

Supporting Information

Table S1. The ETAAS temperature program for the determination of total arsenic.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow rate (mL/min)
Preheating	80	5	15	200
Drying	120	5	15	200
Pyrolysis	800	10	20	200
Atomization	2500	0	5	0
Cleaning	2800	0	4	200

Table S2. Operating parameters of the liquid chromatographic separation-gradient hydride generation-AAS detection system.

LC separation	Column: Wakopak Navi C30-5, $\Phi 6 \times 250$ mm and $\Phi 6 \times 150$ mm; Mobile phase: 5 mmol/L sodium 1-butanedisulfonate, 4 mmol/L malonic acid, 4 mmol/L tetramethylammonium hydroxide, 0.1 % methanol, 10 mmol/L ammonium tartrate, pH 2. Flow rate: 1.0 mL/min; Column temperature: 25°C; Sample volume: 100 μL.
Hydride generation	1% NaBH₄ (m/v, in 0.5% NaOH); 6 mol/L HCl (with 2% L-cysteine (m/v)) for As(V), As(III) and MMA; 0.6 mol/L (with 2% L-cysteine (m/v)) for DMA and TMAO. A same flow rate of 1.1 mL/min was used for both HCl and NaBH₄ solutions. An argon flow rate of 50 mL/min was employed as carrier gas.
AAS condition	Wavelength: 193.7 nm; Lamp current: 12 mA; Burner height: 10.0 mm; Slit width: 1.3 nm; Flame type: air-acetylene; Acetylene flow rate: 1.2 L/min; PMT voltage: 500 V; Air pressure: 160 kPa; Air flow rate: 15.0 L/min; Reading mode: Peak height.

Table S3. The analytical performance of the liquid chromatographic separation-gradient hydride generation-AAS system for arsenic speciation.

Species	Regression equation	Retention time (s)	LODs ($\mu\text{g/L}$)	RSDs (% , n=8)	
				100 $\mu\text{g/L}$	20 $\mu\text{g/L}$
As(V)	$\text{Abs} = 0.0026C_{\text{As(V)}} + 0.0029$	399	0.9	2.8	6.0
As(III)	$\text{Abs} = 0.0015C_{\text{As(III)}} + 0.0033$	437	1.4	2.5	5.9
MMA	$\text{Abs} = 0.0015C_{\text{MMA}} + 0.0009$	474	1.4	2.0	5.7
DMA	$\text{Abs} = 0.0012C_{\text{DMA}} + 0.0041$	560	1.6	2.7	4.9
TMAO	$\text{Abs} = 0.0013C_{\text{TMAO}} + 0.0014$	734	1.5	2.1	4.7

Note: $\text{LOD} = 3H_N C/H$ (the detection limit of each arsenic species was estimated at a concentration level of 100 $\mu\text{g/L}$). H_N : peak height of baseline noise; c: the concentration of an arsenic species; H: peak height of an arsenic species.

Figure S1. The influence of L-cysteine on the hydride generation efficiency. The experimental data were presented as mean value $\pm$ standard deviation (the number of replicates is n=3)

