

THE USE OF POLAROGRAPHY FOR CONTINUOUS AND AUTOMATIC CONTROL OF LABORATORY AND PRODUCTION PROCESSES

Ya. I. Tur'yan and A. M. Murenkov

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Despite numerous review articles on polarography, and also the appearance recently of monographs on the same subject, very little has been published on questions relating to the use of polarography for continuous and automatic control. At the same time, a large amount of work has been carried out in these directions. Since continuous and automatic control places a number of specific requirements on the polarographic method, it would be expedient to consider the results of various investigations relating to the individual sections of the polarographic system.

The Indicator Electrode

The parameters of the indicator electrode used during continuous and prolonged operation should remain constant in order to ensure the reproducibility of the diffusion or limiting current over a long time. Under such conditions one must bear in mind that the surface of the electrode may be contaminated by the products of the electrode reaction and by suspended particles present in production solutions. The electrode should ensure that the new value of the stationary diffusion current is established with the minimum delay when the concentration of the test material in the control liquid or gas stream alters; it should also be insensitive to the vibration of the bracing equipment, and should not require complicated supervision during long and continuous operation. A number of indicator electrodes have been used in the practice of continuous and automatic control.

Wilson and Smith [1] were the first to investigate in detail the operation of the classical dropping mercury electrode in the test solution stream. When the capillary is set up in a horizontal cylindrical cell (the end of the capillary is on the cell axis), linear flow was observed to exert an appreciable effect on the value of the diffusion current at rates exceeding 20 cm/min (cell diameter $d = 25$ mm, discharge about 100 ml/min). When the diameter is smaller ($d = 12.3$ mm), the effect of the flow rate is considerably stronger. One might expect a further decrease in the limiting linear velocity with a decrease in the diameter of the horizontal cylindrical cell. Mann [2], however, has shown that at d about 4 mm (Fig. 1), the limiting value of the velocity is 20 cm/min ($v =$ about 2.5 ml/min).

Wilson and Smith [1] also investigated the flow of a solution in a vertical cylindrical cell ($d = 22$ mm, the capillary being along the cell axis). The limiting value of the linear velocity which still did not appreciably affect i_d , when the liquid moved downwards was found to be 50 cm/min, while in the reverse direction its value was 40 cm/min. When the flow rate is the same, in the second case i_d is greater than when the flow is downward. Nevertheless, this flow direction, in the author's opinion [1], is to be preferred since there is then no necessity to filter the solution.

Jura [3], in order to decrease the effect of the flow, adopted a fairly complicated method of screening the dropping electrode, and obtained, on using a vertical cylindrical cell ($d = 22$ mm), a limiting value of w equal to about 30 cm/min when the solution was moving upward. This flow rate is of the same order as that obtained in Wilson and Smith's cell [1]; it is doubtful, therefore, whether the screening adopted by Jura [3] serves any useful purpose, particularly since in Jura's cell there is a delay of about 2 min.

A number of authors [4-6] have successfully used vertical cylindrical cells in which the capillary is fixed along the cell axis and in which the liquid flows upward (v about 100-150 ml/min), without using any screening. In these cases, as in [1], the limiting value of w which does not essentially affect i_d did not exceed 50 cm/min.

Mancy and Okun [7] have derived the following relation between the diffusion constant of the current of dissolved oxygen G and the electrolyte discharge V :

$$G = 1,52 + V^{2,2}. \quad (1)$$

The formula holds up to $v = 200$ ml/min. The electrolyte moved upward in a conical cell, and the effect of the stream, despite special equipment (tangential injection) was greater in this case than in the ordinary vertical cylindrical cell. In order to eliminate the flow effect completely, some authors [8, 9] have periodically stopped the flow, and taken polarograms after definite time intervals (5-7 min). In such cases, however, the delay should be greater than when operating in a continuous flow.

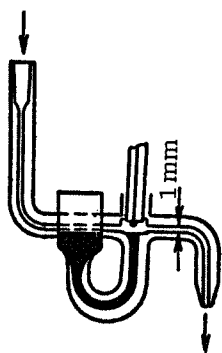


Fig. 1. Mann's dropping mercury electrode.

Miller [10] has suggested an ingenious design for a cell (Fig. 2), in which the flow effect should be completely eliminated during the operation of a dropping mercury electrode. Although the author only designed this cell for mixing the liquid, it is also suitable, in our opinion, for analysis in a flow. The capillary electrode behaves as a pump which draws the test solution into a capillary tube 1 with a diameter of about 1 mm (less than the diameter of the mercury drop). Because of the bend in the lower part of the capillary tube, the mercury drop stays in it until the next drop breaks off, so that during the growth of a new drop, movement of the liquid in the capillary ceases. The liquid is completely renewed after 2-3 drops have fallen off. The delay time is 30 sec. The disadvantage of this setup is the high electrical resistance of the cell. Even when the capillary 2 is 10 mm long, the resistance is 1200 ohms in 0.1 N KCl. Difficulties may also arise as a result of blockage of the capillary along which the liquid is sucked.

Vojir [11] has described the design of a cell (Fig. 3) for analysis of small amounts of a liquid flowing at the rate of 0.1 ml/min. Polarograms are taken on a slowing growing drop of solution 1; the dropping period of the solution is greater than that of the mercury. The anode is a spiral wound on a silver wire capillary 2. The thin film of solution flowing off the surface of the capillary is rapidly saturated by the upward gas stream. We think that such a system would be best suited for the continuous analysis of a gas flow. Under such conditions drawbacks associated with the bubbling of gas through a liquid would be completely eliminated.

In order to eliminate the deleterious effect of gas bubbling on the operation of a dropping electrode during gas analysis, the capillary is placed in a special funnel [12, 13] (Fig. 4). When this is done, immersion of the capillary

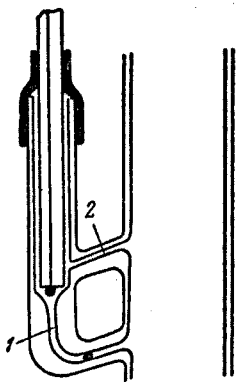


Fig. 2. Miller's cell for stirring the liquid.

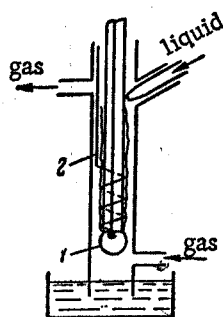


Fig. 3. Vojir's cell for analyzing small amounts of a flowing liquid.

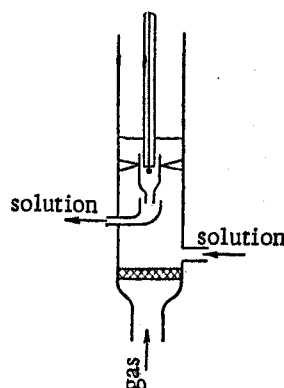


Fig. 4. Design of a funnel for eliminating the effect of bubbling.

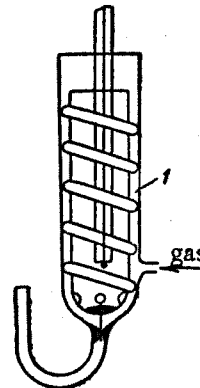


Fig. 5. Nedorost's cell for continuous polarographing.

to a depth of 5 mm in the funnel eliminates the effect of the gas rate, over the range 170-1000 ml/min, on the experimental results. The delay time under these conditions is about 2 min.

Nedorost [14] has designed a cell (Fig. 5) for continuous polarographic analysis, in which thorough saturation of the electrolyte with the gas is coupled with protection of the dropping electrolyte from the turbulence of the electrolyte during bubbling. The electrolyte is saturated with gas in the spiral-like space 1 and then passes into the electrolytic division and then back again into the spiral-like space. The author points out that up to rates of 170 ml/min, the gas rate does not affect the operation of the dropping electrode.

From these papers it becomes clear that with regard to the effect of the flow of liquid and gas on the results of continuous polarographic analysis, the classical dropping electrode can be used with considerable success when certain designs of cells are used. Nevertheless, this electrode has some serious disadvantages, the most essential of these being the breakdown in the reproducibility of the results because of changes in the polarographic characteristics of the capillary with time [12, 15]. Thus, it has been shown in [15] that during continuous determination of oxygen dissolved in natural water, the usual dropping mercury electrode starts to give nonreproducible results after only a few hours because of the entry of CaCO_3 into the capillary mouth. Other drawbacks of the dropping mercury electrode are its sensitivity to vibration, the necessity of transfer by hand, and purification of mercury.

An attempt has been made [16] to use a vibrating dropping electrode for decreasing the effect of mixing of the liquid and bubbling of gas. Such a setup is scarcely promising for continuous production control on account of the complexity of its design.

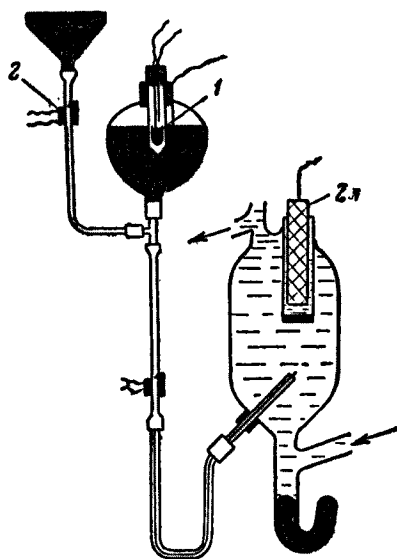


Fig. 6. Dropping mercury electrode with a wide opening.

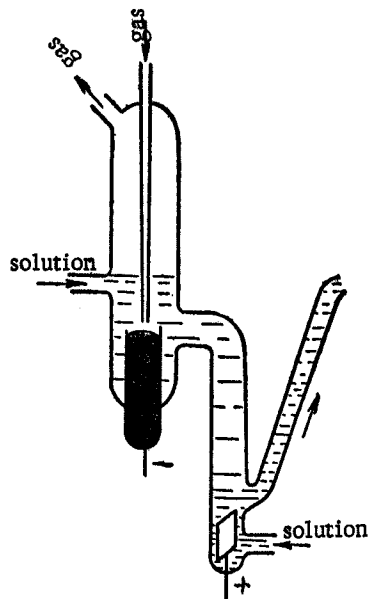


Fig. 7. Massive mercury electrode with a large surface.

Smolar [17] was the first to suggest horizontal dropping electrodes, while Serak [18] has used them successfully for continuous polarographic analysis. Tyler and Karchmer [19] adopted a rapidly dropping electrode with a dropping period of about 0.25 sec for the same purpose. The most essential advantage of this indicator electrode for continuous automatic control is its low sensitivity to vibrations and blows.

A Dropping Mercury Electrode with a Wide Opening for continuous polarographic analysis was suggested by Briggs et al [15, 20]. The electrode was fixed at an angle of 45° (Fig. 6), it had an opening of $d = 0.8$ mm and a dropping period of 2.5 sec. In order to ensure a constant mercury throughput (about 6 ml/hr), the cell was provided with an automatic regulator—a float 1 with electrical contacts and a valve 2. The advantages of this electrode are its good reproducibility during prolonged use, its insensitivity to contamination in solution, and its significantly higher—ten times as much—diffusion current. Of interest in this case is the fact that the flow effect is more marked at lower velocities (about 3 cm/min) than is the case when the usual dropping electrode is used.

Polarographic analysis of unstirred and stirred samples, using a massive dropping mercury indicator electrode was first described in [21-23]. Novak [24] used a massive mercury electrode whose surface was washed with gas (Fig. 7) for continuous polarographic analysis; a sensitivity of 10^{-7} -M was achieved with an electrode surface of 0.2-0.3 cm^2 and a gas flow of 500 ml/min. Starting at 200 ml/min, the limiting current does not increase on increasing the gas flow further, but remains proportional to the electrode surface. The variation in the current is 2-6%, i.e., not more than the usual variation when a dropping electrode is used. In addition to the electrode surface, the following parameters should be kept constant: the diameter of the end of the gas lead-in tube (1-2 mm), the distance

between the end of this tube and the electrode surface (~ 2 mm), and the thickness of the electrolyte layer over the electrode surface (6-12 mm). Novak's electrode is exceptionally promising on account of the reproducibility of the results and its high sensitivity. Novak has shown that the electrode is also completely suitable for the continuous analysis of metals, since the increase in the concentration of the amalgam is very slow. Thus, for $V_{\text{Hg}} = 3$ ml and $i = 100 \mu\text{a}$, during analysis of Cu^{2+} an amalgam containing only 0.21% Cu is obtained after one month, while it is only necessary to change the mercury after several months' use. Nevertheless, when the metal concentration is high, the amalgam becomes concentrated appreciably more rapidly; this limits the possibilities of the use of this electrode. At low throughputs (< 1 ml/min) the concentration of test material may decrease and can lead to analytical errors.

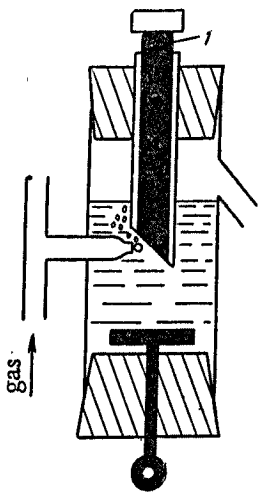


Fig. 8. Graphite indicator electrode.

In another design [25] Novak used a massive mercury electrode which was washed only by a strong stream of test solution, at rates up to 500 ml/min. The opening of the feeding tube was 10-30 mm from the electrode surface. The sensitivity at $S_{\text{Hg}} = 3 \text{ cm}^2$, as in the previous case, is very high ($\sim 10^{-7}$ -M.).

Jessop [26] has patented a polarographic cell for continuous analysis in which a massive mercury electrode ($d_{\text{Hg}} = 2 \text{ cm}$) washed by the test solution is again used.

Zavorka and Strafelda [27] have pointed out that the disadvantage of a massive mercury electrode is the possibility of the contamination of its surface by mechanical impurities and adsorbed materials. To eliminate this, these authors have adopted a complicated system for automatically renewing the mercury surface. The flow of test solution continuously carries off a small amount of the mercury which is then returned to the electrode after purification.

Muller [28] was the first to study the behavior of a Platinum Microelectrode $S = 0.3 \text{ mm}^2$ in a stream of test solution. The electrode was fixed in the capillary constriction ($d = 0.4 \text{ mm}$ and $l = 1 \text{ mm}$) of the feeding tube. The following relation was established between the limiting current (i_n) and electrolyte throughput (V):

$$i_n = a + b \lg V. \quad (2)$$

The formula holds for the range $V = 0.60$ to 18 ml/min ; a and b are constants for a given material—the depolarizer. The values of b bear approximately a diffusion coefficient relationship to each other. In addition to its use for continuous analysis, the electrode can be successfully used for determining the throughput of liquid.

Novak [29] has suggested a platinum electrode in the form of a disc with $S = 1 \text{ cm}^2$, washed by a gas with a constant rate of 20-100 ml/min, for continuous polarographic analysis. The gas should wash as much of the electrode surface as possible. The variation in this case, as in the case of a massive dropping mercury electrode, is 2-6%; the sensitivity is $\sim 10^{-7}$ -M. Vibration does not affect the readings.

Platinum indicator electrodes, like electrodes of other noble metals, are not suitable for anodic polarography, since the current drops with time because of the formation of oxide film [30]. Bearing this in mind, Novak [31] has used a graphite indicator electrode 1, $S = 0.5-1 \text{ cm}^2$ (Fig. 8) washed by gas for continuous anodic polarography. The electrode gives an oxidizing current which is stable with time. The working part is cut at an angle so that the gas is not held on the surface.

An essential drawback of the normal solid electrode is contamination of its surface by electrolysis products, which completely excludes the use of this electrode for continuous analysis of solutions in which metals are deposited.

In order to eliminate this drawback, Tur'yan has developed a design of a polarographic cell (Fig. 9) in which the solid indicator electrode 1 is continuously moved along a circular channel 2, separated by a number of partitions into a series of compartments: a compartment for test solution 3; a compartment for anode 4 and cathode 5 depolarization with electrolytes and auxiliary electrodes 6 and 7 specially chosen for this purpose; a compartment 8 for washing with water; and a compartment 9 for the background or standard electrolyte. The calomel or other reference electrode 10 is common to both test and standard solutions. The electrode is rotated around an axis which coincides with the axis of the circular channel, while transfer of the electrode from one compartment to another is realized by

means of an electromagnet 11 which rotates together with the electrode and lifts it as it approaches a partition. The electromagnet is switched off and on, and the polarization and depolarization conditions selected automatically by means of rubbing contacts. The fact that the same electrode is used in the standard and test solutions appreciably facilitates the possibility of using differential polarography, which is particularly important for continuous automatic polarography. The insignificant carry-over of solution from compartment to compartment is not important owing to the flow of test and standard electrolytes. The electrode is continuously cleaned not only from deposited metals, but also from oxide films, so that it should prove useful in anodic polarography.

It has been pointed out [15, 26] that platinum and gold indicator electrodes are rapidly poisoned during continuous analyses. This drawback can be eliminated in the case of oxygen determination [32, 33] by separating the platinum indicator electrode from the medium being analyzed by a special polyethylene or teflon membrane. The

use of such membranes which are permeable to the gas passing to the indicator electrode but impermeable to the electrolyte, and were first suggested by Clark et al. [34] has great possibilities. The particularly important advantage of membranes is the elimination of the deleterious effect of metals and other materials dissolved in the liquid flow [33]. Membranes made from polyethylene have a thickness of 0.051 mm, while the teflon membranes are 0.027 mm thick. Teflon is 2.5 times more permeable to gas than polyethylene. The delay time is about a minute. The design of such an electrode [33] is shown in Fig. 10, in which the platinum indicator electrode in the form of a disc 1 is wrapped in a polyethylene membrane 2. The electrolyte 4 and the silver reference electrode 5 are located between the membrane and the plastic holder 3. A drawback in the use of membranes is their high temperature coefficient, which amounts to about 5% per 1°.

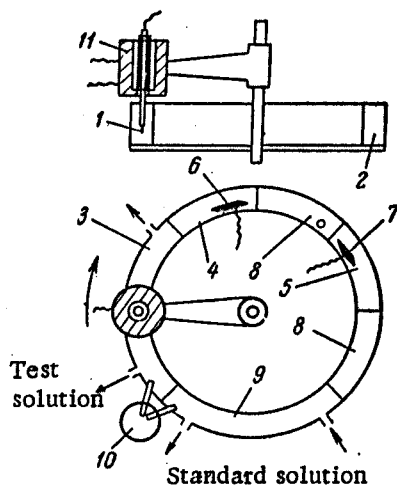


Fig. 9. Polarographic cell for solid indicator electrodes with an attachment for cleaning.

Reference Electrodes

An essential requirement of such an electrode is the absence of polarization during prolonged continuous operation. It is also desirable that the reference electrode should not be separated from the test solution by diaphragms which can lead to a sharp increase in the electrical resistance of the cell [5] during prolonged use. When a mercury pool is used as the reference electrode, in order to avoid polarization, its surface should be continuously purified by the stream of test solution [35].

As Novak [5] has shown, the usual reference electrode of the second kind is very rapidly polarized. Thus, a calomel electrode changed its potential by 1000 mv after only being used for one hour at a current of $100 \mu\text{A}/\text{cm}^2$. Novak [5] has suggested a normal dropping electrode placed in the test solution or in another solution as a reference electrode. When such a technique is adopted, the electrolyte of the reference electrode is not separated from the test solution by any diaphragm. Separation of the solutions is effected purely by differences in their specific gravities.

At high currents a dropping reference electrode (anode) is unsuitable, and Novak, in another paper [6] replaced it by a platinum plate $S = 1 \text{ cm}^2$ (see Fig. 7) in a solution of $\text{FeSO}_4 + \text{Fe}_2(\text{SO}_4)_3 \cdot (0.01 - 0.1 - \text{M}) + \text{H}_2\text{SO}_4 \cdot (0.1 - 1.0 - \text{M})$. Such an electrode has been successfully used under anodic and cathodic conditions (oxidation and reduction of iron ions). A mixture of ferri- and ferrocyanides is used in the case of alkaline solution. The same author has suggested adding para-nitrophenol to the solution when using a platinum nonpolarizing cathode.

Novak [3] has also used a copper disc in a solution of $0.5 - 1.0\% \text{ H}_2\text{SO}_4 + 0.1 - 2\% \text{ CuSO}_4$ as a nonpolarizing cathode in continuous anodic polarography. Changes in the Cu^{2+} concentration even by as much as a half only changed the cathode potential by about 9 mv.

Foyn [36] has suggested the use of a zinc rod (see Fig. 6) in a buffer solution ($\text{CH}_3\text{COONa} + \text{HCl}$) $\text{pH} = 5.5$ as a nonpolarizing anode; it has been tested in continuous analysis [15, 20]. This electrode was not polarized during several months continuous operation without change of solution at a current of $50 \mu\text{A}$.

Measuring Setups and Polarographs

Two methods are used in continuous automatic polarography for recording the analytical results: periodical recording of complete polarograms over a given potential range, and recording of the limiting current with time at a given potential. Although the first technique is rarely used, nevertheless it has, as Valenta has pointed out [37],

a number of advantages: interference from changes in the resistance of the cell and the potential of the reference electrode is eliminated; the appearance of new waves can be detected; and, finally, changes in the concentration of the solution connected with continuous passage of large currents can be eliminated. Nevertheless, continuous recording of complete polarograms requires complicated polarographs.

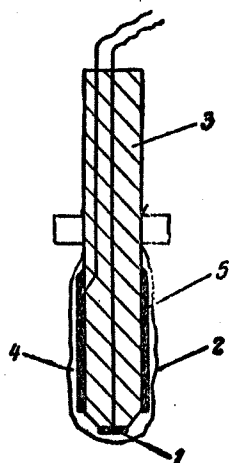


Fig. 10. Platinum indicator electrode with a polyethylene membrane.

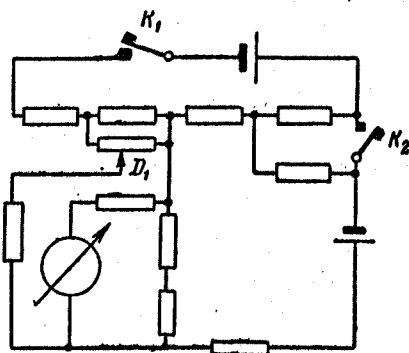


Fig. 11. Electrical circuit for a semi-automatic polarographic setup.

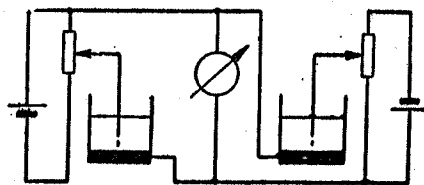


Fig. 12. Electrical circuit of an automatic setup.

in which auxiliary 1, indicator 2, and reference 3 electrodes are used (Fig. 13). The potential applied from the potentiometer 4 at any concentration of the solution should leave the galvanometer in a null position, which is achieved automatically. The potential of the indicator potential is kept constant in this way. Due to the large

Prochazka [38] has constructed a polarograph for periodical recording of oxygen maxima at definite time intervals.

Valenta [37] has described an electronic polarograph for periodical recording of complete polarograms on paper over a given potential range every 15 sec.

A polarograph has been used [8] which automatically recorded derivative polarograms every 5 min over the requisite potential range.

When recordings of the limiting current with time are used in conjunction with electronic polarographs of particular promise is differential polarography which permits compensation for the effect of various impurities which are reduced in the same potential range. Pletnev and Rozov [39] working with a semiautomatic setup, used an electrical circuit (Fig. 11) which enabled the effect of O_2 , Cu^{2+} , and Fe^{3+} on the height of Cd^{2+} waves to be compensated. For this purpose key K_2 is opened and a potential below the reduction potential of Cd^{2+} is applied, then by moving D_1 the currents from O_2 , Cu^{2+} , and Fe^{3+} are compensated; key K_2 is closed and the diffusion current of Cd^{2+} recorded.

In completely automatic setups differential polarography is adopted in which two separate cells, two indicator electrodes and the electrical circuit shown in Fig. 12 are used [4, 26]. The liquids in the cells should not be in electrical contact, accordingly the current through the cell breaks on the drops [4]. This would not be possible if the test solution had a high resistance [26].

The use of Tur'yan's design, described above, enables a differential polarogram to be obtained without additional circuits, and, most important, without eliminating the effect of the differences in the polarographic characteristics of the two indicator electrodes.

Of considerable promise for continuous polarographic control, as Tsfasman et al. [40-42] has shown, is an ac polarograph which eliminates interference from electropositive impurities and also eliminates interference from oxygen to some extent; the method possesses a very high sensitivity. The most essential drawback of this method when applied for continuous control is the difficulty of keeping the value of the half-wave potential constant with time. As the authors have pointed out [40] a change in the half-wave potential of only a few millivolts leads to an error of about 10%.

In contrast to the articles considered above, in which the value of the current is recorded by the usual method with a millimicroammeter or electronic potentiometer, Novak [43] has suggested a compensation scheme for measuring the electrical current

value of the resistance 5, the potential applied can serve as a measure of the current passing through the system. The choice of the indicator electrode is realized by means of the potentiometer 6. Adoption of Novak's suggestion for continuous control, eliminates interference arising from changes in the potential of the reference electrode at high currents, and also eliminates variations in the internal resistance of the cell. It should also be possible to use organic solvents with a high resistance.

Examples of the Practical Application of the Method Determination of Oxygen

Continuous analysis of oxygen content has been carried out both in liquids (natural and tap water [15, 20, 33], boiler water [25-27], biological media [18, 28]) and in gases (natural gas, ethylene, butadiene [24], hydrogen, and generator gas [12]). The sensitivity of the method is 0.1 mg/liter for boiler water [26]. According to Novak [25], 0.05 mg/liter of oxygen in boiler water gives a current of 2 μ a, the accuracy is not less than 10%. In a setup described in [15, 20] the range of tests concentrations of dissolved oxygen is 0.0 to 15 mg/liter. Differential polarography [26] was used for eliminating the effect of heavy metal ions; this is not necessary, however, when a protective diaphragm is used [33]. For gas analysis the sensitivity of the method is 0.1% when an aqueous electrolyte is used [24] and 0.01% when a methanol electrolyte is used [12]. In this paper the upper limit of the test concentration is 5% for an accuracy of 5%. As a rule, the second oxygen wave (about 1 v) is used; nevertheless, when cationic surface active materials are present in the medium it is recommended [7] that the limiting current of the first wave be used.

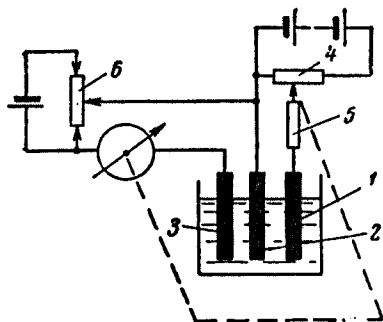


Fig. 13. A compensation scheme for measuring the electrical current when three electrodes are used.

Analysis of Metals and Production Streams.

Most of the work has been devoted to the determination of uranium [8, 44, 45, 46]. Bertram et al. [8] have carried out continuous analysis of production streams. The uranium concentration of the original

solution was 100-200 g/liter, while in the test solution it was ≤ 2.5 g/liter. Automatic dilution involving an error of $\pm 0.5\%$ was adopted. The experimental error was $\pm 5.5\%$. Continuous analysis of radioactive industrial streams for their uranium content has been described in [44]. The upper limit was 5 g/liter, while the accuracy was $\pm 10\%$.

Pletnev and Rozov [39] have developed a setup for the semiautomatic determination of Cd^{2+} in the electrolyte from zinc hydrometallurgical plants. Tsfasman, Bryksin, and Bruk [40] have suggested a more advanced and completely automatic setup for similar purposes. Under their conditions the Cd^{2+} concentration was ≤ 5 mg/liter, while the accuracy was $\pm 4\%$. Even a 200-fold excess of Cu^{2+} did not affect the accuracy of the apparatus readings.

A method for the continuous determination of Cd^{2+} and Bi^{3+} in solutions from hydrometallurgical plants has been suggested in [4]. The application of differential polarography permitted determination of Cd^{2+} in the presence of 1000 times its amount of Bi^{3+} .

Novak [6, 24] has suggested a method for the continuous analysis of mixtures of Ti^{3+} and Fe^{3+} during production of titanium pigments, and of mercury ions in production tap water [24].

Analysis of SO_2 in hydrometallurgical production (solutions) with an accuracy of $\pm 5\%$ has been described in [1], and in sulfuric acid production and cellulose (gas) in [31]; in the latter case the sensitivity was about 0.01% SO_2 .

Analysis of Other Materials. Continuous control of cyanide ions has been suggested in [3]. The concentrated solutions was diluted ten times; the oxygen wave served as the reference level. The accuracy was $\pm 2\%$.

Novak [5, 29] has developed methods for the continuous control of nitrobenzene content during the production of aniline, and of CO in the air (down to $10^{-4}\%$) in metallurgical plants and pits. The CO analyzer is recommended as the best apparatus for pits. Before passing into the CO analyzer, iodine oxide is reduced to iodine, the latter then passes with the gas into the cell and depolarizes a Pt cathode or anode in 0.5-1.0 N H_2SO_4 .

Kemula et al. [47-49] have made the widest use of polarography as a detector-analyzer for chromatographing mixtures of organic compounds. One of the difficulties in this method is continuous removal of oxygen under conditions which preserve the differences in the nature and concentration of materials at different parts of the stream.

For this purpose use is made either of the movement of the solution in the form of a turbulent film in a fine capillary tube through which nitrogen is bubbled [50], or of the movement of a gas and the electrolyte in a tube packed with glass spheres [51]. In general, Kemula [49] did not remove dissolved oxygen, but used two chromatographic columns and adopted differential polarography.

In conclusion, one of the authors of the present review wishes to thank Doctor Novak (Polarographic Institute of the Czechoslovakian Academy of Sciences) for giving him the fullest information on the work carried out in Dr. Novak's laboratory on continuous polarographic analysis.

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DETERMINATION OF ULTRAMICROAMOUNTS OF ZINC, LEAD, AND COPPER PRESENT AS IMPURITIES IN HIGH PURITY TIN BY AMALGAM POLAROGRAPHY

A. G. Stromberg, M. S. Zazharov, V. E. Gorodovykh,
and L. F. Zaichko

Tomsk Polytechnical Institute

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The sensitivity* of the determination of zinc, lead, and copper in high purity tin should not be less than $10^{-5}\%$ in certain cases. Spectrographic methods which have been developed hitherto permit this problem to be solved with respect to lead and copper, but the average experimental error is 30%; the sensitivity of zinc determination is considerably less, while the results are semiquantitative in character.

The new physicochemical method of analysis—amalgam polarography on a stationary mercury electrode using a linearly changing potential—developed recently permits determination of a number of elements at concentrations down to 10^{-9} M [1-6]. However, there are only individual published papers on the application of this method to the analysis of pure materials [7-9].

The authors of the present article have developed a technique for the determination of Zn, Pb, and Cu in high purity tin at a sensitivity which is not less than $10^{-5}\%$.

Of the various methods which we tested for removing the bulk of the tin from the impurities to be determined we finally decided on distillation as SnBr_4 . There are published references to the possibility of removing tin as SnCl_4 , nevertheless, preliminary experiments showed that despite several evaporations with hydrochloric acid in the presence of hydrogen peroxide or nitric acid, significant amounts of tin remained in the residue, presumably in the form of the oxychloride.

* We define sensitivity in this case as that concentration of the element in high purity tin which gives a peak height of 2 mm on the polarogram under the experimental conditions used. Under such conditions we consider that the error in measuring the peak height should be 0.5 mm.