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Separation and determination of dimethylarsenate in natural waters

NUREDDIN BEN ISSA•, ALEKSANDAR D. MARINKOVIĆ*# and LJUBINKA V. RAJAKOVIĆ#

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, P. O. Box 3503, Serbia

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Abstract: A simple and efficient method for the separation and determination of dimethylarsenate DMAs(V) was developed in this work. Two resins, a strong base anion exchange (SBAE) resin and iron-oxide coated hybrid (HY) resin were tested. By simple adjustment of the pH value of water to 7.00, DMAs(V) passed through the HY column without any changes, while all other arsenic species (inorganic arsenic and monomethylarsonate, MMAs(V)) were quantitatively bonded on the HY resin. The resin capacity was calculated according to the breakthrough point in a fixed bed flow system. At pH 7.00, the HY resin bonded more than 4150 μg g^{-1} of As(III), 3500 μg g^{-1} of As(V) and 1500 μg g^{-1} of MMAs(V). Arsenic adsorption behavior in the presence of impurities showed tolerance with the respect to potential interference of anions commonly found in natural water. DMAs(V) was determined in the effluent by inductively coupled plasma mass spectrometry (ICP–MS). The detection limit was 0.03 μg L^{-1} and the relative standard deviation (*RSD*) was between 1.1–7.5 %. The proposed method was established by application of standard procedures, *i.e.*, using an external standard, certified reference material and by the standard addition method.

Keywords: arsenic species; dimethylarsenate; hybrid resin; exchange; adsorption; inductively coupled plasma mass spectrometry (ICP–MS).

INTRODUCTION

Arsenic is typically found in areas with active volcanism, geothermal waters, soil and bedrock.[1–3] Traces of arsenic are found in groundwater, lakes, rivers and ocean water. It is also released during human activities in areas of wood preservation, agriculture, mining[3] and energy production from fossil fuels.[2,3] Many water sources in the world containing high concentration of arsenic cause health

* Corresponding author. E-mail: marinko@tmf.bg.ac.rs
# Serbian Chemical Society member.
• On sabbatical leave at the University of Belgrade.
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problems or diseases such as cancer.[3–7] The provisional guideline value for arsenic in drinking water of the World Health Organization, WHO, is 10 μg L^{-1} (WHO, 1993). Inorganic arsenic, iAs, has two predominant oxidation states in most environmental systems, As(III) and As(V), which are mostly in the form of acids.[8] Organic arsenic, oAs, such as monomethyl-arsonic acid [MMAs(V)] and dimethylarsenic acid [DMAs(V)] are predominant in surface water and sediments.[9]

Both oAs [DMAs(V) and MMAs(V)] are stable in oxidative environments, and could be found in the marine water and biological samples.[10] Despite the fact that iAs species are predominant in natural waters, the presence of oAs has also been reported.[11] The toxicity of oAs species is lower than iAs species.[12,13] Although the main analytical interest is to determine total arsenic in water and prevailing iAs species, it is also important to develop procedures for the separation and determination of oAs species. The distribution of oAs species as a function of pH value of water is presented in Fig. 1.

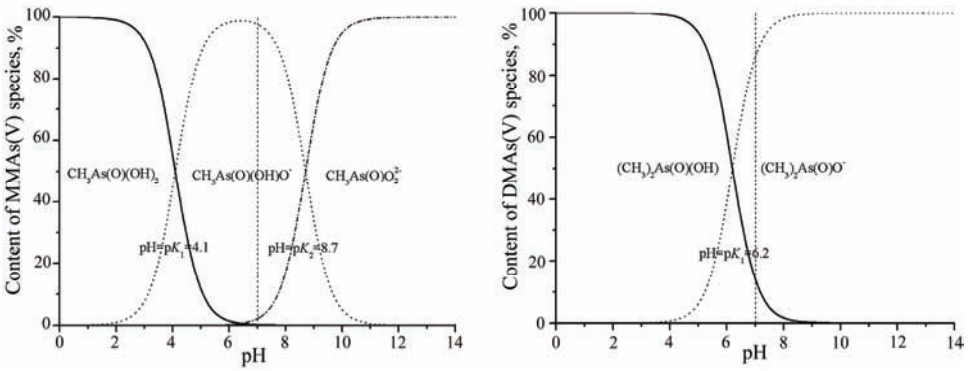

Fig. 1. Speciation of oAs compounds as a function of pH.

The investigation of the content of arsenic species and their behavior in natural waters and environment is important for chemistry and environmental protection. Several methods have been developed for the separation and measurement of arsenic species.

The most common method used to provide detection at low arsenic concentration is the hydride generation technique[15–18] connected with sensitive detection devices such as atomic absorption, fluorescence and atomic emission.[19] Inductively coupled plasma mass spectrometry (ICP–MS) and ICP optical emission spectroscopy (ICP–OES) techniques provides very low detection limits, with a greater accuracy of mass spectra detector than optical methods. The intensity of the arsenic emission is obtained by the sample entering into an ionized plasma thus producing As^{75}. Ion chromatography[20,21] (IC) or ion exchange chromatographic[22,23] methods were coupled with ICP to provide separation and determination of arsenic species.

High-pressure liquid chromatography (HPLC) is the preferred technique used for the separation of arsenic compounds. An HPLC–ICP–MS system was used for the separation and measurement of iAs, oAs, arsenobetaine (AsB) and arsenocholine (AsC) in beer samples by the employment of an anion-exchange column using phosphate buffer as the mobile phase and perchloric acid as the extraction reagent.[24] Similar methods were developed using phosphate buffer with the addition of 2.0 % acetonitrile,[25] and using ICP atomic emission spectroscopy (ICP–AES).[26] An HPLC–ICP–MS system was also used for the quantification of iAs and oAs in rice and soil, whereas AsB and DMAs(V) and an unknown arsenic species were quantified in a chicken tissue.[27] In addition to these, pre-column reduction and complexation of As(V), MMAs(V) and DMAs(V) with L-cysteine at elevated temperature, followed by HPLC separation of the complexes on a strongly acidic cation-exchange column, and arsenic species determination by flow injection hydride generation atomic absorption spectrometry (FI––HGAAS) was achieved.[28] Lopez *et al*.[29] applied post-column derivatization by mixing an HPLC effluent with a persulfate stream before entering into thermo--reactor consisting of a loop of PTFE tubing dipped in a powdered-graphite oven heated at 140 °C. After cooling in an ice-bath, hydrochloric acid and sodium borohydride were added on-line to generate the arsine. Rahman *et al*.[30] achieved good separation results using SPE sorbents (polymeric organic materials comprising an ion-selective sequestering property based on molecular recognition and macrocyclic chemistry) which were coupled with graphite furnace atomic absorption spectrometry (GF–AAS). Additionally, gas chromatography (GC) was used for the determination of arsenic species in seawater. The DMAs(V) and MMAs(V) were derivatized in the sample solutions with methyl thioglycolate and the products were extracted into cyclohexane and used for the analysis.[31]

Moreover, a method based on the transformation of arsenic species to a colored compound using ammonium diethyldithiocarbamate (ADDC), and silver diethyl-dithiocarbamate (SDDC) is widely used.[12,32] Electrical differential pulse cathodic or anodic stripping voltammetry are methods that have very low detection limits.[33–35]

Ben Issa *et al*.[22,23] studied the separation and determination of iAs and oAs species in drinking water. For the separation of iAs and oAs, two types of resins, a strong basic anion exchange resin (SBAE) and hybrid resins (HY–Fe and HY––AgCl) were used. The HY–Fe and SBAE resins retained all arsenic species except DMAs(V) and As(III), respectively, which enabled the direct measurements of these species in the effluents. An HY–AgCl resin retained all iAs, which was convenient for the direct determination the concentration of oAs species in the effluent.[23]

As a continuation of previous work,[22] a method for the separation and determination of DMAs(V) using an HY resin was developed and is presented in this

paper. The hybrid system, which integrates anion exchange with adsorption, is based on the activity of hydrated iron oxides (HFO) adopted for the separation of iAs.[36] The hybrid resin could also be used for the selective removal of MMAs(V), thus providing separation of DMAs(V). Although DMAs(V) is less toxic than iAs, nevertheless, the determination of the DMAs(V) concentration could be of appropriate significance for a better control of environmental pollution.

EXPERIMENTAL

Apparatus

Arsenic was analyzed by ICP–MS following the EPA method 200.8[37] using an Agilent 7500ce ICP–MS system (Waldbronn, Germany) equipped with an octopole collision/reaction cell, Agilent 7500 ICP–MS ChemStation software, a MicroMist nebulizer and a Peltier cooled (2.0 °C) quartz Scott-type double pass spray chamber. Calibration at levels 1.0–80.0 μg L^{-1} was performed with an external standard solution (Fluka, Product No. 01969) by appropriate dilution. The slope of the calibration curve was 0.9999. The calibration blank and standards were prepared in 2.0 % nitric acid for all measurements. The instrument was optimized daily in terms of sensitivity, level of oxide and doubly charged ions using a tuning solution containing 1.0 μg L^{-1} of Li, Y, Tl, Ce, Co and Mg in 2.0 % HNO_3 (v/v). Standard optimization procedures and criteria specified in the manufacturer's manual were followed. The sample solutions were filtered through a Millipore 0.45 μm membrane filter (Bedford, MA, USA) before injection.

The analytical accuracy and precision of the measurements were determined by analysis of certified reference materials NRC SLRS4 (Ottawa, ON, Canada) and NIST 1643e (Gaithersburg, MD, USA). The method detection limit (*MDL*) was 0.03 μg L^{-1}.

A laboratory pH meter, Metrohm 827 (Zofingen, Switzerland) was used for the pH measurements. The accuracy of the pH meter was ±0.01 pH units.

Reagents

The following chemical were used: $HAsO_2(CH_3)_2$ *p.a.*, Sigma–Aldrich (St. Louis, MO, USA); $Na_2AsO_3CH_3{\cdot}6H_2O$ *p.a.*, Sigma–Aldrich; $Na_2HAsO_4{\cdot}7H_2O$ *p.a.*, Aldrich (Munich, Germany); $NaAsO_2$ *p.a.*, Riedel-de Haën (Buchs, Switzerland); HNO_3 *p.a.*, Fluka and NaOH p.a., Merck. Ultra-pure water (resistivity less than 18 MΩ cm^{-1}) produced by a Millipore Milli-Q system was used throughout the experimental work.

Standard solutions of arsenic compounds

A monomethylarsonate, MMAs(V), working stock solution was made by dissolving 389.3 mg of $Na_2AsO_3CH_3{\cdot}6H_2O$ to 1.0 L in deionized water (100.0 mg L^{-1} stock solution). A dimethylarsenate, DMAs(V), working stock solution was made by dissolving 184.0 mg of $HAsO_2(CH_3)_2$ to 1.0 L in deionized water (100.0 mg L^{-1} stock solution).

An As(III) stock solution (3750.0 mg L^{-1}) was prepared by dissolving 4.9460 g sodium arsenite ($NaAsO_2$) and 1.30 g NaOH to 1.0 L in deionized water, stored in an amber bottle at 4 °C. Under these conditions, this working stock solution was found to be stable for at least one year. An As(V) working stock solution was made by dissolving 4.1600 g $Na_2HAsO_4{\cdot}7H_2O$ to 1.0 L in deionized water (1000.0 mg L^{-1} stock solution), which was preserved with 0.50 % HNO_3.

Ion exchange and hybrid resins

The study of the separation and determination of arsenic species was performed by the use of two types of resins: SBAE and HY. SBAE resin is a strong base anionic exchange resin, Lewatit MonoPlus M500, Lanxess (Leverkusen, Germany), which is a gel-type resin based on a styrene–divinylbenzene copolymer with uniform, spherical (monodisperse), light yellow particles of 0.61 mm mean bead size. The HY resin is a hybrid macroporous monodisperse polystyrene-based resin, FO36, Lanxess with spherical, brown particles, mean bead size of 0.35 mm.[35] HY is a new hybrid resin developed for the removal of arsenic species based on two processes: ion exchange and adsorption.

Sorption procedures

Measurements of the resin capacities were performed by two methods, *i.e.*, the standard batch and fixed bed flow techniques. In a preliminary study, evaluation of separation process efficiencies with respect to several parameters, such as pH, contact time, mass of resin and arsenic concentration, was studied. The arsenic model solution was prepared in deionized water at a concentration ranging from 0.50 to 100.0 mg L^{-1} in the batch system and 0.50 to 5000.0 μg L^{-1} in the fixed bed flow system.

Sorption experiments was conducted in a batch system operating under the following condition: 100 ml of an arsenic model solution with 1.0 g of resin were placed in an Erlenmeyer flask and the mixture was shaken (ω = 150 rpm) using an orbital laboratory shaker (Rotamax 120, Heidolph Instruments, Kelheim, Germany) for different times up to 12 h at room temperature. The pH was varied from 3.00 to 12.00 by adjustment with 0.1 M HCl or 0.1 M NaOH.

In the fixed bed flow system, a column of diameter 2.00 cm and length 30 cm was employed. The flow rate, Q, mass of resins, m, and empty bed volume, EBV, were adjusted to obtain the optimal time of contact, τ, for the ion exchange/sorption. The conditions in the flow system were the following: Q = 1.66–2.00 mL min^{-1}, m_{resin} = 6.0–10 g, EBV = 11.0–12.5 mL, τ = 6.6–7.50 min.

Water samples

Water samples were collected from the domestic tap water and wastewater from drainage channels (Vojvodina region in Serbia). Modified water was prepared by addition of ions of interest, usually present in natural water, to study the influence of their appropriate concentrations on the separation and determination of arsenic species by the proposed method. All water samples were filtered through a 0.25 μm membrane filter and collected in polyethylene bottles; if it was necessary to store for a prolonged time, the samples were acidified with HNO_3 and stored at 4.0 °C.

RESULTS AND DISCUSSION

Preliminary investigations

The influence of pH on the separation of arsenic species was studied in the pH range from 3.00 to 12.00, and the results are given in Fig. 2. Separation of the iAs and oAs species both at a concentration of 100 mg L^{-1} was conducted using HY and SBAE resins in the batch system operating under the following condition: contact time τ = 60 min and shaker speed ω = 150 rpm at room temperature.

The resin capacity was calculated according to Eq. (1):

$$q = \frac{c_i - c_f}{m} V \quad (1)$$

where q is a sorption capacity in μg g^{-1}, c_i is initial arsenic concentration in mg L^{-1}, c_f is equilibrium arsenic concentration in μg L^{-1}, V is the volume of the model solution in L and m is the mass of resin in g. All capacities measurements were realized in triplicate.

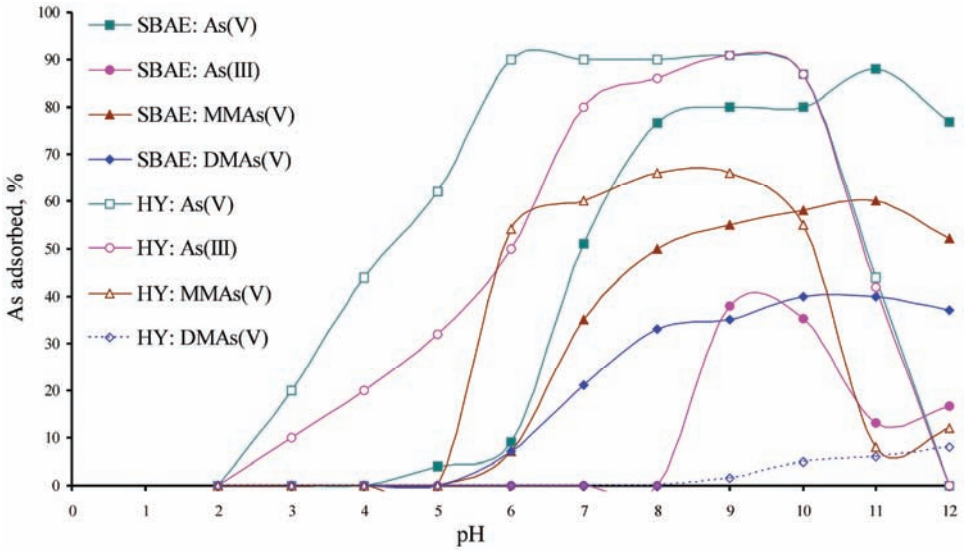

Fig. 2. Efficiency of arsenic adsorption on HY and SBAE resins *vs*. pH. Conditions: $c_{As(III)} = c_{As(V)} = c_{MMAs(V)} = c_{DMAs(V)} = 100.0$ mg L^{-1}, $m_{resin} = 1.00$ g, $t = 20$ °C, $V = 100$ mL, $\tau = 60$ min, $\omega = 150$ rpm.

The results presented in Fig. 2 show that the arsenic separation by the use of HY and SBAE resins was highly affected by the pH value. The adsorption of DMAs(V) on SBAE started at pH 5.00 and on HY resin at pH 8.00. DMAs(V) exists as neutral species at pH < 6.00 (Fig. 1), or even as cations in strongly acidic media, and thus deionized DMAs(V) showed low affinity with respect to both resins. Bonding capacities of SBAE with respect to MMAs(V), DMAs(V) and As(V) species increased starting from pH 5.00 and reached a maxima at pH 11.00. The mono- and divalent anions of MMAs(V) showed better adsorption capabilities on the SBAE resin in the pH range 7.00–12.00; a somewhat higher affinity of the divalent anion could be observed. As(III) did not bond on the SBAE resin at pH < 8.00 as it existed as neutral molecules, which is beneficial for As(III) determination in the SBAE resin effluent.[22]

Bonding capacities of the hydrated iron-oxide particles integrated into the HY resin with respect to iAs was beneficial at pH > 2.00. Adsorption of arsenic

species, except DMAs(V), increased from pH 2.00, small capacities changes could be observed in the pH range from 6.00 to 10.00, and subsequently, a rapid drop of the adsorption efficiency was observed. From this point of view, the HY resin could be used in the pH range from 6.00 to 8.00 for the separation and determination of DMAs(V), as well for the determination of the total iAs.[22]

The pH of the solution plays an important role in the control of arsenic species, which is beneficial for the arsenic separation; thus, by adjusting the pH to 7.00, SBAE resin could not retain the molecular form of As(III) while As(V) was bonded at the resin surface. Hence, the concentration of As(III) could be measured directly in the effluent from the SBAE resin. With this feature, the SBAE resin is a convenient material for the separation of iAs species.[22] However, the result of iAs and MMAs(V) separation from water using the HY resin suggest that HY is efficient for the mutual removal of molecular and ionic forms of iAs, as well MMAs(V) species. Thus, DMAs(V) could be measured directly in the effluent from the HY resin.

Determination of resins capacities in a fixed bed flow system

In order to develop a method for the separation and determination of DMAs(V), it was necessary to determine the capacity and the efficiency of SBAE and HY resins in a fixed bed flow system. Model solutions were prepared from deionized and from modified tap water at an arsenic concentration of 5000 μg L^{-1}, pH 7.00. These solutions were passed through a fixed bed column: m_{resin} = 6.0 g, Q = 1.66–2.0 mL min^{-1} and EBV = 12.5 mL. The breakthrough point was considered to be the point when the arsenic concentration in the effluent was equal to or higher than 10 μg L^{-1}, which is a good criterion for the determination of the resin capacity, as well for resin comparison. The results of the capacities determination for the HY resin are shown in Fig. 3.

The capacity of the HY resin in a fixed bed flow system for the samples prepared in deionized water was 4150 μg g^{-1} for As(III),[22] 3500 μg g^{-1} for As(V)[22] and 1500 μg g^{-1} for MMAs(V),[23] at pH 7.00. Analogous experiments conducted with modified tap water (Fig. 3b) gave slightly lower resin capacities: 3750 μg g^{-1} for As(III), 3330 μg g^{-1} for As(V) and 1466 μg g^{-1} for MMAs(V).

The high capacities provide a good area for research, especially for the separation and preconcentration of arsenic species in different water samples. The presented results indicate that at pH 7.00, DMAs(V) is not bonded by HY, while MMAs(V) show a significant affinity for the HY resin surface. Significant sorption capacities of MMAs(V) were observed in the pH range from 6.00 to 10.00, but at lower pH values, molecular forms become dominant which are less attracted by the positive resin surface. The low sorption capacity for DMAs(V) at pH > 8.00 could be due to steric interference of the two methyl groups and the resin surface groups, and such repulsive forces prevent entrance into the meso-

and micropores.[38] Arsenate adsorption by iron-oxide involves a ligand exchange reaction with surface hydroxyl groups, which results in different surface complexes, *e.g.*, monodentate *vs*. bidentate, mononuclear *vs*. binuclear. Arsenite adsorbs *via* a ligand exchange reaction as well forming mono- and binuclear complexes. At higher surface coverage, bidentate binuclear complex formation is a preferential type of binding, which could be a reason of the low affinity of DMAs(V) toward the HY resin surface.[39,40] The use of HY resin provides the possibility for quantitative separation of DMAs(V) without any interference of other arsenic species present in the sample subjected to analysis.

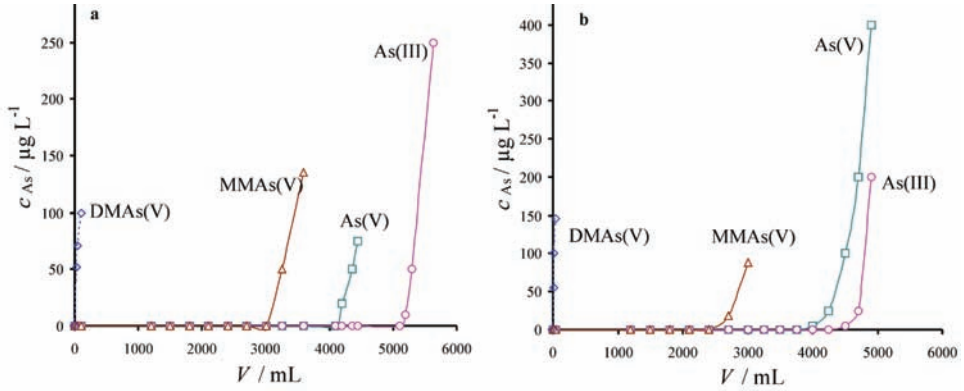

Fig. 3. Breakthrough curves for iAs and oAs species on the HY resin: a) deionized water and b) modified tap water. Conditions: $c_{As(III)} = c_{As(V)} = c_{MMAs(V)} = c_{DMAs(V)} = 5000$ µg L^{-1}, pH 7.00, $m_{resin} = 6.0$ g, $Q = 1.66$ mL min^{-1}, $EBV = 12.5$ mL.

Established procedures

A simple and efficient method for the separation and determination of DMAs(V) was developed in preliminary tests and applied to the standard As solution and drinking water samples. The laboratory column was filled with 6.0 g of HY resin and rinsed with 100 ml of deionized water. The water sampling was performed according to a literature procedure[41] without adding any substances as stabilizers. Before the sorption experiments, the pH of the water sample (100 ml) was pH-adjusted and passed through the separation column at a flow rate of 1.66 mL min^{-1}. Five portions (20.0 mL) of effluent were taken, and each fraction was adjusted to the appropriate pH with 5 % HNO_3 before injection into the ICP–MS instrument.

Application of the proposed method to the standard As solution

For the validation of the proposed method for water analyses, six samples of deionized water were spiked with different iAs and oAs concentrations to check the efficacy of DMAs(V) separation and determination. The testing was based on

the use of standard samples with the addition of iAs and oAs in the concentration range 5–100 μg L^{-1} to approach the concentration of arsenic in natural water. The results of samples analysis prepared in deionized water with the addition of different concentrations of DMAs(V), MMAs(V), As(V) and As(III), are given in Table I.

TABLE I. Analytical data of the separation and determination of DMAs(V) species in standard solutions containing MMAs(V), As(V) and As(III) using the HY resins (σ – standard deviation)

Standard solution	As content, standard addition, μg L^{-1}				Measured, μg L^{-1}	Recovery, %
	DMAs(V)	MMAs(V)	As(V)	As(III)	DMAs(V) average value ± σ	DMAs(V)
1	5.00	5.00	5.00	5.00	4.75±0.06	95.0
2	20.00	40.00	100.0	50.00	18.80±0.22	94.0
3	20.00	50.00	50.00	50.00	21.80±1.60	109.0

Good recoveries of 95.0, 94.0 and 109.0 % were obtained and the *RSD* values were 1.1, 7.50 and 7.50 % for standard solutions 1, 2 and 3, respectively.

The results of analysis of standard samples prepared in deionized water containing different concentrations of DMAs(V) and MMAs(V) are given in Table II.

Good recoveries were found in the samples at DMAs(V) concentrations of 10, 50 and 100 μg L^{-1}, while the *RSD* values were 2.6, 4.6 and 2.4 %, respectively.

TABLE II. Analytical data of the separation and determination of DMAs(V) species in standard solutions containing MMAs(V) using the HY resin (σ – standard deviation)

Standard solution	As content, standard addition, μg L^{-1}		Measured, μg L^{-1}	Recovery, %
	DMAs(V)	MMAs(V)	DMAs(V) average value ± σ	DMAs(V)
4	10.00	10.00	9.00±0.17	90.0
5	50.00	50.00	52.70±2.50	104.5
6	100.0	100.0	104.8±2.50	104.8

Application of proposed method to drinking water samples

The proposed method has been applied to drinking water samples in order to separate and determine DMAs(V). In Table III are presented results of DMAs(V) separation and determination in drinking water samples spiked with different concentrations of arsenic species. The standard addition method is useful because some unknown variations of the matrix can be prevented and this was suggested in some studies.[41,42] Because no water samples with known concentrations of various arsenic species were available the accuracy of the analytical results was evaluated by recovery studies.

The recovery and reproducibility of tap water samples 1–3 and modified water were good, with *RSD* values of 2.9, 7.00, 2.8 and 5.4 %, respectively.

TABLE III. Analytical data of the separation and determination of DMAs(V) species in tap water containing MMAs(V), As(V) and As(III) using the HY resin (σ – standard deviation)

Sample tap water	As content standard addition, μg L^{-1}				Measured, μg L^{-1}	Recovery, %
	DMAs(V)	MMAs(V)	As(V)	As(III)	DMAs(V) average value ± σ	DMAs(V)
1	5.00	5.00	5.00	5.00	4.50	91.0
2	10.00	50.00	100.0	50.00	8.80±0.20	88.00
3	50.00	50.00	100.0	50.00	48.10±1.00	96.2
Modified	50.00	50.00	100.0	50.00	53.30±2.80	106.6

Analytical figure of merit and application

The analytical validity of the proposed method and of the ICP–MS measurements were determined and tested by analyzing fresh water and river water certified reference materials for trace metals NIST 1643e and NRC SLRS4, of certified As concentrations of 60.45±0.72 and 0.68±0.06 μg L^{-1}, respectively. The obtained results were 61.7±0.94 and 0.66±0.05 μg L^{-1} total As. The standard reference materials were spiked with 10 and 25 μg L^{-1} of DMAs(V) in order to check the validity of the proposed method with a known standard concentration of iAs. The results of the DMAs(V) determinations are presented in Table IV.

TABLE IV. Analytical data of the proposed separation procedure using HY resin for the determination of DMAs(V) species in the standard reference material NIST 1643e

Standard solution	As content standard addition μg L^{-1}		Measured μg L^{-1}	Measured μg L^{-1}	Recovery %
	DMAs(V)	iAs	iAs average value ± σ	DMAs(V) average value ± σ	DMAs(V)
1	10.00	61.70	61.50±0.82	9.60±0.20	96.0
2	25.00	61.70	60.80±0.76	24.40±1.50	97.6

The accuracy of the proposed method was additionally proved by analyzing five samples of wastewater from drainage channels taken from the region of Vojvodina. Only in one sample, collected in the region of the city Zrenjanin, was DMAs(V) detected, at a level of 1.2 μg L^{-1}, and total iAs of 22 μg L^{-1}. Separation and determination of As(V) and As(III) species was achieved on SBAE and ICP–MS measurements gave 21.6±0.98 μg L^{-1} of As(V) without detection of As(III). The wastewater sample was spiked with 10 μg L^{-1} of DMAs(V) and subjected to separation and determination of DMAs(V). The obtained result, 10.9±0.84 μg L^{-1}, gave unambiguous proof of the validity of proposed method for the separation and determination of DMAs(V).

The analytic characteristics of the proposed method are given in Table V, and the experimental limit of detection was equal to the method detection limit (*MDL*), 0.03 μg L^{-1} for iAs and oAs. The achieved sensitivity is adequate for arsenic determination in non-polluted water samples.

TABLE V. Analytical characteristics of the proposed method; linear analytical range, 0.03–20 μg L^{-1}; method detection limit (*MDL*), 0.03 μg L^{-1}; *A*: absorbance; [As] expressed as μg L^{-1}; *R* – correlation coefficient

Characteristic	iAs (total iAs)	oAs (total oAs)
Calibration	$A = 1.016\times10^4$[iAs] + 4.671×10^2 $R = 0.9999$	$A = 1.022\times10^4$[oAs] + 4.785×10^2 $R = 0.9996$

Interference of inorganic ions

The ions commonly present in tap water: chloride, sulfate, fluoride and nitrate, could potentially interfere in the proposed analytical method. The separation and determination of DMAs(V) in the presence of ions naturally present in drinking water was investigated using drinking water samples spiked by the gradual addition of the appropriate anion (Cl^-, SO_4^{2-}, F^- and NO_3^-) in a concentration ranging from 10 to 100 mg L^{-1}. The interference of the ions was studied using a 10 μg L^{-1} solution of DMAs(V) at pH 7.00, in order to determine the level of noticeable signal depression (Table VI). The presence of interference ions showed negligible effects on the reproducibility of the DMAs(V) determination providing the total dissolved salts (*TDS*) were less than 450 mg L^{-1}. All samples were tested by ICP–MS measurements.

TABLE VI. Concentration of interfering ions (mg L^{-1}) in tap water samples that cause noticeable signal depression when using ICP–MS

Sample	*TDS*	Cl^-	SO_4^{2-}	F^-	NO_3^-	DMAs(V), μg L^{-1}
Modified tap water	450	52.2	53.0	0.2	3.2	9.5

The interferences of chloride and sulfate ions could be tolerated up to a concentration of 50 mg L^{-1}. A severe problem associated with the determination of As by ICP–MS arises from the interference of chloride, which create polyatomic species observed at m/z = 75. The chloride present in the sample reacts with the working gas, resulting in the formation of $^{40}Ar^{35}Cl^+$ (m/z = 75), the signal of which could interfere with those of the As species, leading to inaccurate results. The determination of arsenic in the presence of chloride was accomplished according to a procedure suggested in the literature.[43] Significant depression of the signal were observed for fluoride and nitrate anions at level of 0.2 and 3.2 mg L^{-1}, respectively. These results could not have a large influence on the method as fluoride and nitrate in drinking water are present at lower concentrations than the detection limit.

Hitherto, the developed methods for the determination of the total concentration of arsenic in natural waters (level of 1 μg L^{-1} or less) can be achieved only by sophisticated analytical techniques for separation and measurement, such as ICP–MS and graphite furnace atomic absorption spectrometry (GF–AAS). For the measurements of iAs species, the HG–AAS[15–18] and hydride generation ato-

mic fluorescence spectrometry (HG–AFS)[44] techniques were successfully employed. However, coupled analytical techniques are the most convenient for the selective and sensitive determination of arsenic species with essentially uniform qualitative and quantitative responses. In many works, nowadays, arsenic species are determined by ICP–MS coupled with various chromatographic methods: IC,[20] HPLC,[24–27,29] or more complex system: performing pre-column[28] or post-column[29] arsenic species derivatization. In contrast to such highly sophisticated and expensive methods, the proposed procedure is cheap, simple, precise and time efficient. The separation procedure of arsenic species was highly efficient and with low interference of the ions, commonly found in water. The method could be applied routinely for monitoring the arsenic level in the various types of water samples (drinking water, ground water and wastewater).

The significance of the presented method lies in the fact that arsenic toxicity, its bioavailability and transport mechanisms highly depend on the chemical form in which it appears. The methylated arsenic species are significantly less toxic than arsenite and arsenate and thus, the determination of arsenic speciation in specific samples is of utmost significance for the consideration of the overall toxicity, which cannot be based only on total arsenic determination. Thus, the developed method represents a great improvement compared with direct ICP–MS measurements, which usually gives data of the total arsenic concentration. This method can be recommended for speciation analysis when appropriate equipment for highly sophisticated coupled techniques is not available. The proposed procedure can be adapted for on-site collection or separation of As(III), As(V) and DMAs(V) where oAs could possible be found, such as in nature where biomethylation is caused by the activity of microorganisms,[45] or as the result of the use of arsenic-based pesticides.[46]

CONCLUSIONS

Studies and research on the separation and determination of arsenic species are of crucial importance for a complete understanding of the properties of elements and for the monitoring and management of natural water pollution, as well for the design of appropriate purification technologies. Two types of resins, SBAE and HY were tested. The adsorption of iAs and MMAs(V) species onto a HY resin was accomplished by adjusting the pH value of the water sample to 7.00, thus providing DMAs(V) separation and determination. The separation and pre-concentration procedures functioned well with the ICP–MS technique for the sensitive determination of DMAs(V) and iAs at low concentrations. Measurements with certified reference materials of known iAs value and spiked with different DMAs(V) concentrations proved the validity and accuracy of the applied method. Detection limit was 0.03 μg L^{-1} and relative standard deviation (*RSD*) of all the investigated arsenic species was between 1.1–7.50 %.

The separation test showed that the resin HY could be used for separation and determination of the concentration of DMAs(V) in arsenic standard solution prepared in the laboratory and in drinking water samples spiked with different concentrations of oAs and iAs. Therefore, the obtained results related to the separation and determination of DMAs(V) indicates that the proposed method is accurate, sensitive and time saving.

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И З В О Д

РАЗДВАЈАЊЕ И ОДРЕЂИВАЊЕ ДИМЕТИЛАРСЕНАТА У ПРИРОДНИМ ВОДАМА

NURREDIN BEN ISSA, АЛЕКСАНДАР Д. МАРИНКОВИЋ и ЉУБИНКА В. РАЈАКОВИЋ

Технолошко–металуршки факултет, Универзитет у Београду, Карнегијева 4, 11120 Београд

У раду је приказан једноставан и ефикасан метод за раздвајање и одређивање диметиларсената, DMAs(V). За издвајања DMAs(V) коришћена је хибридна смола модификована гвожђе-оксидом (HY). За одређивање концентрација арсена примењена је метода масене спектрометрије са индуковано спрегнутом плазмом (ICP–MS). Квантитативно одвајање DMAs(V) од свих врста арсена присутних у природним водам остварено је применом HY смоле уз контролу pH вредности. При pH вредности воде од 7,00 све врсте арсена у води се квантитативно везују за HY смолу изузев DMAs(V). Капацитет HY смоле је израчунат на основу одређивања тачке пробоја у проточном систему, HY смола веже више од 4150 μg g^{-1} As(III), 3500 μg g^{-1} As(V) и 1500 μg g^{-1} MMAs(V). Капацитет смоле је висок и постојан и у присуству јона који су природни састојци воде. У ефлуенту је одређена концентрација DMAs(V) применом ICP–MS. Предложени метод је успостављен и потврђен применом стандардних аналитичких поступака, анализом сертификованог референтног материјала и анализом узорака уз примену спољашњег стандарда и стандардног додатка. Граница одређивања била је 0,03 μg L^{-1}, а релативна стандардна девијација (*RSD*) у опсегу између 1,1–7,50 %.

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