

Methods for As speciation

Water samples and extracts are analyzed by ion chromatography (Hamilton PRP-X100 column in a Bischoff gradient system) with post column hydride generation and detection by inductively coupled plasma mass spectrometry (IC-ICPMS; Thermo Fisher Element 2). The use of hydride generation provides improved sensitivity and thus better limits of reporting, but means that only As(III) (arsenite), As(V) (arsenate), DMA (dimethylarsinate), and MMA (monomethylarsonate) can be detected. Species including arsenobetaine and arsenocholine, the major As containing species in many marine biota, cannot be determined using this method.

Matrix	Fresh water	Marine water and urine	Sediment, soil, sludge (a)	Biota (a)
Shipping	Top filled bottle; store/ship cool and dark; if frozen pack samples individually in sealed zip-lock bags (b). If possible filter and acidify to pH 2 with HCl in the field.	Top filled bottle; store/ship cool and dark; if frozen pack samples individually in sealed zip-lock bags (b). If possible filter and acidify to pH 2 with HCl in the field.	Top filled bottle; store/ship cool and dark	Freeze before shipping and, if possible, ship in freeze box
Minimum amount (c)	1 mL	1 mL	1 g	0.5 g
Preparation	Filter (0.45 μm) and dilute if required (d)	Filter (0.45 μm) and dilute 10-fold or more if required (d)	Homogenize; overnight extraction into 0.1 M phosphoric acid; filter (0.45 μm) and dilute if required (e)	Homogenize; ultrasound-assisted extraction into 1+1 methanol + water; filter (0.45 μm) and dilute 10-fold or more if required (f)
Limit of reporting (g)	As(III) 0.1 $\mu\text{g/L}$ As(V) 0.4 $\mu\text{g/L}$ DMA 0.1 $\mu\text{g/L}$ MMA 0.2 $\mu\text{g/L}$	As(III) 1 $\mu\text{g/L}$ As(V) 4 $\mu\text{g/L}$ DMA 1 $\mu\text{g/L}$ MMA 2 $\mu\text{g/L}$	As(III) 0.01 mg/kg As(V) 0.04 mg/kg DMA 0.01 mg/kg MMA 0.02 mg/kg	As(III) 0.01 mg/kg As(V) 0.04 mg/kg DMA 0.01 mg/kg MMA 0.02 mg/kg

Notes: (a) Please mark the sample documentation "Samples for research purposes only". (b) Do not freeze top filled containers as these will break. Plastic containers holding frozen water samples often break and should therefore be individually packed in zip-lock containers to minimize the risk for sample loss. The outside surfaces of the sample container should be cleaned before packing. (c) This is the minimum amount of sample required for a single analysis to reach the given limits of reporting. Larger samples are required for duplicate measurements and recovery checks. (d) Acid mine drainage and waste waters may require much greater dilution factors than fresh and drinking waters; this will result in poorer limits of reporting for the former than given in the table. (e)

Note that the sum of extractable As species recovered and detected by our method may be much lower than the total As concentration. We can perform other single step extractions for the same price at the customers' request, e.g. US EPA Method 1311 – toxicity characteristic leaching procedure, although this will not recover all As either. (f) Ultrasound-assisted extraction into methanol/water normally provides quantitative recoveries of As(III), As(V), MMA and DMA from fish, shellfish, etc. Recoveries of incipient species from plant materials may not be quantitative. (g) The limit of reporting is normally set at a level corresponding to the limit of quantification (LOQ; 10 x SD for blanks).