ELECTROCHEMICAL DETECTOR WITH AUTOMATIC RENEWAL OF THE WORKING SURFACE OF A SOLID INDICATOR ELECTRODE

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For continuous renewal of the surface of a platinum electrode, equipment has been proposed [1, 2] in which the electrode is continuously pressed against a rotating abrasive drum, which is located in the solution. However, as the same authors have shown [3], graphite can not then be used as the electrode material, since it spreads over the surface of the drum.

We have investigated methods of cleaning graphite indicator electrodes with the object of using them in automatic analysis.

Effective renewal of the electrode surface can be achieved by cleaning it with a cutting tool, using a special apparatus (see Fig. 1). A graphite rod 2, impregnated with silicone liquid and epoxy resin, is press fitted into a

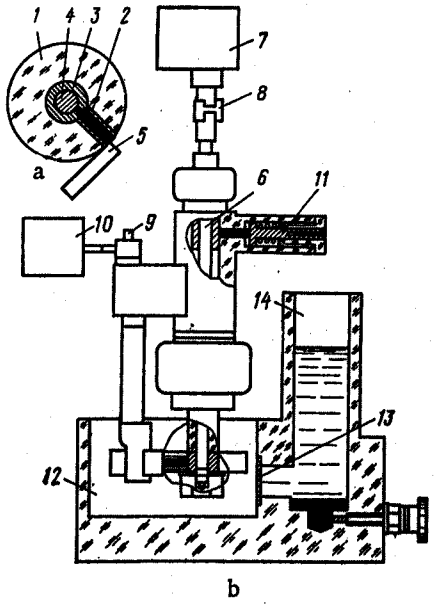

Fig. 1

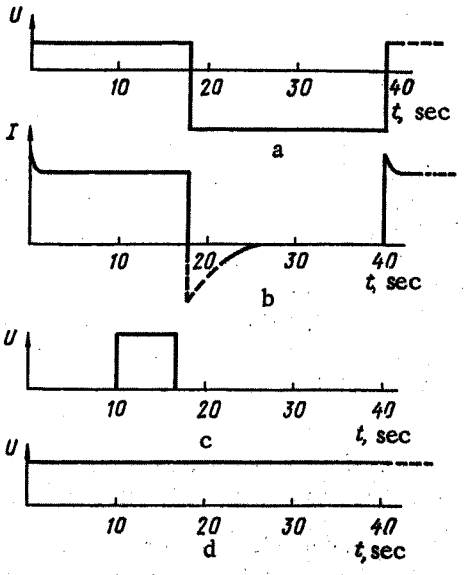

Fig. 2

Fig. 1. Electrochemical detector and indicator electrode holder.

Fig. 2. Time diagrams for the operation of the detector and the measuring equipment: a) Voltage applied to detector; b) current in detector circuit, c) switching in of recorder; d) reading of continuous recorder.

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TABLE 1. Results for the Analysis of Effluent Waters

Element	Concentration determined, mg/liter	Determination error, % relative	Determination duration, min.
Cu	0,1—0,001	4—8	5
Cd	0,5—0,002	3—6	5
Pb	0,1—0,001	5—10	2
As	0,2—0,05	5—10	2—10
Sb	0,1—0,0001	5—10	5

holder 1, made of organic glass, Teflon, or other material. A thin layer of polyethylene is applied to the lateral surface of the rod. Electrical contact between the graphite and the external circuit is achieved by means of a metallic ring 3 and a shaft 4. The electrode is cleaned by the tool 5.

The holder with the graphite rod is fitted on to the metallic shaft 6, which is insulated from the solution, and is connected to the electric motor 7, through the flexible coupling 8. The cutting tool is fixed on the end of a parallel shaft 9. A spring torque is applied to this shaft, so that the cutting edge of the tool is applied to the electrode surface and mounting with a constant force. When the shaft 6 is rotated the tool cuts a thin layer off the electrode holder, continuously renewing its surface. Disconnection of the cutter from the electrode can be done by hand, or by means of a signal from the command unit, using the electromagnetic or mechanical acuator 10. Contact with the electrode is effected through the shaft 6 and the current collector 11.

The indicator electrode and renewal device are located in the electrode cell 12, which is in contact, through an ionic membrane 13, with the reference electrode cell 14. For a calomel electrode, mercury and saturated potassium chloride solutions are poured into the cell.

The detector, designed for analysis under production conditions, differs from that described above in that the shafts for the electrode and cutting tool are mounted in titanium tubes. Their interiors are insulated from the solution by self-sealing one-sided glands. These tubes can also be used as auxiliary electrodes. The detector is fixed in a technological conduit, so as to ensure that it is immersed in the solution to be analyzed to a depth of 500 mm.

The material selected for the indicator electrode was spectral graphite V-3, impregnated successively with silicone oil VKZh94B, and epoxy resin ÉD-5 with hardener UP-609.

We investigated various materials for the cutting tool: quartz glass, agate, pyroceramic, ruby, and thermal corundum. The best for resistance to wear was thermal corundum SM-322. The optimum conditions for mechanical cleaning were with an electrode rotation rate of 100 to 160 rpm. When the products of the electrode reaction are precipitates of metals or sparingly soluble compounds, the rate of their removal from the surface should be increased considerably.

We investigated the possibility of automatic determination of copper (0 to 2 g/liter) and cadmium (0 to 400 mg/liter) ions in technological solutions from electrolytic zinc production, by measuring the limiting reduction current at constant potential. Figure 2 shows diagrams of the measurement cycle. The tests were carried out using a constant-current polarographic concentration meter ION-2 [4], with programmed equipment.

The instrument reading was proportional to the concentration and remained stable for a long time. The root mean square errors, calculated on the basis of 30 measurements taken every hour, were 1.9 and 1.4% for the determination of copper and cadmium respectively.

Industrial trials of the detector were carried out in the lixivation plant of the electrozinc works. The copper content was determined in neutral solutions from the upper drain of the thickener, and cadmium in solutions after the first stage of the process of purification from copper and cadmium. The detector was placed in industrial solutions, containing up to 10 g of ferric hydroxide and copper-cadmium cake per liter. The solution temperature was 50 ± 4°C. Tests were performed around the clock for 3 months. The readings were compared with the results of control analyses, carried out by the plant laboratory, once or twice a shift. During the first test period we obtained 125 comparative determinations of copper and 115 of cadmium. The root mean square error was 3.4% in the first case, and 4% in the second, which completely satisfied technological requirements.

The above design of laboratory electrochemical detector was tested for the determination of traces of the ions of copper, cadmium, antimony, lead, and arsenic, as microimpurities in zinc electrolyte and effluent waters. The measurements were made by the method of inverse voltamperometry, using R-60 and ON-102 polarographs.

Table 1 shows the analytical results for effluent waters from zinc electrolyte plants.

Maintenance work on the detectors, during the test period, was confined to washing the submerged parts free of adherent solid deposit. This operation was performed once a week, and took 10 to 15 min. During the test period

the surface of the indicator electrode remained lustrous, smooth, and hydrophobic. The wear of the electrode during 3 month's operation amounted to 1.5 mm. In 1973 it is proposed to introduce electrochemical detectors in nonferrous metal and chemical plants.

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