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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Fast Procedure for No-Reference Inversion-Voltammetric Determination of Lead in Aqueous Solutions

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Abstract—Possibility of no-reference inversion-voltammetric determination of lead in aqueous solutions with the use of a preliminarily determined coulometric constant of the electrochemical cell, which enables substantially faster analysis as compared with the known analogs, was studied. The coulometric constants of electrochemical cells with a mercury film electrode were found for different solution volumes.

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Reliable and easily automated analytical techniques are necessary for controlling the quality of products and, in particular, the quality of plated coatings and products of hydrometallurgical industries. To such methods belong no-reference electrochemical techniques. This communication considers a version of methods of this kind.

Several alternatives of no-reference inversion-voltammetric methods have been suggested. To these techniques belongs no-reference inversion chronopotentiometry [1] based on multiple-cycle dissolution of a metal from an amalgam produced in the pre-electrolysis stage and subsequent determination of the quantity of electricity, Q_∞, necessary for complete recovery of a substance from solution. In addition, a variation of the no-reference method based on cyclic deposition and dissolution of a metal from the amalgam obtained in the accumulation stage has been suggested, named "dynamic coulometry" [2].

The aboveprocedures of no-reference electrochemical methods were not further developed and have failed to find wide application because of the comparatively intricate and prolonged analytical procedures involved and need to use specialized instruments. The prolonged analysis is also characteristic of an integrated no-reference electrochemical method [3, 4] combining principles of inversion voltammetry (IVA) and controlled-potential coulometry (CPC), based on a calculation of the total quantity of electricity, Q_∞, by the Meites formula [5]. However, three successive measurements with different accumulation times t_{acc} should be made to find Q_∞, making the analysis duration substantially longer than that in the classical IVA procedure.

To develop the previously proposed approach to no-reference determination of lead ions, it was suggested in this study to solve this problem by using the following equation for calculation:

$$Q_\infty = \frac{Q_t}{1 - e^{kt}}, \quad (1)$$

where Q_t is the quantity of electricity consumed for conversion of a given substance during a time t; t, pre-electrolysis duration; and k, coulometric constant of the electrochemical cell [6].

Use of formula (1) can simplify the measurement scheme, because a single determination of the quantity of electricity, Q_t, corresponding to an accumulation time t_{acc} is sufficient in this case. However, its practical application requires a preliminary determination of the coulometric constant k. The value of this constant is determined by the measurement conditions and can be theoretically calculated by the equation

$$k = \frac{SD}{V\delta} \quad (2)$$

where S is the surface area of the working electrode; D, diffusion coefficient; V, solution volume; and δ, diffusion layer thickness.

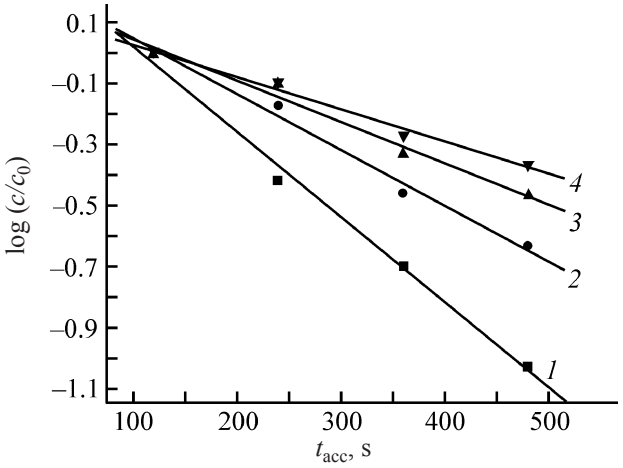

Fig. 1. Logarithm of normalized concentration of lead(II) ions, log (c/c_0), vs. the electrolysis time t_{acc}. Solution volume (ml): (*1*) 2, (*2*) 3, (*3*) 4, and (*4*) 5.

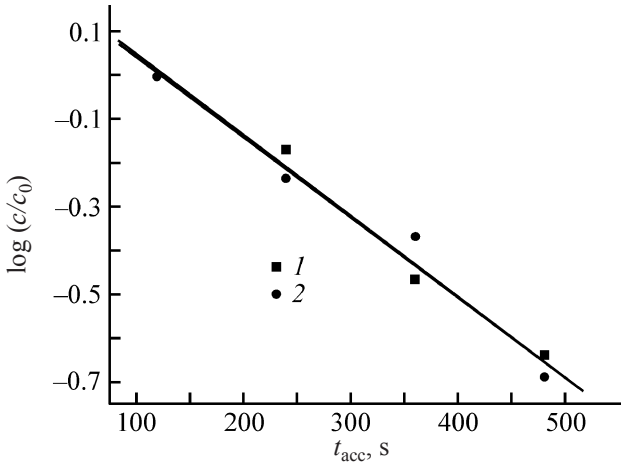

Fig. 2. Logarithm of normalized concentration of lead(II) ions, log (c/c_0), vs. the electrolysis time t_{acc} for solutions with lead(II) ion concentrations of (*1*) 1×10^{-7} and (*2*) 5×10^{-8} M. ($K = 5.4 \times 10^{-3}$ s^{-3}).

Experimentally, the coulometric constant k can be found from the equation

$$\log (c_i/c_0) = -kt, \qquad (3)$$

where c_i is the running concentration at an arbitrary instant of time, and c_0, initial concentration.

The aim of this study was to experimentally verify the suggested rapid procedure of no-reference inversion-voltammetric determination with the use of the coulometric constant of the electrochemical cell for the example of determination of lead(II) in aqueous solutions.

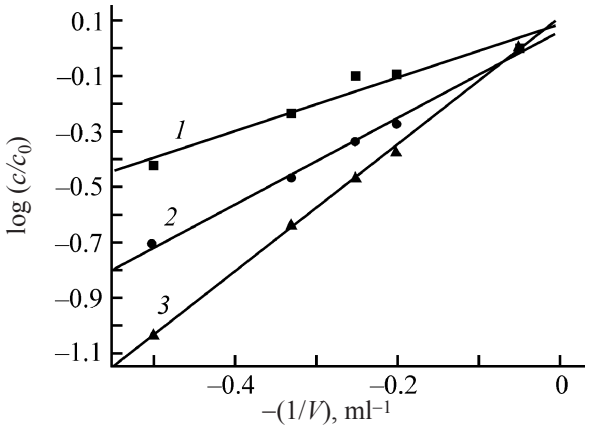

Fig. 3. Logarithm of normalized concentration of lead(II) ions, log (c/c_0), vs. the inverse volume of a solution being analyzed, $1/V$. $c_0^{Pb} = 1 \times 10^{-7}$ M. t_{acc} (s): (*1*) 240, (*2*) 360, and (*3*) 480.

EXPERIMENTAL

The inversion-voltammetric measurements for determining the coulometric constant were made in the ac mode on an AKV-07 MK voltammetric analyzer (NPKF Akvilon Private Company, Moscow) in a supporting electrolyte of composition 5×10^{-2} M HCl + 1×10^{-4} M $HgNO_3$. A film-type mercury rotating-disk electrode with a working surface area $S_{el} = 0.071$ cm^2 was used as the working electrode. The silver chloride reference electrode ($E = 0.2303 \pm 0.001$ V) for measurements in small-volume cells was fabricated as it was done in [3]. A glassy-carbon crucible served as auxiliary electrode and, simultaneously, as measuring cell. Lead(II) was determined in aqueous solutions in the dc mode on a PU-1 polarograph (ZIP, Gomel) with an AKV-07 transducer. Voltammograms were recorded using a personal computer with a Grafit-2 interface unit (NTF Vol'ta, St. Petersburg). The potential sweep rate in dc measurements was maintained within the range 2–5 mV s^{-1} to provide complete transfer of lead from the amalgam into solution in the electrodissolution stage. In the measurements, the accumulation stage was performed at a potential $E_{acc} = -1.1$ V. Small-volume cells were fabricated by gluing-in a poly(ethylene terephthalate) cylinder into the glassy-carbon cell; for volumes of 2 and 3 ml, a glassy-carbon insert was used. It has been shown previously [3, 4] that the concentration strongly changes at an accumulation time of 120 s in a cell with a solution volume of less than 6 ml, and, therefore, all measurements were made in solutions with volumes smaller than 5 ml.

Model solutions containing lead(II) ions were prepared from State standard samples with a rated ion concentration

Table 1. Coulometric constants for lead(II) ion solutions of various concentrations

V, ml	$k \times 10^3$, s^{-1}			$kV \times 10^3$, ml s^{-1}			S_r, %	
	at indicated solution concentrations, M							
	5×10^{-8}	1×10^{-7}	average	5×10^{8}	1×10^{-7}	average	5×10^{8}	1×10^{-7}
2	–	2.7	2.7	–	5.4	5.4	–	0.04
3	1.8	1.8	1.8	5.4	5.4	5.4	0.03	0.04
4	1.3	1.4	1.4	5.2	5.6	5.4	0.04	0.04
5	1.1	1.1	1.1	5.5	5.5	5.5	0.04	0.00

Table 2. Results of lead(II) determination by the fast pocedure of integrated no-reference electrochemical method

V, ml	t_{acc}, s	Q_t	Q_∞	$Q_{\infty theor}$	$c \times 10^8$, M		S_r, %
		μC			introduced	found	
5	360	6.62	11.07	12.06	1.25	1.15	8.0
	360	13.05	21.82	24.12	2.50	2.26	9.6
	480	8.88	12.62	12.06	1.25	1.31	4.8
4	360	14.29	20.97	19.30	2.50	2.72	8.8
	480	6.53	8.35	8.35	1.25	1.08	13.6
3	480	5.99	6.90	7.24	1.25	1.20	4.0
	480	10.57	12.18	14.48	2.50	2.10	16.0

Table 3. Results of lead(II) determination from data obtained in [3]

V, ml	t_{acc}, s	Q_t	Q_∞	$Q_{\infty theor}$	$c \times 10^8$, M		S_r, %
		μC			introduced	found	
3	720	6.36	6.70	6.37	1.10	1.16	5.5
2	600	19.16	19.60	19.30	5.00	5.08	1.6
3	300	20.06	28.19	28.95	5.00	4.87	2.6

of 1 g l^{-1}. All solutions were produced from reagents of chemically pure grade and double-distilled water.

The experimental data were processed using Origin 6.1 software. The quantity of electricity Q_t was found by integrating over time the current of lead dissolution from the amalgam.

To find the coulometric constant of the electrochemical cell, electrolysis of solutions with a known concentration of lead(II) ions was performed at a constant accumulation time. Thus, the total time of electrolysis was constituted by accumulation times. Lead was dissolved from the surface of a mercury-graphite film electrode (MGFE) into a supporting electrolyte solution in another cell of volume V = 20 ml. The completeness of lead dissolution was verified by repeated measurements of voltammograms in the supporting electrolyte solution. The concentration of lead(II) ions in solution was calculated from the heights of lead ionization peaks in the voltammograms. The coulometric constant k was found from the plot of log (c_i/c_0) against t_{acc} (Fig. 1) for the optimal (for the employed measurement technique) solution volumes of 2, 3, 4, and 5 ml for MGFE. The coulometric constants for each solution volume were calculated from Fig. 1. The values of the constants are listed in Table 1.

It follows from Fig. 1 that the quantity $K = kV$ is constant [$K = (5.5 \pm 0.1)\ 10^{-3}$ ml s^{-1}] under the measurement conditions specified.

In accordance with Eq. (3), k must be independent of the initial concentration c_0. To verify the correspondence of the experimental data to Eq. (3), the coulometric

constants were determined for solutions with different concentrations of lead ions in solution. The data obtained indicate that, within the measurement error, the values of the constants are independent of the concentration of lead(II) ions in solution (Table 1, Fig. 2).

It follows from Eq. (2) that the value of the coulometric constant is inversely proportional to the volume of a solution under study. This is experimentally confirmed by the data in Fig. 3. Indeed, the dependences of $\log(c_i/c_0)$ on $-1/V$ at different accumulation times are represented by straight lines converging to a common point at sufficiently large solution volumes at which the concentration is almost invariable in the course of electrolysis.

The experimental data presented above are in good agreement with the basic equations of potentiostatic coulometry [6], whence follows that the values found for the coulometric constants can be used when determining the concentration of lead(II) in solution by Eq. (1).

The resulting value of the coulometric constant K was used to calculate Q_∞ from Q_t found by integrating over time the current of the peak of lead dissolution from the amalgam in dc votammograms measured in supporting electrolyte solutions with addition of lead(II) ions. The measurement results are listed in Table 2. The calculations were made in two ways: using the average value of K, found for different volumes, and with k calculated for a given solution volume. Also, Q_∞ was calculated from the values of Q_t, reported in [3]. The results obtained are listed in Table 3.

The data in Tables 1–3 demonstrate a good agreement between the input and found concentrations.

CONCLUSIONS

(1) It was demonstrated that the rapid no-reference method of lead determination is convenient for automated analysis of technological solutions and wastewater from galvanic and hydrometallurgical shops.

(2) The coulometric constants were found for lead(II) ions at various ion concentrations and solution volumes. The possibility of determining lead(II) by the fast procedure of integrated no-reference electrochemical method in model solutions was demonstrated.

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