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THE USE OF GRAPHITE ELECTRODES IN OSCILLOGRAPHIC POLAROGRAPHY FOR TRACE DETERMINATIONS

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The substance to be determined is first electrochemically concentrated in the form of a film on the graphite electrode. The film which forms is dissolved with linearly changing voltage or a rigidly specified current. Direct proportionality is observed between the anodic peaks and the concentration of the corresponding ions in solution.

The difficulties encountered in the use of solid electrodes in polarography are due to a change in the electrode surface during the measurement.

Using preliminary concentration on a platinum electrode [1, 2] a double positive effect can be obtained: the useful signal can be considerably increased with practically constant value of the capacitance current (which means that electrodes can be used with a less smooth surface than in ordinary oscillographic polarography), and the electrode can be cleaned and prepared for the next experiment during an actual measurement.

We therefore decided to study the possibility of using nonamalgamated solid, especially graphite, electrodes in oscillographic polarography with a fixed current or a voltage varying according to a definite law for trace determinations.

To obtain oscillograms in the method with fixed current we used the P-576 polaroscope (Czechoslovakia) with a photoattachment consisting of a "Zernit" camera with adaptor rings and a relay which makes it possible to photograph oscillograms at a given instant. In the method with continuously changing voltage the oscillograms were obtained with the 02 TsLA oscillographic polarograph.

In both cases the electrodeposition on the electrode was carried out on a stationary electrode with the solution mixed with a magnetic stirrer. In the first case the auxilliary electrode was a silver chloride electrode, and in the second case it was a saturated calomel electrode. In the electrolyzer [3] instead of a hanging mercury drop we used a graphite electrode in the form of a small rod sealed in a polythene tube by paraffin. V-3 graphite was first impregnated in vacuum with molten paraffin or ÉD-6 epoxide resin. In the last case the impregnated electrode was gradually heated to 140°C and kept at this temperature for 4 hours. Maleic anhydride was used as the polymerization catalyst.

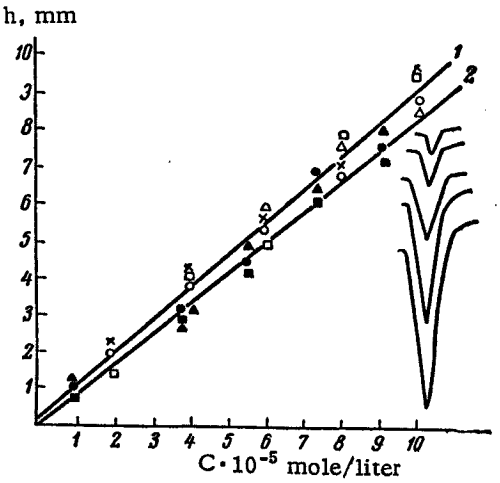

Fig. 1. Oscillograms of copper obtained at a given voltage, and the dependence of the maximum current of electrolytic dissolution on the copper ion concentration on the electrode impregnated with epoxide resin and kept in water 1 and in air 2 (●○– first day, ■□–fourth day, × –seventh day, ▲△– tenth day).

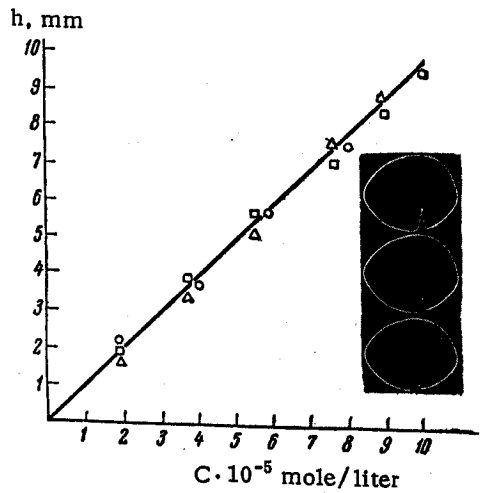

Fig. 2. Dependence of the cadmium peak (in relative units) on the concentration of its ions using a graphite electrode impregnated with wax.

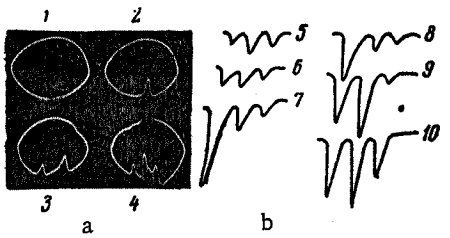

Fig. 3. Oscillograms of cadmium, lead, and copper, obtained with a fixed current a (direct component DC = 0.5, alternating component AC = 1.3; time of electrodeposition 15 sec; φ = -1.1 V) and voltage varying according to a certain law b (rate of change in voltage 0.125 V/sec; time of electrodeposition 60 sec; φ = -1.1 V); 1) Supporting electrolyte; 2) Cd^{2+} $5 \cdot 10^{-5}$ mole/liter; 3) Cd^{2+} $5 \cdot 10^{-5}$ mole/liter; 4) Cd^{2+} $5 \cdot 10^{-5}$ mole/liter + Cu^{2+} $5 \cdot 10^{-5}$ mole/liter + Pb^{2+} $5 \cdot 10^{-5}$ mole/liter; 5) supporting electrolyte, range of current 50; 6) supporting electrolyte Cu^{2+} $2 \cdot 10^{-6}$ mole/liter, range of current 50; 7) supporting electrolyte + Cu^{2+} $2 \cdot 10^{-5}$ mole/liter, range of current 50; 8) supporting electrolyte + Cu^{2+} $2 \cdot 10^{-5}$ mole/liter, range of current 100; 9) supporting electrolyte + Cu^{2+} $2 \cdot 10^{-5}$ mole/liter + Pb^{2+} $1 \cdot 10^{-5}$ mole/liter, range of current 100; 10) supporting electrolyte + Cu^{2+} $2 \cdot 10^{-5}$ mole/liter + Pb^{2+} $1 \cdot 10^{-5}$ mole/liter + Cd^{2+} $0.8 \cdot 10^{-5}$ mole/liter, range of current 100.

The oxygen was removed from the solution by nitrogen which had first been washed with an acidified solution of vanadium (II) sulfate. Zinc amalgam was placed on the bottom of the wash bottles. Traces of hydrogen sulfide were absorbed by a sodium plumbite solution.

We used 1-M NH_4OH + 1-M NH_4Cl + 0.005-M sulfosalicylic acid as the polarographic supporting electrode for nickel. For copper, lead, and cadmium the inert electrolyte was 2 N KCl with pH = 3.0.

Since we were unaware of any literature data on the use of graphite electrodes in oscillographic polarography or in polarography with preliminary concentration of the material on the electrode, we studied a number of problems in procedure.

We found (Fig. 1) that the depth of the peak during electrolytic dissolution of copper was directly proportional to the concentration of reduced ions in the solution; this agrees with theoretical conclusions [2] for the case of electrolytic dissolution of thin solid films deposited preliminarily on the electrode. For the systems Cd^{2+}/Cd^0, Ni^{2+}/Ni^0 we observed the same type of dependence of the maximum current of electrolytic dissolution on the concentration of cadmium and nickel ions. Figure 1 shows that the conditions and length of storage of the electrode have practically no effect on the results. The maximum deviation from the mean does not exceed 10%.

Figure 2 gives oscillograms obtained by the method with a fixed current for the system Cd^{2+}/Cd^0 on a graphite electrode. For the systems Cd^{2+}/Cd^0, Ni^{2+}/Ni^0 in the given range of cadmium ion concentrations direct proportional-

ity was observed between the depth of the anodic peak and the concentration of cadmium ions in the solution, the reproducibility of the results, as in the first case, being satisfactory.

The existence of direct proportionality between the current of electrolytic dissolution and the nickel ion concentration in the solution, which is also analogous for very dilute solutions (10^{-6} M) of copper and cadmium, evidently makes it possible to extend polarographic analysis with preliminary accumulation to the determination of substances which do not form analgams [4, 5]. The same evidently applies to the use of this method to determine substances whose potentials are more positive than the dissolution potential of mercury, since the working region of a graphite electrode in the anode range of potentials is much wider than that of mercury.

Taking into account the difficulties arising due to the formation of intermetallic compounds [6] and the possible formation of solid solutions during the deposition of different metals on the electrode during concentration, we can assume that the anodic electrolytic dissolution curves are distorted with the simultaneous liberation of the sum of metals. Figure 3 shows oscillographic curves for the electrolytic dissolution of copper, lead, and cadmium, obtained by a method with fixed current (a) and voltage varying according to a certain law (b).

The copper and cadmium peaks (see Fig. 3a) are separated fairly well. In the presence of lead the separate measurement of the peaks of copper, lead, and cadmium is difficult but the formation of new peaks is not observed. It is much more convenient to use oscillograms obtained by the second method (see Fig. 3b), on which there is good separation of the peaks for the same amount of electrolytically deposited substance. Experiments show that the addition of one of the substances does not affect the electrolytic dissolution currents of accompanying substances.

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THE COULOMETRIC DETERMINATION OF THALLIUM AT A CONTROLLABLE POTENTIAL

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With the example of the coulometric determination of thallium we have shown the possibility of using the MacNevin and Baker method when working with a mercury cathode as well as a solid cathode. The relative error in the determination of 0.2-2.0 mg Tl is 0.48-11.5%.

In the coulometric determination of metals according to the Lingane method [1], the electrolysis is carried out at the potential of a mercury cathode corresponding to electrolysis at the limiting current. In this case the change in the current intensity with time is given by the expression

$$I_t = I_0 \cdot e^{-\kappa t} = I_0 \cdot 10^{-\kappa' t}. \quad (1)$$

Here I_t is the current intensity at instant of time t; I_0 is the initial current intensity ($t = 0$); t is the duration of