CONTINUOUS POLAROGRAPHIC CONTROL OF THE CONCENTRATION OF INDUSTRIAL SOLUTION COMPONENTS BY COMPUTER-AIDED SOLID RENEWABLE ELECTRODE AND CAMAC APPARATUS

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The peculiarities and technical characteristics are reported of the polarographic sensor having a renewable solid electrode and ensuring the performance of no less than 10^5 cycles. The sensor and special measurement-control apparatus are shown to allow the rapid check of the content of industrial electrolytes.

The methods of electrochemical analysis provide the most favourable premises for the development of reliable and easily automated systems to control components concentrations of various industrial solutions. In this respect a voltametric method seems to be of particular interest. However, its application for automation of analytical control of industrial solutions is rather limited at the moment. This is due mainly to the absence of a sensor that would allow reproduction of the working electrode surface in a long-term continuous automatic regime. According to the requirements imposed by industrial performance, the working electrode surface must be highly stable in mentioned conditions during at least thousand hours with a number of measurement cycles more than 10^5.

The principle of renewing the surface of the solid electrode appears to be very promising for designing a sensor that would meet the requirements of industrial exploitation. Such a method provides complete renewal of the surface and minimum accumulation of contaminants on the surface, since the major part of contaminants precipitates, together with metallic shavings, at the bottom of a vessel.

Polarographic possibilities of the sensor renewable by cutting have been reported in refs[1,2]. Here we consider the peculiarities of designing the sensor applicable for industrial performance, the measurement-control set of apparatus used to feed and regulate the sensor working regimes and process the output signals. Also, the results of the longterm laboratory tests on reproduction of the sensor parameters are discussed.

EXPERIMENTAL

The sensor is shown in a schematic fashion in Fig. 1. An electrotechnical copper wire with a diameter of about 0·4—0·6 mm was used as an electrode. It was plated with a PEV-2 standard enamel isolation. The wire was reeled off coil 1 by means of leading 2 and pressing 3 cylinders and pushed through the levelling tubes 4 and 5 into cutting device. This latter consists of the fixed 6 and moving 7 knives. The knife 8 is drived by means of axis 8. The feeding and cutting of the wire is performed by the electromotor or electromagnet.

The measurement of the sensor parameters and control of its regimes were carried out using the measurement system composed of standard and specially developed devices. Amongst standard commercial devices are mini-computer, CAMAC analog-digital and digital-analog convertors, commutator, output register and CAMAC-mini-computer interfaces. Novel, specially developed devices are the sensor itself, mini-computer controlled potentiostat and line-scanning oscillator of the voltage constructed according to the CAMAC standards.

The digital-analog convertor and non-standard blocks permit one to establish the necessary polarization regimes of the working electrode. The output register serves to control feeding and renewal of the surface of the working electrode. The commutator and the analog-digital convertor are employed to register the sensor response and other signals of the system, which then are transformed to digital codes and introduced into the computer memory. Here they are treated in accordance with a particular program.

RESULTS AND DISCUSSION

As shown by numerous experiments, the choice of materials for the fixed and moving knives of the sensor and their angles of backing-off is very important both for the reproducibility of the cutting area and reliability of the voltage-current curves obtained. These materials must be sufficiently stable to various aggressive media. The different sorts of steel, including stainless steel, and metallized ceramic are not appropriate for this purpose. Synthetic ruby, nephrite, boron nitrite, tungsten, and alloy of titanium of different grades of hardness were tested as materials for cutting pairs.

As a result of these experiments, the following cutting pair was found to be an optimum one: the fixed knife made from boron nitride ("Elboron"-like material) having

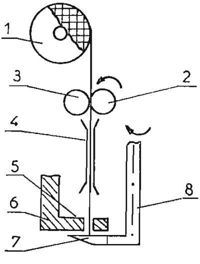

FIG. 1

Schematic representation of the concentration sensor the backing-off angle of 80 – 85°, and the moving knife made from the titanium alloy of increased hardness, its backing-off angle being 30 – 40°. The feeding and curring of the wire was performed by the electromotor drive.

The long-term laboratory tests of the sensor with such cutting pair were carried out in a solution containing 0·1M-$CuSO_4$ and 0·25M-H_2SO_4. In this case the following measurement regimes were chosen: the rate of line-scanning 0·125 V/s; the range of potential scanning from 0 to 0·3 V relative to copper anode with a large surface; temperature +30 ± 0·5°C. A renewal of the electorde surface was per-

TABLE I

Mean values of the peak current (I_{max}) and its relative square-law errors (δI_{max}) *vs* the number of cuts during Cu^{2+} reduction on renewable copper electrode

Number of cuts	I_{max}, 10^{-6} A	δI_{max}, %
3 000	63·1	2·1
25 000	65·0	1·5
50 000	62·6	1·3
70 000	60·5	1·5
85 000	64·7	2·6
100 000	62·8	2·1

TABLE II

Instrumental errors of the current peak measurements for some components of industrial solutions on renewable copper electrode

Electrode process	Component under determination	Solution g/l	Number of cuts	δI_{max}, %
Copper reduction	Cu^{2+}	copper-plating electrolyte, 15 – 150 g/l $CuSO_4$	30 000	3·0
Anode dissolution of copper electrode	S^{2-}	filtrate of pulp flotation of molybdenum concentrate, 0 – 10 g/l Na_2S	10 000	2·0

formed at a rate of 5 cuts/min. After a certain number of cuts had been made (see Table I, column 1), 80 successive cuts-determinations were performed. The mean values of these measurements are compiled in Table I: values of the peak current $\bar{I}_{\max}$) – column 2 and square-law errors ($\delta\bar{I}_{\max}$) – column 3. When using a fresh cutting pair the first several hundred cuts give higher values (by 5–15%) than the subsequent cuts. This difference results from the grinding of the cutting pair. No visual changes on the working edges of cutting pair were observed after the experiments were over.

Assuming that the main experimental error in the sensor current measurements is induced by instability of the working electrode surface, one may conclude from the data in Table I that after grinding of the cutting pair the surface area fluctuates by no more than 3% at the number of cuts equal to or higher than 10^5. This reproducibility of the results is acceptable to resolve the problems of control of most of the technological solutions.

The results of the long-term tests of the sensor with renewable copper electrode conjugated with the above described measurement-control set of apparatus used for the determination of the concentrations of copper (Cu^{2+}) in copper electrolyte and sulfide (S^{2-}) in flotation solutions are summarized in Table II. To measure the current peaks that characterize the concentrations of Cu^{2+} and S^{2-}, the regime of the sensor performance was chosen as follows: the rate of potential scanning 0·25 and 2 V/s; the ranges of potential scanning from 0 to −0·3 V (with respect to copper counter electrode) and from −0·8 to +0·6 V (with respect to graphite counter electrode); the number of cuts 5 per min. In these conditions the concentrations of the above ions were proportional to the peak current values.

Thus, the results obtained by us show that the mini-computer aided sensor with a renewable solid electrode coupled with the CAMAC apparatus is, indeed, very promising for the fast determination of the components concentrations in various industrial solutions.

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