PULSE POLAROGRAPHY AT SOLID ELECTRODES

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The possibility of using a platinum microdisc electrode in pulse polarography has been investigated. A method has been developed for treating a platinum electrode to obtain reproducible results. It has been found that there is a linear relation between the current strength and the cadmium concentration in solutions with 1 M KCl and 1 N NH_4Cl + 2 N NH_4OH as supporting electrolytes.

The method of pulse polarography with a dropping mercury electrode has been widely used in recent years. The use of solid electrodes has been considered in only a few papers by foreign authors.

Juliard [1] investigated the problem of determining iodides by alternating current polarography at solid electrodes. In order to obtain reproducible results, he recorded a so-called cyclic polarogram, over the potential range +15 V to −1 V and back to +1.5 V. Curves for two different iodide concentrations were described. Agreement between parallel experiments was obtained, but the reverse half of the cycle from −1 to +1.5 V showed an additional peak absent from the first half of the cycle.

The use of solid electrodes for determining organic compounds has been described in another paper [2]. The problem of reproducibility and the possibility of quantitative determination were not investigated.

Kojama [3] used a square wave method for determining plutonium at a platinum electrode, with 1 M HCl and 2 M HNO_3 as supporting electrolyte. He showed a calibration curve for 10^{-6} to 10^{-5} mole/liter of plutonium and obtained good agreement between theoretical and experimental results. He emphasized that it was necessary to treat the electrodes periodically in order to obtain reproducible results. The cause of nonreproducibility was attributed to an oxide film on the surface of the platinum electrode.

The object of our work was to determine the ions of certain metals by pulse polarography at solid electrodes. We used a recording pulse polarograph, constructed in the Analytical Chemistry Laboratory with cooperation of the KIL of the Academy of Sciences of the Moldavian SSR [4]. The sensitivity of the instrument was 0.02 μA/mm, and the rate of voltage input was 2.4 mV/sec.

We first recorded the polarogram of 5×10^{-3} M $CdCl_2$, with 1 N KCl as supporting electrolyte, using a microdisc platinum cathode and a bottom mercury electrode. Under these conditions the cadmium peak was recorded at −0.7 V relative to the mercury. However, the peak height was not reproducible from experiment to experiment. It is characteristic that fully consistent results was obtained under these conditions by classical polarography. It is clear from Fig. 1 that the reproducibility of pulse polarography was far worse than that of classical polarography; the errors were 7.7 and 2% relative respectively. The differences between parallel experiments were 46 mm for pulse polarography and 2 mm for classical polarography.

It was obvious that the cause of the nonreproducibility was the continuous action of the alternating voltage on the electrode. This was also shown by Barker [5], whose emphasized that square-wave pulses caused premature break away of the mercury drop. Evidently, the behavior of the metal, deposited on the electrode surface, depended on the action of the alternating constituent of the voltage. On the one hand, this resulted in nonuniform coating of the electrode surface, and, on the other hand, it led to heterogeneity of the metal film on the electrode.

Various means were used to reduce the effect of alternating current on the electrode: 1) The polarization range was reduced; 2) the cell was disconnected between experiments, when the polarization voltage had returned to its original value; 3) the rate of application of the saw-tooth voltage was increased from 2.4 to 12.5 mV/sec; 4) the electrode was cleaned before each polarogram was recorded.

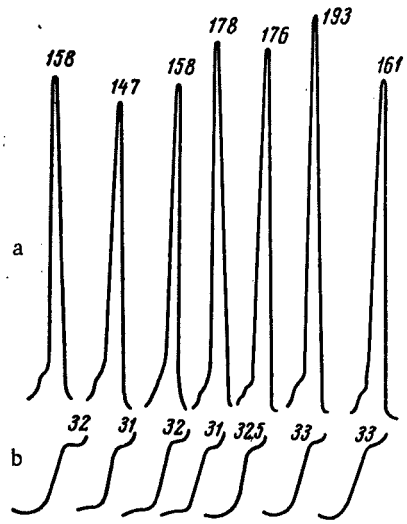

Fig. 1. Polarograms of 5×10^{-3} M cadmium with 1 N KCl as supporting electrolyte: a) Pulse polarograms; b) classical polarograms. The peak heights are shown above each polarogram.

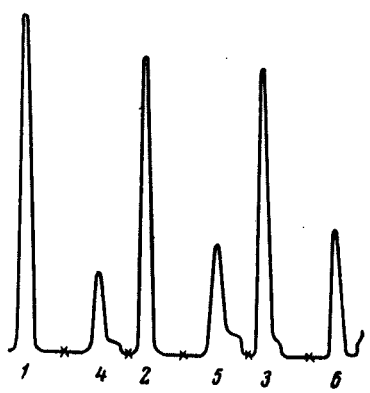

Fig. 3. Pulse polarograms of 5×10^{-3} M cadmium with 1 N KCl as supporting electrolyte: 1-3) Second half cycle; 4-6) first half cycle.

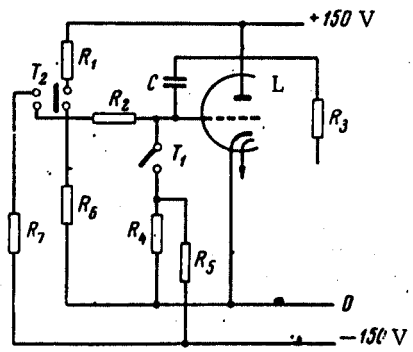

Fig. 2. Basic circuit of generator to give linear change in voltage.

However, these changes did not lead to any positive results. Then following the work of Juliard [1], we recorded polarograms of cadmium in the forward and reverse directions, i.e., for 0 to −1 V and from −1 to 0 V.

For this purpose, the circuit of the generator for giving a linear change in potential was altered so as to give changes in polarization voltage in both directions at the same rate (Fig. 2).

The tumbler switch T_1 was for starting and returning the voltage to its original state, and the tumbler switch T_2 was for determining the direction of the increase in voltage. The resistance R_1 was selected such that the rate of increase in voltage was the same in both directions.

When the saw-tooth voltage was applied in reverse, the surface of the platinum electrode should be restored to its original state, thus ensuring reproducibility. However the results were negative.

The same effect was observed when the electrode was polarized from −1 to +1 V. When a cyclic voltage was applied from 0 to −1 V and from −1 to 0 V, the peak height in the first half cycle was considerably less than in the second half cycle, although there was no accumulation of material (Fig. 3). Moreover, the peak potentials did not coincide in the two half cycles.

It was noted that the electrode operated better after repeated use, evidently because it became coated by a cadmium film. We therefore applied a preliminary treatment in which the platinum microdisc electrode was held, for a definite time, at the limiting current potential of the substance (ion) to be determined, without any accompanying alternating current component through the cell. At the end of the definite time, the alternating current component was switched on, and a pulse polarogram was recorded for the second half of the cycle. This operation was repeated before each polarogram was recorded. In this way the electrode always has a fresh cadmium surface, undisturbed by the action of the alternating current component.

Quite reproducible results were obtained when strict attention was payed to the value of the limiting current potential (−1 V) and to the time (3 min) for which the electrode was maintained at this potential. With 10^{-4} M cadmium solution, the peak heights of three pulse polarograms were 146, 142, and 145 mm.

The effects of the actual value of the potential and the time for which it was applied were not examined in detail. It is reasonable to suppose that similar results would have been obtained at other potentials, close to the limiting current potential for the substance to be determined, and with different times for its application. The peak might be correspondingly larger or smaller, but the proportionality between current and concentration of the substance to be determined should be maintained.

The above conditions for electrode preparation were observed in the construction of calibration curves for the relation between peak height and cadmium concentration, using both 1 N KCl and 1 N NH_4Cl + 2 N NH_4OH as supporting electrolytes. The curves were straight lines in both cases.

LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.