
APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Determination of Arsenic in Aqueous Solutions by No-Reference Inversion Voltammetry

Yu. V. Tsapko, I. I. Tumkin, and S. S. Ermakov

St. Petersburg State University, St. Petersburg, Russia

Received July 17, 2008

Abstract—Electrochemical method for arsenic determination at concentrations characteristic of inversion voltammetry was suggested. The method does not require calibration of the measuring instrument against standard solutions or application of the standard-additive technique. The method of no-reference inversion-voltammetric determination is based on calculating the arsenic concentration in solution with the use of the preliminarily determined coulometric constant of an electrochemical cell.

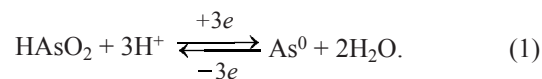
DOI: 10.1134/S1070427209020189

Arsenic and its compounds exhibit a high degree of pathologicity (at present, there are about 19 diseases associated with organism poisoning by arsenic compounds) [1]. Therefore, determination of microscopic concentrations of arsenic compounds is a topical task. This problem is aggravated by the tendency toward increasingly stringent regulations concerning the content of arsenic in various objects [e.g., the maximum permissible concentration (MPC) of arsenic in drinking water, established by the World Health Organization in 2001, was lowered from 50 to 10 $\mu\text{g l}^{-1}$] [2]. Modern laboratory practice widely employs for arsenic determination in aqueous media various techniques, such as atomic-absorption spectrometry with generation of hydrides and mass spectrometry with inductively coupled plasma [3–6]. Together with these methods, the leading position in determination of low concentrations of toxic elements is held by inversion voltammetry (IVA). The comparative simplicity and low cost of the equipment used, high sensitivity, and possibility of automation of the determination process predetermine the wide use of IVA.

A considerable number of publications has been devoted to cathodic and anodic versions of arsenic determination by IVA. Having metrological characteristics close to those of the anodic IVA (AIVA), the cathodic version suffers from significant disadvantages: highly toxic arsine evolves in the stage of the cathodic potential sweep and no less toxic mercury is used as the material

of the indicator electrode. This restricts the applicability area of the cathodic IVA, compared with AIVA.

In the stage of pre-electrolysis in the AIVA version, arsenic is concentrated at the electrode in the form of a deposit of elementary arsenic. The method is based on the following reaction:



It follows from Eq. (1) that arsenic accumulates at the cathode with a lower overvoltage in solutions containing a large excess of hydrogen ions. Therefore, solutions of strong mineral acids (0.1–10 M), such as sulfuric and, most frequently, hydrochloric, are commonly used for these purposes as a supporting electrolyte [7].

Because IVA is a comparative method and involves prolonged routine procedures of construction of calibration dependences with the use of reference samples, several alternations of no-reference electrochemical determination of toxic elements in aqueous solutions have been suggested recently [8–12].

The chronopotentiometric technique is based on multiple-cycle dissolution-deposition of a metal from an amalgam produced in the pre-electrolysis stage and subsequent finding of the quantity Q_∞ of electricity consumed for electroconversion of the whole mass of a substance being determined, present in solution. A similar method of “dynamic coulometry,” suggested

by Sokolkov [9], is based on using a cyclic potential sweep.

Jurica et al. [10] suggested a flow-through version of coulometric determination of arsenic on porous electrodes coated with a film of gold. The method has a comparatively high sensitivity and can be used for routine determination of arsenic contained in aqueous media in various concentrations.

However, these techniques have failed to find wide use because of the relative complexity and long duration of analytical procedures or need to use special instruments.

Two alternatives of combined no-reference electrochemical method based on principles of IVA and coulometry at controlled potential (CCP) have been suggested for determining zinc, cadmium, lead, copper, and mercury [11–14]. Originally, heavy metal ions were determined by a procedure using the Meytes formula for calculating the concentration; later, a version was employed, based on using the coulometric constant k of the electrochemical cell, calculated by the equation

$$\log (c_i/c_0) = kt_{\text{acc}} \quad (2)$$

where c_i is the concentration at time instant t_{acc} , and c_0 , initial concentration of the analyte in solution.

The method does not require any special equipment and is comparatively rapid.

In solving various problems of industrial control and ecological monitoring, it is frequently necessary to use reliable and easily automated analytical techniques. To these belong, in particular, no-reference electrochemical methods. The possibility of using a variation of techniques of this kind for determining arsenic in aqueous solutions and the choice of the optimal measurement conditions are the subject of the present study.

EXPERIMENTAL

Inversion-voltammetric measurements were made on a PU-1 polarograph (ZIP, Gomel) with an AKV-07 transducer (NPKF Avilon, Moscow) and an AKV-07MK voltammetric analyzer with Polar-4.1 software (NPKF Avilon, Moscow) in the ac and dc modes. Solutions with various arsenic(III) ion concentrations were prepared from GSO 1 g l⁻¹ solutions [GSO (State Standard Sample 7143–95)]. The solutions were prepared from reagents of special-purity, chemically pure, and analytically pure

grades and double-distilled water. The measurements were made with a gold rotating-disk electrode (GRDE), with the rotation rate of the electrode in the accumulation stage equal to 1000 rpm. The electrode was prepared for operation by polishing with an emery powder (5 μm) deposited onto a filter paper wetted with ethanol. The electrochemical cleaning of the working electrode was made at a potential $E_{\text{cl}} = +0.3$ V. The design of the electrochemical cell and electrode has been described previously [11, 15]. All the measurements were made relative to a saturated silver chloride reference electrode ($E = +0.203 \pm 0.001$ V relative to s.h.e.). To satisfy the condition of complete dissolution of arsenic deposited onto the GRDE surface, comparatively low potential sweep rates (2–5 mV s⁻¹) were used [15].

Because the method suggested employs the IVA measurement scheme, the first stage of the study was devoted to finding the optimal conditions of arsenic determination by the AIVA technique.

As supporting electrolytes were studied sodium sulfite (0.4 M) and EDTA (0.01 M) solutions and solutions with varied sulfuric acid concentrations (0.1 to 7 M) [6, 16, 17]. Inversion voltammograms of arsenic were obtained in the ac mode at various concentrations of the arsenite ion in the supporting electrolyte. The data obtained upon integration of the anodic current peaks of arsenic dissolution were used to construct dependences of the arsenic dissolution current peak area on the concentration of arsenic(III) ions in solution. As criteria for choosing the composition of the supporting electrolyte served the sensitivity and the scatter of the arsenic dissolution peak areas, obtained at different concentrations of arsenic ions in solution.

In the case when the supporting electrolyte contained sodium sulfite, a comparatively wide scatter of arsenic dissolution peak areas was observed (rms deviation 9.9%), which is presumably so because electrodeposition of arsenic in alkaline solutions occurs only at high cathodic potentials (about –1.6 V) and is accompanied by hydrogen evolution. The most satisfactory results were obtained with hydrochloric acid solutions used as supporting electrolytes (rms deviation 0.5–3%). In this case, as it would be expected, the sensitivity of arsenic determination increased with the hydrochloric acid concentration.

The effect of the HCl concentration on the arsenic dissolution peak area was studied. The plot of the arsenic dissolution peak area against the hydrochloric acid concentration is shown in Fig. 1a, whence follows that in

the HCl concentration range 0.1–5 M a linear increase in the arsenic dissolution peak area is observed. However, further increase in the hydrochloric acid concentration in solution results in a decrease in the sensitivity of its determination, which is probably due to passivation of the gold electrode surface by gold chloride formed in the stage of electrochemical cleaning. Therefore, a hydrochloric acid solution with a concentration of 5 M was chosen as the supporting electrolyte.

To choose the optimal accumulation potential, voltammograms of arsenic were obtained at a concentration of 6.7×10^{-7} M of arsenic ions in solution at various accumulation potentials. The measurement results are shown in Fig. 1b, from which follows that the optimal accumulation potential is $E_{\text{acc}} = -0.3$ V. It should be noted that, with more negative pre-electrolysis potentials used, the arsenic dissolution peak area sharply decreases because the predominant process at these potentials is hydrogen evolution.

It is known [7] that, being deposited in the accumulation state, arsenic forms an amorphous deposit on the surface

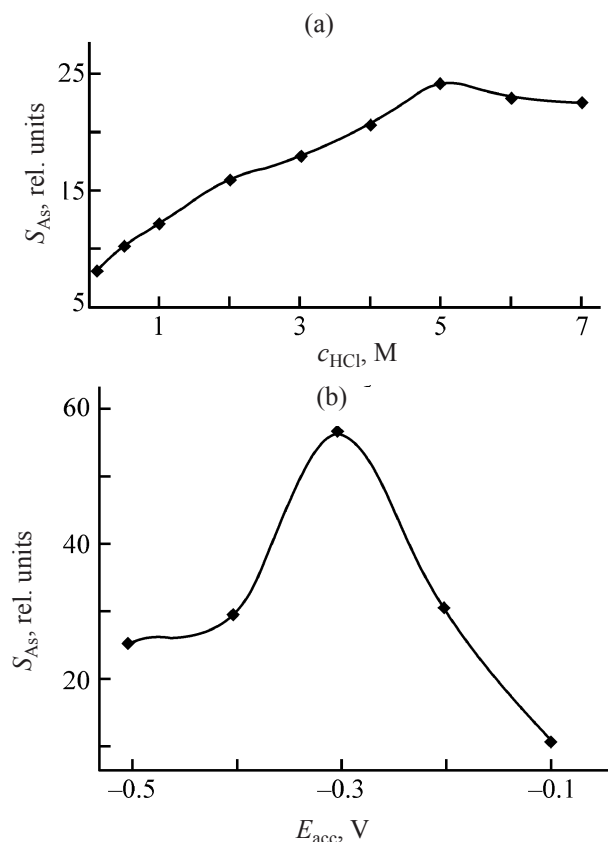


Fig. 1. Arsenic dissolution peak area S_{As} vs. (a) the hydrochloric acid concentration c_{HCl} and (b) the accumulation potential E_{acc} . $S_{\text{el}} = 28.73 \text{ mm}^2$, $c_{\text{As}}^{3+} = 6.70 \times 10^{-7} \text{ M}$, $V = 3 \text{ ml}$, $t_{\text{acc}} = 60 \text{ s}$.

of the indicator electrode and this deposit is a poor electric current conductor. Therefore, the variation of the arsenic dissolution peak area with the accumulation time was studied in order to find the optimal accumulation time interval, during which the limiting dissolution current markedly changes. The plot of the arsenic dissolution peak area against the accumulation time, obtained at a constant arsenic(III) concentration in solution, is shown in Fig. 2.

The dependence obtained confirms that, at a long accumulation time ($t_{\text{acc}} \geq 360 \text{ s}$), the surface is completely covered by a deposit of elementary arsenic, which has a high electrical resistance. This makes lower the limiting anodic dissolution current and thereby restricts the working range of accumulation times. Therefore, a larger-area (28.73 mm^2) working electrode was used in further measurements in order to diminish the saturation effect.

To determine the working concentration range, the dependence of the arsenic dissolution peak area on the arsenic(III) concentration in solution was studied (Fig. 3). Because the MPC of arsenic in natural water is

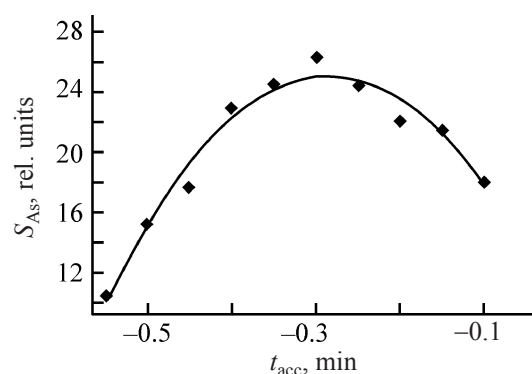


Fig. 2. Arsenic dissolution peak area S_{As} vs. the accumulation time t_{acc} . $S_{\text{el}} = 28.73 \text{ mm}^2$, $c_{\text{As}}^{3+} = 6.70 \times 10^{-7} \text{ M}$, $V = 3 \text{ ml}$, $E_{\text{acc}} = -0.3 \text{ V}$.

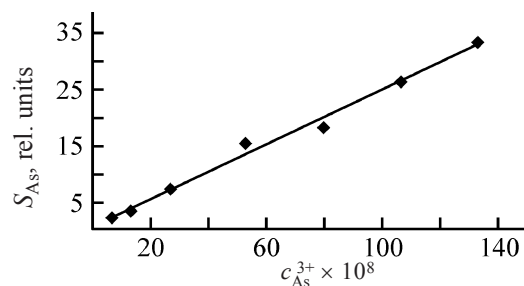


Fig. 3. Arsenic dissolution peak area S_{As} vs. the arsenic(III) concentration c_{As}^{3+} in solution. $S_{\text{el}} = 28.73 \text{ mm}^2$, $V = 3 \text{ ml}$, $t_{\text{acc}} = 60 \text{ s}$, $E_{\text{acc}} = -0.3 \text{ V}$.

10 $\mu\text{g l}^{-1}$, all the subsequent measurements were made at concentrations lower than 10 $\mu\text{g l}^{-1}$.

One of the basic conditions for implementation of the method suggested here is that the coulometric constant of the electrochemical cell should be determined. For this purpose, dependences of $\log(c_i/c_0)$ on t_{acc} on GRDE in a cell with 3 ml of a supporting electrolyte solution were studied at different arsenic(III) concentrations in solution (Fig. 4).

It follows from Eq. (2) that the coulometric constant k is independent of the initial analyte concentration c_0 in solution, and this was confirmed experimentally.

Indeed, it follows from the values of coulometric constants for various arsenic(III) concentrations in solution that these values differ only slightly. The average constant of the electrochemical cell at a solution volume of 3 ml is $(3.13 \pm 0.06) 10^{-4} \text{ s}^{-1}$.

Thus, the fact that the experimentally obtained coulometric constants are in good agreement with theoretical concepts, which made it possible to pass to their use for experimental verification of the applicability of the no-reference IVA method for determination of arsenic in aqueous solutions.

For this purpose, measurements were made by the introduced–found method in a supporting electrolyte solution with a volume of 3 ml at different accumulation times and arsenic(III) concentrations in solution in the dc mode. The quantities Q_t of electricity corresponding to the accumulation time t_{acc} were calculated by integration of the arsenic dissolution current over time. Equation (3) and the resulting values of Q_t were used to calculate the quantities Q_{∞} of electricity that corresponds to complete

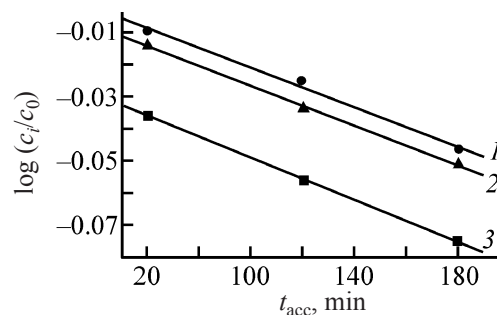


Fig. 4. $\log(c_i/c_0)$ vs. the accumulation time t_{acc} for various As^{3+} concentrations in solution. $S_{\text{el}} = 28.73 \text{ mm}^2$, $V = 3 \text{ ml}$, $E_{\text{acc}} = -0.3 \text{ V}$, $v_{\text{rot}} = 1000 \text{ rpm}$.

electroconversion of arsenic present in the solution bulk:

$$Q_{\infty} = \frac{Q_t}{1 - e^{-kt_{\text{acc}}}}$$

The obtained values of the quantity of electricity, Q_{∞} , were used to calculate the arsenic(III) concentration in solution by the Faraday law (see table). The experimental data presented above confirm that the no-reference IVA method can be used to determine arsenic in aqueous solutions.

It should be noted that applying the no-reference procedure of IVA with the use of the Meites formula to find Q_{∞} [11, 12, 15] fails to produce satisfactory results. A probable reason is that the range of the accumulation times used is limited because of specific features of the element being determined (Fig. 2).

CONCLUSIONS

(1) The possibility of using the no-reference inversion-voltammetric method for determining arsenic in aqueous

Results of arsenic determination on GRDE with the use of the coulometric constant ($n = 3$)

$c_0 \times 10^8, \text{ M}$	$Q_{\infty}^{\text{theor}}, \mu\text{C}$	$t_{\text{acc}}, \text{ s}$	Q_t	Q_{∞}^{calc}	$c^{\text{calc}} \times 10^8$	$c_{\text{av}} \times 10^8$	S_r
			μC		M		
2.7	26.05	60	1.27	30.30	3.1	3.1	18.0
		120	2.82	34.40	3.6		
		180	3.50	22.20	2.3		
6.7	57.32	60	1.96	46.40	5.5	6.0	8.0
		120	4.96	57.15	6.6		
		180	5.84	49.40	5.8		
13.3	115.80	60	3.90	93.50	11.0	11.5	1.0
		120	9.40	112.80	13.0		
		180	10.50	87.10	10.4		

solutions was experimentally established. The optimal experimental conditions for arsenic determination by this method were determined.

(2) The method suggested for determination of arsenic can be employed for automated monitoring of its content in technological solutions and wastewater of metallurgical shops.

REFERENCES

1. *Vrednye khimicheskie veshchestva: Neorganicheskie soedineniya V–VIII grupp* (Noxious Chemical Substances: Group V–VIII Inorganic Compounds), Leningrad: Khimiya, 1989.
2. He, Y., Zheng, Y., Ramnaraine, M., and Locke, D.C., *Analyt. Chim. Acta*, 2004, vol. 511, pp. 55–61.
3. Gong, Z., Lu, X., Ma, M., Watt, C., and Le, C., *Talanta*, 2002, vol. 58, pp. 77–96.
4. Richardson, S., *Analyt. Chem.*, 2001, vol. 73, pp. 2719–2734.
5. Melamed, D., *Analyt. Chim. Acta*, 2005, vol. 532, pp. 1–13.
6. Hung, D., Nekrassova, O., and Compton, R., *Talanta*, 2004, vol. 64, pp. 269–277.
7. Sun, Y.-C., Mierzwa, J., and Yang, M.-H., *Talanta*, 1997, vol. 44, pp. 1379–1387.
8. US Patent 5891322.
9. Sokolov, S.V. and Zagorodnyuk, P.N., *Zh. Ross. Khim., O–va im. D.I. Mendeleeva*, 2001, vol. 45, pp. 78–82.
10. Jurica, L., Manova, A., and Beinrohr, E., *Polish J. Environ. Studies*, 2004, vol. 13, pp. 533–536.
11. Sheremet, A., Averyaskina, E., Chekmeneva, E., and Ermakov, S., *Electroanalysis*, 2007, vol. 19, pp. 2163–2165.
12. Ermakov, S.S., Sheremet, A.A., and Moskvina, L.N., *Zh. Prikl. Khim.*, 2008, vol. 81, no. 3, pp. 434–436.
13. Ermakov, S.S., Tsapko, Y.V., and Chezhina, N.M., Abstracts of Papers, *12th Int. Conf. on Electroanalysis*, Prague, June 16–19, 2008, p. 85.
14. RF Patent 2199734.
15. Ermakov, S.S., Chekmeneva, E.N., and Moskvina, L.N., *Zh. Anal. Khim.*, 2007, vol. 62, pp. 89–94.
16. Zaichko, A.V., Ivanova, E.E., and Noskova, G.N., *Zavod. Lab.*, 2005, vol. 71, pp. 19–23.
17. Zakharova, E.A., Deryabina, V.I., and Slepchenko, G.B., *Zh. Anal. Khim.*, 2005, vol. 60, pp. 571–575.