

SPECIATION ANALYSIS OF ARSENIC IN COPPER ELECTROLYTE BATHS USING LIQUID-LIQUID EXTRACTION AND ICP-OES METHOD DETECTION

The present study describes a method for the determination of As (III) and As (V) in copper electrolytes. The method is based on the separation of As (III) from a copper electrolyte by triple liquid-liquid extraction using a non-polar organic solvent in a medium of 10-12 mol L⁻¹ HCl. The extract contains As (III) and the raffinate-As (V), respectively. As(III) specie can be re-extracted from the organic solvent through the water. Analyzes of the concentration of As in the re-extract and raffinate were performed by ICP-OES spectroscopic method. The average recovery of arsenic by the proposed method is about 99%. Repeatability was estimated with RSD ($n = 6$). Selectivity and accuracy were proven by the standard addition method. The relative error for restoring the standard addition of As (III) is about 0.3%. The speciation method analysis could be applied for determination of the arsenic species in the analytical quality control of refined copper in copper tanks in the production of copper cathodes.

Keyword: arsenic; speciation analysis; copper electrolyte; ICP-OES method; extraction

1. Introduction

Arsenic, antimony, and bismuth are naturally occurring elements [1]. They are found in the composition of complex non-ferrous ores and concentrates in the form of sulfide minerals [2]. During the roasting of copper concentrates, arsenic and other impurities (Sb, Bi e.g.) are distributed to gases, slags, and anode blister copper [3,4]. Usually, the content of copper in anode blister copper is 99.5%. This grade of copper does not meet requirements for major industry applications (electronics, electrical engineering, etc.) and it needs to be further refined in order to decrease the content of impurities [5]. Anode blister copper contaminants are: As, Sb, Bi, Se, Te, Ni, Ag, Au, Pt, Pd, and others. Their behavior is different during the electrolysis. As, Sb and Bi dissolve in electrolyte while the precious metals, Se and Te are more noble elements than Cu and they precipitate into the anode slime [6]. The accumulation of As, Sb, and Bi in the copper electrolytes is related to contamination of the cathode copper [7]. These three elements dissolve in their trivalent state, followed by oxidation of As and Sb to their pentavalent state. The oxidation of Sb(III) to Sb(V) is related to the formation of floating amorphous slime, mainly as Sb₂O₅.nH₂O [8]. The floating slime might contaminate the copper cathodes by physical

entrapment. This effect leads to increased impurities content in refined copper and as a result decreased quality [8].

It has been found that the oxidation of Sb(III) to Sb(V) is a slow process and can be controlled by the presence of arsenic in the electrolyte [6, 9]. The mechanism of this type of control is the competition reaction of faster oxidation of As(III) to As(V). The obtained arsenate ions react with Bi(III) and Sb(III) and the result of these reactions are insoluble arsenates which precipitate into anode slime [9-11]. At arsenic concentrations of 15-20 g L⁻¹ in the copper electrolyte, the oxidation of Sb(III) to Sb(V) is suppressed and floating slime formation can be prevented [12]. This type of purification of the copper electrolyte, known as in-situ impurities control, is commonly used in the refining of anode copper [12]. Hence, the determination of As(III) and As(V) takes a crucial role in the operation of tankhouses.

Several techniques for separation of species of As combined with their determination using spectral methods have been reviewed in the literature [13,14]. One of them is hydride generation atomic absorption spectroscopy (HG-AAS). This technique is based on arsine formation, which is directly analyzed by AAS. The speciation can be done by reduction of arsenic species with NaBH₄. As(III) can be separately analyzed in a higher pH range [15,16]. The conditions of reduction are very important.

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If the concentration of reducing agent-NaBH₄ is higher, the possibility of reducing both forms is higher and this leads to an overestimation of As(III). On the other hand, when the molar ratio Cu/As(III) in the sample is higher than 120, low recoveries for As(III) can be found [16].

Inductively coupled plasma optical emission spectrometry (ICP-OES) is one of the most attractive detection systems. ICP-OES is routinely used in many diverse research fields such as earth, environmental, life, and forensic sciences and in food, material, chemical, and nuclear industries. The technique can be applied for the determination of total arsenic in different types of samples [17]. In addition, the ICP-OES technique is typical for quality control in every smelter or tankhouse laboratory. Unfortunately, the method is only able to determine total arsenic content, but it is not applicable for direct arsenic species determination.

In this context, the aim of this report is an estimation of analytical characteristics of ICP-OES determination of arsenic species, As(III) and As(V) in copper-containing electrolyte bath applying liquid-liquid extraction with a non-polar solvent. Liquid-liquid extraction is the oldest pre-concentration and isolation method for speciation analysis and one of its major advantages is directly applying for samples with complex matrices [14]. It is also known to separate various forms of arsenic into biological materials by liquid-liquid extraction and determine its exact concentration by atomic absorption spectrometry [18]. Initially, after dissolving the sample, arsenic (III) was extracted into a 9 mol L⁻¹ hydrochloric acid solution using toluene as extractant. After extraction, arsenic (V) remains in the raffinate and is reduced to arsenic (II) and re-extracted. Extraction of arsenic (III) in highly concentrated hydrochloric acid solutions (11-12 mol L⁻¹) with chloroform extractant has been described [19]. Arsenic (V) was then reduced and re-extracted as arsenic (III). A method has also been developed for the extraction of arsenic (III) with a 40% solution of tributyl phosphate in xylene [20]. The extraction was performed under 4 mol L⁻¹ hydrochloric acid and 2 mol L⁻¹ lithium chloride. It is stated that arsenic (III) is extracted in the presence of Cu (II), Co (II), Ni (II), Sn (II), Fe (III), Cd (II) and other elements. Given the above and the need for speciation analysis of arsenic motivate us to develop a relatively fast, sensitive, and selective method for determining both forms of arsenic in the electrolyte baths for quality production of copper cathodes based on pre-extraction and ICP-OES detection.

2. Experimental procedures

2.1. Materials

All reagents and solvents were analytical grade. Double distilled water was used for the preparation of the solutions. A stock solution of As(III) was prepared by dissolving 1.056 g of As₂O₃ (Sigma Aldrich) in 100.0 mL of 6 mol.L⁻¹ HCl. The stock solution was analyzed using ICP-OES and the established As concentration was 7.992 g. L⁻¹.

2.2. Apparatus

The ICP-OES spectra were recorded with a Thermo Scientific iCAP 6000 Series instruments. The chosen operating conditions were: nebulizer K-type, auxiliary gas 1.5 L.min⁻¹, nebulizer gas 0.7 L min⁻¹, RF power 1.2 kW, pump rate 50 rpm, sample uptake time 30 sec, integration time 30 sec radial view. High purity Ar 99.999% supplied by SIAD BG was used to sustain plasma and as a carrier gas. Two-point background correction and three replicates were used to measure the analytical signal.

2.2.1. Solutions for calibration

Standards for calibration of ICP-OES were prepared by diluting the As stock standard solution (MERCK) with concentration 1000 ± 4 mg.L⁻¹ (1000 ppm). The media for calibration solutions was 20 % HCl (v/v 37%). The instrument and analytical function were calibrated using standard solutions with concentrations of As(III): 5, 10, 20, 50 and 100 mg.L⁻¹.

2.3. Procedure for sample analysis

The sample was collected from production copper electrolyte bath containing the following main chemical components: Cu: 40.0 g.L⁻¹, H₂SO₄: 175.0 g.L⁻¹, Ni: 2.0 g.L⁻¹, As: 7.0 g.L⁻¹, Sb: 0.2 g.L⁻¹, Fe: 0.2 g.L⁻¹, Bi: 0.6 g.L⁻¹, Zn: 0.3 g.L⁻¹, Cl⁻: 0.05 g.L⁻¹. The chemical content of electrolyte bath is presented in Scheme. 1. For analysis, 5,00 mL fresh sample, previously chilled to 20°C was added to 50 mL of concentrated hydrochloric acid HCl (37%, Merk). Extraction of arsenic was carried out with 15.0 mL benzene at room temperature and vigorous stirring for 5 min. After that the solution was placed to a separating funnel where the two phases were separated. The aqueous phase (raffinate) was stripped and subjected to a further

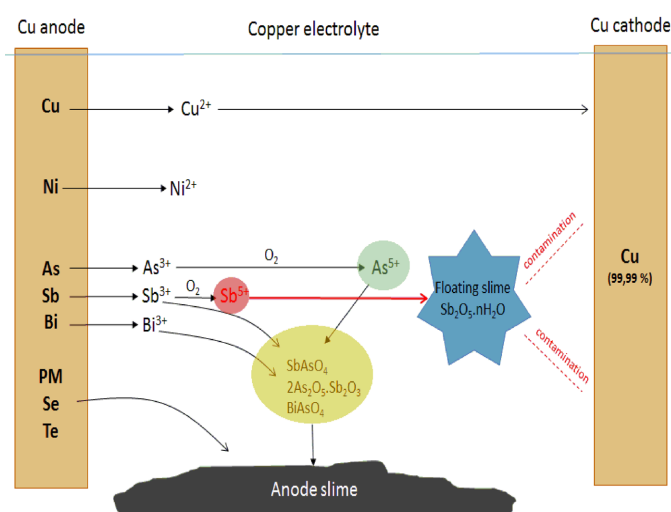


Fig. 1. Scheme presenting the content of analyzed electrolyte bath, where PM is the precious metals referring primarily to platinum, palladium, gold, and silver

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 distilled water at room temperature and vigorously stirred for 3 minutes. After separating of 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 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.

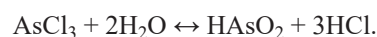
2.4. Statistical analysis

Statistical evaluation of the analytical characteristics of applied method was performed using mathematical software OriginPro8.0 (ANOVA).

3. Results and Discussion

Of key importance in a refinery for the production of copper cathodes is the possibility of analytical control of As (III) and As (V) in the electrolyte to determine the operating concentrations and to monitor the process parameters. It was found that the determination of the two forms in the presence of different ion concentrations in the electrolyte bath is impossible without

prior sample preparation and subsequent analysis. Initially, distillation was tested to separate arsenic (II) from arsenic (V), but it did not give sufficiently reproducible results. Another problem with distillation is the presence of thiourea in the sample, which reduces part of As (V) to As (III) in the strongly acidic medium. This side reaction increases the error in the result for As (III). The requirements for the accuracy of the definitions of a maximum of 5% relative error were achieved by extraction separation of the two forms. The sequence of stages illustrating both the analytical procedure for performing the extraction process and the spectral measurement of the analytical signal is given in Figure 2. In an aqueous medium, arsenic halides (III, V) hydrolyze to form arsenic and arsenic acid, respectively:



In order to exist as a whole molecule (AsCl_3), the solution must be strongly acidified with hydrochloric acid or the hydrolysis equilibrium is thus shifted completely to the left. At the lower concentration of the corresponding acid, the salts easily hydrolyzed in solution according to $\text{AsCl}_3 + 3\text{H}_2\text{O} \leftrightarrow \text{As}(\text{OH})_3 + 3\text{HCl}$ as the dissociation constant of $\text{As}(\text{OH})_3$ is $5 \cdot 10^{-15}$, and its isoelectric point is observed at pH 4. Arsenic (III) halides are covalent, non-polar compounds and are accordingly well soluble in non-polar solvents such as benzene, toluene, carbon tetrachloride and the like. Another proof that these halides, and in particular arsenic trichloride, are non-polar, is the fact that arsenic trichloride dissolves sulfur and phosphorus well and is mutually soluble in carbon disulfide. It is known that in media of $10\text{--}12\text{ mol L}^{-1}$ HCl, As(III) is present as non-polar molecules of AsCl_3 [21]. At the same conditions As(V) is present as arsenate ion [16]. The non-polar molecules of AsCl_3 are preferably

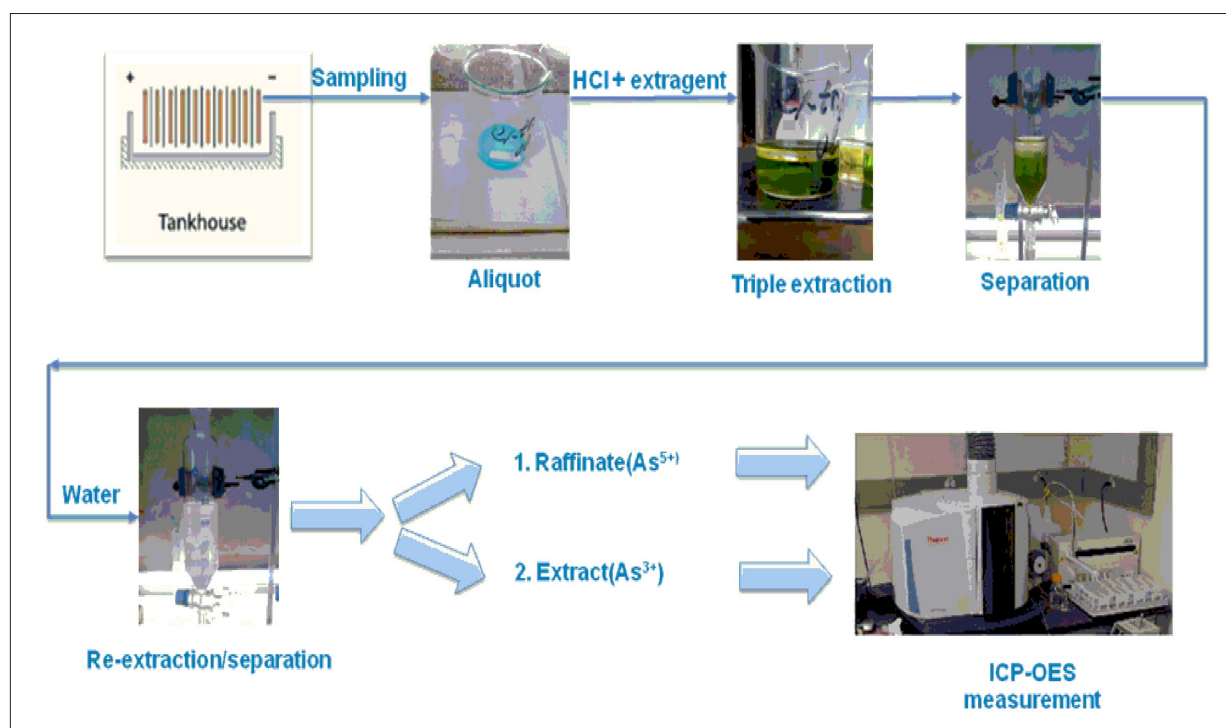


Fig. 2. Stages of analytical procedure for speciation analysis of arsenic in copper electrolyte baths

dissolved by the non-polar solvent because of the similarity of their molecules: $\text{AsCl}_3(\text{w}) \leftrightarrow \text{AsCl}_3(\text{o})$ [22]. Therefore, for the development of the new method, benzene, a non-polar solvent as an extraction agent for the determination of arsenic forms, was selected.

The peak intensity of the arsenic using the ICP-OES method at a specific wavelength – 189.04 nm was measured (Fig. 3). Analytical characteristics of the method were studied using an external standard method for calibration by plotting the intensity of emission radiation versus concentration of As in a concentration range from 5 to 100 ppm and the coefficient of analytical function equal to $5.28 \times 10^{-5} \text{ mL.g}^{-1}$ was determined (Fig. 3). The results presented in Fig. 3 showed high sensibility and excellent linearity of the measurement in the presented concentration interval.

3.1. Analytical characteristics of the method

The data for the quantitative determination of arsenic (III), arsenic (V), and total arsenic (As(III) + As(V)) in the analysis

of one sample using the extraction and direct ICP-OES method are given in TABLE 1. For evaluation of the analytical characteristics of the method for arsenic species determination the sensitivity, accuracy, and reproducibility of the new method were estimated. The efficiency of the applied arsenic species extraction method was verified by analyzing six samples from the same electrolyte bath on different days. This was achieved by bypassing the same sample volume throughout the analytical procedure described above. Results for six replicates of the same sample analysis are presented in TABLE 1. The mean values from six parallel determinations of As(III), As(V), and total arsenic are as follows: 0.63 ± 0.02 for As(III); 6.40 ± 0.07 for As(V), and 7.03 ± 0.06 for total arsenic, respectively (TABLE 2). The relative standard deviation is 0.82%. The total arsenic values obtained by the extraction ICP-OES method were compared with those obtained by direct ICP-OES analysis of the arsenic in the same sample (TABLE 1). One can conclude that the results obtained by both ICP-OES methods are identical in the limit of random errors (TABLE 1 and 2). The relative standard deviation (s_r) from $\approx 2\%$ for As(III) was also calculated (TABLE 2).

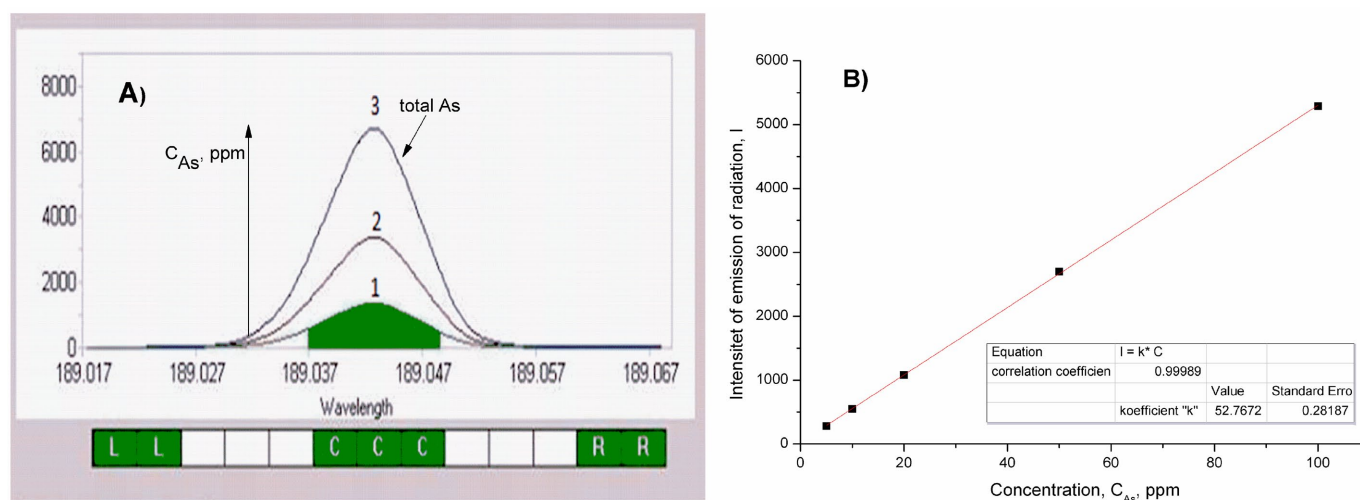


Fig. 3. ICP-OES spectrum of arsenic at different analyte concentration (1-20.00 mg L⁻¹; 2-50.00 mg L⁻¹; 3-100.0 mg L⁻¹) (A) and a plot of intensity of emission radiation vs. total arsenic concentration (ppm) (B)

TABLE 1

Results from samples analysis, obtained by the new (Extraction ICP-OES) and Direct ICP-OES method

Sample volume, mL	Extraction ICP-OES method				Total As(III) + As(V), g.L ⁻¹	Direct ICP-OES method Total As(III) + As(V), g.L ⁻¹	Percentage of total As, %
	As(III)-Re-extract		As(V)-Raffinate				
	C _{As(III)} , g L ⁻¹	DF*	C _{As(V)} , g L ⁻¹	DF*			
5.000	0.6355	1	6.294	10	6.93	7.05	98.3
5.000	0.6365	1	6.394	10	7.03	7.05	99.4
5.000	0.6304	1	6.416	10	7.05	7.05	100
5.000	0.6186	1	6.390	10	7.01	7.05	100
5.000	0.6482	1	6.416	10	7.06	7.05	100
5.000	0.6069	1	6.494	10	7.10	7.05	101

* Dilution of the sample volume : $DF = \frac{V_{flask}}{V_{sample}}$

Statistical characteristics for evaluation of accuracy of the method

Statistical characteristics	Concentration of As(III), g L ⁻¹	Concentration of As(V), g L ⁻¹	Concentration of total As, g L ⁻¹
\bar{X} (at $n = 6$)	0.63	6.4	7.0
S	0.0146	0.064	0.0584
S_r , %	2.32	1.01	0.83
S_x	0.01	0.03	0.02
$t_{table} (P = 95\%)$	2.57	2.57	2.57
confidence interval (at $P = 95\%$)	± 0.02	± 0.1	± 0.1
true content, μ	N/A	N/A	7.05
$ \Delta C = C - \mu $	N/A	N/A	0.0200
$\% \delta = \Delta C \cdot 100/\mu$	N/A	N/A	0.28
t -calculated	N/A	N/A	0.84

The percentage (R , %) of arsenic in the six repetitions was calculated by Eq. (1) and the results are also presented in TABLE 1

$$R = \frac{C_{As(III)} + C_{As(V)}}{C_{Total}} \cdot 100, \% \quad (1)$$

To verify the accuracy of the method, a statistical evaluation of a series of results was performed in the analysis of samples from one electrolyte bath. The data from the statistical evaluation are also given in TABLE 2. The data shows that a system error for the total arsenic determination absent as the results from the direct method is within the range of confidence interval of the result obtained by the extraction ICP-OES method (TABLE 1 and 2). In the results for the total arsenic there is an accepted true value (μ), which is obtained by direct analysis of the sample (TABLE 2). The absolute error ($|\Delta C| = |C - \mu|$) is calculated as the difference, and the relative percentage error ($\% \delta = |\Delta C| \cdot 100/\mu$) has a value of $\approx 0.3\%$ (TABLE 2). For the results of total As the Student's test is calculated. Its value does not exceed the tabular

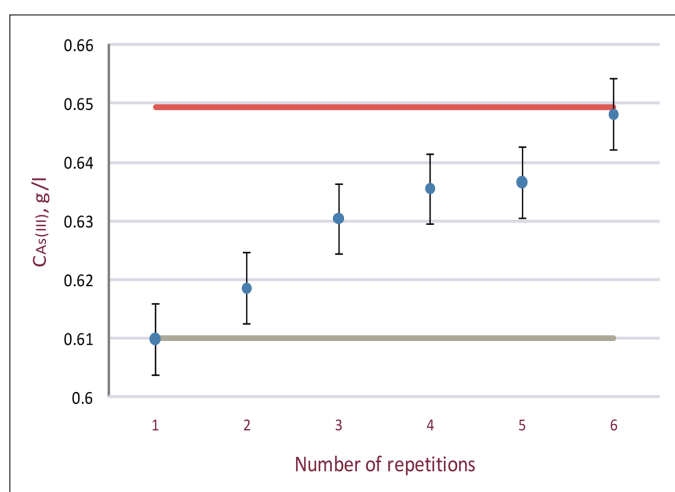


Fig. 4. Confidence interval and values founded for As (III) concentration. Error bars are the calculated uncertainties from the apparatus and from the glassware

value for the given number of parallel analyzes, ie. no system errors. For the other two studies (results for As (III) and As (V) content) a graphical model was used to prove the absence of systemic errors. Fig. 4 and 5 show the confidence interval for arsenic (III) and arsenic (V). One can see that the 6 results for investigated samples lie in the border of confidence interval which proves the accuracy of the determination.

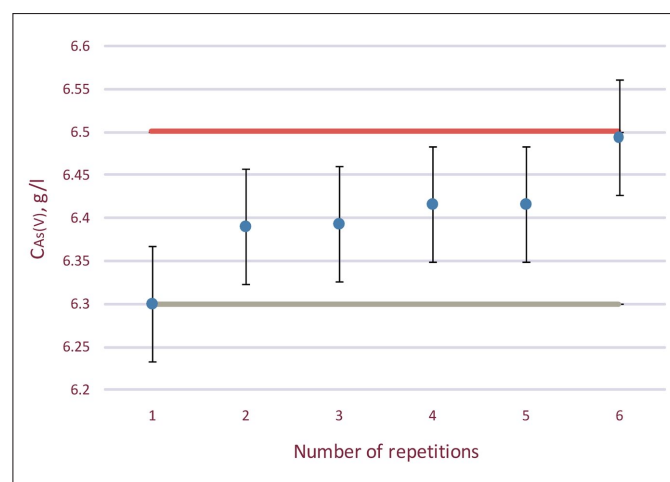


Fig. 5. Confidence interval and values founded for the concentration of As (V). Error bars are the calculated uncertainties from the apparatus and from the glassware

3.2. Evaluation of the selectivity of the method

The evaluation of the selectivity and the full extraction of As (III) was done by adding a standard solution of As(III) into the sample solution as the mass of As (III) solution was determined by ICP-OES. The addition solution also passed the described procedure with benzene. The relative error of the found mass of the additive was calculated. The summarized results for the benzene extraction supplements made are shown in TABLE 3.

Percentage recovery of As(III) in spiked sample, using spiking levels of 0.002398, 0.004796 and 0.007194 g

Solution	Mass of As(III) total (Real sample + spike), g	Mass obtained, g	Mass recovered, g	Recovery, %	Relative error, %
1	0.005480	0.005423	0.002341	97.62	-2.4
2	0.005480	0.005445	0.002363	98.54	-1.5
3	0.007878	0.007766	0.004684	97.66	-2.3
4	0.01028	0.01024	0.007158	99.50	-0.5

The influence of matrix components was evaluated by determination of recovery after spiking of the sample. The recovery was calculated by Eq. (2), as follows:

$$R = (m_{a+spike} - m_a) / m_{spike} \quad (2)$$

where $m_{a+spike}$ is the mass of As(III) after spiking, m_a – the mass of As(III) and m_{spike} – mass of analyte in spike. The recovery results are presented in TABLE 3. The obtained recovery varied between 97.62% and 99.50% proving good accuracy of the extraction procedure [21]. According to the literature [23] when the spikes are added at the sample preparation stage, the recovery at the range of 80-120% is acceptable and does not require matrix corrections. This wide interval depends on the nature of the samples, extraction procedure, and concentration levels of the elements.

4. Conclusions

Due to the extraction of As(III) with non-polar solvent a new ICP-OES method for the determination of arsenic with liquid-liquid extraction and re-extraction of the analyte has been developed. The analysis is performed easily, needs a small sample quantity and the results are accurate and precise. The standard deviation of the total arsenic concentration determination is 0.058. The precision in relative units (s_r) is 0.82%. Thus, the new method would be useful for the analytical control of the arsenic species in a copper-containing electrolyte bath. Moreover, the method proposed allows the determination of the mass and concentration of As(V) in the raffinate from the extraction. The method is tested in a laboratory of the Research and Development department of Aurubis, Bulgaria because the concentration of As(III) is essential for the quality of the copper cathodes produced and showed positive results for future application.

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