POLAROGRAPHIC ELECTROLYZER WITH A SOLID INDICATOR ELECTRODE FOR CONTINUOUS AUTOMATIC RECORDING

Ya. I. Tur'yan

Lisichan Branch of the State Institute of the Nitrogen Industry

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A polarographic electrolyzer with a solid indicator electrode intended for continuous automatic recording is described. The design provides for: 1) a continuous cleansing of anode-cathode polarization products from the surface of the electrodes and, if required, the coating of the electrodes with mercury, lead or other metals; 2) the use of the same electrode in the solution being analyzed, the background solution or the standard solution; 3) the accumulation of the substance on the surface of the electrode during the analysis of small quantities of impurities which is followed by anode polarization.

A continuous polarographic analysis with a solid indicator electrode requires continuous cleansing of the surface, the removal of the film of metal being analyzed, or of the film of impurities from the solution during polarographic electrical reduction, the removal of the oxide film which damages the surface of the electrode during polarographic electrolytic oxidation, etc. The reversal of a pulsating depolarizing current ensures a continuous cleansing of the electrode surface. However, this arrangement cannot always be used.

In the apparatus being described the electrode surface is cleansed by moving the electrode from section II, containing the solution being analyzed, into section III, in which the anode depolarization takes place. After the electrode has been washed with water in section IV it is transferred into section V, for cathode depolarization. This depolarization is best performed in a 0.1 N solution of H_2SO_4; it is necessary for removing the oxide film and any traces of chlorine after anode depolarization in a chloride solution, or in a 1 N solution of HCl.

After this operation and washing with water in section VI, the electrode is transferred into section I containing the background or the standard electrolyte; it is subsequently returned into section II. The cycle is repeated automatically. The adopted design also solves several other problems.

In continuous polarographic analysis use is often made of the second indicator electrode held in the background electrolyte or in the standard solution. This method eliminates the need for the previous removal of oxygen from the solution.

In our apparatus this is effected by means of a single indicator electrode which is passed through the background or standard electrolyte before being placed into the solution being analyzed; this results in the recording of the initial current at a certain moment. In this case an ordinary polarograph can be used.

The use of a solid indicator restricts the applicability of cathode polarography because of the low excess pressure of hydrogen on the platinum and other solid indicator electrodes. In order to eliminate this shortcoming the solid indicator electrode can be either mercury or lead coated in the cathode depolarization section V during every cycle; i.e., it is continuously and automatically regenerated. For this purpose a solution of mercury nitrate or some other coating electrolyte is filled into section V of the channel. In section III the electrode is cleansed by anode depolarization in a 0.1 N HNO_3 solution or in some other electrolyte.

For polarographic analysis of very small concentrations (10^{-7} mole or less) a preliminary accumulation of the substance on a drop of mercury, the cathode, is necessary; this is followed by analysis by the anode-polarography method. In this apparatus the accumulation of the substance on the surface of the solid indicator electrode (the cathode), can be effected in section II containing the solution being analyzed, while the analysis based on the determination of the anode current is carried out in section III. This eliminates the need for the use of separate mercury drops with equal surface areas.

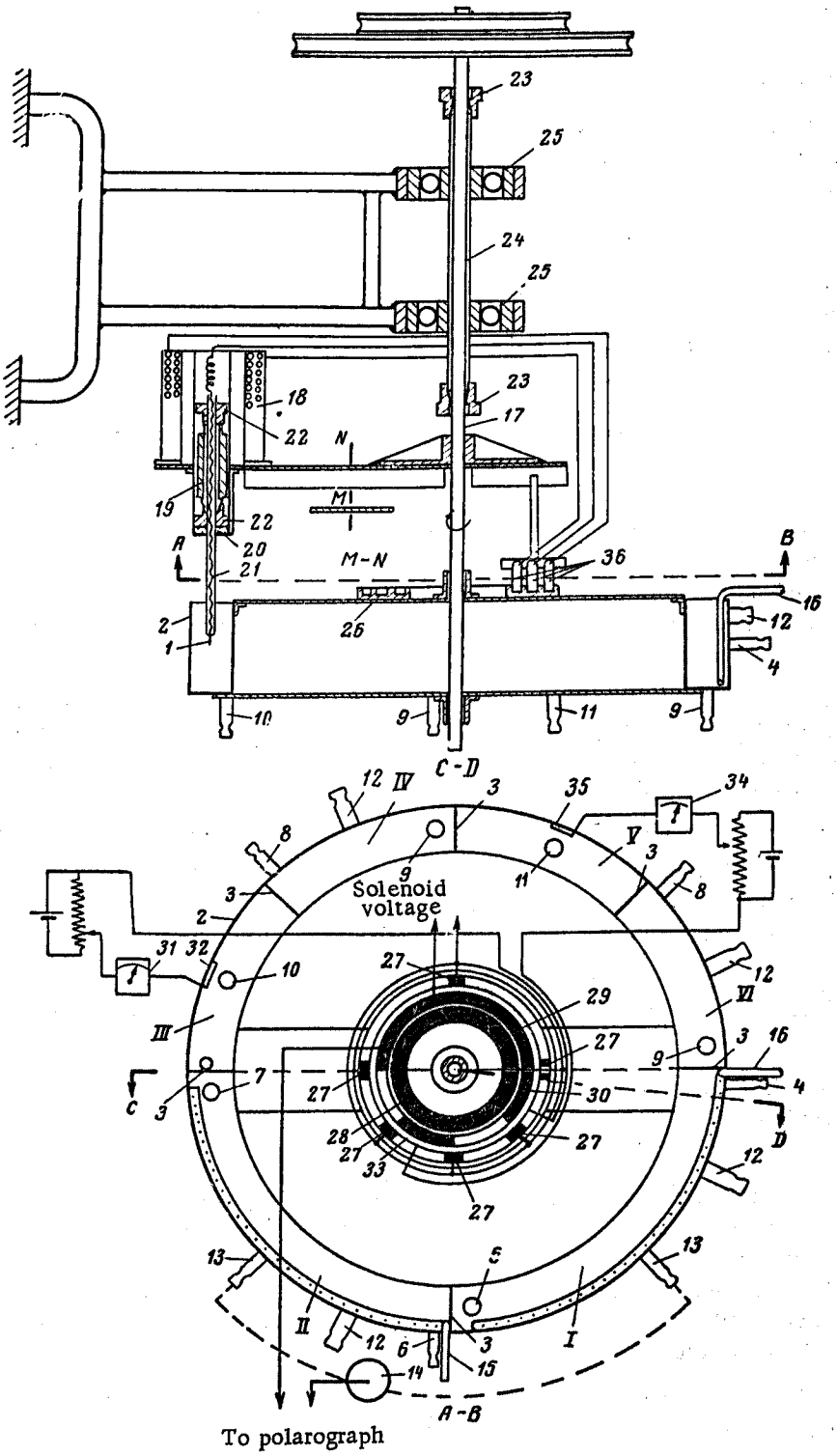

Fig. 1. Polarographic electrolyzer with solid indicator electrode.

The electrolyzer consists of electrode 1 and the circular channel 2, which is divided into six sections by partitions 3.

Connection 4 is the inlet and connection 5 the outlet of the background or the standard solution. The same function is performed by connections 6 and 7 with respect to the solution being analyzed, and connections 8 and 9 for the distilled washing water. Connections 10 and 11 are provided for removing the solutions of the anode (connection 10), and cathode (connection 11), depolarizers. Connection 12 is used for pouring the solutions or water when the flow rate is increased. Connection 13 is filled with an agar-agar solution of an electrolyte, and serves as an electrolytic connection for the solution being analyzed and for the background solution with the comparison electrode 14.

The circular channel, the partitions and all the pipe connections are best made of plastic glass.

The gas being analyzed and the standard (comparison) gas, whose concentration is known, can be supplied through perforated pipes 15 and 16 made of glass or other material. The same pipe is used to supply air into the solution being analyzed, and into the background solution, in order to equalize the concentrations of dissolved oxygen; they can also be used to feed nitrogen, hydrogen, or carbon dioxide in order to remove oxygen.

The indicator electrode rotates at a constant speed in a clockwise direction about its axis 17, and passes through all sections of the circular channel. Solenoid 18 lifts the electrode over the partitions 3; it is energized and lifts the electrode when this approaches the partition. After the electrode has passed over a partition the solenoid is automatically deenergized and the electrode is lowered into the solution by its own weight and the weight of the solenoid core 19.

In order to reduce the shock when the electrode was returned into the solution a fine-pore rubber washer 20 was used. The glass tube 21 containing the electrode is secured in the core by means of tapered nuts 22. Similar nuts 23 are used to secure shaft 24 in ball bearings 25.

The electrode is rotated by the motor and the reduction gear of the KÉP unit, which is an electropneumatic control device. The special holder 24 carries the following conductor bars above the electrolyte: 27 and 28 for feeding the solenoid; 29 for feeding current from the polarograph to the indicator electrode, 30 for supplying the anode depolarization current to the indicator electrode through milliammeter 31 and the auxiliary platinum cathode 32, while the conductor bar 33 carries the cathode depolarization current to the indicator electrode through the milliammeter 34 and the auxiliary platinum cathode 35.

The current is taken from the conductor bars by means of three brushes 36, which rotate together with the electrode and solenoid.

Owing to the high linear velocity of the electrode the steady diffusion current is reached very rapidly.

It should be pointed out that the rotation of the electrolyte with respect to the stationary solid indicator electrode has been successfully used earlier in polarographic analysis. As far as hydrodynamics is concerned, the electrode is identical to the one described by Chirkov [1].

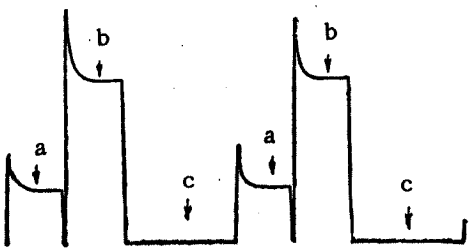

Fig. 2. Recorded polarographic analysis: a) background electrolyte; b) solution being analyzed; c) anode, cathode depolarization and washing with water.

The electrolyte consumption can vary since its linear speed in the channel is not very high, and the effect of fluctuations of this velocity on the diffusion current is very small.

The amount of electrolyte carried from section to section is very small because the glass part of the electrode is coated by a silico-organic film.

A special regulation of the temperature of the electrolyte being analyzed is not necessary, but the temperatures of the standard solution and the solution being analyzed should be the same.

The suggested electrolyzer can also be used for the polarographic analysis of a stationary solution.

About 100 ml of the solution being analyzed is poured into the corresponding section of the channel. The electronic polarograph is used for the continuous recording of the results of the analysis.

A representative curve of the polarographic analysis for a given voltage is shown in Fig. 2 for two revolutions of the electrode.

The concentration of the substance is determined from the difference between the heights of the plateaus obtained for the background solution and the solution being analyzed, using for this purpose the previously plotted calibration curve.

For example, in analyzing $2 \cdot 10^{-3}$-10^{-2} M solutions of lead nitrate in 1-M KNO_3, the sensitivity of the method was $5 \cdot 10^{-5}$ mole and the accuracy—3-7% rel. Oxygen was not removed from the solutions since the electrode passed through the background electrolyte (1 M KNO_3 first). For the automatic anode cleansing of the electrode we used a 5 M NaOH solution containing 5% Seignette's salt; the anode depolarization current was 0.1-0.2 ma. The reproducibility of results was fully satisfactory.

LITERATURE CITED

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A FLUOROPLAST PISTON - TYPE MERCURY ELEMENT

B. Ya. Kaplan and P. M. Chigirev

State Scientific Research and Design Institute of the Rare-Metals Industry

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Polarographic anode ultramicroanalysis, preceded by the electrolytic concentration of the element being determined on a stationary mercury electrode, is now one of the most widely used methods of analyzing high-purity substances. The electrodes with platinum or gold wires described in technical literature have a limited field of application because of the formation of intermetallic compounds between the metal of the wire and the element being determined. All single-drop glass electrodes require a thorough hydrophobic treatment and are therefore difficult to use in alkaline solutions. The best of the single-drop electrodes described hitherto is the "Kemula screw" [1] which consists of a glass vessel with a glass capillary closed by a fluoroplast plug. A steel screw is passed through the plug; the mercury is pressed through the capillary tube by this screw. However, the life of electrodes of this type is short because the thread seal soon fails.

In the proposed piston-type mercury electrode we use a fluoroplast capillary tube which requires no hydrophobic treatment and which eliminates any possibility of contamination by minute quantities of impurities. The sealing of a plastic-glass piston moving in a fluoroplast cylinder is very reliable; the small size of the piston (3.5 mm dia.) and the small pitch of the thread (0.5 mm) combined with a large dial (31 mm dia.) make it possible to obtain a very fine regulation (within a few %) of the surface area of the drop. This was found by measuring the volume of the droplet on Barker's square-wave polarograph.

The design of the piston electrode is shown in the figure.

The fluoroplast cylinder 2 with a 0.14-0.2-mm hole 3 in the bottom is screwed to the stainless steel body 1 of the electrode*. The ground-in plastic-glass piston 4 moves in the cylinder; it is fixed by means of metal ring 5 and pin 6 to the stainless steel rod 7.

In order to improve the electrical contact between the rod and the mercury in the cylinder, the end of the piston carries a platinum contact 8, both ends of which are riveted. In order to improve the reliability of this contact

* The design of the cylinder was slightly modified to eliminate any possibility of the accumulation of bubbles on the cylinder base and to reduce the effect of the diffusion of amalgam into it. The length of the fine hole was increased to 7-10 mm and the end of the cylinder was made tapered.