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# DETERMINATION OF ARSENIC BY CATHODIC STRIPPING VOLTAMMETRY: SENSITIVITY IMPROVEMENT USING HIGH CONCENTRATION OF HYDROCHLORIC ACID AND HIGH TEMPERATURE

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## SUMMARY

A sensitivity improvement for arsenic determination in the presence of copper by cathodic stripping voltammetry, using a high concentration of hydrochloric acid (3 mol/L) and high cell temperature (40 °C), is described. The optimum conditions were established, and LOD and LOQ for determination of As(III) were calculated from the calibration curve to be 7 ng/L and 22 ng/L, respectively. The accuracy of the method was checked by analyzing a certified reference material (LGC 6010-Hard Drinking Water). The method was applied to drinking water samples in Balıkesir city of Turkey.

## KEYWORDS:

arsenic, cathodic stripping voltammetry, drinking water.

## INTRODUCTION

Arsenic in nature is present in both organic and inorganic forms, and arsenic contamination risks of food, plants, air and drinking water have been increased by human activities. Toxicity of arsenic is dependent on its chemical form. It is generally accepted that soluble inorganic arsenicals are more toxic than the organic ones, and As(III) is more toxic than As(V). Both the EPA and International Agency for Research on Cancer (IARC) have classified inorganic arsenic as a known human carcinogen. On the other hand, it has been considered as an oligo-element with unknown physiological function because of its presence in living organisms [1]. But, there is no conclusive evidence of arsenic essentiality in humans, while it is an essential nutrient for animals, such as minipigs, goats, chicken, hamsters and rats [2]. The World Health Organization (WHO) standard for

arsenic is 10 µg/L for drinking water, and those in Canada, the European Union and Australia are 25 µg/L, 10 µg/L and 7 µg/L, respectively [3]. According to the Agency for Toxic Substances and Disease Registry (ATSDR), provisional minimal risk levels of arsenic are 5 and 0.3 µg/kg/day for acute and chronic oral exposure, respectively [1, 2]. Therefore, it is important to have simple, cheap, sensitive and accurate methods for the determination of arsenic in different samples.

Arsenic levels have been determined by a wide variety of methods, such as ultraviolet (UV) spectrometry, atomic absorption spectrometry (AAS); mainly coupled to hydride generation (HG-AAS) or electro-thermal atomization in graphite furnace (ET-AAS), atomic emission spectrometry (AES), generally with inductively coupled plasma (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), X-ray spectrometry, neutron-activation analysis (NAA) [6, 7], and stripping techniques including anodic stripping voltammetry (ASV) [7-12], cathodic stripping voltammetry (CSV) [7, 14-21] and stripping potentiometry [22]. However, it is well-known that stripping techniques present low investment and maintenance costs with good precision, accuracy and sensitivity. Therefore, arsenic determinations in water, food and some plant samples have been recently made using stripping techniques [7-22]. Among these techniques, CSV is the most sensitive one. Holak [13] developed a CSV technique for the determination of As(III) in the presence of Se(IV), forming inter-metallic compounds in acidic media and depositing them on the hanging mercury drop electrode (HMDE) [13]. It has been also described a similar one in different studies using Cu(II) in various concentrations instead of Se(IV), and applied to water samples [14-17]. Furthermore, CSV procedures have been used for the determination of As(V) in acidic medium containing man-

TABLE 1 - Some CSV methods for the determination of As in various samples.

Technique	Analyte	Supporting electrolyte	Reducing agent for determination of As(V)	Sample	LOD ( $\mu\text{g/L}$ )	Ref.
DPCSV	As(III)	0.75 mol/L HCl, 5 mg/L, $\text{N}_2\text{H}_4\cdot\text{HCl}$ (25%)	-	water	1	[14]
DPCSV	As(III)	2 mol/L HCl, 50 mg/L Cu (II), $4 \times 10^{-5}$ mol/L $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$	-	natural water	0.2	[15]
SWCSV	As(III)	1 mol/L HCl, 50 mg/L Cu(II)	$\text{S}_2\text{O}_3^{2-} + 500$ mg/L Cu	natural water	0.06	[16]
SWCSV	As(III)	1 mol/L HCl, 5 mg/L Cu(II)	KI+ ascorbic acid	natural water	0.7 (1min)	[17]
SWCSV	As(V)	0.3 mol/L NaCl, 2 mol/L $\text{NaClO}_4$ , 100 mg/L $\text{CuSO}_4$	0.5 mol/L mannitol + $\text{HClO}_4$ (pH=1.7)	water	4.4	[18]
SWCSV	As(V)	0.4 mol/L $\text{H}_2\text{SO}_4$ , 10 mg/L Cu(II), 70 mg/L Se(IV)	0.22 M D-mannitol	natural water	0.52	[19]
DPCSV	As (III)	0.33 mol/L HCl, 5 mg/L Cu (II) $5 \times 10^{-4}$ mol/L $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$	$\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$	refined beet sugar	not reported	[20]
DPCSV	As(III)	1 mol/L HCl, 5 mg/L Cu(II)	KI + ascorbic acid	plant material	0.06	[21]
SWCSV	As(III) As(V)	3 mol/L HCl, 38.5 mg/L Cu(II)	KI + ascorbic acid	drinking water	0.007 0.06 (5 min, 40 °C)	proposed method

DPCSV: Differential Pulse Cathodic Stripping Voltammetry, SWCSV: Square Wave Cathodic Stripping Voltammetry, LOD: Limit of Detection

nitro and Cu(II) [18], or mannitol, Cu(II) and Se(IV) [19]. A few CSV applications reported on As analysis in refined beet sugar and plant material, in the presence of Cu(II) [20, 21]. Some arsenic CSV determination methods with different detection limits are summarized in Table 1, with regard to different experimental conditions in the various samples.

The main purpose of this work was to investigate whether the sensitivity of CSV arsenic determination can be further improved by changing critical experimental parameters, such as copper concentration, hydrochloric acid concentration, cell temperature, deposition potential, and deposition time. Indeed, this sensitivity could be improved by using a high HCl concentration at high cell temperatures.

## MATERIALS AND METHODS

### Apparatus and Reagents

Voltammetric measurements were carried out with a Radiometer Pol 150 Polarographic Analyzer, connected to a MDE 150 polarographic stand, controlled with a PC via Trace Master 5 software. HMDE was used as working electrode, whereas a platinum rod and a Ag/AgCl,  $\text{KCl}_{\text{sat}}$  electrode were used as auxiliary and reference electrodes, respectively. Hexadistilled mercury (Radiometer-Copenhagen) was used for HMDE throughout the study.

The As(III) stock solution (1000 mg/L) was prepared by dissolving 0.132 g  $\text{As}_2\text{O}_3$  (Riedel, Germany) in 1 L water, and that of As(V) (1000 mg/L) from a Titrisol ampule (Merck, Darmstadt, Germany). Both solutions were stored at 4 °C. The required standard solutions were prepared daily by dilution of the stock solutions. Hydrochloric acid (Merck) and sulphuric acid (Merck) were used for acidification without further purification. The other chemicals used throughout the study were of analytical grade. Hydrazinium sulfate was used to prevent oxidation of As(III) to As(V) and prepared daily. All the solutions were prepared with deionized water having the resistivity of 18.2 M $\Omega$ .

Various trademark drinking waters were collected from the market in Balikesir city of Turkey. Surface water samples were collected from the Dam Lake's water treatment plant, at the input (untreated) and output (treated) in Balikesir city of Turkey, and stored at 3 °C in 250 mL polyethylene bottles.

The flasks were cleaned by soaking them in 4 mol/L nitric acid solution for 24 h, and then excessively washing them with deionized water.

### Procedure

In all experiments, aliquots of the standard solutions were transferred to voltammetric cell, and then, different amounts of the reagent solutions were added and the volume was completed to 10 mL with deionized water. In all measurements,  $4 \times 10^{-5}$  mol/L hydrazine sulfate was used to protect the oxidation of As(III) to As(V) during deposition step. The jacketed voltammetric cell was put into place and temperature adjusted to 40 °C using a thermostat. Then stripping was carried out using square wave mode after deposition step. All measurements were done in the presence of dissolved oxygen, without nitrogen purging to shorten the analysis time [17]. For the analysis of samples, the test solution was placed in a voltammetric cell and diluted to 10 mL with deionized water after addition of HCl,  $\text{Cu}^{2+}$  and hydrazine sulfate, to give final concentrations of 3 mol/L, 38.5 mg/L and  $4 \times 10^{-5}$  mol/L, respectively. A new mercury drop was extruded and arsenic deposited as intermetallic compound at -400 mV for 300 s. The other instrumental conditions were set as follows, SW frequency: 25 Hz, pulse amplitude: -50 mV, step amplitude: 1 mV, step duration: 0.04 s, scan rate: 25 mV/s, stirring rate: 800 rpm, and waiting time: 20 s.

For determination of As(V) in drinking water, it was reduced to As(III) using a KI and ascorbic acid mixture as reducing agent. For this purpose, 1 ml of conc.  $\text{H}_2\text{SO}_4$  and the mixture of KI and ascorbic acid (final concentrations  $2.4 \cdot 10^{-2}$  mol/L) were added to 5 ml of each sample. The

solution was allowed to stand for 10 min, in order to complete the reduction. This solution was analyzed as stated above by using As(V) standard solution for calibration.

## RESULTS AND DISCUSSION

It has been reported that square wave (SW) voltage modulation is more sensitive than either differential pulse and linear sweep [15]. Therefore, SW voltage mode was used for experiments. The effect of SW frequency was also investigated for our experimental conditions. For this purpose, SW frequency was varied in the range between 2.5-200 Hz. The peak current increased with SW frequency, but peak-broadening and signal noise were observed at frequencies higher than 25 Hz. Therefore, 25 Hz was selected as optimum frequency for subsequent experiments.

In previous studies, the methods using various concentrations of hydrochloric acid ( $C_{\text{HCl}}$ ) and copper (II) ( $C_{\text{Cu}}$ ) for As determination by CSV have been reported (see Table 1). As it can be seen in Table 1, these methods have different detection limits. Therefore, the critical parameters were re-optimized to improve the sensitivity.

### Influence of hydrochloric acid concentration

Hydrochloric acid is the most suitable and widely used supporting electrolyte in electrochemical stripping determination of arsenic. It is well-known that the use of higher HCl concentrations increase the stripping signals of arsenic [8, 15, 22]. HCl concentration ( $C_{\text{HCl}}$ ) was varied to obtain the optimum one, and the results are shown in Figure 1. Three plateaus indicating the probable formation of a stable Cu-As inter-metallic compound were observed. The peak current has increased dramatically with  $C_{\text{HCl}}$  after the second plateau, then increased slightly giving a maximum at 3 mol/L, and finally decreased. A positive shift in peak potential ( $\sim 25$  mV) was observed at increased  $C_{\text{HCl}}$  levels from 1 mol/L-3 mol/L. Baseline deterioration and significant peak-broadening affecting the analysis were not observed at higher  $C_{\text{HCl}}$ .

### The effect of deposition potential

The other significant parameters affecting accuracy and sensitivity of the method are deposition potential ( $E_d$ ), deposition time ( $t_d$ ), and copper concentration ( $C_{\text{Cu}}$ ). In previous studies, these parameters were suggested to be dependent on each other, and  $C_{\text{Cu}}$  oppositely proportional to  $t_d$  [15, 16].

Figure 2 illustrates the variation of peak current as a function of  $E_d$ . It can be seen that the peak current was increased with  $E_d$ , a maximum at  $-400$  mV, and then decreased at more negative values. This current decrease has been attributed to the reduction reaction of As(0) to arsine being faster than the reaction between arsenic and copper. It has also been reported that As-Cu inter-metallic compound in different stoichiometry is the other factor decreasing the peak current at more negative potential [15]. In

our study, we observed a shift in peak potential, when the variation of  $E_d$  was performed sequentially in the same solution, whereas no shift was observed by changing the solution for each measurement. These observations suggest that the reaction between arsenic and copper is not complete, and the stoichiometry of As-Cu intermetallic compound depends on time as well as  $E_d$ . ( $-400$  mV was chosen for optimum  $E_d$ , which is the same given in literature).

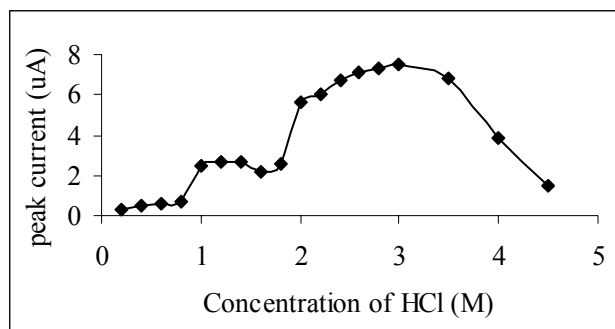


FIGURE 1 - The variation of peak current as a function of HCl concentration: As(III) 20  $\mu\text{g/L}$ ,  $\text{CuCl}_2$  40 mg/L, hydrazine sulfate  $4 \times 10^{-5}$  mol/L,  $E_d = -400$  mV,  $t_d$  60 s, cell temperature  $22.9 (\pm 0.1)^\circ\text{C}$ , and stirring rate 800 rpm.

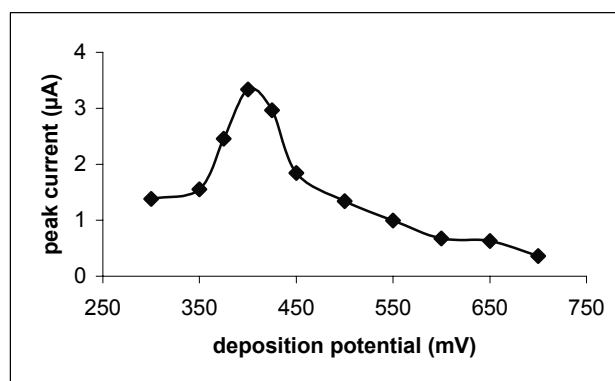


FIGURE 2 - The variation of peak current as a function of deposition potential: As(III) 10  $\mu\text{g/L}$ , HCl 3 mol/L,  $\text{CuCl}_2$  40 mg/L, hydrazine sulfate  $4 \times 10^{-5}$  mol/L,  $t_d$  60 s, cell temperature  $22.9 (\pm 0.1)^\circ\text{C}$ .

### The effect of copper concentration

The variation of peak current with Cu(II) concentration ( $C_{\text{Cu}}$ ) is shown in Figure 3. The peak current increased with  $C_{\text{Cu}}$ , and reached a maximum at 37.5-40 mg Cu(II)/L. Current decreasing and leveling-off was observed, when  $C_{\text{Cu}}$  was further increased. Therefore, optimum  $C_{\text{Cu}}$  was selected to be 38.5 mg/L. Different  $C_{\text{Cu}}$  values have been selected in several studies, such as 5 mg/L [14, 17, 20, 21], and 50 mg/L [15, 16]. Furthermore, we also observed that the  $C_{\text{Cu}}$  value, corresponding to the maximum peak current, depends on  $E_d$ .

### The effect of deposition time and cell temperature

It was reported that a decrease in peak current and some changes in voltammograms, such as potential shift towards

negative values and peak-broadening resulting in splitting, are observed for longer deposition times [17], and additionally, similar effects occur when copper concentration is increased. These alterations have been attributed to a change in the stoichiometry of As-Cu deposits at the electrode surface. Figure 4 shows the variation of peak current as a function of  $t_d$  for an initial  $C_{Cu}$  of 38.5 mol/L. The peak current has increased with  $t_d$  giving a maximum at 60 s, then decreased and remains constant at further increased deposition times. It was also observed from the studies performed for different  $C_{Cu}$  and  $t_d$  values that the optimum  $t_d$  depends on  $C_{Cu}$ . Therefore, the selection of these parameters is important to obtain good precision and sensitivity.

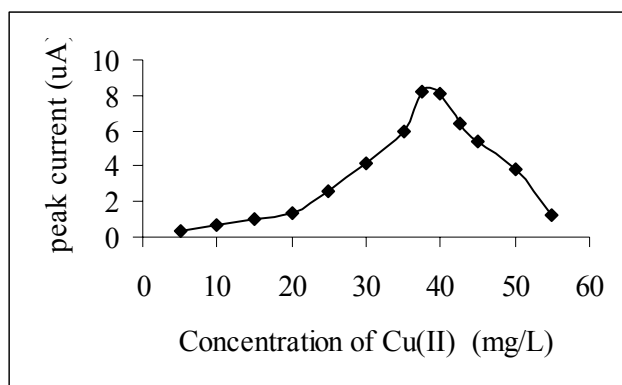


FIGURE 3 - The variation of peak current as a function of Cu(II) concentration: As(III) 20  $\mu\text{g/L}$ , HCl 3 mol/L, deposition potential -400 mV, hydrazine sulfate  $4 \times 10^{-5}$  mol/L, deposition time 60 s, and cell temperature  $22.9 (\pm 0.1) ^\circ\text{C}$ .

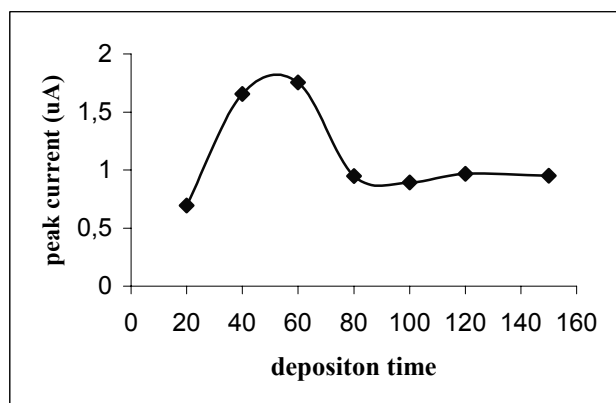


FIGURE 4 - The variation of peak current as a function of deposition time: As(III) 5  $\mu\text{g/L}$ , HCl 3 mol/L,  $\text{CuCl}_2$  38.5 mg/L, deposition potential -400 mV, hydrazine sulfate  $4 \times 10^{-5}$  mol/L, and cell temperature  $22.9 (\pm 0.1) ^\circ\text{C}$ .

The effect of cell temperature was also examined in order to improve sensitivity of the method. Figure 5 shows the variation of peak current as a function of cell temperature. The peak current has increased with cell temperature and no peak deterioration and splitting were observed in 3 mol/L HCl at 50  $^\circ\text{C}$ . However, a slight negative shift in peak potential was observed at high temperatures. On the

other hand, non-systematic peak deterioration and splitting were observed in 1 mol/L HCl at  $\geq 30$   $^\circ\text{C}$ . This result indicates that the sensitivity can be improved in the presence of 3 mol/L HCl by using high temperatures as well as increasing deposition times. The optimum cell temperature was selected to be 40  $^\circ\text{C}$ . However, nonsystematic potential shift and peak splitting were observed at 60 s for  $t_d$  and 38.5 mol/L for  $C_{Cu}$ , for arsenic concentrations below 0.1  $\mu\text{g/L}$ , when high temperature was used to improve sensitivity. It is noteworthy that these observations are opposite to those reported above. On the other hand, a well-defined peak was obtained for low arsenic concentrations, when long  $t_d$  was used at high temperature. For this reason,  $t_d$  was selected to be 300 s for low arsenic concentrations at high temperature.

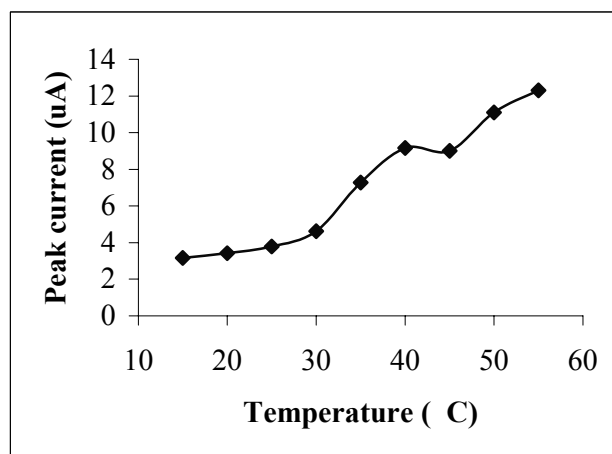


FIGURE 5 - The variation of peak current as a function of cell temperature: As(III) 10  $\mu\text{g/L}$ , HCl 3 mol/L,  $\text{CuCl}_2$  38.5 mg/L, hydrazine sulfate  $4 \times 10^{-5}$  mol/L, deposition potential -400 mV, and  $t_d$  60 s.

#### Analytical Characteristics of the Procedure and Application to Drinking Water Samples

Under the optimum conditions achieved, a linear calibration curve

$$I_p(\text{nA}) = 1141.4C_{As}(\mu\text{g/L}) + 0.131$$

with a regression coefficient of 0.9987 was obtained at 40  $^\circ\text{C}$  and  $t_d = 300$  s. By using standard deviation about regression ( $s_{y/x}$ ) instead of standard deviation of blank ( $s_B$ ), as described elsewhere [23], the limit of detection (LOD) and limit of quantification (LOQ) were calculated from the calibration curve to be 7 ng/L and 22 ng/L, respectively. The voltammograms obtained from these measurements and the calibration curve are given in Figure 6. The relative standard deviation for five replicate measurements of 60 ng As (III)/L was found to be 8.7 %.

On the other hand, for As(V) determination, a potassium iodide-ascorbic acid mixture was used as reducing agent. For this purpose, solutions with different concentrations of both chemicals, ranging between  $8 \times 10^{-3}$ - $6.4 \times 10^{-2}$  mol/L, were tested for reduction of As(V) to As(III).

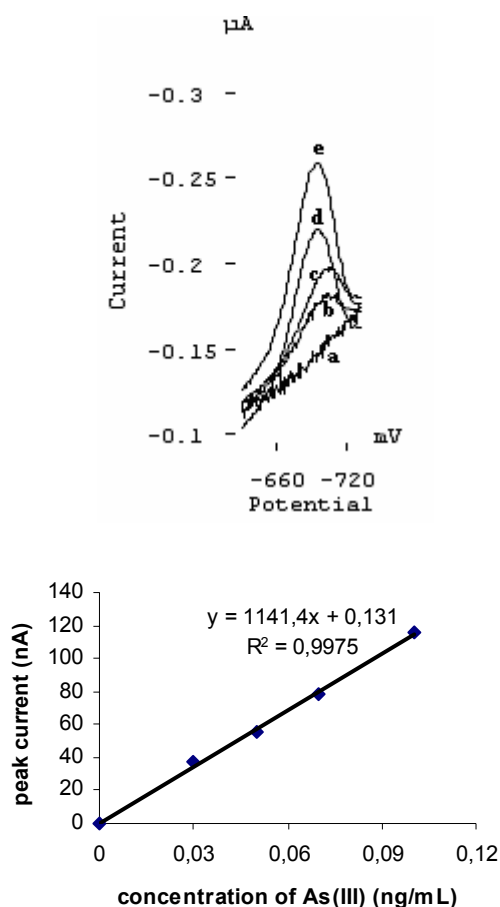


FIGURE 6 - Voltammograms and calibration curve obtained at high temperature (0-0.1µg/L As(III),  $t_d=300$  s,  $T=40$  °C).

The best results were obtained for potassium iodide/ascorbic acid, each at  $2.4 \times 10^{-2}$  mol/L. The efficiency of As(V) reduction to As(III) was also investigated, and 10 min seem to be sufficient for complete reaction.

A calibration curve was plotted at the same conditions for determination of As(V) after reduction of As(V) to As(III). The equation of the calibration curve is:

$$I_p(\text{nA/mV}) = 55.13C_{\text{As}}(\text{ng/mL}) + 0.75$$

with a regression coefficient of 0.993 between 0-0.3 ng/mL of As (V). LOD and LOQ were calculated to be 60 ng/L and 200 ng/L, respectively. The relative standard deviation for five replicate measurements of 200 ng/L As (V) was found to be 6.2 %. The different LOD and LOQ values of the two curves are attributed to the presence of potassium iodide and ascorbic acid in the solution.

The proposed conditions were validated by the analysis of certified reference material (LGC6010-Hard Drinking Water). The arsenic content of this material (certified value for As =  $55 \pm 5$  for 95% confidence level) was found to be  $57 \pm 4$  in average (95% confidence level) for seven independent determinations (RSD = 6 %). Statistical evaluation of the results using Student's t-test (at 95% confidence

level) show that there are no significant differences in the results. The method applied to real samples, and the results obtained are given in Table 1.

TABLE 1 - As(III) and As(V) contents of various drinking water samples and recovery rates (R).

Sample	As(III) added	As(V) added	As(III) found	As(V) found	R (%) for As(III)	R (%) for As(V)
DW-B 1	-	-	nd	$1.8 \pm 0.2$		
DW-B 1		0.8		2.5		87.5
DW-B 2	-	-	nd	$5.2 \pm 0.5$		
DW-B 3	-	-	nd	nd	-	-
DW-B 3	0.06		0.05	nd	83.3	
DW-B 4	-	-	nd	nd	-	-
DW-B 5	-	-	nd	nd	-	-
DLW-untreated			nd	$16.7 \pm 0.6$		
DLW-treated			nd	nd		

DW-B: drinking water in bottles, DLW: Dam lake's water (concentrations are expressed in µg/L, and the standard deviations corresponding to three independent analyses are also reported).

As(III) was not detected in all of the samples, but As(V) was found in two drinking water samples ( $1.8 \pm 0.2 \mu\text{g l}^{-1}$  and  $5.2 \pm 0.5 \mu\text{g l}^{-1}$  -  $N = 5$ , 95 % confidence level). The amount of As(V) was determined to be  $16.7 \pm 0.6$  in untreated Dam lake's water. However, As(V) was not found in treated water samples. The results show that arsenic is absorbed on the filter during coagulation-assisted microfiltration of treated water, and arsenic contents of the water samples analyzed are below  $10 \mu\text{g l}^{-1}$ , recommended by WHO. However, it must still be monitored.

## CONCLUSIONS

We have presented a modified CSV method for As(III) determination, using 3 mol HCl/L at 40 °C, improving its sensitivity approx. ten-fold, when compared to the present methods. However, a decrease in linearity of calibration curve was observed at high temperatures. The method is suitable for trace amounts of inorganic arsenic in water samples. Additionally, it has been demonstrated that the peak current increases with the increase of cell temperature without peak deterioration and splitting in 3 mol HCl/L, whereas non-systematic peak deterioration and peak splitting occur in 1 mol/L HCl at high temperature. On the other hand, it was found that the conditions optimized ( $C_{\text{HCl}}$ : 3 mol/L,  $C_{\text{Cu}}$ : 38.5 mg/L,  $E_d$ : -400 mV, and  $t_d$ : 60 s) are also valid at room temperature.

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