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SUPPLEMENTARY MATERIAL TO

Analytical methods for arsenic speciation analysis

LJUBINKA V. RAJAKOVIĆ[1]*, ŽAKLINA N. TODOROVIĆ[2], VLADANA N. RAJAKOVIĆ-OGNJANOVIĆ[3] and ANTONIJE E. ONJIA[2]

[1]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia, [2]Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, 11001 Belgrade, Serbia and [3]Faculty of Civil Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, Belgrade, Serbia

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TABLE S-I. Some review articles from 2003 to 2011 dealing with aspects of arsenic speciations relevant and complementary to this review (for the reference number refer to the Reference list in the paper)

Title of the review	Comments	Ref.
Determination of arsenic species: A critical review of methods and applications, 2000–2003	A detailed review of more than 400 published papers on the speciation of arsenic in the period from 2000–2003. Different methods of extraction and stability of arsenic species and advances in separation and detection techniques are analysed.	14
Arsenic and its speciation analysis using HPLC and ICP-MS	Applications and work using only HPLC and ICP-MS for arsenic speciation of environmental and biological samples are presented in this review.	17
Analytical methods for inorganic arsenic in water	Reports an overview of more than 100 papers, regarding existing methods for analysis of As(III) and As(V) in water, including various spectroscopic, ICP and electrochemical techniques. Recent field portable analytical applications are also reviewed.	18
Analysis and speciation of arsenic by stripping potentiometry	Summarized several examples of the literature from 1980 to 2003, to illustrate the applications of stripping potentiometry for the determination and speciation of arsenic in several samples.	19
Isotope dilution analysis for elemental speciation	Describes the application of isotope dilution analysis to quantitative elemental speciation.	20
Current perspectives in analyte extraction strategies for tin and arsenic speciation	Summarises different extraction techniques for arsenic and tin speciation as one of the most important error sources in modern analytical methods.	26

* Corresponding author. E-mail: ljubinka@tmf.bg.ac.rs

TABLE S-I. Continued

Title of the review	Comments	Ref.
Effect of thermal treatments on the contents of arsenic species in food	This article summarizes and discusses the published papers on the effect of thermal treatment used in the cooking or processing of food, including sterilization and preservation stages, on total arsenic and arsenic species content. It also reviews possible transformations of arsenic species.	27
Speciation and surface structure of inorganic arsenic in solid phases	The objective of this paper was to examine advancement in the speciation and surface structure identification of inorganic arsenic species in solid phases. An analysis of related methodological, analytical and surface structure modelling aspects is made.	28
A review of non-chromatographic methods for speciation analysis	Describes the relevant scientific literature concerning speciation of trace elements using non-chromatographic methods.	16
Aquatic arsenic: Toxicity, speciation, transformations, and remediation	Describes the toxicity, speciation and biogeochemistry of arsenic in aquatic environmental systems.	29
Voltammetric methods for determination and speciation ofinorganic arsenic in the environment	Reports recent work on the separation and detection of arsenic compounds using voltammetric methods.	30
HPLC coupled to AFS for the speciation of the hydride and chemical vapour-forming elements As, Se, Sb and Hg	The review focuses on sample preparation, post-column treatments and on the applications of HPLC hyphenated to hydride generation or chemical vapour generation and atomic fluorescence spectrometry (HG/CVG-AFS) to various liquid and solid samples for the determination and speciation of the selected hydride-forming elements As, Se and Sb and the chemical vapour-forming metal Hg.	31
Analytical methods for the determination of arsenosugars – A review of recent trends and developments	Describes the typical experimental approaches for sample pre-treatment, extraction, separation and detection.	32
Environmental application of elemental speciation analysis based on HPLC or GC hyphenated to ICP-MS	This review summarizes developments in environmental applications of elemental speciation analysis using ICP-MS coupled with HPLC and GC.	33
Preservation of inorganic arsenic species in environ-mental water samples for reliable speciation analysis	Describes stability of inorganic arsenic species in water samples as a key item in the speciation analysis.	34
Sample pre-treatment and extraction methods that are crucial to arsenic speciation in algae and aquatic plants	Using information covering the period since 2000, summarized and discussed sample handling, cleaning, drying and powdering of fresh samples and the later extraction of As species.	35

TABLE S-I. Continued

Title of the review	Comments	Ref.
As speciation in biomedical sciences: Recent advances and applications	Deals with recent advances and applications of methods for arsenic speciation in biomedical sciences, with emphasis on the specimens commonly encountered in biomedical laboratories.	36
As, Hg, I, Sb, Se and Sn speciation in body fluids and biological tissues using hyphenated-ICP-MS techniques	Focuses on different technique for speciation of As, Hg, I, Sb, Se and Sn in biological tissues. The focus is on ICP-MS as a powerful analytical tool for elemental speciation analysis.	37
As speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry	Overview of analytical methods, pre-concentration and separation techniques using hydride generation and electrothermal atomic absorption spectrometry for the determination of inorganic As and organoarsenic species in environmental samples.	38
As and its speciation in water samples by HPLC and ICP-MS	Covers last decade research in speciations of arsenic compounds in water samples by high performance liquid chromatography inductively coupled plasma mass spectrometry.	1

TABLE S-II. Sample preparation methods, separation and detection for arsenic species in different matrices; LC/ESI-MS/MS – liquid chromatography/electrospray ionisation tandem mass spectrometry; DRC – dynamic reaction cell; CE/UV – capillary electrophoresis/ultraviolet detector (for the reference number refer to the Reference list in the paper)

Matrix	Species	Sample pre-treatment	Separation/detection technique	Analytical features	Ref.
Whole blood and urine	As(III), As(V), MMA, DMA, AB	Dilution with $HgCl_2$ and ultrafiltration	LC/ICP-MS	*LoD* / μg L^{-1}: <0.3	47
Urine	As(III), As(V), MMA, DMA	Dilution with deionised water and filtration	IC/ICP-MS	*LoD* / μg L^{-1}: 0.11 As(III), 0.25 As(V), 0.18 MMA, 0.17 DMA, 0.75 AB; Repeatability, %: 1.9 As(III), 2.7 As(V), 2.1 MMA, 1.9 DMA, 2.8 AB	48
Urine	As(III), As(V), MMA, DMA, AB	Dilution with deionised water and filtration	HPLC/ICP-MS	Recovery: 85 to 100 %	49
Urine	As(III), As(V), MMA, DMA, TMAO	Dilution with mobile phase and filtration	HPLC/HG-AAS	From 1.1 μg L^{-1} for TMAO to 2.6 μg L^{-1} for As(V)	50

TABLE S-II. Continued

Matrix	Species	Sample pre-treatment	Separation/detection technique	Analytical features	Ref.
Urine	As(III), As(V), MMA, DMA	Dilution HCl and L-cysteine	HPLC/electro-thermal -AAS	*LoD* / μg L^{-1}: 0.038	51
Urine	As(III), As(V), MMA, DMA	Dilution with deionised water and filtration	HPLC/HG-ICP-MS	*LoD* / μg L^{-1}: 0.37 As(III), 0.22 As(V), 0.18 MMA, 0.17 DMA; Precision, %: 4.1 As(III), 5.4 As(V), 6.0 MMA, 6.6 DMA	52
Whole blood	MMA, DMA	Centrifuge	CE/ICP-MS	*LoD* / μg L^{-1}: 1; *LoQ* / μg L^{-1}: 0.8 As(III), 1.0 As(V), 1.0 MMA, 0.9 DMA	53
Fish and oyster tissues	As(III), As(V), MMA, DMA	Lyophilisation / microwave digestion	CE/ICP-MS	–	54
Fish	As(III), As(V), MMA, DMA	Ultrasonic extraction and 4 different experimental conditions	HG-AFS	*LoD* / μg kg^{-1}:0.62 As(III), 2.1 As(V), 1.8 MMA, 5.4 DMA; *RSD*: 6.8 % As(III), 10.3 % As(V), 8.5 % MMA, 7.4 % DMA; Recovery > 93%	55
Fish sauce	AB, AC, TMAO	Extraction with water/ /methanol (1+1,v/v)/ /shaking/cen-trifugation	HPLC/ICP-MS	*LoD* / mg kg^{-1}: 0.01	56
Beverages (soft drinks, lemon juice, beer)	As(III), As(V), MMA, DMA	Sample were passed through a C18 sep-pack and filtered	HPLC/ICP-MS	*LoD* / mg kg^{-1}:0.2, 0.2, 0.3 and 0.5 for As(III), DMA, MMA and As(V), respectively; *RSD* of As(III), DMA, MMA and As(V) were 1.2, 2.1, 2.5 and 3.0 %, respectively	57
Cereals	As(III), As(V), MMA, DMA	Ultrasonic extraction with H_3PO_4 and Triton XT-114	HG-AFS	*LoD* /mg kg^{-1}: 1.3, 0.9, 1.5 and 0.6 for As(III), As(V), DMA and MMA, respectively; Recoveries: > 90 %; Repeatability, %: As(III), 3; DMA, 5; As(V) and MMA, 6	58

TABLE S-II. Continued

Matrix	Species	Sample pre-treatment	Separation/detection technique	Analytical features	Ref.
Wines	As(III), As(V), MMA, DMA	Treatment with cysteine in HCl for total As; dilution with citrate buffer or acetic acid for As species	HG-AFS	*LoD* / μg L^{-1}: 0.12, 0.27, 0.15 and 0.13 (as As); *RSD* / %: 2–6, 5–9, 3–7 and 2–5 for As(III), As(V), MMA and DMA, respectively	59
Vegetables	As(III), As(V), MMA, DMA	Ultrasonic extraction with H_3PO_4 and Triton XT-114	HG-AFS	*LoD* / mg kg^{-1}: 3.1 As(III), 3.0 As(V), 1.5 DMA, 1.9 MMA; Recovery / %: > 91%	60
Milk	As(III), As(V)	Ultrasonic extraction with/without KI	HG-AFS	*LoD* / mg L^{-1}: 8.1 and 10.3 for As(III) and As(V); *RSD* / %: 5.7 and 5.5 for As(III) and As(V)	61
Water	As(III), As(V), MMA, DMA	Pre-treatment with KI and HCl or acetic acid or tartaric acid	HG-AAS	–	62
Water	As(III), As(V), DMA	Treatment with cysteine, KI, urea or acids	HG-AAS, CE/UV, LC/ICP-MS	*LoD* / mg L^{-1}: 0.10 As(III), As(V), 0.19 (DMA) for HG-AAS, 100 (As(III), DMA) to 500 (As(V)) for CE/UV and 0.1 (DMA, MMA) to 0.2 (As(III), As(V)) for LC/ICP-MS; Precision (*RSD* / %): < 5; Recovery, %: 80–110 except CE/UV only 50	4
Water and urine sample	Inorganic, organic As	Treatment with/without cysteine	HG-ICP-MS	*LoD* / ng L^{-1}: 6	63
Water and reference materials	As(III), As(V)	Treatment with HCl and $NaBH_4$	HG-AAS	*LoD* / μg L^{-1}: 0.1 for As(III) and 0.06 for total As. Precision (*RSD* / %) is 2.9 for As(III) and 3.1 for total As	64

TABLE S-II. Continued

Matrix	Species	Sample pre-treatment	Separation/detection technique	Analytical features	Ref.
Water	As(III), As(V)	None	HG-AAS	*LoD* / μg L^{-1}: 0.019 total As, 0.031 As(III)	65
Water	As(III), As(V)	Reaction with cysteine, $NaBH_4$	HG-AAS	*LoD* / μg L^{-1}: 0.1	66
Water	As(III), As(V)	Reaction with cysteine	HG-ETAAS	–	67
Water	As(III), As(V)	None	HG-AFS	–	68
Water	As(III), As(V)	pH adjustment	HG-AAS	*LoD* / μg L^{-1}: 0.07–0.4 As(V) and 0.1–0.5 As(III + V); Recovery, %: 90–102	69
Water	As(III), As(V)	Treatment with $KMnO_4$	ICP-AES	*LoD* / μg L^{-1}: 0.1–0.6	9
Water	As(III), As(V), MMA, DMA	None	HPLC/ICP-MS	*LoD* / μg L^{-1}: 0.33 As(III), 0.69 As(V); *LoQ* / μg L^{-1}: 50	70
Water	Inorganic As	Pre-reduction of As(V) with cysteine	HG-AAS	*LoD* / μg L^{-1}: 0.15; *LoQ* / μg L^{-1}: 0.5; *RSD* (n = 10): <8 %	71
Seawater	As(III)	Complexation with pyrrolidine dithiocarbamate	ET-AAS	*LoD* / μg L^{-1}: 0.008; *RSD* (n = 11): 4.5 %	72
Water	As(III), As(V), MMA, DMA	None	HG-ICP-AES	Recovery, %: As(V) 97.6, As(III) 100, MMA 99.8, DMA 99.9	73
Water	As(III), As(V)	Treatment with $KMnO_4$	ET-AAS	*LoD* / μg L^{-1}: 0.35; Recovery, %: 93.5––106.4; *RSD* / %: 3–7	74
Water	As(III), As(V), MMA, DMA, AB	None	HPLC/ICP-MS	*LoD* / μg L^{-1}: 0.017 As(III), 0.026 As(V), 0.026 MMA, 0.023 DMA, 0.024 AB; *LoQ* / μg L^{-1}:0.056 As(III), 0.085 As(V), 0.088 MMA, 0.076 DMA, 0.080 AB	3
Ground-water	As(III), As(V), MMA, TMAO, PAA and PAO	None	HPLC/ICP-MS	*LoQ* / μg L^{-1}: 0.2- 0.8	9

TABLE S-II. Continued

Matrix	Species	Sample pre-treatment	Separation/detection technique	Analytical features	Ref.
Groundwater	As(III), As(V), PAA, diphenylarsinic acid (DPAA) and PAO	None	HPLC/ICP-MS	–	75
Groundwater	As(III), As(V)	None	HPLC/HG-AAS	*LoD* / μg L^{-1}: 7.8 As(III), 12.0 As(V); Precision (*RSD* / %): 10.5 As(III), 12.1 As(V)	76
Hot spring water	As(III), As(V), MMA, DMA, TMAO, TMA, AC and AB	None	HPLC/ICP-MS	*LoD* (μg L^{-1}): 0.2; *RSD* / % (n = 6): < 2	77
Human hair	As(III), As(V)	Reduction of As(V) to As(III)	HG-AAS	*LoD* / μg L^{-1}: 0.2 As(III), 0.5 As(V); *RSD* / %: 2.1 As(III), 2.5 As(V)	78
Sediment and fly ash	Water soluble and phosphate-exchange-able As(III) and As(V)	Extraction with water and phosphate buffer	HG-AAS	*LoD* / μg L^{-1}:0.06-0.10; *LoQ* / μg L^{-1}: 0.20–0.31. Repeatability expressed as *RSD*: <1 %	79
Landfill leachate	As(III), As(V), MMA, DMA, TMAO, AB	Filtration	HPLC/ICP-MS	*LoD* / ng L^{-1} between 11 for DMA to 27 for As(V). *LoQ* / ng L^{-1} between 36 and 90	80
Municipal landfill leachates	As(III), As(V), MMA and DMA	Filtration	LC/ESI-MS/MS and HPLC/DRC–ICP-MS	Recovery, %: 68–94	81
Soil	Total As	Extraction with HNO_3, acetic acid, EDTA and Mehlich III	HG-AAS	–	82

TABLE S-III. The most important analytical performance parameters in arsenic speciation analysis (for the reference number refer to the Reference list in the paper)

Author(s)	Title	*LOD*/*DL* Method	Ref.
Sakai and Wilbur, 2006	Routine Analysis of Toxic Arsenic Species in Urine Using HPLC with ICP-MS	Detection limits (*DL*) for each arsenic species were calculated as three times the chromatographic peak-to-peak signal to noise. All species met the goal of ≈0.1 μg L^{-1}, *RSD* ranged from 1.3 to 2.8 % and recoveries from 93 to 101 %	84
K. Ito *et al*., 2010	Determination of Five Arsenic Species in Whole Blood by LC Coupled with ICP-MS	The method *LoD* < 0.3 μg L^{-1} for each arsenic species, range from 2 to 200 μg L^{-1} for urine, and 2 to 12 μg L^{-1} for blood. Method detection limits (*MDL*) were estimated from concentrations at which the peak intensities were 3 standard deviation (*SD)* of the blank background signal for each of the five arsenic species, *LOQ* as 1 mg L^{-1} based on 10 *SD*. Recovery > 80 %.	47
Xie *et. al*., 2006	Arsenic Speciation Analysis of Human Urine Using Ion Exchange Chromatography Coupled to ICP-MS	For this study, the detection limits of speciation were defined as three times the standard deviation of seven replicate measurements of a standard solution with the lowest concentration of species whose peaks could be distinguished from the baseline in the speciation chromatogram. Obtained values (μg L^{-1}) were: 0.11 As(III), 0.25 As(V), 0.18 MMA, 0.17 DMA, 0.75 AB, repeatability <5 %.	48
Heitland and Köster, 2008	Fast Determination of Arsenic Species and Total Arsenic in Urine by HPLC–ICP-MS: Concentration Ranges for Unexposed German Inhabitants and Clinical Case Studies	*LOQ* (0.1 μg L^{-1}) were defined as the analyte concentration corresponding to 10 times the *SD* of 5 measurements of a spiked sample. This sample was urine. Recoveries estimated from the standard reference materials (SRM) only for total As and *RSD* of the average concentrations were in the range 6.3–8.7 %.	85
Hirata *et al*., 2006	Determination of Arsenic Species in Marine Samples by HPLC–ICP-MS	*DL* were calculated based on 3 *SD* of baseline noise at the peaks retention time (*n*=9). The *DL* ranged from 0.02 to 0.10 μg L^{-1}. The precision (*RSD*) were 3.1–7.3 % for all eight species.	86

TABLE S-III. Continued

Author(s)	Title	*LOD*/*DL* Method	Ref.
Ronkart *et al*., 2007	Speciation of Five Arsenic Species (Arsenite, Arsenate, MMA, DMA and AB) in Different Kinds of Water by HPLC–ICP-MS	*LoD* and *LoQ* were evaluated by analysing ten samples containing an arsenical concentration close to the expected *LoD* and *LoQ* under repeatability conditions and using Eqs. (below), where *y* signal is the medium value and *S* signal is the standard deviation. $LoD = y_{signal} + 5S_{signal}$ (1) $LoQ = y_{signal} + 10S_{signal}$ (2) *LoQ* values were confirmed by analysing ten replicates of a solution containing all arsenic species at the *LoQ*. Variation coefficient of 9.87, 8.38, 8.33, 12.3 and 8.84 % were obtained for respectively AB, DMA, As(III), MMA and As(V). Recoveries were calculated through analysis of three spiked real samples and ranging from 95–108 %.	3
A. H. E. Petursdottir, 2010	Determination of Toxic and Non-Toxic Arsenic Species in Icelandic Fish Meal	*LoD* was taken to be three times the noise (3σ) and the *LoQ* was evaluated as the area of the smallest standard analysed and was 0.04 mg kg^{-1}. Recovery ranged from 82–111 %.	87
Komorowicz and Barałkiewicz, 2011	Arsenic and Its Speciation in Water Samples by High Performance Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry – Last Decade Review	*DL* was mainly calculated as three times the *SD* of the background signal or replicate analyses of spiked deionised water samples. *RSD* values did not exceed 20 % and the recoveries were between 80 and 120 % in all reviewed water samples.	1
Sathrugnan and Hirata, 2004	Determination of Inorganic Oxyanions of As and Se by HPLC–ICP-MS	*DL* was calculated based on 3σ of the blank intensities at respective retention time and were less than 80 and 0.77 g L^{-1} for As and Se, respectively. The standard addition in the order of 6 *s* (*LoQ*) into sample extracts produced significant peaks from baseline. The *RSD* of the proposed method for As was less than 4.8 % and recovery were in the range of 98–102 %	88
Ponthieu *et al*., 2007	Speciation Analysis of Arsenic in Landfill Leachate	Detection limits were calculated for the HPLC–ICP-MS system using the IUPAC (International Union of Pure and Applied Chemistry) definition as three times the *SD* of noise level. Relative detection limits varied between 11 ng L^{-1} for DMA to 27 ng L^{-1} for As(V). The *LoQ* ranged between 36 and 90 ng L^{-1}	80

TABLE S-III. Continued

Author(s)	Title	*LOD*/*DL* Method	Ref.
Rajaković *et al*., 2012	Review: The Approaches for Estimation of Limit of Detection for ICP-MS Trace Analysis of Arsenic	Detection limits were reviewed and calculated for the ICP-MS system using different approaches: – *LoD* values calculated according to the traditional approaches (Currie, IUPAC, US EPA 200.8), $n = 26$ – *LoD* values calculated according to the prediction interval approaches (Hubaux–Vos, ISO), $n = 8$ The most appropriate values were obtained according to Currie's variation of the traditional method; the critical value was 0.011 mg L^{-1} and the *LoD* was 0.022 mg L^{-1}.	83