

Table 1S.

Pre-concentration/separation methods to accomplish the speciation of inorganic As species by HG-based non-chromatographic techniques.

Matrix	Species	Procedure	Detection	LOD ^a , µg L ⁻¹	EF ^b	Ref.
<i>CPE</i>						
natural waters	As(III) As(V)	Selective reaction between As(III) and Pyronine B in presence of SDS at pH 10 followed by extraction of As(III)-Pyronine B complex into Triton X-114. Total i-As was extracted after pre-reduction of As(V) to As(III) with Na ₂ S ₂ O ₃ ; As(V) calculated by difference.	HG-AAS	0.008	25.7	[18]
Lake water	As(III) As(V)	Selective formation of As(III)-APDC (at pH 4.6) and As(V)-molybdate (at pH 2.4) complexes followed by extraction into Triton X-114. As species determined separately.	HG-AFS	As(III): 0.009 As(V): 0.012	As(III): 9.3 As(V): 7.9	[23]
<i>DLLME</i>						
Fruit juices	As(III) As(V)	Selective reaction between As(III) and APDC at pH 3 followed by As(III)-APDC complex extraction into CCl ₄ in dispersive medium (methanol). Total i-As was extracted after pre-reduction of As(V) to As(III) with Na ₂ S ₂ O ₃ (pH 1.7-1.8); As(V) calculated by difference.	HG-AFS	1.2		[30]
<i>ATPS</i>						
tap water	As(III)	Selective extraction of As(III)-APDC at pH 6 using ATPS (electrolyte and polymer based) composed of L64 (copolymers) + Na ₂ SO ₄ + H ₂ O.	HG-ICP-OES	0.20 (µg kg ⁻¹)		[84]
<i>co-precipitation</i>						
drinking water	As(III) As(V)	Selective co-precipitation of As(III) with DBDTC at pH 2. After separation, the co-precipitated As(III)-DBDTC was dissolved with NaOH-H ₂ O ₂ . Total i-As was co-precipitated after pre-reduction of	HG-AFS	0.05		[5]

As(V) to As(III) with KI-K ₂ S ₂ O ₇ ; As(V) calculated by difference.						
<i>SPE</i>						
natural waters	As(V) As(III)	Selective adsorption of As(V) at pH 6 on aluminum hydroxide gel followed by dissolution in concentrated HCl and pre-reduction with thiourea-ascorbic acid. Total i-As was adsorbed after pre-oxidation of As(III) to As(V) with KMnO ₄ ; As(III) calculated by difference.	HG-AFS	0.003	167 ^c	[14]
natural waters	As(III) As(V)	Selective reaction between As(III) and APDC with next retention of the As(III)-APDC complex on the column packed with cigarette filter. Total i-As was extracted after pre-reduction of As(V) to As(III) with thiourea-ascorbic acid; As(V) calculated by difference. Eluent: 1.68 M HCl.	HG-AFS	0.0074	25.6	[9]
sea water	As(III) As(V)	Selective formation of As(III)-APDC complex followed by its sorption on the mini-column contains PTFE particles as sorbent. Total i-As was extracted after pre-reduction of As(V) to As(III) with thiourea; As(V) calculated by difference. Eluent: 2 M HCl.	HG-AAS	As(III): 0.02 As(V): 0.03	20.4	[25]
natural waters	As(V) As(III)	Selective sorption of As(V) at pH 3.5 on the G-COOH (column technique). Retained As(V) was eluted with 0.5 M NaOH and then pre-reduced to As(III) with KI-ascorbic acid. Total i-As was extracted after pre-oxidation of As(III) to As(V) with KMnO ₄ ; As(III) calculated by difference.	HG-AAS	0.0021	50.3	[4]
natural waters	As(III) As(V)	Selective formation and retention of the As(III)-APDC complex at pH 3 on the micro-column packed with SWCNTs followed by elution with 20% HNO ₃ . Total i-As was extracted after pre-reduction of As(V) to As(III) with thiourea; As(V) calculated by difference.	HG-AFS	As(III): 0.0038 As(V): 0.0043	25.4	[10]

natural waters	As(V) i-As	As(V) was selectively separated from As(III) at pH 5.8 with the MWCNTs-BPEI packed mini-column. Retained As(V) was desorbed using 0.6% NH_4HCO_3 . Total i-As was extracted after pre-oxidation of As(III) to As(V) with H_2O_2 .	HG-AFS	As(V): 0.014	16.3	[26]
natural waters	As(V) As(III)	As(V) sorbs selectively at pH 3 on the nano $\text{ZrO}_2/\text{B}_2\text{O}_3$ hybrid sorbent (column technique) and then desorbs by 3 M HCl followed by pre-reduction with KI-ascorbic acid. Total i-As was extracted after pre-oxidation of As(III) to As(V) with KMnO_4 . As(III) calculated by difference.	HG-AAS	0.00925	20	[16]
natural waters	As(III) As(V)	Selective sorption of As(III) and As(V) at pH 4 in two knotted reactors filled with PSTH-MNPs followed by elution using 7% HNO_3 –0.1% thiourea–2.8% L-cysteine and selective HG for As(III) and i-As. As(V) calculated by difference.	HG-ICP-MS	As(III): 0.0027 As(V): 0.0032	As(III): 1.9 As(V): 2.1	[11]
natural waters	As(III) As(V)	Selective biosorption of As(III) into the baker's yeast (<i>Saccharomyces cerevisiae</i>). At pH 7 As(III) was accumulated by the yeast cells, while As(V) remained in solution. After separation, the solid phase was prepared to be slurry for determination. As species determined in separate phases.	HG-ICP-AES	As(III): 0.1 As(V): 0.5	7 ^c	[8]
herbicide, pesticide, cigarette	As(V) As(III)	Selective biosorption of As(V) using column packed with yeast (<i>Saccharomyces cerevisiae</i>) immobilized on the CPG. At pH 7 As(V) sorbs selectively, whereas As(III) was not retained and passed directly through the column. Both As(III) and As(V) determined separately. Eluent: 3 M HNO_3 .	HG-ICP-AES			[37]

ground water	As(V)	Selective retention of As(V) on the ESM at pH 11. Eluent: 2 M HNO ₃ .	HG-AFS	0.001	33.3	[21]
rice products,	i-As (as	Strong anion exchange (SAX) cartridges for selective sorption of i-As	HG-AAS		0.02 mg kg ⁻¹	[41]
marine organism,	As(V))	coexisting with o-As at pH 6. Eluent: 0.4 M HNO ₃ [41] or 0.5 M HCl	HG-AFS		0.08 mg kg ⁻¹	[79]
rice		[42,79].			1.3 ng g ⁻¹	[42]
marine algae	i-As (as	Polystyrene (PS) resin cartridge for selective sorption of AsBr ₃ [55] or	HG-AFS		3.0 ng g ⁻¹	[55]
	As(III))	AsCl ₃ [43] coexisting with As-sugars and/or o-As under strongly acidic condition. Eluent: H ₂ O			1.1 ng g ⁻¹	[43]

APDC: ammonium pyrrolidinedithiocarbamate. ATPS: liquid-liquid extraction of aqueous two-phase systems. DBDTC: dibenzylthiocarbamate. DLLME: dispersive liquid-liquid microextraction. SDS: sodium dodecyl sulfate. CPE: cloud point extraction. CPG: controlled pore glass. ESM: eggshell membrane. G-COOH: carboxylated nanoporous grapheme. HG-AAS: hydride generation atomic absorption spectrometry. HG-AFS: hydride generation atomic fluorescence spectrometry. HG-ICP-AES: hydride generation inductively-coupled plasma atomic emission spectrometry. HG-ICP-OES: hydride generation inductively-coupled plasma optical emission spectrometry. HG-ICP-MS: hydride generation inductively-coupled plasma mass spectrometry. i-As: the inorganic tri- and pentavalent As species (As(III) and As(V)). M: mol L⁻¹. MWCNTs-BPEI: multi-walled carbon nanotubes functionalized with branched cationic polyethyleneimine. o-As: the organic, i.e. methylated pentavalent As species (DMA and MMA). PSTH-MNPs: magnetic ferrite (Fe₃O₄) nanoparticles functionalized with [1,5-bis (2-pyridyl) 3-sulfonophenylmethylene] thiocarbonohydrazine. PTFE: polytetrafluoroethylene. SWCNTs: single-walled carbon nanotubes.

^a For As(V) as As(III) without or after previous pre-reduction step.

^b Enrichment factor: the ratio of the slopes of the calibration curves for As with and without pre-concentration.

^c Pre-concentration factor: the ratio of initial to final volume of enriched solution after pre-concentration.