Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc. *78* (10) 1461–1479 (2013)

JSCS–4510

UDC 543.632.472:628:504.53

Review

REVIEW

Analytical methods for arsenic speciation analysis

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(Received 15 March, revised 29 May 2013)

Abstract: Arsenic exists in the form of various chemical species differing in their physicochemical behaviour, toxicity, bioavailability and biotransformation. The determination of arsenic species is an important issue for environmental, clinical and food chemistry. However, differentiation of these species is a quite complex analytical task. Numerous speciation procedures have been studied that include electrochemical, chromatographic, spectrometric and hyphenated techniques. This review presents the relevant research in the field of arsenic speciation analysis with novel applications and significant advances. Stability of arsenic species and each of the analytical steps (sample collection, storage, preservation, extraction) of the arsenic speciation methods is particularly evaluated. Analytical validation and performance of these methods are also reviewed.

Keywords: arsenic speciation; adsorption; extractions; water, soil; biological sample.

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doi: 10.2298/JSC130315064R

1. INTRODUCTION

Arsenic research is opening up new scientific topics, especially in speciation analysis. Methods for determining traces of total arsenic and different chemical forms of arsenic have become increasingly important due to the different toxicity and chemical behaviour of the various forms of arsenic. Consequently, various speciation procedures have been proposed and reviewed.[1] For the routine determination of a large number of arsenic samples, well-established methods that involve the coupling of separation techniques, such as ion chromatography (IC)[2] and high performance liquid chromatography (HPLC)[3], with a sensitive detection system, such as inductively-coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry-hydride generation (AFS-HG) and atomic absorption spectrometry-hydride generation (AAS-HG)[4] are the methods of choice. Procedures for the separation of arsenic species on various sorbents and exchange resins have also been developed and proposed.[5–9] The most important aspect in non-chromatographic and chromatographic methods is the selective separation of the arsenic species. Recently, our research group was involved in finding a procedure and material that are efficient for the selective separation of arsenic species[6–8] and arsenic removal from water.[10,11]

The maximum permissible concentration (*MPC*) of total arsenic in drinking water is set at 10 μg L^{-1}, while the limit values for arsenic species have not been established.[12,13] For this toxic element and its species, highly sophisticated equipment and sensitive methods should be applied. An adequate method for the estimation of the limits would facilitate the necessity and relevant progress in determining arsenic and its species. Numerous methods for total arsenic concentration and speciation are reported in the literature.[14] The ICP-MS method is highly sophisticated technique that enabled a decrease in the limit of detection (*LoD*) from 5 or even 25 μg L^{-1} established at the end of the 20th century[15] to values below 1 μg L^{-1} for arsenic determination.

This review considers primarily the remarkable developments in speciation analysis of arsenic in the last decade.

The chemical species are specific forms of an element defined though its: 1) isotopic composition, 2) electronic or oxidation state, 3) inorganic and organic compounds and their complexes, 4) organometallic species and 5) macromolecular compounds and complexes.[16] Speciation analysis involves analytical activities for identifying and measuring the quantities of individual chemical species in a sample.[17] Determination of total element concentration does not provide adequate information to understand the effects observed in the environment and in living systems.

The toxicity, bioavailability, physiological and metabolic processes and mobility are greatly dependant on the specific chemical form of the element. Potentially, toxic arsenic compounds are found in every aspect of the environ-

ment. Inorganic arsenic occurs on earth naturally in small amounts. Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic. Arsenic exists in different inorganic and organic chemical forms and different arsenic species exhibit different toxicities.[18] Inorganic arsenic compounds are more toxic than organic compounds and the acute toxicity generally decreases with increasing degree of methylation.[19] Depending on the source, a metal or metalloid can enter the environment, where it might be converted into another compound. Therefore, in order to obtain information on the activity and toxicity of a specific element it is necessary to know its specific chemical and physical forms.[20]

2. ARSENIC CHEMISTRY AND ARSENIC SPECIATION – PREVIOUS REVIEWS

Arsenic has more than fifty identified different naturally occurring arsenic containing chemical species.[21] The names, abbreviations and structure of the most widespread arsenic species in the environment are presented in Table I. Arsenic occurs in the environment in four oxidation states (As^{3+}, As^{5+}, As^{0} and As^{3-}) in inorganic as well as in organic forms.[1,21,22] Inorganic arsenic comprises two oxyanions, arsenite As(III) and arsenate As(V). Different organoarsenic compounds exist but the most common in the environment are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). In addition, simple methylated arsenic species are trimethylarsine oxide (TMAO) and the tetramethylarsonium ion (TETRA). A number of organoarsenic compounds are present in biological samples: arsenobetaine (AB) as a dominant species in fish, arsenocholine (AC) and trimethylarsoniopropionate (TMAP). Other forms of As, such

TABLE I. Names, abbreviation and structure of the most common arsenic species

Name of arsenic species	Abbreviation	Structure
Arsenous acid, arsenite	As(III)	H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}
Arsenic acid, arsenate	As(V)	H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}
Monomethylarsenic acid	MMA	$CH_3AsO(OH)_2$
Dimethylarsinic acid	DMA	$(CH_3)_2AsO(OH)$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Trimethylarsoniopropionate	TMAP	$(CH_3)_3As^+CH_2CH_2COO^-$
Tetramethylarsonium ion	TETRA, TMA	$(CH_3)_4As^+$
Arsenobetaine	AB	$(CH_3)_3As^+CH_2COOH$
Arsenocholine	AC	$(CH_3)_3As^+CH_2CH_2OH$
Dimethylarsinyolacetic acid	DMAA	$(CH_3)_2AsOCH_2COOH$
Phenylarsine oxide	PAO	C_6H_5AsO
Phenylarsonic acid	PAA	$C_6H_5AsO(OH)_2$
Arsenosugars $C_7H_{14}AsO_3CH_2CH(OH)CH_2R$		
Arsenosugar 1 (glycerol sugar)	–	R=OH
Arsenosugar 2 (phosphate sugar)	–	$R=OP(O)(O^-)OCH_2CH(OH)CH_2OH$
Arsenosugar 3 (sulphonate sugar)	–	$R=SO_3^-$
Arsenosugar 4 (sulphate sugar)	–	$R=OSO_3^-$

as arsenosugars, occur mainly in water organisms. Extensive toxicity studies of As showed that different forms exhibit different toxicities. Inorganic arsenic species are about 100 times more toxic than organic arsenic compounds.[22] Trivalent arsenic is about 60 times more toxic than the oxidized pentavalent state.[23] Methylation of inorganic arsenic in the body is a detoxification process, which reduces the affinity of the compound for tissue as an adsorbent.[23]

In natural waters, arsenic appears most often in inorganic forms and to a lesser extent in organic form such as MMA and DMA. As(V), MMA and DMA are stable in oxidized systems, while As(III) is unstable under oxidizing conditions and is readily oxidized.[24] In natural water, As(III) occurs at much lower concentrations compared to As(V), which makes its direct detection difficult and inevitably pre-concentration steps are required.[25]

Recent complementary reviews on specific aspects of arsenic speciation analysis are listed in Table S-I of the Supplementary material to this review. The review starts from Francesconi[14], who gives the base on how to understand the complexity of arsenic environmental and biological chemistry and it ends with Komorowicz,[1] a paper devoted to HPLC–ICP-MS techniques for arsenic and its speciation in water samples.

During the last decade, a significant number of scientific papers reporting the development in arsenic speciation have been published. The focus of research was the development and improvement of methods for arsenic extraction, separation and detection. The selection of an appropriate method for the extraction of arsenic species from different matrices without changing the oxidation state or with minimal loss by volatilisation or adsorption is still a challenging topic for research.

Liquid separation techniques, such as high-performance liquid chromatography (HPLC) and less popular capillary electrophoresis (CE) are the most frequently used techniques for the separation of soluble forms of arsenic species. The advantage of HPLC is the extended range of separation mechanisms by different mobile and stationary phases. The most applied detection technique is ICP-MS, especially after HPLC separation. This technique was applied in many studies for different sample types (environmental, biological and food samples). Application of ICP-MS has great capabilities since it can be used as a highly sensitive and element specific detector. Hydride generation atomic absorption spectrometry (HG-AAS) is a relatively simple and inexpensive technique but suitable only for hydride active As species. Electrochemical methods are suitable only for direct measurements in simple solutions.

The number of publications on arsenic speciation analysis has increased steadily since 2003. The number of publications, as shown in Fig. 1 from Science Direct, has increased from 32 articles per year (published in 2003), up to 125

articles per year (published in 2012). As presented, the interest for arsenic species is permanently growing.

3. ANALYTICAL METHODS FOR SPECIATION ANALYSIS

The ideal solution for direct measurement of species would be *in situ* analysis. However, very few techniques provide the necessary selectivity and sensitivity required for trace element speciation analysis. Those are: nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), electron spectroscopy for chemical analysis (ESCA), X-ray absorption fine structure spectroscopy (XAFS), electron spin resonance (ESR), tandem mass spectroscopy (TMS) and Mössbauer spectroscopy**.**

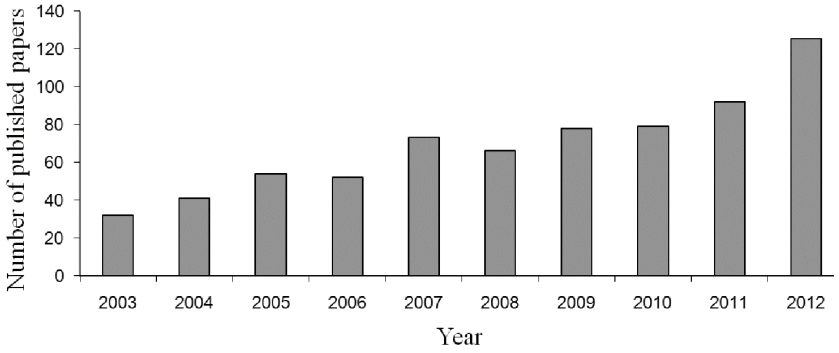

Fig. 1. Evolution of the number of published papers on arsenic speciation since 2003.

However, for species determination in practice at least two steps are usually applied: separation and detection. The most commonly used detection methods in speciation analysis are atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), atomic emission spectrometry (AES) and inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, electrochemical methods are also powerful tools for speciation analysis.[39]

Coupled techniques combining the separation power of a chromatographic or equivalent separation technique with the detection power of the most sensitive atomic spectroscopic techniques are the most applicable hyphenated techniques. Nowadays, hyphenated techniques couple the separation technique on-line with the detection technique. The advantages of such hyphenated techniques are manifold: a high degree of automation, a high sample throughput and a good reproducibility, a short analysis time, reduced risk for species transformation during analysis, a reduction in contamination due to a closed system and a high degree of information due to enhanced combined selectivity of the involved techniques. Different separation techniques that could be successfully coupled with sensitive detection techniques are presented in Fig. 2.[40]

Analytical methods for determining different arsenic species have become increasingly important due to the different toxicity and chemical behaviour of the various arsenic forms. Well-established methods that involve the coupling of separation techniques, such as ion chromatography (IC)[41,42] and high performance liquid chromatography (HPLC)[43,44] with a sensitive detection system, such as inductively coupled plasma-mass spectrometry (ICP-MS),[6] hydride generation-atomic fluorescence spectrometry (HG-AFS), hydride generation-atomic absorption spectrometry (HG-AAS)[45] and graphite furnace-atomic absorption spectrometry (GF-AAS)[46] are the methods of choice for the routine determination of a large number of water samples.

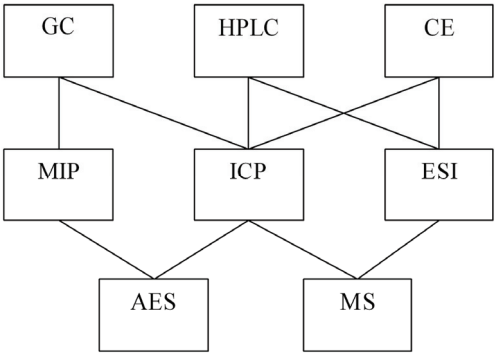

Fig. 2. Actual techniques for speciation analysis.[40] Legend: GC – gas chromatography; HPLC – high performance liquid chromatography; MIP – microwave-induced plasma, ICP – inductively coupled plasma; CE – capillary electrophoresis; ESI – electrospray ionization; AES – atomic emission spectrometry; MS – mass spectrometry.

A compilation of the developed methods commonly employed in speciation analyses is provided in Table S-II of the Supplementary material. The HPLC–|–ICP-MS method was applied in many studies with all types of sampled and this was the main step in improving arsenic speciation analysis. The only other technique that had application for all sample types is HG-AAS, usually after on-line HPLC separation. X-ray spectroscopic methods dominate in solid sample analyses. This is not surprising since all the coupled techniques require the arsenic species to be in solution, and suitable extraction procedures have not yet been developed for sediments and soils. Indeed, sample extraction is becoming one of the key issues in arsenic speciation analysis.

The analytical performance of an analytical method must be evaluated through validation protocols. Besides specificity and/or selectivity, linearity of calibration, repeatability and accuracy, the most important parameters are *LoD* (limit of detection) and *LoQ* (limit of quantification). All of the limits are related and have distinct definitions. Through the limits, it is possible to define the lowest concentration of an analyte that can be reliably detected and quantified. In this part of the review, the focus is analytical limits in the determination of arsenic species.

The obtained values for *LoD* and *LoQ* (Tables S-II and S-III of the Supplementary material) depend not only on the different matrices, extraction techniques and instruments for the measurements, but also on the different approaches for calculation. It could be noticed that several protocols are commonly used for *LoD* estimation: traditionally the 3σ method, method detection limit (MDL) according to US EPA and method of calculating signal to noise ratio based on manual measurements of peak heights on chromatogram printout. These methods are popular due to their simplicity, but at the same time characterized as not valid. Once again, the proper use of basic Currie definitions should be emphasized. The procedure for *LoD* determination should include testing whether the analytical measurement system is homoscedastic (standard deviation of measurement error is constant) or heteroscedastic (standard deviation of measurement error changes with concentration), and subsequently the adequate formulae for both the critical value and *LoD* should be used. Incorporating a blank subtraction factor and taking heteroscedasticity into account leads to unbiased and efficient estimates of the limits.[83]

Some recent articles dealing with arsenic speciation are reviewed concerning limit of detection, *LoD* and limit of quantification, *LoQ*, determined by different analytical techniques and different sample preparation procedure, are listed in Table S-III of the Supplementary material. The precision, most often determined as a value of relative standard deviation, is also analyzed and presented in Tables S-II and S-III of the Supplementary material. The obtained values of precision do not exceed 20 %. The recovery of the methods is usually calculated from spiking of the samples or from standard reference materials (SRM). The values for the recovery were also studied and the obtained values, which were greater than 70 %, are listed in Tables S-II and S-III of the Supplementary material.

4. STABILITY OF ARSENIC SPECIES: SAMPLE COLLECTION, STORAGE AND PRESERVATION

Sampling problems such as loss of analyte or contamination have long plagued trace element analyses, but they are nowadays reasonably well understood and controlled. The situation with arsenic speciation analysis is much more complex, and for many types of samples/species, there is still a long way to go before the problems can be adequately addressed.[14] Sampling and storage procedures could be considered as a key requirement in order to preserve the species information during the whole analytical process. Two main strategies could be distinguished for achieving this goal. Firstly, species preservation should keep the chemical species of interest unchanged during all steps of analysis to avoid changes in the oxidation state, changes induced by microbial activity and losses by volatilization or adsorption. Secondly, the species could be quantitatively

transformed into suitable derivatives for further separation, accumulation and quantification.[89]

The most reliable method for preserving natural water samples is, therefore, acidification to pH 2, refrigeration and deoxygenation.[90] According to Segura *et al*.[43], arsenic species in water are stabile under neutral conditions for a period of 4 months if they are placed in polypropylene bottles in a refrigerator. Using phosphoric acid as a preservation agent, samples remain stable for 3 months, even if they show evidence of high concentrations of iron or manganese.[91] Phosphoric acid at a final concentration of 10 mM is recommended as a preservation agent, combined with keeping the samples cool (6 °C) and in the dark.

McCleskey *et al*.[92] investigated the influence of preservation of water samples for As(III) and As(V) determinations. To stabilize dissolved As redox species, it is imperative for the samples to be filtered, preserved with HCl, H_2SO_4, or ethylenediaminetetraacetic acid (EDTA) to stabilize Fe, and to be stored in the dark. Filtering the sample removes most of the colloidal material and micro-organisms that can affect the dissolved As(III/V) ratio. Acidification prevents oxidation and precipitation of Fe and Mn hydroxides that could co-precipitate or adsorb As. EDTA sequesters Fe and the formation of precipitates is inhibited. Arsenic has never been shown to be photochemically reactive, but oxidation of As(III) in conjunction with the photoreduction of Fe(III) could occur unless light is excluded. Excluding light prevents photochemical reactions that could affect the As redox distribution. Preservation of As depends on the analytical technique and the need to stabilize other redox species, especially Fe(II/III). Hydrochloric acid works well as a preservative for As, Fe and Se redox species for a wide range of natural water samples when the samples are properly filtered and stored in the dark and is preferred when using HG-AAS for determining hydride-forming elements. For HPLC–ICP-MS applications, EDTA is the preferred preservative.

There is no general agreement on stability procedures and reports are sometimes even contradictory. This is especially true for complex solid matrices, such as soils, sediments and biological tissues. Dahl *et al*.[93] showed that processing or storage by freezing did not change the total arsenic content in seafood samples, or alter the speciation pattern greatly. According to Pizarro *et al*.,[94] arsenic species in rice extracts remained stable during a three-month test period, whereas in fish and chicken tissue extracts, AB was transformed into DMA over time. As species from chicken and fish (higher protein content than rice and/or soil) became more stable as the methanol content in the employed extractant mixture increased.

Salgado *et al*.[95] investigated the stability of total arsenic and arsenic species in alga samples (*Sargassum fulvellum* and *Hizikia fusiformis*), as well as in their aqueous extracts, which were stored in amber glass and polystyrene containers at

different temperatures. The results obtained for solid alga samples showed that total arsenic (for *Hizikia* alga) and arsenic species present (As(V) for *Hizikia* and NIES No. 9 – reference material of a lyophilised *Sargasso* material, *Sargassum fulvellum*, National Institute for Environmental Studies (Japan)) were stable for at least 12 months when samples are stored in polystyrene containers at 20 °C. On the other hand, different behaviours in the stability of total arsenic and As(V) species in aqueous extracts were observed for both samples. The best storage conditions for the *Sargassum* extracts were in polystyrene containers at temperature of −18 °C, when they were stable for at least 15 days, while *Hizikia* extracts had to be stored in polystyrene containers at 4 °C in order to ensure stability for 10 days.

5. SAMPLE EXTRACTION

Extraction is the selective separation of target species from their matrix (water, soil, sediment, biological tissue or fluid). Table III summarises recent application and research papers dealing with arsenic speciation, and the different methods applied for sample preparation for different matrices. The most commonly used extraction methods are: solvent extraction, enzymatic hydrolysis, solid phase extraction (SPE), solid phase micro-extraction (SPME) and microwave extraction.

However, there is no universal extraction procedure for different species and different matrices, which means that for each application and target analyte, a specific sample treatment method has to be developed. This has been realized for arsenic speciation from biological samples, coal and ash, plant, water and soil samples.

Solvent extraction. The solvent extraction technique is commonly used for the determination of organic arsenic compounds, especially in biological samples. Methanol/water mixtures are widely used for extracting less polar species. Ciardullo *et al*.[96] used a 1/1 (v/v) methanol/water mixture for the quantification of water-soluble As compounds in the muscle tissues of freshwater fish. In addition, extraction with water, or extraction with methanol/water followed by centrifugation and filtration,[35] or extraction with chloroform/methanol/water and sonication[97] are very powerful extraction media and often used extraction procedures. The total arsenic in different samples is usually extracted using the microwave extraction procedure.[98] In order to avoid species losses or transformation, parameters such as extraction medium, applied microwave power and exposure time have to be carefully optimized.

On the other hand, it has been repeatedly proven that a simple, inexpensive reagent, such as tetramethylammonium hydroxide (TMAH) in alkaline medium, is useful as a solubilising agent for a wide variety of biological matrices. Speciation analysis of arsenic in fish-based baby foods by electrothermal atomic

absorption spectrometry (ET-AAS) using suspensions prepared in a 0.01 mol L^{-1} tetramethylammonium hydroxide (TMAH) solution has limits of detection for the determination of AB, DMA and inorganic arsenic 15, 25 and 50 ng g^{-1} expressed as arsenic, respectively.[99]

Methods such as these in which methanol/water is used have the feature of extracting only a small percentage of the arsenic in soil and sediment samples. Accordingly, methods for soils and sediments and other abiotic samples are often based on those used in classical fractionation studies, using aqueous solutions of varying ionic strengths/pH/redox potential to release arsenic bound to the various mineral phases in the samples. Speciation information on the solid fraction is more difficult to acquire. For some time, a series of sequential extractions has been employed to acquire the information required to understand the cycling of As in sediments (on water-soluble, phosphate-exchangeable, organically bound and residual phases in such media).[100,101] Digestion using the mixture of acids: nitric and sulphuric in presence of vanadium pentoxide as catalyst is a powerful technique for the separation and determination of arsenic in coal and coal ash.[46,102]

Giacomino *et al.*[103] investigated the fractionation and speciation of As in contaminated soil. Regarding speciation, they found that As(V) prevailed over As(III), while more than 40 % of total arsenic was in an organic form. The fractionation of As was investigated with two sequential extraction methods: with concentrated hydrochloric acid and using the solvent extraction technique. The concentration of organic arsenic was determined by the difference between the total concentration of arsenic determined by acid digestion and total inorganic arsenic. Determination was realized by ICP-AES and GF-AAS. The extraction percentages for As ranged from 30 to 65 %.

Enzymatic hydrolysis. The use of enzymes, mainly those of a proteolytic nature, is another approach for speciation studies.[104] Enzymes are able to break down specific bonds of the substrate (biomolecules hydrolysis) under neutral pH and room temperature, and they allow a selective analyte release from the sample matrix without chemical species changes. However, enzymatic hydrolysis methods offer as a disadvantage the long time required for completing the substrate hydrolysis (several hours), which strongly conditions the applicability of the methods. To overcome this problem, pioneering developments based on the use of ultrasound energy (sonication probes) to assist the hydrolysis process have been proposed for extracting arsenic species.[105] The reduction of the hydrolysis time when using ultrasound could be attributed to fast cell membrane disruption, which allows a direct contact of cytosolic structures and the enzymes. Enzymatic hydrolysis procedures can also be assisted by microwave irradiation. In this case, improvements on enzymatic hydrolysis efficiency under microwaves are attributed to pressure effects on the enzyme and/or the substrate–enzyme interaction

and conformational changes in the protein. Moreda-Pineiro *et al.*[106] proposed enzymatic hydrolysis of seafood materials for isolating arsenic species (As(III), As(V), DMA and AB) by assisting the procedure with ultrasound energy supplied by an ultrasound water bath. The use of pepsin, as a proteolytic enzyme, under optimized operating conditions (pH 3.0, temperature 40 °C, enzyme to sample ratio of 0.3) led to an efficient assistance of the enzymatic process in a short period (from 4.0 to 30 min). The method was successfully applied to different seafood samples (molluscs, white fish and cold-water fish).

Microwave-assisted extraction. Microwave extraction is a frequently used technique for the extraction of biological and environmental matrices, considerably faster than conventional Soxhlet extraction procedure. Parameters such as extraction medium, applied microwave power and exposure time have to be carefully optimized in order to avoid species losses or transformation. Sample preparation for speciation analysis can be improved using a focused-microwave oven owing to a better control of the energy delivered to the sample. Extraction procedures using dilute acid or organic solvents at low temperature can be easily realized in focused-microwave ovens.

Microwave-based strategies for speciation analysis of arsenic, mercury, tin and selenium from matrices such as urine, fruit juices, fish, mussel, sediments and diatomea were reviewed by Nobrega *et al*.,[107] emphasising both its suitability for the leaching of labile species and to support derivatisation reactions. Raber *et al*.[108] used microwave extraction for the determination of inorganic arsenic in food. The method was based on sample extraction with trifluoroacetic acid/H_2O_2, and measurement of arsenate by anion-exchange HPLC–ICP-MS using aqueous malonic acid as the mobile phase. The method showed good extraction efficiencies (generally >90 %) for samples of rice, tuna fish and wheat.

Solid phase extraction. Solid phase extraction (SPE) is a frequently used method for pre-concentration and/or separation. The principle of SPE is partitioning between a liquid (sample matrix) and a solid (sorbent) phase. The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, chelation, ion-exchange or ion-pair solid phase extraction. SPE offers the advantages of high sensitivity due to the possibility of performing a simultaneous enrichment step, and versatility, since different substrates interact with different metal species. SPE is a popular technique because of its ability to work in combination with different detection techniques: on-line and off-line. In on-line techniques, there is no sample manipulation between pre-concentration and analysis, so the risks of loss and contamination are avoided and reproducibility is better. Likewise, all species are analyzed, so the volume of the sample can be smaller than the off-line procedure, the consumption of organic solvents is less and the potential for automation is greater. Nevertheless, the off-line SPE approach remains useful for analyzing complex samples due to its greater flexi-

bility and its ability to analyze the same extract using various techniques.[109] Various sorbents (*e.g.*, activated alumina, zirconium-loaded polymeric resin, Fe(III)-loaded resin, metal-loaded active charcoal and lanthanum hydroxide) have been reported for the separation of oxo-species of arsenic but a metal leaching problem and their poor stability in alkaline or acidic medium restrict their use. The application of chelating resins became extremely popular with the successful introduction of chelating groups (*e.g.*, imidazole, benzimidazole, 6-mercaptopurine, 2-naphthol-3,6-disulphonic acid, thiosalicylic acid, and bis(2--aminophenyl) disulphide) into a resin matrix, and has been reported for arsenic speciation.[109]

For the development of an extraction method, it is necessary to bear in mind that various arsenic species have different physical and chemical properties. The same extraction procedure applied to different samples can result in various extraction recoveries. Sometimes sequential extraction with a combination of different solvents and different extraction techniques should be developed.

6. SEPARATION AND DETERMINATION OF ARSENIC SPECIES IN WATER

Determination of arsenic is of the cardinal importance for water quality analysis. Arsenic has been reported as a groundwater pollutant in India, Bangladesh, Vietnam and Cambodia. It has also been detected in the south-eastern European Pannonian Basin region, where increased arsenic concentrations were found in the groundwater of Hungary, Romania and Serbia. The concentration of arsenic in the Banat region of Serbia ranges from 50 to 250 μg L^{-1}.[110] This was the reason for scientific investigations in Serbia of arsenic compounds and the possibilities of their removal from water.[111] Conventional and non-conventional treatment technologies for aqueous arsenic remediation were the subject of many studies. Adsorption is considered a relatively simple, efficient and low cost removal technique, especially convenient for application in rural areas. A wide range of sorbent materials for aqueous arsenic removal is available nowadays: biological materials, mineral oxides, different soils, activated carbons and polymer resins. Nevertheless, finding inexpensive and effective sorbent for arsenic removal from water is still highly desirable.

Chemisorption filters (activated with Ag^{+}, Mg^{2+}, Cu^{2+}, Al^{3+} and Fe^{3+}) made by the paper manufacture method and consisting of cellulose, cationic and anionic ion exchangers, activated carbon and a corresponding chemical agent were used as adsorbents for the removal of arsenic from water.[112] Cu^{2+} ions exhibited the most efficient removal. The mechanisms of total arsenic removal were determined based on measurements of active Cu^{2+} ion propagation inside the filter structure. A decrease in the arsenic concentration was determined using a continuous chromatographic system with multifunctional filters combining the effects of adsorption, ion exchange and filtration; for an active layer of 8 mm and

a contact time of 2 s, the decrease was more than 1000-fold. Investigations have shown that arsenic removal is valence dependent (the removal of pentavalent arsenic was more effective). The initial concentration, pH value of the water and the concentration of anionic pollutants, which affected the selectivity, were important for all the investigated processes.

Activated carbon impregnated with metallic silver and copper is also a very powerful adsorbent for the removal of arsenic from water.[113] The ability of activated carbon to adsorb arsenic depends on the arsenic oxidation state, the pH of water and the activity of the metal used for impregnation of the activated carbon. Physical adsorption is effective only for As(V) species in water. Activated carbon adsorbs As(V) with a saturation adsorption capacity of 0.27 mmol g^{-1}. The chemisorption process is effective for both As species. When active carbon is impregnated with copper, the sorption process for As(III) species was significantly improved, with saturation adsorption capacities of 0.41 and 0.23 mmol g^{-1} for As(III) and As(V) species, respectively. The pH value of the water is important for the adsorption of both As species because of the change in the ionic forms of arsenic. The optimal pH range is between 4 and 9, which is a consequence of the affinity between the carbon surface and H_3AsO_3 and $H_2AsO_4^-$ that are the predominant As species at this range of pH values.

Arsenic sorption onto hydrated iron(III) oxide (HFO)-coated materials, at neutral pH values, when As occurs in both molecular and ionic forms, is a multistage process consisting of both macropore and intraparticle diffusion.[10] Higher sorption values were obtained for As(III), which was attributed to the beneficial features of HFO.

Natural materials (zeolite, bentonite, sepiolite, pyrolusite and limonite) and industrial by-products (steel-mill waste, waste filter sand as water treatment residuals and blast furnace slag from steel production)[11,114] are low-cost adsorbents for inorganic arsenic removal from water. The natural zeolite and the industrial by-products were found to be good and inexpensive sorbents for arsenic while bentonite and sepiolite clays showed little affinity towards arsenic. The sorption capacities for As(V) compared to As(III) were significantly higher when natural zeolite and blast furnace slag were investigated, while the waste filter sand exhibited similar removal efficiencies for both As species. In equilibrium studies, the efficiency of As removal was found to be valence dependent, suggesting that the molecular forms of As bond less efficiently compared to its ionic forms.

Future research should involve the analysis of the desorption mechanisms for the examined waste materials and investigations of fixed-bed sorption systems, as well as the economic aspect of iron waste slag modification in terms of the possible application of this material in real water treatment systems.

A simple method for the preparation, separation of As(III) and As(V) species and pre-concentration of the total As on fixed bed columns in natural and drink-

ing water was developed by ben Issa e*t al*.[6] Two resins, a strong base anion exchange (SBAE) resin and a hybrid (HY) resin were utilized. The inductively-coupled plasma-mass spectrometry method was applied for the determination of the arsenic concentration in water. The governing factors for the ion exchange/sorption of arsenic on resins in a batch and a fixed bed flow system were compared. Acidity of the water, which plays an important role in the control of the ionic or molecular forms of arsenic species, was beneficial for the separation; by adjusting the pH values to less than 8.00, the SBAE resin separated As(V) from As(III) in water by retaining As(V) and allowing As(III) to pass through. The sorption activity of the hydrated iron oxide particles integrated into the HY resin was beneficial for the bonding of all inorganic As species over a wide range of pH values from 5.00 to 11.00. In other papers,[7,8] a simple and efficient method for the separation and determination of inorganic arsenic and organic arsenic in drinking, natural and wastewater was proposed. A procedure for the separation and determination of arsenic species in water is presented in Fig. 3. Three types of resins: a strong base anion exchange (SBAE) and two hybrid (HY) resins: HY–Fe and HY–AgCl based on the activity of hydrated iron oxides and silver chloride, respectively, were investigated. The procedures showed that they were accurate, precise and time efficient, and that just a very simple sample treatment is required.

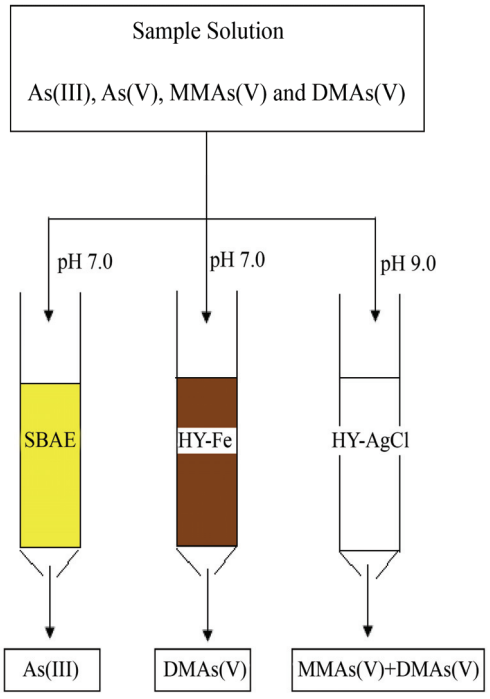

Fig. 3. Scheme for the selective separation of the arsenic species in water using SBAE, HY–Fe and HY–AgCl resins.[7]

7. CONCLUSIONS

The speciation analysis of arsenic is of great importance for human health, but it is challenging for analysts and is still a challenge for analytical chemistry. Complete characterization of arsenic compounds is necessary due to the different toxicological effects demonstrated by particular arsenic species. The chemical nature of arsenic compounds, in particular their tendency to change valence states or chemical form under a wide range of pH and redox conditions, makes it difficult to assess their fate and mobility in the environment.

There are a large number of papers on arsenic speciation in various matrices including a number of different extraction techniques. It is not possible to set an universal extraction procedure for different species and different matrices.

The most commonly used method for arsenic speciation involves liquid chromatographic separation followed by element detection (ICP-MS, AAS, and HG-AFS). Selecting the most appropriate method for the determination in arsenic species can be of vital importance in the achievement of reliable and accurate results.

SUPPLEMENTARY MATERIAL

Tables S-I–S-III are available electronically at http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

Acknowledgements. This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia through the Research Project III 43009.

И З В О Д

АНАЛИТИЧКЕ МЕТОДЕ ЗА АНАЛИЗУ АРСЕНОВИХ ЈЕДИЊЕЊА

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Арсен се налази у многобројним хемијским врстама које се разликују по физичко–хемијском понашању, токсичности, биодоступности и биотрансформацији. Одређивање појединих арсенових једињења је неопходно у хемији животне средине, клиничкој хемији и хемији хране. Међутим, диференцијација ових врста је врло сложен аналитички задатак. За анализу арсенових врста развијен је велики број метода и поступака које укључују хроматографске, спектрометријске и електрохемијске технике и њихове комбинације. У овом прегледном раду обухваћена су релевантна истраживања у области специјационе анализе арсена са нагласком на најзначајнија достигнућа и примену. Одржавање непроменљивог, оригиналног састава арсенових специја у току појединачних аналитичких корака (прикупљање узорака, чување, конзервисање, екстракција) посебно су разматрани. Издвојене су методе за директно и индиректно одређивање арсенових врста. Побројане су спрегнуте технике које се најчешће примењују у пракси применом методологије која подразумева прелиминарну сепарацију једињења, а затим поједи-

начно одређивање. Дат је преглед аналитичких својстава, предности и недостатака најпримеренијих аналитичких метода, развијених управо за анализу трагова арсенових врста од неорганских до органских у различитим матрицама. Издвојене су и детаљније презентоване најзначајније студије о арсеновим једињењима у води.

(Примљено 15. марта, ревидирано 29 маја 2013)

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