Isolation of Mn(II), Fe(III), Cu(II) and Ni(II) Ions on Strongly Acidic Cation-Exchange Resins Followed by Determination of Inorganic Arsenic by Anodic Stripping Voltammetry

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Abstract. The possibility of ion exchange technique with of *IC-H Hypersep* cartridge (*Metrohm, Switzerland*), sulfonated cation-exchange resins *KU-2-8* (Russia) and *Purolite C100* (UK) has been shown for ion separation of Mn (II), Fe(III), Cu(II) and Ni(II) ions from arsenite and arsenate ions. The conditions for ion-exchange removal of interfering cations in water when determining different arsenic(III, V) by stripping voltammetry have been optimized. The *KU-2-8* cation-exchange resin based cartridge was found to be appropriate for use in the proposed sample preparation for water. The developed technique of analysis has been applied for the separated determination of inorganic arsenic forms in waters of different origin by anodic stripping voltammetry. The correctness of experimental results has been confirmed by the standard addition method.

INTRODUCTION

Arsenic is considered one of the most immunotoxic elements; its chronic effect can cause skin, lungs and liver cancers [1]. Maximum permissible concentration of arsenic in drinking water is 10 $\mu g \cdot L^{-1}$ [2]. In soil and in ground water, arsenic exists mainly in a form of inorganic compounds of As(III) and As(V) [3]. The As(III) compounds suppress cellular metabolism and inhibit various ferments. The As(V) compounds are less toxic. However, there are more biochemical disturbance caused by arsenates. Arsenates are analogues of phosphates, so they can replace phosphates in hydroxyapatite of bone tissue in case of commensurable quantities [4]. Therefore, today the determination of inorganic forms of arsenic in aquatic ecosystem is an important problem.

The majority of high-sensitive methods of analysis can detect only one inorganic form and total arsenic in different types of water, and another form has to be calculated as a difference. Ion chromatography (IC) combined with spectroscopic methods is often used for separate determination of arsenite and arsenate ions [5]. For example, IC with inductively coupled plasma mass spectrometry (ICP-MS) is used for determination of As(III) and As(V) in drinking and waste waters with the detection limit of 0.5-1 $\mu g \cdot L^{-1}$ [6]. The preliminary separation of arsenic forms is usually done by extraction with sodium dithiocarbamate or ammonium pyrrolidinecarbodithioate.

Anodic stripping voltammetry (ASV) is successfully used for the determination of micro quantities of inorganic arsenic in various samples [7–12]. Arsenic(III) is usually analyzed in acidic medium with dilute hydrochloric acid. Recently, the possibility of direct separate determination of As(III) and As(V) ions on gold microelectrodes in

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neutral and weak acidic solutions has been reported [13, 14]. In addition, stripping voltammetry is an attractive method due to its ease of use and cost effectiveness.

The speciation of inorganic arsenic forms depend on pH of a solution. In acidic solutions, As(III) changes to As(V) affected by air oxygen. Arsenite and arsenate ions can exist together under anaerobic conditions in neutral and weak acidic medium. However, As(V) is electrically inactive in neutral medium and cannot be detected by ASV. The solution of Na_2SO_3 was proposed as a supporting electrolyte for As(V) detection on gold microelectrodes in neutral and weak alkaline solutions when there are Mn(II) ions in a solution that act as mediators in a process of As(V) reduction [14, 15]. When there are Mn(II) ions in a solution, the following reactions take place on the electrode:

- electroplating step

$$\mathrm{Mn(II)} + 2\bar{e} \rightarrow \mathrm{Mn(0)} \quad (1)$$

$$\mathrm{As(V)} + \mathrm{Mn(0)} \rightarrow \mathrm{As(III)} + \mathrm{Mn(II)} \quad (2)$$

$$\mathrm{As(III)} + 3\bar{e} \rightarrow \mathrm{As(0)} \quad (3)$$

- anodic dissolution of As(0)

$$\mathrm{As(0)} - 3\bar{e} \rightarrow \mathrm{As(III)} \quad (4)$$

According to the proposed technique of separate determination of arsenic forms, firstly the analytical response, which is proportional to As(III) concentration, is detected in the supporting electrolyte of Na_2SO_3 and estimated; then, Mn(II) ions are added to the solution. The existence of As(V) in a solution is confirmed by the increase of the same response (Eq. 4) and estimated with the standard addition of As(V).

However, the impact of interfering ions, e.g. Mn(II), Fe(III), Cu(II), Ni(II) and others which 10 and 100 fold exceed arsenic concentration in water, can occur when analyzing As(III) and As(V) on gold microelectrode by ASV. Arsenic concentration in drinking water is often less than its threshold limit value (TLV). For reliable quantitative determination of arsenite and arsenate ions in a sample, it is necessary to isolate Mn(II) and other interfering metal ions, and to add then the definite quantity of mediator into a cell in order to obtain an excellent As response. The As(III) response can be unselective without isolation of Mn ions in a sample because there are both As(III) and As(V) ions in a solution. Therefore, the appropriate sample preparation is necessary for ASV analysis of water on arsenic.

Ion exchange is often used for the isolation of Mn(II), Fe(III), Cu(II) and Ni(II) cations from As(III, V) anions [16]. In acidic solutions, the isolation is conducted on a strongly acidic cation-exchange resin (SAC resin). The isolation of trace contaminants (Fe, Cu, Co, Ni, Al and others) was proposed for atomic emission analysis of high-purity arsenic in order to concentrate them on *KU-2-8* cation-exchange resin at pH 1.4–1.6 [17]. In [18], the isolation of Cu(II) on *KU-2-8* at pH 4–5 for arsenic determination in water by ASV. For the isolation of metal ions on selective complexing sorbents, the weakly acidic or neutral medium is needed so that active groups are dissociated. In [19], the authors have shown total isolation of Cu(II), Fe(III) and Hg(II) ions on carboxylic cation-exchange resins *KB-2E*, *KBS* and *KB-2T* (Russia) at pH 3–5 for analysis of arsenic in natural objects by ASV. For ASV analysis of water on arsenic, the chelated ion-exchange resin *Chelex 100* contained iminodiacetic active groups was proposed for the removal of interfering cations of transition metals at pH > 4 [20, 21]. For sample preparation, the authors used the cartridge filled with *Chelex 100* ion-exchange resin.

In this connection, the purpose of the present paper is to assess the possibilities of ion exchange using different cation-exchange resins for removal of interfering metal ions in water samples in analysis of inorganic arsenic forms by ASV.

EXPERIMENTAL PART

Apparatus, Materials and Methods

The following ion-exchange resins were used in the investigation: ion-exchange cartridge *IC-H Hypersep* (Switzerland), sulfonated cation-exchange resins *KU-2-8* (Russia) and *Purolite C100* (UK). Total exchange capacity of *KU-2-8* cation-exchange resin is 5.4 $\mathrm{mmol \cdot g^{-1}}$; of *Purolite C100* is 6.0 $\mathrm{mmol \cdot g^{-1}}$. *Purolite C100* cation-exchange resin differs from *KU-2-8* its better capacity and chemical purity that can be essential for ASV analysis. The possibility of ion-exchange isolation of Mn(II), Fe(III), Cu(II) and Ni(II) ions on SAC resins was investigated in a pH range of 1–7. Hydrochloric acid and pH voltmeter – millivoltmeter *PP-15* (Germany) were used to adjust pH of a solution.

The working capacity E_{work} of a cartridge was determined relatively to the hardness salts. For this, tap water was filtrated trough the cartridge, and filtrate was collected with portions of 10 ml. Then, the sum of Ca^{2+} and Mg^{2+} salts was determined by complexonometric titration; the breakthrough curve of concentration (Ca^{2+}, Mg^{2+}) vs. volume of water flow was plotted and the working capacity was calculated using the breakthough volume (V_{break}) of the cations in a solution according to Eq. 5:

$$E_{work} = V_{break} \cdot c, \tag{5}$$

where c is water hardness in [$\text{mmol} \cdot L^{-1}$] units calculated according to the following equation:

$$c = [(c_{EDTA} \cdot V_{EDTA})/V_{H2O}] \cdot 1000. \tag{6}$$

In order to isolate the interfering cations, the solution being analyzed was flown through a cartridge with a syringe or was filtrated through the ion-exchange column filled with sulfonated cation-exchange resin with flow rate of 1 $\text{ml} \cdot \text{min}^{-1}$. The glass column sized 4×120 mm filled with 2-3 g of ion-exchange resin in H^+-form was used. The analyte was filtrated through a column. Then, the column was washed with 2-3 ml of double-distilled water. A filtrate and washing water were collected in a 10 or 25 ml capacity measuring flask; the pH was adjusted (to the range of 1-3 using hydrochloric acid, to the range of 8-9 using ammonia buffer solution); the solution was adjusted to a volume with double-distilled water, stirred and finally analyzed by ASV. A cartridge and a column were recharged with 2 M hydrochloric acid after every collection. For the investigation, the simulating solutions were used, in which the concentration of arsenic was on the same level or lower than the TLV (0.004–0.01 $\text{mg} \cdot L^{-1}$), and the concentration of interfering ions was similar to their level in natural and drinking waters.

The As forms were detected with voltammetric analyzer *TA-4 (LTD "RPE “Tomanalyt”*, Tomsk, Russia) which has three electrode cells so that three samples can be processed simultaneously. The model *TA-4* is one of the latest modern voltammetric analyzers. It can detect the elements on the level of 1/10 of the TLV. The *VALabTx* software was used for the detection and processing of an electrochemical response. Oxygen was removed from a solution with the use of sodium sulfite. Stirring of a solution being analyzed was performed by the electrode vibration.

The conventional three-electrode cell was used for the electrochemical measurements. Gold modified carbon composite electrode was used as a working electrode; $Ag/AgCl_{(1\ KCl)}$ were used as a reference electrode and as a counter electrode. The technique of working electrode preparation is described in [22].

The commercial reagents HCl, HNO_3 and NH_3 were of analytical grade and used without purification. All solutions were prepared with double-distilled water. The standard solutions of Mn(II), Fe(III), Cu(II) and Ni(II) were prepared using the State Standard Samples 1000 $\text{mg} \cdot L^{-1}$; the solution of As(III) was prepared using State Standard Samples 100 $\text{mg} \cdot L^{-1}$, and 0.2 M H_2SO_4 by diluting of double-distilled water without added acid and were hold in dark. There were two techniques used for As(III) solution preparation; i.e., using $Na_2HAsO_4 \cdot 7H_2O$ (the concentration was determined by iodometric titration) and 10 $\text{mg} \cdot L^{-1}$ standard solution of As(III) by ozonation during 10 minutes every other week. The solution concentrated 1 $\text{mg} \cdot L^{-1}$ was prepared the same day prior the experiment by dilution with water.

The supporting electrolyte of Na_2SO_3 was prepared from its saturated solution (the excess of Na_2SO_3 salt was dissolved in near boiling water; the prepared solution was stored in dark). The concentration was determined by potentiometric titration with 0.1 M HCl and was 2.25 $\text{mol} \cdot L^{-1}$. The concentration of Na_2SO_3 in analyzing solutions was 0.1 $\text{mol} \cdot L^{-1}$.

RESULTS AND DISCUSSION

Quantification of As (III, V) by Anodic Stripping Voltammetry

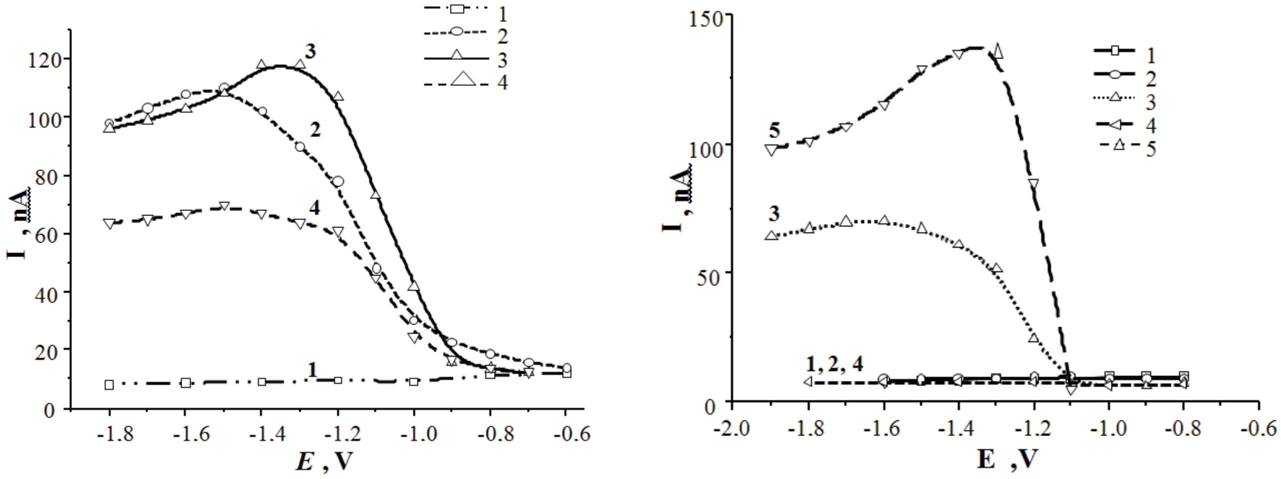
For As(III, V) stripping voltammetric detection, the optimal conditions from [14] were used (Table 1). According to the Eq. 4, As peak at –0.2 ... –0.25 V (Fig. 1, 2) is the same for the both forms. But the height of a peak depends on arsenic(V) impact in electrode process. When there is a sulfite in a solution (without Mn(II) ions, only As(III) is active and the peak height is proportional to its concentration in a range of linearity of calibration curve in case of current does not exceed 150-200 nA (for example, in concentration range of 0.002-0.015 mg·L^{-1} for 40 s electrolysis time). When there is Mn(II) ions in a sulfite solution, both arsenic form make a contribution in a electroanalytical signal (at –0.2 V), and special conditions (i.e., addition or masking of Mn(II) ions) are needed for separate measurement. These conditions were optimizes in [14].

TABLE 1. Conditions for arsenic electroanalytical responses

Conditions	As(III) response	As(V) response
Supporting electrolyte	Na_2SO_3 , (Na_2SO_3 + EDTA)*	Na_2SO_3 + Mn^{2+}
Cleaning step	E = 0.200 V, t = 10 s, vibration	E = 0.200 V, t = 10 s, vibration
Electroplating step	E = –1.400 V, t = 40 s, vibration	E = –1.400 V, t = 40 s, vibration
Equilibration step	E = –1.200 V, t = 5 s	E = –0.500 V, t = 5 s
Stripping step	E = [–0.800 ... +0.200] V	E = [–1.200 ... +0.200] V
Scan rate	120 [mV/s]	120 [mV/s]

* EDTA is used as a masking agent for Mn ions

The procedure of direct determination of As(III) and As(V) by ASV in simulating solutions and drinking water. 7 ml of double-distilled water and 0.5 ml of saturated solution Na_2SO_3 are placed in every electrochemical cell. The voltammetric curve is recorded under such conditions when the As analytical response does not exceed 100-150 nA. Then, 1-3 ml of a prepared sample is added and the cells and the voltammorgam is recorded under the same conditions. The electrochemical response observed at –0.2 V points at As(III) ions in a solution. The voltammorgam is then used as a background line when As(V) is estimated. After, Mn(II) ions (0.1 mg·L^{-1}) are added to the cells and the voltammorgam is recorded again. The increase of electrochemical response indicates the existence of As(V) ions in a solution. The addition of a standard solution of As(V) is put to the cells and the voltammorgam is recorded in the same conditions in order to quantify As(V). The quantity of As(III) is estimated in the same samples according to the following procedure. EDTA (1·10^{-5} M) is added to a solution in order to mask As(V) ions by the formation of coordination complex. Then, the voltammorgam is recorded and As(III) is quantified by the standard addition method. All the calculations are done automatically considering the background voltammetric curve.



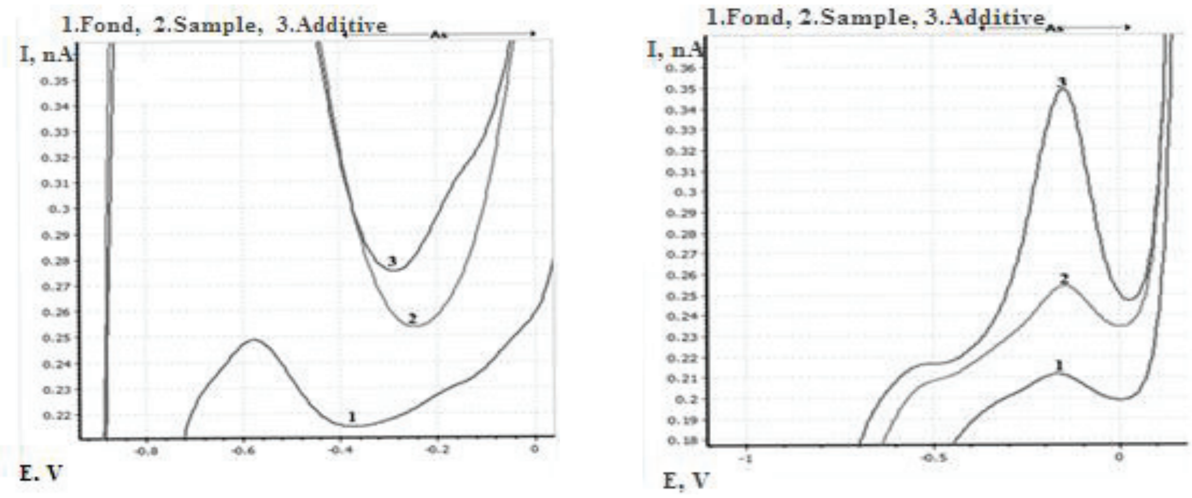
(a) (b)

FIGURE 1. (a) . Current–potential dependence of As(III) (1) 0.1 M Na_2SO_3; (2) 0.005 mg·L^{-1} As(III); (3) As(III) + 0.10 mg·L^{-1} Mn(II); (4) As(III) + Mn(II) + 10^{-2} M HPO_4^{2-}. Electroplating time is 15 s; (b). Current–potential dependence of As(V) and Mn(II): (1) 0.1 M Na_2SO_3; (2) supporting electrolyte + 0.01 mg·L^{-1} As(V); (3) 0.1 mg·L^{-1} Mn(II); (4) supporting electrolyte + 10^{-2} M HPO_4^{2-}; (5) Mn peak vs. E, supporting electrolyte + 0.1 mg·L^{-1} Mn(II). Electroplating time is 20 s [14].

Ion-Exchange Isolation of Interfering Metal Cations in A Solution for the Determination of Inorganic Arsenic(III, V) by Anodic Stripping Voltammetry

The possibility of isolation of Mn (II), Fe(III), Cu(II) and Ni(II) ions from As(III, V) with the use of *C-H Hypersep* cartridge and a columns filled with sulfonated cation-exchange resins *KU-2-8* and *Purolite C100* has been investigated using simulating solutions according to the method described in experimental part.

The figures 2a and 2b show voltammetric curves of As(V) before and after ion-exchange isolation of Fe(III). The As(V) response at –0.2 V obviously is masked when there is Fe(III) (Fe:As = 100:1) in a solution. The excess of Cu(II) and Ni(II) salts demonstrates the same effect. When there is an excess of Mn(II) ions in a solution, the As(III) and As(V) electrochemical peaks are not being masked (the peaks are only decreased slightly), but the determination becomes incorrect because of the simultaneous impact of both forms of arsenic (III, V) to the electrode reaction.



(a) (b)

FIGURE 2 Voltammetric curves: (a) As(V) + Fe(III); (b) As(V) after ion-exchange isolation of Fe(III)

The conditions (e.g., pH) for ion-exchange isolation on SAC resins were optimized at pH range of 1–3 in order to prevent Fe(III) hydrolysis and for total removal of interfering ions. For this, the state diagram of arsenic acid was plotted (Fig. 4) and molar fractions of Fe(III), Cu(II) and Ni(II) hydroxocomplexes in the pH range of interest (0.1–0.001 M HCl) were calculated (Table 2).

TABLE 2. Molar fractions of Cu(II), Fe(III) and Ni(II) ions and their hydroxocomplexes in HCl solutions

c_{HCl}, M	[OH$^-$], M	Cu^{2+}		Fe^{3+}			Ni^{2+}	
		Cu^{2+}	$Cu(OH)^+$	Fe^{3+}	$Fe(OH)^{2+}$	$Fe(OH)_2^+$	Ni^{2+}	$Ni(OH)^+$
10^{-1}	10^{-13}	0.9900	$1\cdot10^{-7}$	0.941	0.059	$2\cdot10^{-4}$	0.9899	$1\cdot10^{-9}$
10^{-2}	10^{-12}	0.9899	$1\cdot10^{-6}$	0.605	0.382	0.013	0.9899	$1\cdot10^{-8}$
10^{-3}	10^{-11}	0.9899	$1\cdot10^{-5}$	0.106	0.667	0.227	0.9899	$1\cdot10^{-7}$

The results presented in Table 2 show that all the interfering elements in defined concentrate range of HCl exist in a solution mainly in cation-form and can be isolated on a SAC resin.

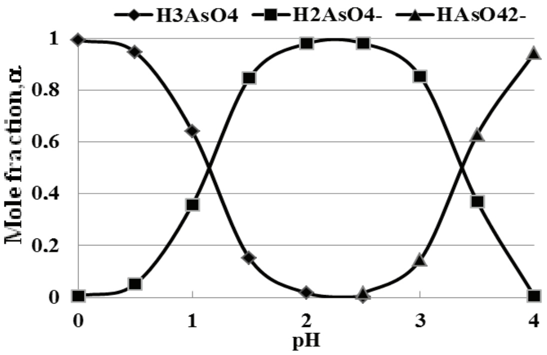


FIGURE 3. Fragment of H_3AsO_4 state diagram in dependence on pH

Figure 3 shows that arsenic acid exists mainly in a form of single-charged ion in defined pH range. The pH range of 1.5-2 is optimal for the isolation when Fe(III) cations have the highest charge in a solution and the acid exists in anion form, because the selectivity of ion exchange increases with the increase of ion charge and non-ion-exchange sorption of H_3AsO_4 is eliminated.

Table 3 presents the results of arsenic(III) determination in simulating solutions contained the ion of interest and interfering ion after isolation of interfering ions using cartridge *IC-H Hypersep* and cation-exchange resin *KU-2-8*. It can be seen that the determined concentration of As(III) are in agreement with its real concentration within the measurement accuracy; therefore, As(III) totally have moved into a filtrate.

The investigation of possibilities of ion-exchange isolation of Mn(II) and other interfering ions in a pH range of 6–7, which is close to the natural water acidity, for the separate determination of arsenite and arsenate ions was of interest. The Table 4 presents the results of separate determination of arsenic(III, V) in a simulating solution containing Mn(II), Fe(III) and Cu(II) ions and standard solutions of As(III) and As(V) after isolation of interfering ions using the cartridge and cation-exchange resins *KU-2-8* and *Purolite C100*. The arsenic concentration was on the TLV level and the content of interfering ions was similar to that one in natural waters.

TABLE 3. The results of arsenic(III) determination in simulating solutions (metal ions – As) after isolation of interfering ions using cartridge *IC-H Hypersep* and a column filled with cation-exchange resin *KU-2-8* at pH 1.5

Interfering element	**Me:As ratio**	**As(III) added, mg·L^{-1}**	**As(III) found, mg·L^{-1}**	
			Cartridge IC-H	**KU-2-8,H$^+$**
Fe(III)	20:1	0.005	0.0044 ± 0.0006	0.0046 ± 0.0005
Cu(II)	50:1	0.005	0.00484 ± 0.00018	0.0045 ± 0.0005
Mn(II)	20:1	0.005/0.01	0.00490 ± 0.00015	0.0090 ± 0.0016
Ni(II)	10:1	0.010	0.00982 ± 0.00019	0.0095 ± 0.0013

The results of determination of As(III) and As(V) in a filtrate after ion exchange are in agreement with their real concentration within the measurement accuracy, and the cation-exchange resins of *KU-2-8* and *Purolite C100* can be utilized for the sample preparation. Hence, arsenite and arsenate ions are not being *lost* during ion exchange; i.e., all of the studied ion-exchange systems can successfully isolate interfering ions so that both arsenic forms can be analyzed by ASV.

TABLE 4. The results of As(III) and As(V) determination in a simulating solution after ion-exchange isolation of interfering ions at pH 6.5 ($c_{As(III)}$ = 0.004 mg·L^{-1}; $c_{As(V)}$ = 0.01 mg·L^{-1}; n = 3; P = 0.95)

Ion	**Ratios**		**As found, mg·L^{-1}**					
			Cartridge IC-H		**KU-2-8**		**Purolite C100**	
	Me: As(III)	**Me: As(V)**	**As(III)**	**As(V)**	**As(III)**	**As(V)**	**As(III)**	**As(V)**
Fe	500:1	200:1	0.00401 ± 0.00012	0.00980 ± 0.00023	0.00393 ± 0.00018	0.0091 ± 0.0016	0.00391 ± 0.00022	0.01032 ± 0.00028
Mn	25:1	10:1						
Cu	25:1	10:1						

Determination of As (III, V) in Different Waters after Ion-Exchange Isolation of Interfering Ions

The sample preparation technique using the cartridge *IC-H Hypersep* and cation exchange resin *KU-2-8* was utilized for the analysis of drinking water on As(III) and As(V). The prevailing cations in natural and drinking water are the water hardness salts (Ca^{2+}, Mg^{2+}), ions Na^+ and K^+ that can be removed by cation-exchange resin from a solution and preserve the isolation of interfering ions; therefore, the working capacity of a cation exchange resin was determined relatively to the water hardness salts. The working capacity was determined to be 0.22 mmol-eq confirming high efficiency of a cartridge, and the bigger aliquot of tap water (up to 40 ml) can be used.

The analytical response of arsenic in ASV method is measured as a height from a peak current to background curve. Peak marking, which is made by extrapolation, is prominent in quantity analysis. Figure 4 shows different methods of peak marking of arsenic(V) analytical response on a voltammogramm, i.e. automatic and manual marking.

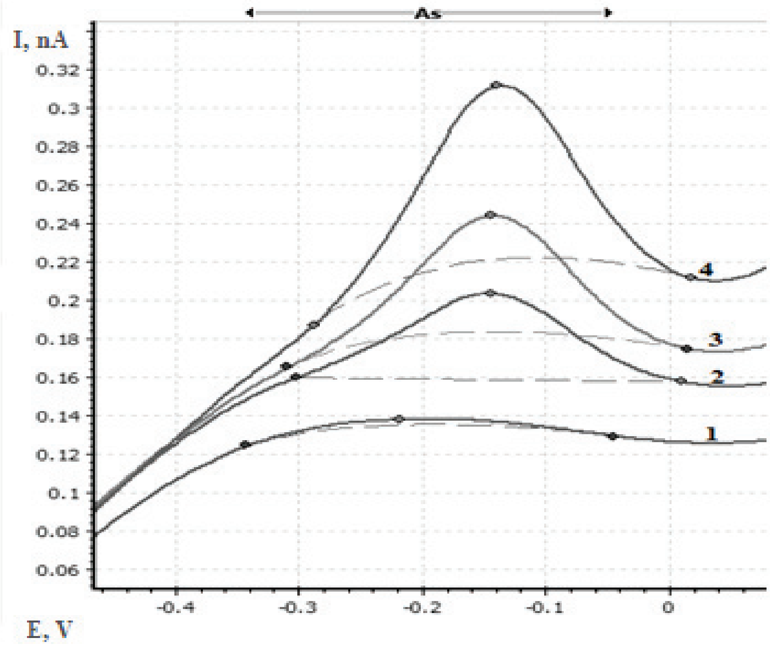


FIGURE 4. Different marking methods for As(V) analytical curve: (1) supporting electrolyte; (2) manually with a straight line; (3) manually with a wavy curve; automatically with a straight line

The effect of marking method on the accuracy of separate determination of arsenic(III, V) in case of tap water analysis in which As(III) and As(V) ions were added was of our interest. The results of ASV analysis of water on As(III) and As(V) after ion-exchange isolation of interfering ions using the cartridge *IC-H Hypersep* and cation-exchange resin *KU-2-8* are presented in Table 5.

TABLE 5. The determination results of As(III) and As(V) in tap water by ASV using different methods of analytical signal marking (0.002 mg·L^{-1}As(III) and 0.005 mg·L^{-1} As(V) were added)

Method of analytical response marking	**Found, mg·L^{-1}**			
	IC-H cartridge		**KU-2-8**	
	As(III)	**As(V)**	**As(III)**	**As(V)**
Automatic marking with wavy curve considering background curve	0.00200± 0.00008	0.00526± 0.00016	0.00197± 0.00004	0.00500± 0.00011
Manual marking with straight line considering background curve	0.00240± 0.00014	0.0046± 0.0003	0.00223± 0.00009	0.0056± 0.0003
Automatic marking with wavy curve not considering background curve	0.00300± 0.00016	0.0064± 0.0003	0.00310± 0.00017	0.0065± 0.0003
Manual marking with straight line not considering background curve	0.0029± 0.0007	0.0069± 0.0006	0.0030± 0.0006	0.0079± 0.0027
Manual marking with wavy curve (separately)	0.0016± 0.0003	0.0037± 0.0011	0.00160± 0.00024	0.0035± 0.0012

TABLE 6. The results of As (total) determination in natural water by ASV and ICP-OES

Sample No	Concentration, mg·L^{-1}				As Determination method				C_c	C
					ASV with ion-exchange		ICP-OES			
	Fe	Cu	Mn	Ni	C, mg·L^{-1}	s_r,%	C, mg·L^{-1}	s_r,%		
1	0.14	<0.010	2.25	0.014	0.0280 ± 0.0015	5.4	0.0270 ± 0.0026	9.8	0.0010	0.0030
2	0.97	0,015	11.00	0.150	0.0139 ± 0.0033	23	0.0150 ± 0.0009	5.9	0.0011	0.0034
3	0.54	<0.010	0.39	<0.010	0.0103 ± 0.0009	9.7	0.0104 ± 0.0013	13	0.0001	0.0016
4	15.00	0.015	4.40	<0.010	0.0085 ± 0.0009	10	0.0100 ± 0.0012	12	0.0015	0.0015
5	1390.44	0.110	15.40	5.800	unknown	–	4.9000 ± 0.3690	7.5	–	–
6	0.15	<0.010	0.11	<0.010	0.025 ± 0.005	19	0.023 ± 0.003	13	0.002	0.006
7	0.60	<0.010	0.37	<0.010	0.0110 ± 0.0019	17	0.0120 ± 0.0015	8.3	0.0010	0.0024

Note: The samples 1–3 are the water from different quarries and deposits of ore bodies (Central Kazakhstan); samples 4 and 5 are the water from wells; samples 6 and 7 are the river waters (the Russian Federation, Bakhchysarai and Central Kazakhstan).

Therefore, the determination of arsenic without ion exchange is not possible. The ion exchange method for the separation of interfering cations makes it possible to estimate the total arsenic content in natural waters.

In order to confirm the accuracy and correctness of the developed procedure of As stripping voltammetric determination in natural water, the comparative study of the experimental data obtained by stripping voltammetry with ICP-OES and the control procedure for precision control using control analytical procedure [22] has been done. For this purpose, the result of the control procedure C_c and the inspection standard C were calculated according to the following equations:

$$C_c = \bar{X} - X_c \tag{7}$$

$$C = \sqrt{\Delta_1^2 + \Delta_2^2}\ , \tag{8}$$

where $\bar{X}$ and X_c are the results of the same sample obtaining by the testing and control procedures, respectfully; Δ is the interval estimate of the precision factor for analysis results of the control analytical procedure, which corresponds to the component content in a sample.

It can be seen from the Table 6 that the result of the control procedure does not exceed the inspection standard. Therefore, the analytical results obtained by the developed method are accurate and meet the precision requirements.

SUMMARY

The effective and environmentally friendly method for sample preparation of water by ion-exchange for the direct determination of As(III) and As(V) by stripping voltammetry on gold microelectrodes. The ions Fe(III), Cu(II) and Ni(II) which interfere the arsenic(III) determination are isolated by strong-acidic cation-exchange resin in water (pH 1–7). Mn(III) ions act as a mediator in As(V) determination and are also isolated by the cation-exchange resin for the following precise addition of them. For determination of As(III) or total inorganic arsenic in arsenite form, it is possible to isolate the ions in acidic medium at pH 1.5–2 with HCl supporting electrolyte when As(V) is inactive. The natural water acidity (pH 6-7) is needed to save the arsenic forms for separate determination of As(III) and As(V). It has been shown that the ion-exchange cartridge *IC-H Hypersep*, sulfonated cation-exchange resins *KU-2-8* and *Purolite C100* can be recommended for the creation of affordable cartridges. The procedure of the direct stripping voltammetric determination of As(III, V) with the developed sample preparation procedure has been applied to drinking water analysis. The comparative analysis of natural waters on arsenic by stripping voltammetry preceded by the ion exchange and ICP-OES has been done. The correctness of the analysis results has been confirmed by the control analytical procedure for precision control [22]. The results have demonstrated similar precision; however, stripping voltammetry determination has the advantage of low cost and affordability.

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