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ATTEMPT TO REPLACE THE MERCURY DROP ELECTRODE WITH SOLID METAL ELECTRODES

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/Figures referred to are appended./

The experiments of certain researchers, well-known from literature (Ya. Heyrovskiy, Polarographic Method - Theory and Practical Application /Polyarograficheskiy method - teoriya i prakticheskoye primeneniye/, ONTI, 1937), to replace the mercury drop electrode for polarographic analysis with electrodes of a solid metal were based, in the main, on the principle of the mechanical elimination of results of physical and chemical changes taking place in the solution and on the surface of the polarized electrode during electrolysis.

We tested another method for using solid electrodes in their polarizable state, this application being based on their periodic depolarization through an electrochemical process.

The procedure of this method is as follows:

The polarizable electrode is represented alternately by two or more solid electrodes of small surface area (relative to the "unpolarized" large electrode) which are kept simultaneously in the solution being tested. In each period when one of the small electrodes is polarized, the remaining are short circuited with the large electrode having a potential opposite to it; in this manner each is subjected to periodic depolarization, after which they successively enter into the process in a "regenerated" state.

In Figure 1 is given the principal circuit for cathode polarization with two small electrodes, the circuit which served as the subject of our investigation.

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The systems of electrodes which were used consisted of: (a) a large mercury anode and two small electrodes of platinum amalgam, and (b) a large platinum electrode and two small platinum electrodes.

A system of two small platinum electrodes and a large mercury anode also was tested. The dimensions of the separate pairs of small electrodes were varied within the following limits: diameter of the electrode - 0.5, 0.3, and 0.1 mm; length - from $\backsim$6 to $\backsim$0.5 mm.

The switching over of the small electrodes as shown in the diagram is accomplished automatically with the help of a throw-over switch of extremely light construction (of the "spider" type), devised by us for this circuit, whose throwing over to right and left positions was accomplished by the rhythmic strokes of the arm of a metronome.

For the first part of the work we used the galvanometer NIIF LGU (Scientific - Research Institute of Physics, Leningrad State University) with a sensitivity of $1.1 \cdot 10^{-9}$ a, an internal resistance of 7800 ohms, a critical resistance of 3020 ohms, and an oscillation period of 5.1 seconds. Through experiments conducted on a series of solutions (neutral, alkaline, and acid), we succeeded in the attempt to obtain polarization curves whose curve characteristics were not distinguishable from curves obtained with a mercury drop cathode. This is sufficiently verified by the polarograms cited below.

The results of experiments to study the influence on polarograms of the switching frequency of the electrodes permit it to be asserted that the latter /i.e., frequency/ has a rather narrow optimum which approaches in value the velocity of dropping of mercury which is usually employed in polarographic analysis.

In Figure 2 are reproduced polarograms of an alkaline solution of lead with a concentration of $\backsim 10^{-3}$ N which were recorded for various velocities of switching the electrodes: from 2.3 to 0.3 seconds for each switching.

It is not difficult to detect the general rule for the variation of these curves where, with an increase of the frequency of switching, together with a decrease of /the period of/ oscillations, the current component which depends linearly on the voltage increases, and the heights of the waves of electrolytic reduction of the metals also increase.

We chose a switching period of the order of one second for each extreme position of the switch.

The question of the influence of the surface dimensions of the small electrodes on the polarization curves was considered for the present only within the above-specified limits. It was shown that variation of the surface area within these limits led only to a corresponding variation of the strength of the current, but not to any variation of the character of the polarogram. This is illustrated by Figure 3, in which are reproduced the curves for lead and zinc in a 10% solution of Rochelle salt which were obtained by using amalgamated platinum electrodes.

Curve I, corresponding to a lead concentration of $\backsim 2 \cdot 10^{-3}$ N, a zinc concentration of $\backsim 7.10^{-3}$ N, and electrodes with a length of 6 mm and a diameter of 0.5 mm, were recorded at a galvanometer sensitivity of 3.5/3020. Curves II and III show the results of the electrolysis of the same solution with another pair of electrodes of 0.3 mm diameter and $\backsim$1.5 mm length. These curves correspond to a 28/3020 galvanometer sensitivity, i.e., to obtain waves approximating in amplitude those obtained with the first (large) pair of electrodes, it was necessary to increase the sensitivity of the galvanometer eight times.

This demonstrates an increased possibility, compared with the method of the mercury drop electrode, for the arbitrary choice of the strength of the electrolytic current through a simple change of the surface area of the polarizable electrodes; this can be of interest from the point of view of the technical application of the method.

It is interesting to note that the current maxima characteristic of certain solutions which occur in electrolysis with the mercury drop cathode did not appear in the work with the circuit described here; this is in agreement with the new representations of the theory of the nature of maxima advanced by A. N. Frumkin and Bruns (Acta Phys-Chim, URSS No 2, 1938 [in English]).

The disadvantage of the method in the first stage of its development, in comparison to the method of the mercury drop electrode, is the inferior definition of the development of the waves in the curves, which lowers the sensitivity of the analysis, particularly when some reducible components are present in small concentrations in the solution.

The above is illustrated by the example shown in Figure 4, where there are reproduced polarograms taken with a solution of 10% Rochelle salt which contained copper, lead, cadmium, and zinc in concentrations of $\sim 8 \cdot 10^{-4}$ N with the use of the described circuit of solid electrodes (curve I) and with a mercury drop electrode (curve II).

For practical utilization of this method, it is necessary to further investigate and perfect it, and in particular to guarantee the possibility of regulating the depolarizing current's density, the depolarization time of each small electrode, and the time of its "rest" before it is connected for its turn of polarization (note: the construction of a commutator which will satisfy these conditions for a system of several solid electrodes can be successfully accomplished in different variations of design).

Furthermore, the problem of the rational selection of electrode materials for different electrolytic agents should be examined (we tested only platinum and mercury).

Also, for any polarographic method of analysis the problem of compensation for the current, which varies proportionally with the voltage, must be solved. For this an ohmic resistance was connected in parallel with the electrolyzer, the terminals g [galvanometer?] on the polarograph were short-circuited, and the windings of a differential galvanometer were connected to both parallel branches of the circuit (electrolyzer and ohmic resistance). Synchronization of the connection and disconnection of the electrolyzer and rheostat was accomplished by changing the double-pole switch to triple-pole, as shown in Figure 5 (note: it is evident in Figure 5 that this simple circuit not only permits the ohmic resistance R to be connected to compensate for a linearly growing current; in addition to R a second electrolytic cell with any composition of electrolyte can be connected).

For recording the current a "Hartman and Braun" differential galvanometer of type 172 B, with an internal resistance of 60 ohms, critical resistance of 400 ohms, half-period of oscillation of 4.5 seconds, and sensitivity of $75 \cdot 10^{-10}$a was used.

An example of the compensation obtained through this circuit is shown in the polarograms cited in Figure 6, where curves I and II represent a lead nitrate solution with a concentration of $\sim 7 \cdot 10^{-4}$ N, the polarograms being taken without the use of compensation (at various sensitivities) with amalgamated platinum small electrodes and a large mercury electrode. Curve III was obtained as a result of connecting the compensation circuit.

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Curves IV and V represent the same solution and were taken with small and large platinum electrodes, without and with compensation for the linear increase of current, respectively.

Utilization of the proposed circuit permitted the determination in individual cases of metal in concentrations down to $\backsim 2.10^{-4}$ N.

In conclusion, we ought to devote some time to the direct determination of cations of precious metals (note: the mercury drop electrode does not allow this possibility, for ions of metals more noble than mercury (Ag, Au) are reduced by mercury itself; moreover, ions of mercury are also very difficult to locate polarographically by use of a mercury electrode).

The possibility of using electrodes of a more noble metal than those which were being determined made this problem easily solvable. The experiment for the polarographic determination of silver, gold, and mercury is illustrated by Figures 7, 8, and 9.

Curve I in Figure 7 shows the polarogram taken with a 10% solution of sodium nitrate, with a silver content of $\backsim 5 \cdot 10^{-3}$ N and an HNO_3 content of 10^{-1} N. Curve II corresponds to the same solution, to which is added silver up to a concentration of about 10^{-2} N. Curve III was taken following the addition of silver up to $\backsim 1.7 \cdot 10^{-2}$ N.

In Figure 8 are shown polarograms of gold.

Curve I corresponds to the original solution, containing 9 cc of a 10% solution of potassium chloride and 1 cc of a 1% solution of gold chloride in 0.1 hydrochloric acid.

The other curves (II, III, IV, and V) were taken with the original solution after the addition of new portions of gold chloride.

Mercury also was determined satisfactorily with platinum electrodes, as is illustrated by the examples of curves which are cited in Figure 9. The first four of these correspond to the joint determination of mercury and lead in a 5% solution of sodium mitrate. Curve V shows the results of the joint determination of mercury, lead, and copper at ionic concentrations of mercury $\sim 10^{-2}$ N, copper $\backsim 5.10^{-3}$ N, and lead $\backsim 1.5 \cdot 10^{-2}$ N.

Conclusions

1. Solid metal electrodes were tested by using a circuit providing for the periodic depolarization of the surface area of the polarizable electrodes by means of an electrochemical process.

2. Favorable results were obtained in the polarographic determination of metals.

3. The proposed method of polarographic analysis can expand the area of the application of this method significantly; in particular, it makes possible direct polarographic determination of metals more noble than mercury, as well as polarographic investigation of molten electrolytes.

4. The aim of further research should be the study of optimum conditions of electrolysis to obtain the greatest reliability, accuracy, reproducibility, and sensitivity from the method.

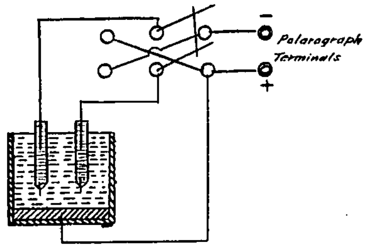

Figure 1. Principal Circuit of Cathode Polarization With Two Small Solid Electrodes

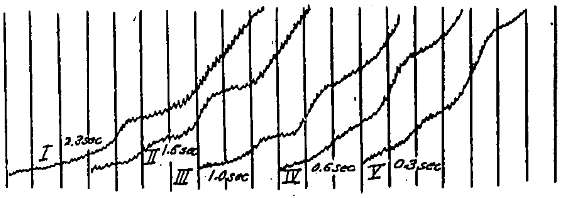

Figure 2. Polarogram of a 0.01N Alkaline Solution of Pb at Various Velocities of Switching the Electrodes

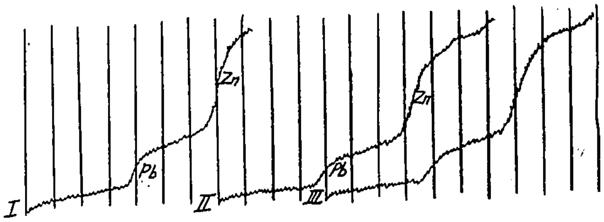

Figure 3. Curves for Pb and Zn in 0.01N Solution of Rochelle Salt With the Use of Amalgamated Hg Electrodes

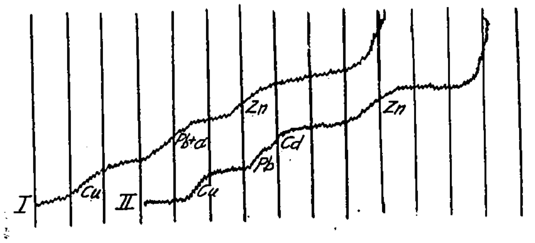

Figure 4. Curves for Cu, Pb, Cd, and Zn in 10% Solution of Rochelle Salt

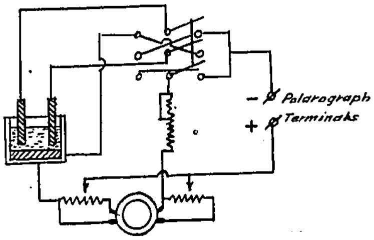

Figure 5. Principal Compensation Circuit of Cathode Polarization

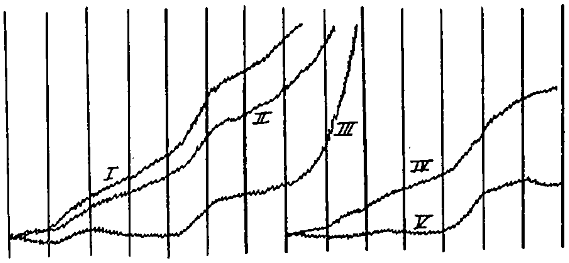

Figure 6. Polarogram of Pb, Taken Without Compensation for Current (curves I, II, IV), and With Compensation for Current (curves III, V)

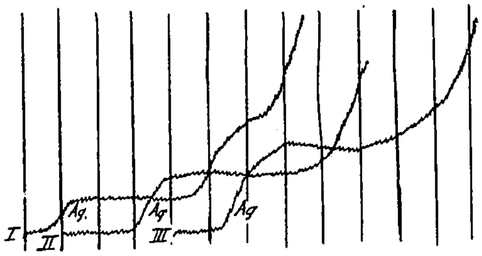

Figure 7. Polarogram of 10% $NaNO_3$ With a Varied Content of Ag

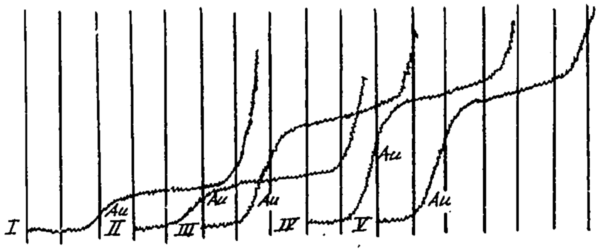

Figure 8. Polarogram of Au in 10% Solution KCl + 0.1N HCl

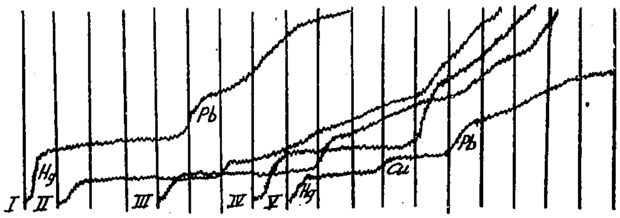

Figure 9. Polarogram for Hg, Pb, and Cu in 5% Solution of $NaNO_3$

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