DETERMINATION OF MICROQUANTITIES OF METALS BY THE METHOD OF ALTERNATING CURRENT FILM POLAROGRAPHY WITH A GRAPHITE ELECTRODE

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A method is proposed for the preparation of a graphite electrode, for use in alternating current polarography, in conjunction with a TsLA vector polarograph. It has been shown that it is possible to determine microquantities of Pb, Cu, and Cd by alternating current polarography, after preliminary concentration on the electrode. The time taken for determination of a reversibly reducible metal was reduced by a factor of 20, as compared with the method of direct current film polarography.

Graphite electrodes have been widely used in recent years in electrochemical methods of analysis [1]. However, only one paper [2] has appeared on the use of graphite and carbon paste in alternating current polarography.

There would appear to be good prospects for increasing the sensitivity of the determination by preliminary electrochemical concentration of the material on the surface of a graphite electrode [3], followed by registration of an alternating current polarogram for electrodissolution of the deposit.

We used the TsLA vector polarograph for investigating the possibility of using graphite electrodes in alternating current polarography. The electrodes which we employed recently for direct current film polarography were unsuitable for use with the TsLA vector polarograph, since the residual current, observed in measurement of the active component of the current, was too high (about 15 μA).

For the impregnation of these electrodes, in vacuum over a period of 4 to 6 h, we had used a mixture of epoxy resin (ÉD-6) with a hardener (polyethylenepolyamine) in the ratio of 100 : 1 or 100 : 2. The electrodes were sealed into glass tubes with polyethylene powder, and could be used at a sensitivity of 10^{-8} A/mm for recording direct current polarograms.

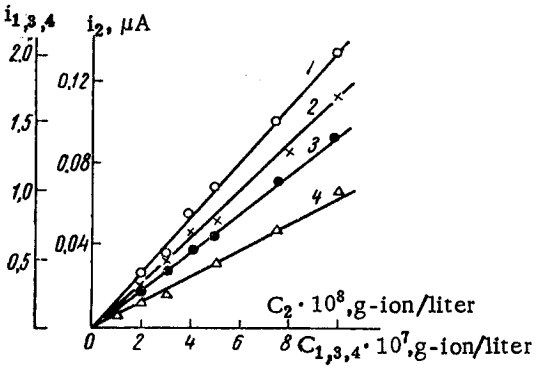

Fig. 1. The relation between the maximum active component of the alternating current obtained during electrodissolution of 1) cadmium, 2, 3) lead, and 4) copper, previously deposited from N HCl ($\tau_{electrolysis}$ = 1 min, $E_{\sim}$ = 4 mV, v = 15.5 mV/sec,

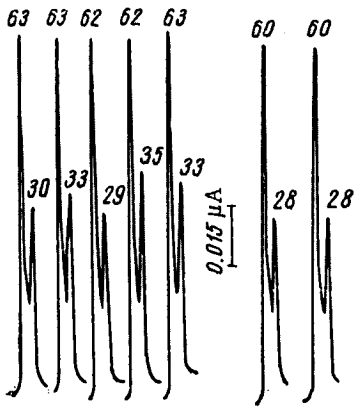

Fig. 2. Vector polarograms of successive determinations of 10^{-2} g-ion of Pb^{2+} per liter and of $3 \cdot 10^{-7}$ g-ion of Cu^{2+} per liter.

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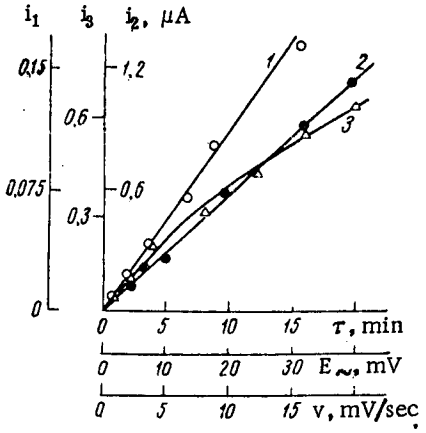

Fig. 3. Variation of the maximum active component of the alternating current in the electrodissolution of lead, with 1) the rate of change of the constant component of the potential, 2) the duration of electrodeposition, and 3) the amplitude of the alternating voltage. 1 and 3) τ electrolysis = 1 min; 1 and 2) $E_{\sim}$ = 4 mV; 2 and 3) v = 15.5 mV/sec.

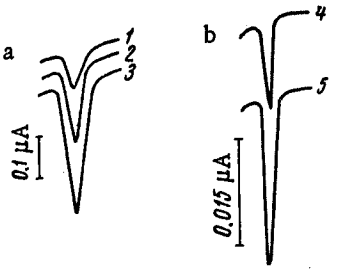

Fig. 4. a) Normal and b) vector polarograms of the electrodissolution of lead, previously concentrated on an electrode. The solvent was N HCl, and the solutions contained 10^{-8}, $2 \cdot 10^{-8}$, and $3 \cdot 10^{-8}$ g-ion of Pb^{2+} per liter for curves 1 and 4, 2 and 5, and 3 respectively. The electrolysis times were a) 20 min and b) 1 min.

Electrodes impregnated with molten paraffin wax in vacuum gave a capacity current of 3 to 5 μA. These electrodes were used with a vector polarograph to obtain a polarogram corresponding to the process of electrodeposition and electrodissolution for various metals. However, the results showed poor reproducibility.

The best results were obtained with electrodes prepared as follows. Twenty to thirty g of paraffin wax was placed in a crucible and melted on a hotplate. Small portions of low pressure polyethylene powder were added to the melt, until the total amount added was 25 to 30% of the weight of the paraffin wax. Each portion of polyethylene was allowed to dissolve completely before adding the next one.

The hot mixture was transferred to a tube and a cylindrical rod of spectrally pure graphite, of purity V-3, 2 mm in diameter and 10 to 15 mm long was immersed in it. The tube was connected to a vacuum pump and evacuated for 6 to 8 h, while the tube was heated on an electric hotplate. The electrode was then removed from the mixture, cooled, and pressed firmly into a glass tube, the inside of the end of which had previously been cleaned. The lateral surface of the electrode and adjacent end of the glass were insulated by the impregnation mixture. Mercury was poured into the inside of the tube to make contact.

Electrodes prepared as above were used in all the subsequent investigations. Measurements were carried out with the three-electrode system of the vector polarograph, with saturated silver chloride reference and auxiliary electrodes. In other respects the experimental technique did not differ from the normal use of a polarograph with accumulation.

As a check on the measurements with the vector polarograph, polarograms were recorded under the same conditions with a Hungarian OH-101 direct current polarograph.

Figure 1 shows the relation between the maximum active component of the alternating current, during electrodissolution of cadmium, lead, and copper, and the concentration of the corresponding ion in the solution. The relation observed was a direct proportionality, and could therefore be used for determining microquantities of various metals. The maximum active component of the alternating current, obtained during electrodissolution of the metal deposit, greatly exceeded the corresponding signal obtained by direct polarography of the solution.

The use of preliminary concentration of metals on a solid electrode in alternating current polarography considerably increased the sensitivity of a determination. A useful signal was obtained during the process of electrodissolution, and the electrode was made ready for a subsequent determination. Accordingly, in direct current film polarography, a graphite electrode could be used for a long time in solutions of chemical reagents without renewal of the surface. However, in the case of alternating current polarography, the reproducibility of results obtained with a stationary electrode was much more affected by the adsorption of traces of surface-active compounds. This affected the velocity constant of the electrode process and its degree of reversibility, and hence the value of the signal measured.

Our experiments showed that mechanical renewal of the surface of a graphite electrode, impregnated with a mixture of paraffin and polyethylene, before each determination gave results which were satisfactorily reproducible.

Figure 2 shows the results of successive determinations of 10^{-7} g-ion of Pb^{2+} per liter and $3 \cdot 10^{-7}$ g-ion of Cu^{2+} per liter, in N hydrochloric acid. The maximum deviation for individual measurements did not exceed 20% relative. In this case, the working surface of the electrode was cleaned with a fine abrasive and polished with filter paper before each determination. When the electrode surface was not renewed in this way, each successive determination gave an alternating current peak which was approximately 20 to 30% smaller than the previous one. This was due to poisoning of the working surface of the electrode by traces of surface-active compounds.

Figure 3 shows the variation of the maximum active component of the alternating current, during the electrodissolution of lead concentrated from solutions containing 1) $5 \cdot 10^{-8}$ and 2) and 3) 10^{-7} g-ion of Pb^{2+} per liter, with 1) the rate of change of the constant component of the potential, 2) the duration of the electrodeposition, and 3) the amplitude of the alternating voltage. The first two relations were linear over the range of variation studied, and the last was linear as long as the amplitude of the alternating voltage was small.

Under similar conditions, with amalgam alternating current polarography with accumulation [4, 5], the second of these relations was curved, and in some cases the maximum current fell with increasing duration of electrodeposition. This can be explained by a reduction in the rate of the electrode process, as the result of adsorption of surface-active compounds during the electrolysis. The linear character of the relations observed, in the case of film vector polarography with accumulation on a graphite electrode, gave a basis for supposing that the sensitivity of this method could be considerably increased by using a long preliminary period of electrolysis.

The difference between the relations could be explained by the supposition that, in film polarography with accumulation, the film of electrically deposited metal, formed on the electrode surface during the concentration process, is less affected by the adsorption of surface-active substances than is a film on mercury. Lyalikov and his co-workers [6, 7] have shown that formation of a film of electrodeposited metal on the surface of a solid electrode favorably affects the reproducibility of the determination of similar ions by the direct method of alternating current polarography.

Figure 4 shows polarization curves for the electrodissolution of lead, recorded by direct current and alternating current film polarography. A convenient signal for measurement, in the determination of lead by film vector polarography, was obtained when the duration of preliminary electrolysis was only about a twentieth of that required when a direct current polarogram was recorded. It may be assumed that the same reduction factor applies to the minimum concentration of lead determinable by vector polarography with accumulation, as compared to determination by direct current polarography with the same time for preliminary concentration.

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