# CONTINUOUS POLAROGRAPHIC DETERMINATION OF HEAVY METALS IN ELECTROLYTES

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The authors describe a method for determining cadmium, in solutions of salts and electrolytes in the zinc industry, by using a graphite disk electrode with periodic accumulation and recording the curve of electrosolution of the metal. They show the possibility of purifying the electrode from surface-active substances.

The method of determining micro-quantities of metals [1, 2] by concentrating them on a solid electrode, followed by recording of the electrosolution current with a linearly changing potential and the determination of admixture concentration in the solution by the maximum value of this current, was used for continuous automatic determination of micro-admixtures in electrolyte solutions.

Previously, solid electrodes have been used for continuous determination of gaseous products [3, 4] or substances not forming (as a result of the electrode reaction) sparingly soluble compounds deposited at the electrode [5].

In our work the indicator electrode was a graphite disk of diam. 2 mm, prepared from Class V3 graphite, impregnated and insulated with ÉD-6 epoxy resin. The polymerization and plastification catalysts were polyethylenepolyamine and dibutylphthalate. Impregnation was accomplished in vacuum. For work with acid solutions the side surface of the electrode was also insulated with polyethylene. The auxiliary electrode was of saturated calomel. The solution to be analyzed was passed at constant speed through the electrolytic cell, which consisted of two compartments separated by a Schott filter. In the first compartment oxygen was removed by a current of nitrogen. In the second compartment the electrolysis was carried out. The graphite electrode was so placed that it was washed by the solution, before this contacted the auxiliary electrode. The pressure vessel was of the constant-level type; this secured constant flow velocity. Continuous polarization of the electrode and registration of the polarization curves were effected by a TsLA-02 oscillographic polarograph.

The form of the voltage pulses fed to the cell, and obtained on the polarograms, is shown in Fig. 1. On section AB (14 sec at constant potential $\varphi_1$) the impurity to be determined separates as metal on the electrode. On section BC (linear potential change at 0.125 V/sec), the metal separating at the electrode dissolves; the oscillograph screen records the polarization curve shown at the bottom of the diagram. On section DEF the peak is repeated, and so on.

Table 1 gives the results of determinations of copper and cadmium in solution of nickel sulfate and zinc sulfate, made over several hours. The decrease in electrosolution current is apparently caused by adsorption of the surface-active substances present as impurities in the solutions. This hypothesis is supported by the quicker changes found for solutions of zinc sulfate containing large quantities of adsorbable substances.

We can suggest two ways of separating harmful substances from the electrode surface: 1) periodic strong cathodic polarization of the electrode, during which the adsorbed layers are removed both by displacement of organic molecules by the strong electric field, and by mechanical action of the hydrogen bubbles formed; 2) mechanical cleaning of the electrode surface. The first method is technically the easier. However, it can be used only in the analysis of acid solutions, the main substance in which is more electronegative than hydrogen (allowing for the corresponding overvoltages). The feasibility of this method is illustrated by the data in Table 2, which gives determinations of copper in an acidified solution of sodium sulfate. Copper was precipitated at $-1.5$ V, hydrogen ions being discharged at the same time. The results obtained in these conditions show fairly good stability.

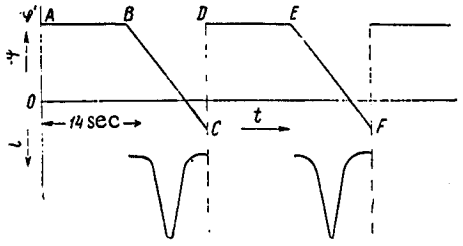


Fig. 1. Shape of voltage pulses fed to electrolytic cell.

In continuous analysis of industrial solutions of zinc sulfate and nickel sulfate, the electrode is periodically subjected to mechanical cleaning with an abrasive (SK10), glued with epoxy resin to the bottom of the electrolyzer below the electrode.

Table 3 gives results of continuous determination of copper ($5 \cdot 10^{-5}$ mole/liter) in a solution containing 300 g/liter sulfate and 0.1 N sulfuric acid. Electrodeposition was carried out at −0.4 V. As seen from the table, the stability of the results did not alter during 100 h, which included both continuous working and interruptions.

Table 3 also gives results of continuous determination of cadmium in zinc sulfate solutions, sampled at various stages of their industrial processing.

It seemed possible to dispense with the displacement of oxygen from the solution. It is apparently separated during the treatment of the solutions with zinc dust, which is used in industry to recover copper and cadmium. In this connection we used a cell without a Schott filter, which would be clogged by fine dust in the solution. Zinc dust is preliminarily filtered off. The solution to be analyzed contained $5 \cdot 10^{-7}$ mole/liter $Cu^{2+}$ and $Pb^{2+}$ and $\sim 5 \cdot 10^{-4}$ mole/liter $Cd^{2+}$. The electrode must be cleaned more frequently than in the case of solutions of reagent salts, especially during the analysis of solutions containing large amounts of organic substances. Such solutions can be analyzed automatically only by using a special attachment which periodically transmits pulses to the apparatus for mechanical electrode cleaning.

In [6, 7] it was shown that there is a linear relation between the maximum electrosolution current of a metal and the concentration of its ions in solution; this enables us to use this method for analytical purposes.

Figure 2 gives the distribution curves of the deviations from the mean for all the cases studied. Even for the analysis of a solution containing large amounts of organic substances, the probability curve is adequately sharp. It shows that in 90% of the cases, the deviation from the mean is less than 6.4%. The probable relative error for the determination of copper in sodium sulfate is 3%; for copper in nickel sulfate, 4%; for cadmium in zinc sulfate after removing heavy metals, 4%; and for cadmium in zinc sulfate undergoing electrolysis, 2%.

In the above method, the information on the inpurity content is obtained continuously in the form of an electric pulse which can be used in an automated system to regulate various technical processes, in particular the purification of the solution. Appropriate choice of precipitation duration (the length of section AB in Fig. 1) enables us to vary the sensitivity over a wide range.

TABLE 1. Determination of Copper in $NiSO_4$ Solution and Cadmium in $ZnSO_4$ Solution

| Duration of operation of electrode, h | Maximum electrosolution current of Cu, μa | Duration of operation of electrode, min | Maximum electrosolution current of Cd, μa |
|---|---|---|---|
| 0 | 6.9 | 0 | 7.2 |
| 1 | 7.0 | 10 | 7.0 |
| 2 | 6.8 | 15 | 6.9 |
| 3 | 6.8 | 20 | 6.7 |
| 4 | 6.9 | 25 | 6.4 |
| 5 | 6.8 | 30 | 6.1 |
| 6 | 6.4 | 40 | 5.8 |
| 7 | 5.8 | 50 | 5.5 |
| 8 | 5.2 | 60 | 5.2 |
| 9 | 4.8 | | |
| 10 | 4.5 | | |

TABLE 2. Continuous Determination of Copper Ions in Solution of 0.1 N $Na_2SO_4$ + 0.1 N $HNO_3$ + $1.10^{-4}$ M $CuSO_4$

| Duration of operation of electrode, h | Maximum electrosolution current of Cu, μa | Duration of operation of electrode, h | Maximum electrosolution current of Cu, μa |
|---|---|---|---|
| 1 | 15 | 30 | 15 |
| 10 | 14.5 | 40 | 15.5 |
| 20 | 15.5 | 50 | 15.5 |

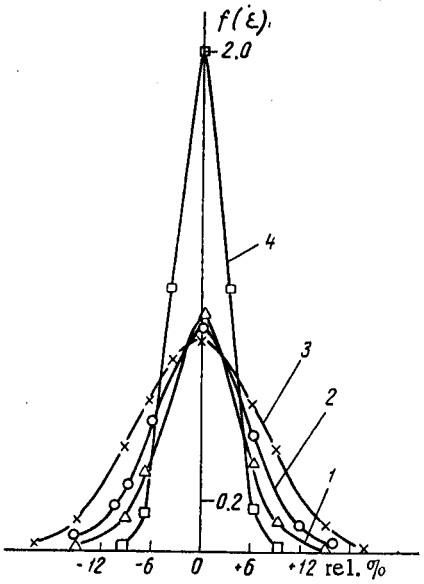


Fig. 2. Distribution function of errors in automatic continuous determinations: 1) of copper in solution of sodium sulfate; 2) copper in solution of nickel sulfate (pH = 1); 3) cadmium in saturated solution of zinc sulfate freed from heavy metals; 4) cadmium in saturated solution of zinc sulfate undergoing electrolysis.

TABLE 3. Continuous Determination of Copper and Cadmium Present as Impurities in Industrial Solutions

| Solution composition | Frequency of cleaning, min | Duration of electrode operation, h | Maximum electrosolution current of Cu, Cd, μa |
|---|---|---|---|
| 300 g/liter $NiSO_4$ + $5 \cdot 10^{-5}$ g-ion/liter $Cu^{2+}$ | 300 | 0 | 6.5 |
| | | 5 | 6.8 |
| | | 10 | 6.5 |
| | | 20 | 6.8 |
| | | 30 | 6.1 |
| | | 40 | 7.0 |
| | | 52 | 6.7 |
| | | 64 | 5.1 |
| | | 90 | 5.4 |
| $ZnSO_4$ + $5 \cdot 10^{-4}$ g-ion/liter $Cd^{2+}$. Solution freed from heavy metals | 30 | 0 | 7.5 |
| | | 5 | 8.5 |
| | | 10 | 8.5 |
| | | 15 | 8.0 |
| | | 20 | 8.2 |
| $ZnSO_4$ + $5 \cdot 10^{-4}$ g-ion/liter $Cd^{2}$ . Solution contains xanthates and extract of soaproot | 15 | 0 | 7.5 |
| | | 2 | 7.0 |
| | | 5 | 7.1 |
| | | 10 | 7.4 |
| | | 15 | 7.2 |

To use this method in industrial conditions, it is necessary to use a special device to obtain the required electrode polarization conditions, periodic feeding of correction pulses to the automatic electrode cleaning system, recording of the electrosolution polarization curves, and output of information to the actuating mechanism which regulates the composition of the solution being analyzed.

## LITERATURE CITED


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