by Metsorb™ DGT.

pH/Ionic Strength	C_{DGT}:C_{ICP-MS}[a]		
	As^{III}	As^{V}	Se^{IV}
pH 3.5	0.99 ± 0.02	1.11 ± 0.03	1.05 ± 0.05
pH 5.0	0.99 ± 0.05	1.12 ± 0.03	0.96 ± 0.02
pH 7.0	1.03 ± 0.05	1.02 ± 0.03	0.97 ± 0.05
pH 8.5	1.06 ± 0.03	0.92 ± 0.02	0.86 ± 0.02
0.0001 mol L^{-1}	1.07 ± 0.08	0.78 ± 0.02	0.86 ± 0.04
0.001 mol L^{-1}	1.10 ± 0.05	1.07 ± 0.15	1.02 ± 0.07
0.1 mol L^{-1}	1.02 ± 0.02	1.06 ± 0.08	0.92 ± 0.03
0.75 mol L^{-1}	1.02 ± 0.10	1.08 ± 0.11	0.92 ± 0.08

[a] *Ratio of DGT measured concentration to ICP-MS measured concentration ± 1 standard deviation.*

Table S-2. Calculated DBLs and DGT-measured arsenic concentrations for field deployments. All values are means ± 1 standard deviation.

Field Site	Calculated DBL (cm)	DGT-measured As (μg L^{-1}) (C_a)	DGT-measured As (μg L^{-1}) assuming no DBL (C_b)	C_b:C_a
Site 1 – Freshwater Stream	0.080 ± 0.013	3.04 ± 0.24	2.05 ± 0.04	0.67
Site 2 – Saltwater Marina	0.067 ± 0.007	0.89 ± 0.04	0.60 ± 0.01	0.67

References

(1) Le, X. C.; Yalcin, S.; Ma, M. *Environ. Sci. Technol.* **2000**, *34*, 2342-2347.
(2) Gomez-Ariza, J. L.; Giráldez, I.; Morales, E.; Pozas, J. A. *Analyst* **1999**, *124*, 75-78.