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Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications

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Abstract

Multiple acute and chronic toxicity of arsenic species and its mobilisation from geological deposits into ground and drinking water resources are one of the greatest threats to human health. Arsenic speciation analysis, mostly done by liquid chromatography, is a challenging task which requires an intense high quality work with respect to extraction, preservation, separation, detection and validation. A growing number of As-species and low regulatory limits (10 μg/L) may require more than one speciation method preferably performed by species specific procedures and detectors. Beside As-fractionation for special application there are many selective speciation methods based on high performance separation techniques like capillary electrophoreses, gas and liquid chromatography. Both, fractionation and speciation methods are reviewed. However, the focus is on scopes and limits of ion chromatographic separations, the most frequently used methods. Based on IC-principles the methods applied are critically discussed and recommendations given which should result in more robust and reliable As-speciation.

1. Introduction

Accumulating evidence on multiple toxicity aspects [1] including mutagenic, teratogenic and general genotoxic [2,3] and neurotoxicity [4] effects of several arsenic species curbed down regulatory limits to 10 μg/L As (WHO, US-EPA) in drinking water. Considering chronic toxicological effects in combination with As-mobilisation from geological deposits into ground water [5], an essential source of drinking water, As is likely to pose one of the greatest threat to human health worldwide. Since years this is reality for up to 100 million people in India [6], Bangladesh [7,8], Vietnam [9,10], Cambodia [11] and other places on the world [1]. Fears have been expressed [12] that this is only the visible tip of the iceberg. These intensified As-problems initiated many investigations to reassess the mobilisation, transformation and toxicity of even low concentrated As-species.

Among oxyanion-forming elements, As shows a unique mobilisation [5] over the pH-range of natural waters under both oxidising and reducing conditions. Inorganic redox species arsenite (AsIII) and arsenate (AsV) are far the most abundant and the most toxic species in environmental waters. In biologically mediated transforma-

tions these species are converted into numerous organic As-species [13,14]. All As-related problems like toxicity, adsorption and transport, biogeochemical cycling and treatment of drinking water depend on As speciation.

For several reasons As speciation remains a challenging task which requires a lot of high quality speciation work: the toxicity of many As-species is not jet elucidated and often a single separation procedure is not reliable since most toxic species can be interfered by As-species of much lower toxicity [15]. Arsenic has a unique rich chemistry [16] with a huge number of organic As-species [17] reflecting the capability of this element to adapt to almost any condition. On the other hand, investigations addressing a large number of species are inevitably forced to reduce costs. However, cost reduction can become so dominant that it restricts the number of questions which can be answered, or worse, narrowing it to what can be achieved by the lowest cost procedure which is unable to answer important open questions. Another difficulty is that the separation procedure has to be adapted to the species preservation or vice versa. But, what is the best preservation during storage and separation? It depends on the matrix and the As-species present. However, if the latter are not com-

pletely known one finds itself in a real speciation dilemma.

Previous reviews provide a helpful orientation by emphasizing different aspects in As-speciation. An over view on recent reviews can be found in [18]. Francesconi *et al.* [19] gave short synopsis and characterisations of all the different methods in a broad (450 references) and comprehensive coverage. The nomenclature given there is followed in this review and listed in **Table 1** together with other abbreviations. The chemistry of As-species in the aquatic environment was extensively reviewed [20] just recently. B'Hymer *et al.* [21] focused on the role of HPLC coupled to ICP MS. Analytical methods for inorganic As have been reviewed by Hung *et al.* [22] and

Table 1. Names and abbreviations of chemicals[a].

Abbrev.	Names	Formula
Arsenicals		
AsIII	Arsenite (arsenous acid)	$As(OH)_3$
AsV	Arsenate (arsenic acid)	$AsO(OH)_3$
AB	Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$
AC	Arsenocholine	$(CH_3)_3As^+(CH_2)_2OH$
DMA	Dimethylarsinic acid	$(CH_3)_2AsO(OH)$
MMA	Monomethylarsonic acid	$CH_3AsO(OH)_2$
TETRA	Tetramethylarsonium ion	$(CH_3)_4As^+$
TMAO	Trimethylarsineoxide	$(CH_3)_3AsO$
p-ASA	p-Aminobenzenearsonic acid	$p-NH_2C_6H_4OAs(OH)_2$
p-PSA	4-Hydroxybenzenearsonic a.	$p-OHC_6H_4OAs(OH)_2$
Rox	4-HO-3-nitrophenylarsonic a.	$OHNO_2C_6H_3OAs(OH)_2$
Other		
AcO	Acetate	CH_3COOH
BDSA	Benzene-1,2-disulfonic acid	$C_6H_4(SO_3)_2^{2-}$
Cit	Citric acid	$(CH_2COOH)_2COHCOOH$
DL	Detection limit	
EDTA	Ethylenediaminetetraacetate	$((^-OOCCH_2)_2N)_2(CH_2)_2$
HSA	Hexanesulfonic acid	$CH_3(CH_2)_5SO_3H$
PS-DVB	Polystyrene-divinylbezene	
SDS	Sodiumdodecylsulfate	$CH_3(CH_2)_{11}OSO_3H$
Tart	Tartrate	$(CH_2)_2(COO^-)_2$
TBA	Tertrabutylammonium	$(C_4H_9)_4N^+$
TRIS	Tris (hydroxymethyl) amino-methan	$(HOCH_2)_3CNH_2$

a) The nomenclature follows the recommendations given by Francesconi *et al.* [19].

voltammetric methods for the same purpose just recently by Mays *et al.* [23].

For a toxicity assessment, ionic As-oxo-species are far more decisive than others and hence ion chromatography (IC) the most often applied method. In this review advantages and shortcomings of specific IC procedures are critically discussed, rather than completely covering in details all the numerous As-speciation methods.

2. Methods for As Speciation

Arsenic speciation analysis can be categorized according to the speciation definition given by IUPAC [24] which is based on selectivity and specificity. Methods which inherently cannot differentiate among chemical species are named fractionation and those with a higher or tuneable resolution are called speciation methods. Following this definition, distinctions like AsIII and AsV, inorganic and organic or smaller and larger size belongs to fractionation since each of this categories consists of several chemical species which are indistinguishable by such methods. So chromatographic separations, except size exclusion (SEC), are considered speciation methods since they can be tuned or used in combinations [25] to separate essentially all chemical species.

A successful speciation requires not only an accurate species determination but also to be in an optimal accordance with the sample treatment (extraction, preservation). Because many speciation methods are based on IC-principles, particular attention is paid to IC-methods and their applications.

2.1. Arsenic Fractionations

2.1.1. Inorganic AsIII/AsV Fractionation
The fact that the two most toxic As-compounds are the inorganic AsIII and AsV justify this fractionation for samples influenced by pure geochemical processes (e.g. groundwater) where no or very minor fraction of organic arsenicals occur. The hydride generation, oxidation state selective fractionation, makes use of the ease As-compounds form hydrides under different conditions: AsIII reacts at slightly acidic pH (6) with borohydrides whereas AsV-arsenicals require pH 1 or a pre-reduction, e.g. by thiols (cysteine [26,27], thioglycolic acid [28]). However, organic arsenicals can require harsh oxidation conditions ($HNO_3/HClO_4/H_2SO_4$ at 300°C) for decomposing, especially AC and AB are the most recalcitrant [29]. Once formed, As-hydrides are volatile and easily separable from the matrix by gas liquid separators or gas diffusion [30]. After this step, they can be diverted directly to a detector or cryo-trapped, pre-concentrated and selectively evaporated in the sequence of their boiling points [31].

In-situ AsIII/AsV fractionation can also be obtained by very sensitive electrochemical methods (20 ng/L [32,33]) which are continuously developed [23]. By exclusively measuring AsIII at natural sample pH 7-8 and AsIII + AsV in an acidified (pH 1) sample aliquot, AsV is assigned to the difference of the two AsIII measurement [32].

2.1.2. Extraction and Preservation Procedures

The time between sampling and analysis often requires a preservation which has not only to be reliable but also compatible with the subsequent speciation method, which is often a difficult task. Species extraction from difficult matrices (soil, sediments, food) can alter the As-speciation and pose a problem for separation procedures.

Most extraction procedures have to be considered as fractionation because of the inherent difficulty to extract completely all species [34-37] by a single procedure. The widespread use of one single extraction method only inspired others to define a new class of "hidden species" [38,39]. Even in case of a hypothetical 100% recovery of each species, inherent procedural species instabilities can cause a shift in species ratio which is difficult to prevent (e.g. instabilities of the oxidation states [14,40], or the thio vs oxo-form [41-43]). A control might be possible for a limited set of As-species as they occur in certified reference materials [44,45], despite total As only is certified in the material.

A variety of extraction procedure have been developed and optimized for several matrices: terrestrial plants [46-48], algae and aquatic plants [49], soils [50-52], food [52] and microwave-assisted extraction from soil [53] and vegetables [54,55]. Solvent extraction (SE) are now investigated with a high enrichment factor (115) [56], ultrasound assisted [57,58] and microwave assisted SE [59], solid phase micro-extraction [60-64].

For the stabilization of As-species low temperatures were sufficient, e.g. freezing (liquid N_2) for clinical samples [65] and $-16°$ for algae extracts [66]. Moreover, diverse additives have been proposed: methanol [52], mineral acids like HCl [67-69] and phosphoric acid [52], phosphoric acid in combination with cooling (6°) [70,71], chelators like EDTA [72-74] against metal precipitation. Some of these preservation procedures have been compared [40,69] using the same set of samples. Low temperatures in combination with preservatives which account for matrix particularities are most effective.

2.1.3. Specialized Fractionation Procedures

In recent years, there has been some progress in isolating special As-fractions like bio-available, volatile or size fractions, exclusively defined by the procedure applied.

A bio-available fraction has been obtained extracting seafood continuously by synthetic body-fluids (saliva, stomach- and gastric juice) [75] and by an in vivo assay [76]. Capture of volatile As-species is indispensable for a total As-balance in a dumpsite [77] or in biogas [78].

Biological samples are often fractionated on a size exclusion column to isolate as much as possible As-species in one run from the complex matrix. This can serve as a cleaning step for further chromatographic speciation [79]. SEC was useful in detecting thioarsenicals as As-phytochelatins from plants [80] and methylated thio-arsenicals in urine [81].

2.2. Sensors and Field Tests

In a large area with a high number of sampling sites it gets impractical to collect and transfer samples to a laboratory. It is more convenient to perform analysis or tests on site in the field and evaluate critical samples only in the laboratory. However, the recommended limit for As (10 ppb (μg/L)) is a very tough hurdle for a sensor or field test which usually operate with compromised detection limits, accuracy and precision in favour of low cost portable instrumentation [82] or test kits [83,84]. If hundreds of volunteers are required, simple and fast test kits are indispensible which can be easily handled by non-scientific staff. Such a screening fulfils a different purpose that is to provide approximate concentrations allowing a sample classification and splitting (below, around and above a limit) for a reduced workload. Detailed requirements and the chemistry applied by field test were discussed and reviewed [85,86]. Biological-based assays have been developed and are reviewed in [87]. Microelectronic sensing of the biological response to arsenicals [88] has a not yet exploited potential.

2.3. As-Speciation Using IC Methods

2.3.1. Detectors in As-Speciation

The method sensitivity has not only a decisive influence on which samples (concentrations) can be analyzed or which method has to be chosen to analyze envisaged species in given samples (concentrations), but the performance and the complexity of the method too depend on the sensitivity. E.g. lower sensitivity detectors require sample clean up procedures and pre-concentrations steps which in turn increase the labour load and the possibility of speciation alterations. In chromatography, the detector sensitivity is linked to the chromatographic performance as a more sensitive detector allows sample dilution or larger dilution factors. More diluted samples can show less severe matrix interference, thus enabling a more robust procedure.

Sensitivity and providing species specific information are the two main abilities detectors meet As-speciation demands. Detectors which are sensitive to only a small number of species require that other species must be chemically transformed in high recovery prior to detection which can cause problems. Bulkiness and costs are other important properties. The smaller, less sensitive and less expensive detectors like UV, conductivity and chemiluminescence [30] are not As-specific and not sensitive enough, whereas the more demanding (cost and space) are more sensitive and deliver species specific data. Among the specific detectors there are atomic fluorescence (AFS) and electrochemical instruments which can be applied to a few As-species only. Volatile hydrides are required for detection by AFS [58,89-91] and only inorganic AsIII [92,93], or AsIII/AsV [32] by electrochemistry. Element-specific detectors like atomic absorption (AAS) and optical emission (OES) traditionally used to determine total element concentrations provided a first generation of universal As-species detectors.

However, sensitivity requirements in As-speciation can bee roughly 1-2 order of magnitude more demanding compared to total element determinations since the element is distributed on several species and many of them have to be separated and detected individually. Element mass spectrometers (MS) extend the detection limit (DL) noticeably. Simple quadrupole ICP MS are the most widely used detectors in general trace element speciation analysis [94-96] as well as in arsenic speciation [21] since they are versatile and the most sensitive instruments [97]. The same is valid for a high resolution (HR) ICP MS except that its sensitivity is at least 10 times better [98]. The particular advantages of plasma source MS have been pointed out in [21,97,99].

Organic MS, detecting molecules and molecule fragments, responded to research and validation needs for more information and proof of the species structure [97]. The advantages and the limitations of various detectors and their couplings to different separation methods are discussed in [100,101]. Considerable evidence in reliable structural assignment was obtained by divers molecule and fragment ionisation MS techniques [100,102] and by x-ray absorption [103] that gives information on As-bonding in the solid state [104-107] which can eliminate artifacts generating extraction steps.

2.3.2. Selective Separation Methods

A sensitive As-specific detector coupled to a sufficiently selective separation method is the heart-piece in As-speciation [108-110]. In most cases a traditional high performance separation technique such as gas chromatography (GC), capillary zone electrophoresis (CE), several liquid chromatographic (LC) methods like ion exchange chromatography (IEC) and ion pair chromatography (IPC) on reversed phase HPLC columns are linked to diverse detectors according to the analytical task.

Volatile arsenicals found under natural conditions were separated highly efficient by GC. Arsenolipids were determined in fish oil [111]. Several mixed arsenosulfur compounds which were produced by intestinal microorganisms [112] were analyzed. Typically, volatile arsenicals are produced in derivatization steps like hydride generation [113,114] and methyl thioglycolate derivatives were extracted into hexane and determined by GC atomic emission [115]. With respect to the growing number of volatile arsenicals, GC remains an important separation method as reviewed in [116]. However, many naturally occurring arsenicals are not volatile and not stabile at the temperature required to keep them in the gas phase. For these compounds liquid separation methods like CE and LC are better suited.

High separation efficiencies made CE an attractive method [97]. However, its low amount of analyte mass applied in combination with low sensitivity detectors provides insufficient DL. For the most common As-species, DL of 5-17 μg/L were reached [117], detecting with a high sensitivity UV-cell and high sample volume stacking. In situ heteropolyacid formation with molybdate and UV-detection gave similar DL [118]. Without sensitivity enhancement in UV-detection, DL between 0.1 and 1.2 mg/L have been reported [119] in aqueous soil extracts. UV detection was 10^3-10^4 times less sensitive compared with ESI MS [120] and with ICP MS [121]. CE coupled to more sensitive detectors requires special interfaces and attention to some particular issues [122,123]. With ICP MS, DL of 0.04 μg/L have been reported [124]. Comparing CE and IEC both coupled to the same HR ICP MS gave 100 times higher DL with CE [125].

HPLC and Ion Chromatography. The most often encountered As-species cover the whole range of molecule polarities, e.g. anions (AsV, MMA, DMA), cations (AC, TMA) and, depending on the pH, neutral molecules (AB, AsIII) [126]. The diverse polarities, the growing number and the different types of As-compounds are a permanent challenge to IC. The method should be robust in routine speciation analysis, provide lowest DL, and separate as many as possible of diverse As-species. Strategies for arsenic speciation analysis have been presented by Larsen [126] and Feldmann *et al.* [13].

As the most toxic As-species are ionic, the overwhelming part in As-speciation is done by IC. IC-methods were previously reviewed, but IC principles and their role within the whole context of As-speciation (species stability and preservation, on column stability,

detector compatibility and variable selectivity) has not been critically discussed, making it difficult for non-experts to gain a comprehensive understanding. This review is intended to better clarify the role of IC in As-speciation and to highlight improved procedures. The different types of IC methods [127], e.g. anion exchange (AEX), cation exchange (CEX), ion exclusion (IEC), ion pair chromatography (IPC) and combinations there of are potentially suitable for As-speciation and are discussed below.

The affinity of an analyte ion towards an ion exchanger depends on the charge density and the polarizability of the two opposite charges. For a given exchanger material, the ion density is given by the number of exchange sites per material mass (capacity) and the polarizability is similar among columns functionalized by the same ionic groups. So far, R_4N^+, SO_3^-, $RCOO^-$ were most often used as ion exchanging groups [127,128]. The analytes charge density and polarizability depends on the molecule size and the charge which is often controlled by a proton association-dissociation equilibrium. The pK_a of arsenicals are spread over a large range, but many of them are $pK_a > 8$ [129]. Hence, their negative charge depends on the pH and the same is valid for protonable or deprotonable column exchange sites. All these variables are controlled by the eluent-pH which becomes the master variable. Unfortunately, the pH of the frequently used eluents (see below) cannot be freely adjusted to the As-species pK_a to tune their retention behaviour and improve the selectivity of the method [130]. The pH is rather dictated by the column capacity that requires an equivalent eluent concentration to reach the eluent strength that can elute species. With such eluents, there is no other choice than to perform the separation at a fixed value or, in case of acids and bases, even at an extreme pH (< 3 or > 9) where many As-compounds are not stabile. Such extreme eluent-pH practically excludes silica-based columns, so separations are usually done with synthetic columns. On organic polymers, ion exchange can be combined with hydrophobic interaction on the column core material, aiding in retention of neutral As-species.

Adjusting the analyte charge density by the eluent pH can be best realized by AEX [126]. In the beginning of ion exchange development it was found [131] that AEX separated common As-species whereas CEX did not retain the two most toxic and most common species, AsIII and AsV, but eluting them together in the front. This has been confirmed in many follow-up comparisons. A recently developed CEX gradient separation (0-20 mM $^+NH_4$, pH = 2.5 [77]) on a PRP-X200 column improved the separation somewhat, but again confirmed the prob-

lems by eluting AsIII, MMA, AsV and Cl$^-$ (interfering as $^{40}Ar^{35}Cl^+$ on $^{75}As^+$-detection by ICP MS [132]) within 3 min in the front and co-eluting AC with TAMO at 15 min. A more promising CEX, just recently published [133], uses acidified (HCOOH) acetonitrile.

Therefore AEX is recommended [13,134] as the primary separation and, if required, CEX as a secondary option to separate the less toxic organic cationic arsenicals not resolved on an anion exchanger. This can be achieved by a dual mode method, which consists on one hand of an additionally applied CEX procedure (as two columns two procedures [13] or as two columns in series in one procedure [135,136]). On the other hand, a mixed mode ion exchanger (mostly AS7 column,) can be used, containing both, anionic and cationic exchange sites [127]. In many cases, AEX, single or mixed mode, sufficiently separates a restricted number of cationic arsenicals, making a separate CEX-run obsolete.

Ion Pair Chromatography [137]. In IPC a simple reversed phase column is dynamically coated by a lipophilic counter ion in the eluent. While this is an attractive access to IC without purchasing additional expensive covalently functionalised columns, problems arise by the dynamic exchange capacity which depends on the sample matrix. Results obtained by this technique until 2002 were reviewed in [134] and an overview is given in **Table 2**. The dynamic in-situ coating in AEX was compared to permanent bound exchanger sites. The latter method [138] gave better results because of the higher and more stable exchange capacity. The dynamic coating can easily be disrupted by matrix components [139], e.g. salts and surface active organics of unknown concentrations. It was also demonstrated that the concentration of the ion pair reagent is very critical, a slight excess can reduce the selectivity substantially [140] and a calculation assisted method optimization found no ion pairing effect at all [59]. Nevertheless, it has been shown that a dynamic ion pair coating withstanding the coat disrupting ability of the sample matrix and an accurately developed method can result in robust and unique separation conditions [141]. Ion pairing reagents can also strongly increase the separation efficiency of AEX (see below).

Anion Exchange Chromatography. AEX separations are done almost exclusively on higher capacity, highly hydrophobic synthetic columns from several manufacturers (**Table 3**-**5**) and with eluents which severely restrict the eluent-pH. Accordingly, three types of restrictions can be distinguished for the following discussion: 1) a strong acidic HNO_3-eluent at two isocratic steps (pH < 3) mostly on a mixed-mode anion-cation exchanger AS7 (**Table 3**), 2) Strongly basic eluents like carbonate or hydroxide (pH > 8.5) on diverse columns (**Table 4**) and 3) phosphate

Table 2. Ion pair chromatographic separations.

IP reagent (mM)	Eluent (pH)	Modifier	Matrix	As species[a] (t_R, min)	Detector (DL, µg/L)	Comment	Ref.
anion pairing							
TBAOH (5)	H_2O (6.0)	4% MeOH		AB, AsIII, DMA, MMA AsV (12.5)	ICP MS (3)	matrix interf.	[139]
TBAPO$_4$ (2.5)	H_2O (5.2)			AsIII, AB, AC, DMA, MMA AsV (8.0)	HG AAS (100)	AB, AC coelute	[157]
TBAPO$_4$ (10)	PO$_4$ 20 mM (6.0)			AsIII, DMA, MMA AsV (9.0)	HG AAS (100)		[172]
TBAOH (5)	H_2O (6.2)		wine, kelp extr.	AsIII DMA, MMA AsV (1.7), pPSA, As-sugars	ICP MS (0.7)	narrow bore HPLC	[140]
TBAOH (13)	H_2O (5.8)	1.3% MeOH	urine	AB, AsIII, DMA, MMA AsV (6.4)	ICP MS (0.2)		[173]
TBAPO$_4$ (5)	H_2O (5.9)			AsIII, DMA, MMA AsV (8), pASA	ICP MS (4)	nano HPLC	[174]
TBAOH (5)	PO$_4$ SO$_4$ (6.0)		urine, plant extract, river water	AsIII, DMA, MMA AsV (6.2) 4 Se-comp.	ICP MS (0.02)	simult. As and Se - speciation	[141]
cation pairing							
SDS (10)	H_2O (2.5)	5% MeOH 5 2.5% AcOH	fish tissue	AB, AsIII, DMA, MMA AsV (12.5)	ICP MS (3)		[139]
HSA (10)	40 mM Cit (2.3)	2-12% MeOH gradient	apple extr.	AsV (1.8) AsIII, MMA, DMA, AB, AC (24)	ICP MS	AsIII, MMA coelute	[175]

a) The elution sequence is given.

Table 3. Anion exchange with eluents restricted to low pH (HNO$_3$).

Column[a] (capacity)	Eluent[b] HNO$_3$ steps	Modifier	Matrix	As species[c] (t_R)	Detector (DL, µg/L)	Comment	Ref.
AS7 (125)	0.5, 50	0.05 BDSA		AsIII, DMA, AsV, AB, AC,	ICP MS (0.5)		[142] [143] [176]
AS7 (125)	0.5, 50	0.05 BDSA	plant extract				[177]
AS7 (125)	0.5, 50	0.05 BDSA	oyster, rice, algae	17 arsenicals	ICP MS (0.01-0.05)	AB & Cl$^-$ coelute	[145] [146]
AS7 (125)	2.5, 50	non	poultry waste	AsIII, MMA, AsV, DMA, ROX	ICP MS (0.02)		[144]
AS7 (125)	0.5, 50	1% MeOH	seafood extr.	AsIII, MMA, DMA, AsV (6), AB, AC	ICP MS (0.01-0.04)	calc.assisted se.optimization	[59]
AS4 (25)	0.4, 50	non	algae extract	AsIII, MMA, DMA, AsV (6), AB, AC	ICP MS (0.03-1.5)	better without modif.	[178]

a) Manufacturer of AS7 and AS4: Dionex. b) Step concentrations in mM. c) Elution sequence is given.

eluents of various composition and pH on different columns (**Table 5**). Separations based on these procedures have been compared [72] to a field speciation method using more than 100 surface waters, ground waters, and acid mine drainage samples. Alternatively, the advantages of non pH restricting eluents (see **Table 6**) are discussed. In some work, organic anions were used as eluent ions which produce a high carbon load to ICP detectors. In low concentrations and as polycarboxylates they play a role as ionic strength modifier.

Strong acidic eluents on the mixed mode exchanger

AS7 were often used (compare **Table 4**) to separate anionic, cationic and neutral As-species [142]. The high hydrophobic nature of the exchange sites provided additional selectivity in conjunction with an ion pair reagent [143] and methanol [144]. The strongly acidic BDSA, which is anionic at low pH (pK$_{a1}$ < 1), was so far the most beneficial one. It interacts better with the positively charged As-centre than with the positive charges on the column, forming more negatively charged ion pairs with neutral or positive arsenicals [143]. Best separation is achieved by eluting at two isocratic nitric acid concentra-

Table 4. Anion exchange with eluents restricted to high pH (HO⁻, CO₃²⁻).

Column[a] (capacity)	Eluent mM (pH)	Modifier	Matrix	As species[b] (t_R, min)	Detector (DL, µg/L)	Comment	Ref.
ICPak MS[1] IC AN2[2]	HCO_3^- 25 (9.25) CO_3^{2-} 100 (10.25)	-	soil extracts	AB, AC, TMA, DMA, AsIII, MMA, AsV	ICP MS (3)	AB, AC, TMA coelute	[138]
ICPakA HC[1]	CO_3^{2-} 2.5 (10.25)	-		AB, DMA, AsIII, MMA, AsV, AC	ICP MS (0.1)	dual column system	[135]
IC AN2	CO_3^{2-} 50 (10.3)	-	groundwater	AB, DMA, AsIII, MMA, AsV (8)	ICP MS (0.2)	60°	[126]
AS11 (56)[3]	NaOH 30	1% MeOH	sediment	AsIII, AsV (3.5)	HG AAS (1)		[152]
AS11 (56)	NaOH 0-40	-	urine	AB, DMA, AsIII, MMA, AsV (9.1)	ICP MS (0.1-0.8)	AB, MMAIII and DMAIII not sep.	[155]
AS14 (80)[3]	NH_4HCO_3 2 (8.2) Tart 2 or 45	-		AsIII, DMA, MMA, AsV	ICP MS (0.5)	Se-species	[156]
AS9HC (237)[3]	Na_2CO_3 5-70 (12)	-	food stuff extracts	AB, DMA, AsIII, MMA, AsV	ICP MS (0.3)	AsIII is oxidised	[149]
AS16 (174)[3]	NaOH 30, 50 (12.7)	1% MeOH	poultry waste	DMA, AsIII, MMA, p-ASA, AsV (6.6), Rox(9.2)	ICP MS (0.02)		[144]
AS16 (174)[3]	NaOH 1.5-55	-	groundwaters	AsV(26)	suppr. conduct.	other oxyanions	[153]
PRP X100[4] (190)	NH_4HCO_3 15-50 (8.5)	-	lobster tissue extr.	AC, AB, AsIII, DMA, MMA(17), AsV (25)	ICP MS		[154]
AS9HC (237)[3]	Na_2CO_3 3, 70 (12)		soil water	AB, DMA, AsIII, MMA, AsV (6)	HR ICP MS (0.01)	spilt 1:10	[125]
AS7 (125)[3]	NH_4CO_3 0-25 (10)		algae extr.	DMA, AsIII, MMA, AsV (30)	ICP MS (0.01)		[179]
As11 (56)[3]	NaOH 0-40 (12.6)		urine	AB, DMA, AsIII, MMA, AsV (7.2)	ICP MS (0.02)		[155]
PRP X100	NH_4CO_3 20 (9.0)		molluscs	thio As-sugars			[180]
PRP X100	NH_4CO_3 20 (10)			50 As-species	ESI SRM MSMS (0.02)		[17]
PRP X100	NH_4CO_3 10-50 (9)	2% MeOH	urine, fish	AB, AsIII, DMA, MMA, AsV (7)	DRC ICP MS (0.01)	Se-compounds	[181]

a) Manufacturer (1-4): 1 Waters (polymetacrylat), 2 Merck, 3 Dionex (PS-DVB), 4 Hamilton (PS-DVB). b) Elution sequence is given. ESI SRM MSMS: electrospray ionisation selected reaction monitoring tandem MS. DRC: dynamic reaction cell.

tion (0.5 and at 50 mmol/L (pH 3.4 and 1.3 resp.), but a gradient is not successful. The procedure [145,146] was developed to a high resolution IC method. A concentration gradient of the ion pairing reagent, however, resulted in irreproducible retention times (t_R) of all analytes [143] and methanol in the sample can cause different response for As-species [146]. Surprisingly, independent work [59,147] reported that the BDSA-concentration has no influence on the separation. With respect to metal precipitation on the column, such an acidic eluent was considered preferable because it keeps metals in solution and continuously removes metals from the column. However, on column deposition of matrix components and loss of chromatographic performance after a few sample injections have been reported [143] for HNO_3 eluents as well. The aggressive and oxidising nitric acid significantly reduces the lifetime of organic polymeric column material. While the procedure is perfectly compatible with the sample introduction and the

plasma of an ICP instrument, it is not compatible with sample preservation procedure and on column stabilities of sensitive As-compounds. Oxidation of AsIII to AsV in nitric acid preserved samples [40] and large differences in species concentrations compared to other IC methods [144] have been observed. The oxidation was found to be catalysed by metals [148] and mediated too by light [69].

High pH eluents substantially increase the dissociation of protonated As-species and increase their affinity for the anion exchanger. The advantages of this type of AEX were discussed by Larson [126]. Under oxic basic conditions oxidation of AsIII to AsV is fast and was reported to occur during chromatography [40,144,149,150]. This method seems to be suited for NaOH extracted soil samples, to perform the separation without adjusting the sample pH. Beside K_2SO_4 (10 mmol/L, pH 10.2) [151], hydroxide and carbonate containing eluents have widely been used on a variety of polymeric anion exchanger columns (see **Table 4**). The higher the column capacity

Table 5. Anion exchange with eluents restricted to medium pH values (PO$_4$, org. acids).

Column[a] (capacity μeqv.)	Eluent mM (pH)	Modifier	Matrix	As species[b] (t$_R$, min)	Detector (DL, μg/L)	Comment	Ref.
Anion HC [1] (150)	NH$_4$PO$_4$ 0-10 (5.8)	-	soil extract	AsIII, DMA, MMA, AsV (11)	HG ICP OES	gradient	[57]
Adsorbo-sphere [1]	NH$_4$PO$_4$ 15 (5.75)	30% MeOH 5 mM AcO	urine	AsIII, DMA, MMA, AsV (9)	ICP MS (0.2)	AsIII & Cl$^-$ coelute	[159]
PRP X100 [2] (190)	NaPO$_4$ 16 (7)	5% MeOH		AsIII, DMA, MMA, AsV (8)	ICP MS (2)		[139]
PRP X100 (190)	NaPO$_4$ 12 (6)	-	groundwater sedim. extr.	AC, AB, AsIII, DMA, MMA, AsV (9)	HG AAS (20)	on line MW digestion	[157]
PRP X100 (190)	NaPO$_4$ 12 (7)	-	tap water	AsIII, DMA, MMA, AsV (9.1)	ICP MS (0.3)	sensitivity decreased	[160]
	TRIS 30-100 (7)	-	tap water	same, AsV (12)	ICP MS (0.06)		[160]
PRP X100 (190)	NH$_4$PO$_4$ 10 (8.5)	30 mM B(OH)$_3$	food extracts	AB, AsIII, DMA, MMA, AsV (10), As-sugars	HG ICP MS		[182]
LC-18 [3]	NaPO$_4$ 20 (6.0)	10 mM TBA	human serum	AsIII, DMA, MMA, AsV (10)	HG AAS (0.5)	not suitable	[172]
LC-SAX [3]	PO$_4$ 30 (4.5)	non	human serum				[172]
LC-SAX	NH$_4$PO$_4$ 20 (3.9)	1% MeOH	water urine	AC, AsIII, DMA, AB, AsV (6), MMA (7)	ICP MS TN (0.1)		[183]
LC-SAX1 [3]	NH$_4$PO$_4$ 5-25 (6)	-	algae	As-sugars, AsIII, AB, DMA, MMA, AsV (19)	ICP MS		[184]
PRP X100 (190)	NH$_4$PO$_4$ 15 Na$_2$SO$_4$ 15 (5.9)	-	groundwater	AsIII, AsV (4)	HG AAS (6) off line		[185]
AS14 (80) [4]	NaPO$_4$ 2 10 (7.2)	1% MeOH	Poultry waste	AsIII, DMA, MMA, p-ASA, AsV (5.3),	ICP MS (0.08)	2 steps	[144]
GL IC A15 [5] (40)	H$_3$PO$_4$ 4 (2.6)	-	urine	AsIII, DMA, AB (7), MMA, AC (21), AsV (27)	ICP MS (0.03)	2 columns separation	[136]
G5134A (40) [6]	NaPO$_4$ 2 (6)	EDTA 0.2 mM	water	AsIII, DMA, MMA AsV (9)	ICP MS (0.07)		[186]
PRP X100 (190)	NH$_4$PO$_4$ 20 (6.0)	-	wastewater	AsIII, DMA, MMA AsV (7.3)	HG AFS (1)		[187]
PRP X100 (190)	NH$_4$PO$_4$ 10 (6.0)	-	food, sediment	AsIII, AB, DMA, MMA AsV (13)	ICP MS (0.07)	AsIII, AB coelute	[52]
PRP X100 (190)	NH$_4$PO$_4$ 20 (5.6)	-	water, plants, sediment,	AsIII, DMA, MMA AsV (10)	HR ICP (0.004)	AsIII, AB coelute	[163]
G5134A (40)	NH$_4$PO$_4$ 7.5 (7.9)	-	groundwater	AsIII, AB, DMA, MMA AsV (7.5)	ICP MS (0.2)		[161]

a) Manufacturer (1-6): 1 Alltech (Si-C18), 2 Hamilton, 3 Supelco (LC-SAX (Si-N$^+$(But)$_3$, LC-SAX1 (Si-N$^+$(CH$_3$)$_3$), 4 Dionex, 5 Agilent, 6 Hitachi. HG: Hydride Generation. MW: microwave. TN: thermospray nebulization.

is, the higher the eluent concentration (isocratic or gradient ramp) has to be. On a low capacity AS11 short t$_R$ were obtained applying 30 mmol/L hydroxide [152] whereas on a AS16 column [144,153] up to 55 mmol/L were required. Short t$_R$ (< 4 min) for AsV were reported [138] with high isocratic carbonate concentrations, 25 mmol/L and pH = 9.25 on IC-PAK-HS or 100 mmol/L and pH = 10.25 on IC-AN2. Carbonate up to 70 mmol/L (pH 12) had to be applied on a AS9HC column to separate As-species within 5 minutes [40]. The advantage of a gradient (15-30 mmol/L) vs. isocratic (30 mmol/L) separation was demonstrated [154] using NH$_4$HCO$_3$ pH = 8.5 on a PRP-X100 column. The gradient provided almost baseline separation of the cationic AC and the neutral AB. However, the low eluting power of the HCO$_3^-$ anion required over 26 minutes to elute AsV from this column. A hydroxide gradient (0-40 mM NaOH) on AS11 was applied to separate inorganic and organic AsIII and AsV in urine samples [155].

A low carbonate concentration (2.5 mmol/L, pH = 9.3) was applicable on IC-PAK-A-HC (150 × 4.6 mm) serially connected to a cation exchange column [135]. Carbonate and hydroxide were used in combination, e.g (5 mmol/L, 20 mmol/L resp.) on AS12 column [71] and (5 mmol/L, 40 mmol/L resp.) on AS4-SC [142]. In order to lower the pH but increase the ionic strength, inorganic eluent anions have been combined with organic anions, e.g. NH$_4$HCO$_3$ (2 mmol/L) with tartrate (2 and 40 mmol/L,

Table 6. Anion and cation exchange with an eluent of a large pH-variability (NH$_4$NO$_3$).

Column[a] (capacity)	Eluent[b] NH$_4$NO$_3$	pH	Matrix	As species[c] (t$_R$, min)	Detector (DL, µg/L)	Comment	Ref.
AEX							
PRP-100X	20, 60	8.7	surf. water	AsIII, DMA, MMA, AsV (7.1), SeIV, SeVI, CrVI	ICP MS (0.05)	multielemental det.	[169]
PRP-100X	4, 60	8.7	earthworm extracts	AB, AsIII, DMA, MMA, AsV (9)	ICP MS (0.3-1)		[188]
PRP-100X	5, 80	8.3	env. waters	AsIII, DMA, MMA, AsV (7.1), SeIV, SeVI,	ICP MS (0.03-0.04)	micro IC-system	[171]
AS11 (14)	0.5-70 gradient	8.3	groundwater	AB, AsIII, DMA, MMA, AsV (7)	HR ICP MS (0.005-0.01	narrow bore system	[130]
Methacrylate[1]	15	3	test water	AsV (7), MMA, DMA, AsIII (10.7), AB	ICP MS (0.02-0.4)	AsV & Cl$^-$ coelute multimode exch.	[170]
CEX							
PRP-200X[2]	0-20 gradient	2.5	landfill leachate	AsIII, MMA, AsV (4), DMA, AB, TETRA, AC (15), TMAO	ICP MS (0.01-0.03)		[77]

a) Manufacturer as in **Tables 2-5**, 1 Micromass nano IC capillary, 2 Hamilton. b) Step or gradient concentrations in mM. c) Elution sequence is given.

pH = 8.2) [156]. Separations at a high pH can suffer from metals (Mg, Ca, Al, Mn, Fe, Cu, etc) precipitating as hydroxides providing fresh adsorbing surfaces for As-species.

Phosphate as an eluent anion was used since a long time because of its particular advantages, but there are also some shortcomings which have to be considered. Compared to other eluents, phosphate is a real buffer able to alter on column the pH of the injected sample to the eluent pH. As an AsV-analogue, it plays an indispensable role in displacing AsV from strong adsorbing sites and providing optimal recoveries in chromatography [130] or in extraction procedures [57]. Higher capacity anion exchangers (compare **Table 5**) required higher eluent pH and/or high phosphate concentrations to compete for arsenicals and elute AsV in a reasonable t$_R$. On the other hand, phosphorus and sulphur in the plasma produce polymeric depositions on the cones and inside of an ICP instrument. Therefore, procedures to reduce the P-load to the instrument have been developed. As-species were often transferred into volatile As-hydride and separated from the eluent in a post column reaction [72]. Organic As-species, however, react sluggishly at room temperature and need a particular fast on line digestion procedure [157] to reach a comparable mass transfer from a column effluent into the gas phase. A newly developed electrochemical hydride generation [158] might be an alternative in-line digestion for coupling to a detector. For a direct inlet into the ICP MS at 1 mL/min, phosphate concentration should clearly be lower than 15 mmol/L since at this concentration a rapid damage of expensive cones [159] and a drop in sensitivity due to clogging [160] was reported. Recently it has been shown that ammonium instead of Na-salts in the plasma pro-

duce less deposits [161]. Eluent splitting before the instrument inlet was used too in order to reduce the P-load. E.g., arsenate was eluted with 20 mmol/L phosphate (pH 5.6, t$_R$ = 10 min) from a PRP-X100 column [162] and the eluent was split before HR ICP MS detection [163]. In cases where an eluent splitting is not an option, lower phosphate concentrations are mandatory. On the PRP-X100 column 12 mmol/L [157] and 10 mmol/L [52] phosphate have been applied which eluted AsV in 12 minutes and compounds in biological samples have been identified which strongly bind to the column and to AsIII producing artefacts in As-species ratios [65]. In combination with poly-anionic EDTA (1 mmol/L), 2.6 mmol/L phosphate eluted AsV in 12 minutes as well and was splitless introduced into a HR ICP MS [164]. Just recently, a phosphate gradient (0-10 mmol/L, pH = 5.8) has been applied on a shorter (4.6 × 100), high capacity column (~150 µequiv.), eluting AsV in 11 min [57].

Phosphate has less pH-restrictions than acids or bases and can be applied within a middle pH-range (3-9). In this range the charge of the phosphate eluent anion varies (between -1 and -2) depending on the degree of deprotonation (pK$_{a1}$ = 2.1, pK$_{a2}$ = 7.2, pK$_{a3}$ = 12.6). Hence, approaching pH 7, phosphate is much more ionized which drastically increases its eluent strength. This was used to selectively increase the t$_R$ of DMA (pK$_a$ = 6.1) while the t$_R$ of other species remained [161]. Further deprotonation at higher pH, however, counteracts the selectivity among other As-species since the increased negative charge on phosphate shortens t$_R$ of arsenicals [157,161]. This makes the separation of the most toxic AsIII from the non toxic AB impossible [52] as the two are separated only at a higher eluent pH (e.g. 10.7 [157] or 8.2 [164]). The problem was addressed by combining phosphate with

other eluting anions which do not change its eluting strength with pH above seven, like EDTA [164] or SO_4^{-2} [141].

Organic eluent anions were used for special separations. A steep gradient of potassium hydrogenphthalate (0-100 mM, 0-5 min) separated organic from inorganic arsenicals on a short column (25 mm) in less than three minutes [165] and AsIII/AsV were separated (12.5 mM malonate and 17.5 mM AcO pH 4.8) on another short column (50 mm) in less than 2 minutes [72,73]. Such short t_R were also obtained on a micro column (ANX 1606AS, CETAC) with tartrate (5 mM, pH 8.5) separating AsIII and AsV [40,166]. A TRIS-buffer gradient (30-100 mM, pH 7) on a PRP-X100 column gave a better separation compared to phosphate [160]. Non preserved organic eluents promote rapid bacterial growth in the eluent [73] and on the column. However, organic carbon eluents are not often applied since the carbon introduced into the plasma modulates the As-ion formation by factors [167]. Unfortunately, organic and even inorganic carbon can vary the As-response [168] detected by ICP in an unexpected manner, particularly after chromatography.

Alternative eluents. Non buffer salts open up interesting alternatives. Mostly NH_4NO_3 (**Table 6**) has been used as fully pH-flexible and outstanding plasma compatible eluent. A two step method (20 mM and 60 mM NH_4NO_3, pH 8.7) demonstrated these unique properties in multi-elemental speciation [169]. This eluent was also chosen for a reliable detection in nano multimode-IC (15 mM NH_4NO_3, pH 3, [170]), micro-AEX (5 mM and 80 mM NH_4NO_3-steps, pH 8.3, [171]) and in narrow bore AEX (0.5-70 mM NH_4NO_3-gradient, pH 8.3, [130]). Up to now, this is the only eluent used to perform the separation around the sample pH or at any other freely selectable pH since its eluent strength does not depend on the pH. Large NH_4NO_3-gradients can be applied [130, 171] and independently an eluent-pH can be selected according to the analyte protonation equilibrium for retention time adjustment and selectivity optimisation [130, 169,171]. The same eluent was also applied in gradient cation exchange separation (0-20 mM pH 2.5) of As-species [77].

3. Conclusions

Most As-species separation was done by anion exchange, so it is worth to look for possible optimizations of this important technique. In trace As-species analysis by AEX, the column capacity and the sample matrix has a dominant influence on separation conditions. Columns caring a lower exchange capacity and requiring lower eluent concentrations are seldom applied despite the of-

ten deployed ICP MS is sensitive enough allowing for sample dilution. Separating diluted samples on low capacity columns reduces the eluent load to the plasma and the sample matrix load to the column as well, which would be the most simple and convenient way to a more robust chromatography.

Facing increasing evidence on As-species instabilities and artefacts in the matrix and during separation, the adaption of the eluent-pH close to the sample-pH is mandatory which is just contrary to what was extensively done in As-speciation so far. What so ever, extreme eluent pH cannot be used without a rigorous control of the species ratios over the whole analytical process. Moreover, in order to use a gradient for the separation of a larger number of As-species and to use the eluent-pH as an independent parameter to tune and enhance the AEX-selectivity, the eluent-pH should be completely independent from the eluent strength which is clearly not the case for acids, bases and most buffer salts, their pK_a being order of magnitudes different from those of As-species. A non-buffer eluent salt, NH_4NO_3, that is known to fulfil all the requirements like best plasma compatibility, pH-adjustable to any pH without affecting ionic strength and high purity has rarely been used so far. For plasma based detectors, eluent components containing carbon, phosphorus and sulphur are problematic since they require a lot of attention due to plasma incompatibilities causing sensitivity variations between injections and during a run (carbon).

These few important issues demonstrate that there is still a potential ahead for serious improvements in As-species analysis by AEX.

4. Acknowledgements

5. References

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