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Application of the Liquid-Liquid Extraction Method and Subsequent ICP-MS Detection for Speciation Analysis of Arsenic in Wastewater Samples

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ABSTRACT

The current paper describes a method for determining As(III) and As(V) concentrations in wastewater samples. The approach is based on the extraction of As(III) from water samples using a non-polar organic solvent in a 10-12 M HCl medium. The extract contains As(III), while the raffinate contains As(V). Distilled water can be used to re-extract As(III) from the organic solvent. ICP-MS was used to analyze As concentrations in the reextract and the raffinate. The average recovery of arsenic by the proposed method is 99.6 %. It was calculated as the sum of As(III) and As(V) concentrations. The collected data demonstrated high repeatability. The standard addition procedure demonstrated the selectivity and accuracy of the employed method. The relative error of recovery of the standard As(III) addition is about 2 %, which is similar to the RSD found under repeatability conditions.

Keywords: *liquid-liquid extraction, As(III), As(V), speciation analysis, ICP-MS.*

INTRODUCTION

Arsenic appears in both organic and inorganic forms in water, with the inorganic forms being more dangerous. Arsenic's toxic behavior in water is a hot topic throughout the world. Its distribution in the earth's crust is limited to 1.5 - 2 ppm [1]. The major sources of arsenic in nature are the minerals arsenopyrite (FeAsS), enargite (Cu_3AsS_4), and realgar (As_4S_4), from which arsenic naturally transfers into natural waterways.

Dissolved oxygen is low in groundwater, and arsenic is present in its arsenite form - AsO_3^{3-}. Surface water contains an abundance of dissolved oxygen, which oxidizes arsenic in its arsenate form - AsO_4^{3-}. Arsenite arsenic is many times more poisonous than arsenate arsenic [2]. The mining and metallurgical industries are primary sources of arsenic, as it is typical by-product or waste product [3]. Controlling water quality after treatment has become more important as industry has grown, thanks to national and international standards. The number of articles on arsenic wastewater treatment and the importance of arsenic forms in wastewater has increased dramatically in recent years. The types of arsenic found in wastewater are determined by the pH of the medium and the matrix components. To create the necessary and right technology for their treatment in treatment plants, it is necessary to study the forms of arsenic in wastewater. Because

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arsenites are more soluble than arsenates, they are more challenging to extract from wastewater. Often, an oxidation step of the arsenites by adding an oxidizing agent is required before the removal of arsenic from wastewater. Knowing the form of arsenic in wastewater provides a better understanding of the technology needed to clean it up in a treatment plant by developing the proper treatment process.

The literature describes several approaches for analyzing arsenic speciation: quantitative [4 - 6], electrochemical [7 - 11], spectral [12 - 15], and chromatographic [16, 17]. Methods involving the preliminary separation of arsenic forms and subsequent detection using an instrumental approach - spectral or chromatographic [17] are especially relevant. Extraction, adsorption (solid phase extraction), and distillation are the most commonly used procedures for separating arsenic forms mentioned in the literature [18]. The most appropriate method for quantitative separation of analytes is liquid-liquid extraction. Its benefits are numerous, including fast extraction, high extraction and concentration levels, and the absence of co-extraction [18]. As(III) exists as $AsCl_3$ in a solution of hydrochloric acid (6 - 12 mol L^{-1}). As(V) hydrolyzes and becomes H_3AsO_4 in such solutions [19]. These features of As(lll) and As(V) are employed to separate them through extraction procedure. Because $AsCl_3$ is a covalent halide with a low affinity for water, it extracts effectively in organic nonpolar solvents. The following equations can be used to characterize the process‘s equilibrium:

$HAsO_2\ \ 3HCl \leftrightarrow AsCl_3 + 2H_2O;$

$AsCl_3(w) \leftrightarrow AsCl_3(o)$

According to literature data, benzene and toluene could extracted $AsCl_3$ completely [3]. Benzene from highly concentrated hydrochloric acid solutions practically does not extract As(V). This feature is used to differentiate the two inorganic forms of arsenic. Multiple extractions using modest quantities of extractant are more efficient than single extractions using high quantities of extractant. The distribution coefficient D in this situation is affected by both the amount of extractant and the concentration of hydrochloric acid. E. Stefanov et al. present a developed analytical procedure for the speciation analysis of arsenic in electrolytic baths by the liquid-liquid extraction of the forms of As(III) and As(V) using the non-polar extractant benzene in a medium of concentrated hydrochloric acid and subsequent detection of the analytical signal by ICP-OES method [18]. The mention above inspired the current effort, which is to evaluate the feasibility of using the developed approach stated in [18] for speciation analysis of arsenic in wastewater as a means of assessing the accessible arsenic and its dangerous form.

EXPERIMENTAL

Materials and aparatus

Reagents, certified reference materials and solutions were used to conduct the analyses, as follows: HCl ≥ 37 % (ρ = 1.19 g mL^{-1}); Benzene, ≥ 99.7 % (ρ = 0.879 g mL^{-1}), Hydrogen peroxide, 30 %, Certified standard solution with As content 100.09±0.95 mg L^{-1}, CPAchem; Certified standard solution with Rh content 99.98±0.39 mg L^{-1}, CPAchem. The ICP-MS spectra were recorded with a Thermo Scientific iCAP RQ Quadrupole. The characteristics of the Thermo Scientific iCAP RQ ICP-MS are summarized in Table 1, and the operating conditions of the ICP-MS method are presented in Table 2.

Calibration of analytical function and apparatus

To calibrate the analytical function, the external standard method was used, and a multipoint calibration graph was constructed. Depending on the concentration of arsenic, the solutions were analyzed in two concentration ranges shown in Table 3. Standard calibration solutions were prepared from a certified standard solution of arsenic in 0.5 v/v % HCl medium. The concentration of hydrochloric acid in the calibration and measurement solutions is

Table 1. Characteristics of the Thermo Scientific iCAP RQ ICP-MS.

Component	Description
RF generator	Control ranging from 400 W to 1600 W.
“skimmer” cone	Reduction of background interference, high matrix tolerance and high ion transfer.
90° cylindrical lenses	Removal of neutrally charged particles from the ion stream and high ion transfer.
Combining QCell with Flatapole technology	High ion transfer and low background interference to achieve better analytical performance.
Collision Cell (CCT) with one CCT electronic gas controller	Interference reduction using Helium as collision gas. The unique design allows the passage of low-mass ions through the cell in He KED mode, enabling the detection of Li, Be and B.
A system of hyperbolic rods	A virtual field is created under the action of a solid-state 2 MHz power supply
Mass stability	< ± 0.025 u/24 hours
Scan speed	> 3700 amu/s
Mass range	2 - 290 amu
Detector	Discrete electronic multiplier with 10-order dynamic range and analog/pulse readout

Table 2. Operating conditions of ICP-MS when measuring As.

Interface cones	Ni sampler and skimmer (with High Matrix insert)
Nebulizer and spray chamber	Micromist and Quartz cyclonic spray chamber
Spray chamber temperature	2.7°C
Cool gas	14.0 L min^{-1}
Auxilliary gas	0.7 L min^{-1}
Forward power	1550 W
Nebulizer flow rate	1.0 L min^{-1}
Reaction cell gas	NO
Reaction cell gas flow rate	4.00 mL min^{-1}
Measurement mode	Kinetic energy discrimination (KED)

Table 3. Concentration ranges at analyzed by ICP-MS.

Concentration ranges I	*Concentration ranges* II
Concentration of As, μg L^{-1}	Concentration of As, μg L^{-1}
Blank	Blank
1	20
5	50
10	75
20	100

taken into account, since it is possible to create interference from high levels of chlorides due to the formation of argon chloride ($^{40}Ar^{35}Cl$) in the plasma, which has the same mass as arsenic (^{75}As) [14]. Instrument calibration and sample measurements were performed in KED mode to minimize polyatomic interference [20]. Analyzed solutions were diluted 10- or 100-fold depending on the arsenic concentration in 0.5 v/v % HCl medium in order to fall within the calibration range. To check the calibration graph, standard solutions (QCS) with an arsenic concentration of 3 µg L^{-1} for concentration range I ($y = 1436.2x + 4447.88$; $R^2 = 0.9998$) and 80 µg L^{-1} for concentration range II ($y = 1217.6x + 673.99$; $R^2 = 0.9998$) were measured before the series of samples. Sample measurement is continued only if the QCS standards have a relative error of ±5 %.

Sample calibration and measurement were performed by adding 20 µg L^{-1} Rh internal standard (in 0.5 v/v % HCl) before the cyclone chamber via a triplane. The internal standard compensates for several factors that can degrade analytical performance, such as instrument drift (e.g., changing ambient temperature), variation in sample introduction efficiency (e.g., different solution density), and matrix effects (e.g., suppression of the analytical signal of As) [20]. The measured concentration of the samples is considered reproducible if the yield of the internal standard has a relative error of ±5 %. When calibrating the equipment and measuring the samples, the isotope ^{75}As was used, and the isotope used for the internal standard was ^{103}Rh.

Analytical procedure for performing liquid-liquid extraction

Liquid-liquid extraction was performed according to the method given in [18]. A sample of wastewater tempered to 20°C is homogenized. Using a foil pipette, an aliquot of 5 or 10 mL depending on the concentration content of total arsenic in the sample (< 50, mg L^{-1}- 10.0 mL; > 50 - 5.0 mL) was measured and transferred to a 200 beaker. ml, in which a magnetic stirrer has previously been placed. 50 mL of concentrated hydrochloric acid - HCl to the sample in the beaker was added. After that, the solution was placed in a separating funnel where the two phases were separated. The aqueous phase (raffinate) was stripped and subjected to a further extraction twice with 15.0 mL of benzene at the same conditions. After that, the raffinate (containing As(V)) was transferred to the 100.0 mL volumetric flask and diluted to the mark with distilled water. The organic phase was re-extracted twice with 45.0 mL of distilled water at room temperature and vigorously stirred for 3 minutes. After separating the two phases, the aqueous phase (extract) was collected again. To ensure complete extraction of As(III), this procedure was repeated two more times by adding benzene to the aqueous phase. The extract (containing As(III)) was transferred to a 100.0 mL volumetric flask and diluted to the mark with distilled water. The extract and the raffinate were analyzed by ICP-OES method. 1.00 mL from non-extracted sample was also diluted and analyzed for the total arsenic content determination at the same conditions.

Procedure for proving selectivity

To prove the selectivity of the procedure and the complete extraction of arsenic, a sample was chosen in which the majority of the arsenic was in its reduced form. 10 mL of hydrogen peroxide 30 % was added to a solution of the sample and 50 mL of concentrated hydrochloric acid to the aliquot in the separatory funnel. After that, a volume (15 mL) of benzene was also added. Due to the different densities of the solutions, two phases were separated. The separatory funnel was shaken vigorously for 5 minutes. After 5 minutes, the delamination of the two phases is awaited. The aqueous phase was transferred to the separatory funnel and two more extractions were carried out with a 15 mL portion of benzene for 5 min. In the third extraction, the separatory funnel is washed with concentrated hydrochloric acid to avoid losses. The aqueous phase-raffinate is transferred to a 100 mL volumetric flask and made up to the mark with distilled water. The collected organic phase was re-extracted by transferring it to a 100 mL separatory funnel and 45 mL of distilled water was added. The separatory funnel is shaken vigorously for 3 minutes and the separation of the two phases is waited for. The two phases separate. Two more re-extractions are carried out with a portion of 45 mL of distilled water. The collected re-extract was transferred to a volumetric flask and 5 mL of concentrated hydrochloric acid was added and made up to the mark with distilled water. The organic phase is a waste product and is collected in a separate closed container because of its danger. The raw sample was diluted to analyze the total arsenic content. The extract, raffinate and dilution for total arsenic content were subjected to an ICP-MS method to measure the arsenic concentration. As(III) was analyzed in the extract, and As(V) in the raffinate.

RESULTS AND DISCUSSION

Aliquots of four wastewater samples were tested sequentially to validate the applicability of the approach for arsenic speciation analysis by preliminary separation of the two forms by liquid-liquid extraction and subsequent detection by the ICP-MS method (Table 4). The analysis results are shown as the concentration value of the arsenic forms. As the sample is diluted (the original aliquot is transferred to a new, bigger amount), the concentration must be recalculated using a dilution factor (DF) as shown in equation 1:

$$DF = \frac{V_{flask}}{V_{aliquot}} \tag{1}$$

Table 5 shows the sample's component composition as well as the total arsenic concentration. The acquired results were assessed for accuracy, precision, selectivity, and the limit of identification and detection of arsenic forms.

To assess the influence of random factors, statistical processing of the obtained results was carried out by calculating the relative standard deviations (eq. 2), standard deviations (eq. 3), standard deviations of the average result (eq. 4) and confidence intervals (eq. 5) [21].

$$Sr = \frac{s}{\bar{x}}.100 \tag{2}$$

$$s = \sqrt{\frac{(xi-\bar{x})^2}{n-1}} \tag{3}$$

$$S_x = \frac{s}{\sqrt{n}} \tag{4}$$

$$\bar{x} \pm \frac{S.t}{\sqrt{n}} \tag{5}$$

The results for As(III), As(V) and total As were checked for errors using the Dixon criterion [18]. The check showed that all checked results belong to the series. The results for As(III)+As(V) and total arsenic were tested for differences between standard deviations due to random errors, using the F-test. The calculated empirical values of the F-criterion (F=S12/S22, S12>S22) are compared with its table value. The statistical tests and comparisons made are summarized in Tables 6 (A and B) and 7 (A and B) for the four samples studied.

Checking the results accuracy

The accuracy of the obtained results was investigated by calculating the analytical yield R for each analysis of each sample (Eq. 6).

$$R = \frac{C_{As(III)} + C_{As(V)}}{C_{As(total)}}.100,\% \tag{6}$$

A requirement for the analytical method is that the analytical yield to be in the range of 80 - 120 %. If the result falls within this interval, it is considered correct. The obtained results for R show that the obtained results are accurate and there is no presence of matrix effects.

The differences between individual values for arsenic concentration can be attributed to the influence of random factors rather than systemic ones (Tables 6 and 7). A quantitative assessment of the accuracy was made by calculating the absolute and relative errors. The absolute error was calculated as the difference between the mean value of the data from each series of results and the assumed true value: for sample 1 ΔC = 19 mg L^{-1}, sample 3 $\Delta C = 2$ mg $L^{-1}$and for sample 4 ΔC = 0.6 mg/L. The relative percentage error has values: for sample 1 $\delta = 4$ %, for sample 3 δ = 0.3 % and for sample 4 $\delta = 6.3$ %.

Table 4. Summary results for As(III), As(V) and total As in wastewater samples.

Number	Sample	Aliquot	As(III)-re extract				As(V)-rafinat				Total As(III)+As(V) mg L^{-1}	Total As, mg L^{-1}
			Volume mL	ICP-MS(75As KED),ppb	DF	As(III)	Volum, mL	ICP-MS(75As KED),ppb	DF	As(V), mg L^{-1}		
1	1	5.000	500,0	42,524	100	425	100,0	8.175	100	16.350	442	465
2	1	5.000	500,0	42,201	100	422	100,0	9.108	100	18.216	440	465
3	1	5.000	500,0	43,256	100	433	100,0	9.199	100	18.398	451	465
4	1	5.000	500,0	41,904	100	419	100,0	8.869	100	17.738	437	465
5	1	5.000	500,0	43,709	100	437	100,0	10.11	100	20.220	457	465
1	2	5.000	100,0	3,948	10	1	100,0	11.501	1000	230.020	231	223
2	2	5.000	100,0	2.798	10	1	100,0	11.574	1000	231.480	232	223
3	2	5.000	100,0	4.128	10	1	100,0	12.155	1000	243.100	244	223
4	2	5.000	100,0	3.003	10	1	100,0	11.931	1000	238.620	239	223
5	2	5.000	100,0	6.326	10	1	100,0	11.682	1000	233.640	235	233
1	3	5.000	500,0	45.4970	100	455	100,0	65.861	100	131.722	587	583
2	3	5.000	500,0	45.4650	100	455	100,0	66.162	100	132.324	587	583
3	3	5.000	500,0	44.4000	100	444	100,0	65.571	100	131.142	575	583
4	3	5.000	500,0	46.1790	100	462	100,0	66.225	100	132.450	594	583
5	3	5.000	500,0	44.8710	100	449	100,0	65.488	100	130.976	580	583
1	4	10,000	100,0	7.995	100	8	100,0	1.227	100	1.227	9.2	8.8
2	4	10,000	100,0	7.851	100	8	100,0	1.621	100	1.621	9.5	8.8
3	4	10,000	100,0	7.941	100	8	100,0	1.771	100	1.771	9.7	8.8
4	4	10,000	100,0	7.497	100	7	100,0	1.712	100	1.712	9.2	8.8

Table 5. Component composition of the samples determined by the ICP-MS method.

Component, mg L^{-1}	Sample 1	Sample 2	Sample 3	Sample 4
Al	7	4	-	-
Bi	4	20	40	-
Ca	30	15	1500	1300
Cd	50	30	60	-
Cl	500	300	-	-
Co	0.15	0.07	-	-
Cu	120	70	170	0.1
F	250	100	-	-
Fe	80	50	30	0.1
Mg	7	3	-	-
Mn	0.2	0.1	-	-
Mo	2	1	-	-
Ni	0.8	0.3	40	-
Pb	7	3	7	-
Se	5	3	5	-
Zn	100	60	250	-
H_2SO_4	20000	12000	-	-
SO_2	5000	3000	-	-
SO_4^{2-}	-	-	20000	17000

Table 6. Statistical evaluation of the test procedure for A) Sample 1.

A) Sample 1				
n	$C_{As(III)}$, mgL^{-1}	$C_{As(V)}$, mg L^{-1}	C_{As}, mg L^{-1}	$C_{(As)total}$, mg L^{-1}
1	425	16	442	442
2	422	18	440	460
3	433	18	451	463
4	419	18	437	492
5	437	20	457	
x	427	18	445	465
Qmin	0.16	0.36	0.17	0.35
Qmax	0.25	0.47	0.31	0.58
Qtabl.(P=95%)	0.71	0.71	0.71	0.89
S	7	1	8	21
Sr, %	2	8	2	4
Sx	3	1	4	10
Ftable(P=95%)	-	-	6.59	-
Confidence interval, (P=95%)	9	2	11	33
µ	N/A	N/A	465	N/A
ΔC	N/A	N/A	19	N/A
%δC	N/A	N/A	4%	N/A
F-calculted	N/A	N/A	5.94	N/A

Table 6. Statistical evaluation of the test procedure for A) Sample 1 - *continued.*

n	C(As), mg/L	μ, mg/L	R, %
1	442	465	95
2	440	465	95
3	451	465	97
4	437	465	94
5	457	465	98

Table 6. Statistical evaluation of the test procedure for B) Sample 2.

A) Sample 2				
n	$C_{As(III)}$, mgL^{-1}	$C_{As(V)}$, mg L^{-1}	C_{As}, mg L^{-1}	$C_{(As)total}$, mg L^{-1}
1	0.8	230	231	219
2	0.6	231	232	223
3	0.8	243	244	226
4	0.6	239	239	
5	1.3	234	235	
x	0.8	235	236	223
Qmin	0.06	0.11	0.09	0.53
Qmax	0.62	0.34	0.36	0.47
Qtabl.(P=95%)	0.71	0.71	0.71	0.97
S	0.3	5	5	4
Sr, %	35	2	2	2
Sx	0.1	2	2	2
Ftable(P=95%)	-	-	19.25	-
Confidence interval (P=95%)	0.3	7	7	10
μ	N/A	N/A	223	N/A
ΔC	N/A	N/A	14	N/A
%δC	N/A	N/A	6	N/A
F-calculted	N/A	N/A	1.93	N/A
n	C(As), mg/L	μ, mg/L	R, %	
1	231	223	104	
2	232	223	104	
3	244	223	110	
4	239	223	107	
5	235	223	106	

Table 7. Statistical evaluation of the test procedure for A) Sample 3 and B) Sample 4.

A) Sample 3				
n	$C_{As(III)}$, mgL^{-1}	$C_{As(V)}$, mg L^{-1}	C_{As}, mg L^{-1}	$C_{(As)total}$, mg L^{-1}
1	455	131.7	587	576
2	455	132.3	587	585
3	444	131.1	575	587
4	462	132.5	594	
5	449	131.0	580	
x	453	131.7	585	583
Qmin	0.26	0.11	0.24	0.87
Qmax	0.38	0.09	0.38	0.13
Qtabl.(P=95%)	0.71	0.71	0.71	0.970.97
S	7	0.7	7	6
Sr, %	1	0.5	1	1
Sx	3	0.3	3	3
Ftable(P=95%)	-	-	19.25	
Confidence interval (P=95%)	8	0.8	9	14
μ	N/A	N/A	583	N/A
ΔC	N/A	N/A	2	N/A
%δC	N/A	N/A	0.3	N/A
F-calculted	N/A	N/A	1.74	N/A
n	C(As), mg/L	μ, mg/L	R, %	
1	587	583	101	
2	587	583	101	
3	575	583	99	
4	594	583	102	
5	580	583	99	

B) Sample 4				
n	$C_{As(III)}$, mgL^{-1}	$C_{As(V)}$, mg L^{-1}	C_{As}, mg L^{-1}	$C_{(As)total}$, mg L^{-1}
1	8.0	1.2	9.2	8.7
2	7.9	1.6	9.5	8.8
3	7.9	1.8	9.7	8.8
4	7.5	1.7	9.2	9.0
x	7.8	1.5	9.4	8.8
Qmin	0.71	0.59	0.03	0.05
Qmax	0.11	0.19	0.48	0.65
Qtabl.(P=95%)	0.89	0.89	0.89	0.83
S	0.2	0.2	0.2	0.1
Sr, %	2.9	14	2.5	1.5
Sx	0.1	0.1	0.1	0.1
Ftable(P=95%)	-	-	9.28	

Table 7. Statistical evaluation of the test procedure for B) Sample 4 - *continued*.

B) Sample 4				
n	$C_{As(III)}$, mgL^{-1}	$C_{As(V)}$, mg L^{-1}	C_{As}, mg L^{-1}	$C_{(As)total}$, mg L^{-1}
Confidence interval (P=95%)	0.4	0.3	0.4	0.2
μ	N/A	N/A	8.8	N/A
ΔC	N/A	N/A	0.6	N/A
%δC	N/A	N/A	6.3	N/A
F-calculted	N/A	N/A	3.33	N/A
n	C(As), mg/L	μ, mg/L	R, %	
1	9.2	8.8	104	
2	9.5	8.8	107	
3	9.7	8.8	110	
4	9.2	8.8	104	

Table 8. Distribution of As(III) and As(V) in sample 2 after oxidation.

$C_{As(III)}$, mgL^{-1}	$C_{As(V)}$, mg L^{-1}	Total (AsIII)+As(V), mg L^{-1}	Distribution As(III)	Distribution As(V)
0.8	230	231	0.3%	99.7%
0.6	231	232	0.2%	99.8%
0.8	243	244	0.3%	99.7%
0.6	239	239	0.3%	99.7%
1.3	234	235	0.5%	99.5%

Evaluation of the selectivity of the analytical procedure

The authors of the study assessed the selectivity of the approach by a single standard addition in a real sample in development for the speciation measurement of arsenic in a copper electrolyte [18]. A wastewater sample with a high concentration of sulfite ions, about 3 g L^{-1}, was chosen to demonstrate the procedure's selectivity and separation of As(III) from As(V). Because the sulfite ion is a strong reducing agent, it converts arsenic to As(III), which means that the majority of the arsenic in the water sample will be in its reduced form As(III). To oxidize As(III) to As(V), the sample was pre-oxidized with excess hydrogen peroxide. The sample was extracted and re-extracted by the analytical test protocol. The distribution of As forms in the preoxidized wastewater sample is shown in Table 8. The table demonstrates that As(V) is present in greater than 99.5 % of the sample following oxidation. Because the extraction is effective in terms of separating As(III) and As(V), no increase in extraction rate is required. According to the data in the table, the applied approach is selective to As(III) and As(V) forms in wastewater.

Evaluation of detection limit and determination limit

The limit of detection (LD) and limit of quantification (LQ) of the ICP-MS method for the determination of total arsenic based on the standard deviation of 10 blank results were evaluated [22]. A detection limit is the minimum value at which the analyte is identified by the instrument. Limit of quantification is the lowest amount of substance that the instrument can distinguish from the absence of arsenic in the solution with a specified level of confidence. They are evaluated by equations 7 and 8 [22].

$$LD = 3.s_0 + x_{Bl} \tag{7}$$

where: 3 - coefficient for 10 determinations, according to literature data; coefficient 3 corresponds to a significance level of $\alpha = 0.01$; s_0 - standard deviation of 10 results without the presence of a gross error of a matrix blank, [µg L^{-1}]; x_{Bl} - mean value of the concentration of blank matrix sample, [µg L^{-1}]. The results obtained from the estimation of limit of detection and limit of determination of total arsenic content were 0.10 µg L^{-1} and 0.30 µg L^{-1}, respectively. The linearity of the ICP-MS method was statistically evaluated by the F test "lack of fit" for the two calibration rang (experimental part). The degree of deviation of the points from the linearity characteristic of the calibration line, which is due to random scatter, is calculated from the repeated measurements (mean sum of squares of random error (MSSerror)). It is compared to the degree of deviation of the points from the line caused by misfit of the calibration model (mean sum of squares (MSSLof)) [23]. For the calibration function constructed with standard solutions by the external standard method, each of which was measured ten times, the test was applied according to eq. 8. The calculated F-criterion was compared with a table value.

$$F = \frac{\text{lack-of-fit sum of squares/degrees of freedom}}{\text{pure-error sum of squares/degrees of freedom}} = \frac{\sum_{i=1}^{n} n_i\left(\bar{Y}_{i\bullet} - \hat{Y}_i\right)^2 \Big/ (n-2)}{\sum_{i=1}^{n}\sum_{j=1}^{n_i}\left(Y_{ij} - \bar{Y}_{i\bullet}\right)^2 \Big/ (N-n)} \tag{8}$$

where: *Yij* is the experimental value of the signal at each concentration i; *Yi·* is the mean value of the experimental signal from the ten measurements at each concentration i; $\hat{Y}i$ is the signal value at one concentration i calculated using the calibration function equation; *n* is the number of standard solutions used to construct the calibration without a zero level; *N* is number of measurements of one standard solution.

The calculated values of the empirical value of the F-criterion for the two calibration ranges are presented in Tables 9 and 10. For calibration range

Table 9. F test for linearity "lack of fit" - calibration range I .

c_{as} ppb	cps1	cps2	cps3	cps4	cps5	cps6	cps7	cps8	cps9	cps10	average cps	calculated cps, ppb	(av-calc)^2	mss(lof)
1	2010.2	1800.1	1720.1	1770.1	1890	1640	1810	1910	1750	1810	1811	1974	26546	40356
5	8022.6	7892.5	7572.3	7742.4	7893	8173	7772	7332	8043	7272	7771	7692	6258	
10	14868.9	14989	14488.4	15380	15099	1509	15029	14989	15029	15519	15031	14840	36441	
20	28352.2	29786	29134	28974	28914	28944	29545	28463	28573	2905	29136	29136	11456	
(cps1-av)^2	(cps2-v)^2	(cps3-av)^2	(cps4-av)^2	(cps5-av)^2	(cps6-av)^2	(cps7-av)^2	(cps8-av)^2	(cps9-av)^2	(cps10-av)^2	мss(error)				
1308	30254	64484	41590	7046	111514	26876	4088	50148	26876	128132				
109079	40068	14407	2507	40068	230756	6411	129693	122689	176508					
824.107	22144	123758	290852	67085	28529	35686	3447	35686	461730					
614217	421954	368621	26315	49426	36987	167428	452956	317217	220130					
Slope	1429.6													
Intercept	544.5													
n	4													
p	10													
F calculated	0.315													
F table	3.259													

I Fcalc.< Ftab. (0.315 < 3.259) and calibration range II Fcalc.< Ftab. (0.699 < 3.259) it is proved that the functions of the two calibration ranges are linear. The limit of quantification (MQL) of the analytical procedure is defined as the minimum measured concentration of a substance that can be reported with 99 % confidence that the measured concentration differs from the results of a method blank [24]. Estimating the MQL includes the influence of reagents in the sample preparation, what is the limit of determination of the instrument, matrix effects, sample dilution factor. The MQL score is in dimension, as the final result of a real sample. The MQL is calculated using Eq.9. Table 11 shows the MQL at different sample aliquots and different dilutions, and Table 12 shows the overall standard deviations of the analytical procedure for the given arsenic concentration ranges.

Table 10. F test for linearity “lack of fit” - calibration range II.

c_{as} ppb	cps1	cps2	cps3	cps4	cps5	cps6	cps7	cps8	cps9	cps10	average cps	calculated cps, ppb	$(av - calc)^2$	mss(lof)
1	25516	25135	24985	25757	24755	25125	25246	24755	25576	25015	25184	25172	19545	856567
5	62145	61893	62848	61712	62094	62627	61592	61119	63370	61954	62135	61621	264391	
10	93912	92149	91162	91091	90769	90346	89248	89721	89963	90860	90922	91995	1151579	
20	124104	121660	122427	123215	122094	123619	123085	122690	122296	123952	122914	122369	296967	
$(cps1-av)^2$	$(cps2-av)^2$	$(cps3-av)^2$	$(cps4-av)^2$	$(cps5-av)^2$	$(cps6-av)^2$	$(cps7-av)^2$	$(cps8-av)^2$	$(cps9-av)^2$	$(cps10-av)^2$	мss(error)				
118068	1376	35152	341418	174631	2227	5359	174631	162982	24803	1225628				
273791	73902	1505406	8290	223587	1011131	861	251853	3059525	110523					
3672908	23741	693750	817246	1503362	2720575	7547749	5171607	4129498	1289852					
3008200	503225	3389	715067	75781	1561291	511820	103051	5327	2505625					
Slope	1215													
Intercept	873													
n	4													
p	10													
F calculated	0.699													
F table	3.259													

$$MQL = \left(\frac{LQ.V_{\text{Мерителна колба}}.\frac{DF}{1000}}{V_{\text{Аликвота}}.1000} \right). \qquad (8)$$

$$.100.10000, \quad \frac{mg}{L}$$

Table 11. Limit of quantification of the analytical procedure for speciation analysis of arsenic in wastewater.

Aliquat, mL	Measure flask, mL	DF	MQL, mg L^{-1}
10	100	100	0,03
10	100	10	0,3
5	100	100	0,06
5	100	10	0,6

Table 12. Total standard deviation of the analytical procedure for speciation analysis of arsenic.

Arsenic concentration range, mg L^{-1}	Total standard deviation, mg L^{-1}
0.6 – 2	0.48
2 – 10	0.35
200 – 250	7
400 – 500	17
550 – 600	6

CONCLUSIONS

Arsenic is involved in complicated biological and chemical processes and occurs naturally in the environment (soil, air, water, etc.) in many oxidation states and species with varying chemical behavior and toxicity that affects human health directly or indirectly. Trivalent arsenic As(III), a reduced inorganic species, is roughly 60 times more toxic than oxidized pentavalent arsenic As (V). This needs a speciation investigation of arsenic forms in various objects from the environment in real-time and, if possible, in field conditions. The approach for liquid-liquid extraction of arsenic forms during sample preparation and subsequent detection using ICP-MS appears to offer an alternative to existing methods for identifying the hazardous form of this component in wastewater samples. The approach was tested on wastewater samples. The devised approach demonstrated good selectivity, sensitivity, precision, and accuracy and may be used to successfully determine the forms of arsenic in wastewater in the concentration range: 0.3 to 100 $\mu g\ L^{-1}$.

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