Non-chromatographic speciation of inorganic arsenic by atomic fluorescence spectrometry with flow injection hydride generation by a tetrahydroborate-form anion-exchanger

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Supplementary information.

The well water and seawater samples were analyzed for 21 elemental constituents by plasma source mass spectrometry. The samples were acidified with 2% high purity nitric acid (Fisher Scientific certified ACS grade), filtered through 0.45µm polyethersulfone membrane Whatman Puradisc syringe filters that were 25 mm in diameter, stored at 4 °C until analysis and measured without further dilution.

The instrument (a PerkinElmer Sciex Elan model 6100) was operated according to the manufacturer's recommended conditions, which are shown in Table S1. Correction for isobaric overlap was applied according to the default conditions of the manufacturer's software. External calibration, with standards prepared by serial dilution of Quality Control Standard 21 (PerkinElmer, Waltham, MA, USA), covering the range 0 – 100 mg L^{-1}, was used. The results are given in Table S2, including the values for arsenic, which is one of the 21 elements in the standard solution.

Table S1. Operating conditions for plasma source mass spectrometer

Parameter	Setting
RF Power	1500 W
Nebulizer Gas Flow	1.01 L min^{-1}
Nebulizer Type	Gem Tip Cross-Flow II
Spray Chamber	Scott
Detector Mode	Dual mode
Sample/Skimmer Cones	Nickel
Dwell Time	100 ms per point
Scanning Mode	Peak hopping

Number of replicates	10
Isotopes	^{75}As, ^{9}Be, ^{43}Ca, ^{111}Cd, ^{59}Co, ^{52}Cr, ^{63}Cu, ^{57}Fe, ^{7}Li, ^{24}Mg, ^{55}Mn, ^{98}Mo, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{82}Se, ^{88}Sr, ^{47}Ti, ^{205}Tl, ^{51}V, ^{66}Zn

Table S2. Elemental concentrations (μg L^{-1}) in natural water samples measured by ICP-MS

Element	Well Water 1[f]	Well Water 1	Well Water 2[f]	Well Water 2	Seawater 1	Seawater 2
As	1.45	1.29	1.01	0.81	41.6	42.2
Ti	1.71	1.60	2.64	2.83	45.6	56.1
Be	ND	ND	ND	ND	ND	ND
Ca	18800	19200	4390	4340	107000	114000
Cd	0.035	0.010	0.016	0.014	0.101	0.094
Co	0.309	0.166	0.097	0.094	0.863	0.824
Cr	1.03	1.20	0.57	0.51	0.89	0.84
Cu	296	213	27	22	18	16
Li	2.6	2.9	2.2	2.3	106	115
Fe	196	202	50	48	1150	1220
Mg	1830	2040	1590	1610	NM	NM
V	0.76	0.62	0.62	0.58	19.7	21.4
Mn	1.37	1.99	1.39	1.30	39.6	1.21
Ni	9.18	2.05	3.78	0.57	6.70	7.24
Zn	2084	19	320	17	13	6
Se	ND	0.15	0.15	0.33	ND	ND
Sr	423	43	30	30	3330	3390
Mo	0.04	0.02	3.0	3.0	3.1	5.5
Sb	1.14	0.03	0.02	0.02	0.11	0.09
Tl	0.06	0.05	0.04	0.04	0.05	0.05
Pb	1.26	0.43	0.40	0.50	0.38	0.23

f first draw sample
ND not detected
NM not measured as concentration too high

It may be seen that the values for arsenic are consistent with those obtained by HG-AFS yields for the well water samples, that the values for the seawater samples are much higher than the results from the AFS measurements. There are several possible polyatomic interfering species, including ^{40}Ar^{35}Cl, ^{40}Ar^{34}SH, and ^{40}Ca^{35}Cl, that could be responsible.

Typical operating conditions of the AFS spectrometer in continuous-flow mode are given in

Table S3 for the three replicate measurements, and for the column-based HG mode in Table S4. The major difference is that in the continuous-flow mode, the hydrogen for the flame atomizer is generated continuously from the reaction between the borohydride and hydrochloric acid, requiring continuous deliver of a relatively high concentration of acid.

Table S3 Operating conditions for AFS continuous flow HG-AFS system

Parameter	Value
HCl Concentration	4 M
HCl flow rate	9 mL/min
Sample preparation volume	50 mL
$NaBH_4$ Concentration	0.7%
$NaBH_4$ flow rate	4.5 mL/min
Sample running time	80s
HCl consumption from sample (4 M x 50 mL)	200 mmol
HCl consumption from blank (4 M x 9 mL/min x 3 x 80 s/60 s min^{-1})	144 mmol
HCl consumption in total	344 mmol
$NaBH_4$ consumption (0.7% x 4.5 mL/min x 80 s/60 s min^{-1} x 3)	126 mg

Table S4 Anion-exchanger HG conditions

Parameter	Value
HCl Concentration	0.1 M
Sample Volume	0.5 mL
Sample preparation volume	25 mL
$NaBH_4$ Concentration	5%
$NaBH_4$ flow rate	4.5 mL/min
$NaBH_4$ loading time (for triplicate)	60 s
HCl consumption (0.1 M x 25 mL)	2.5 mmol
$NaBH_4$ consumption (5% x 1 min x 4.5 mL/min)	225 mg