METHODS OF CHEMICAL ANALYSIS

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GRAPHITE ELECTRODES IN ELECTROCHEMICAL METHODS OF ANALYSIS (REVIEW)

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This paper is concerned with the various methods of using graphite indicator electrodes in electrochemical analysis. The limitations of the mercury drop electrode have given rise to the problem of using other electrode materials in volt-amperometry. Precious metal electrodes, of platinum, gold, and silver, make it possible to work in positive regions of potential, and are widely used in polarography, amperometric titrations, and other electrochemical investigations. However, these precious metal electrodes also have certain disadvantages. The reproducibility of the results depends very much on the previous history of the electrodes. Moreover they are not always sufficiently inert; under certain conditions their surfaces become covered with oxide films, which can affect the electrode processes occurring [1].

Graphite (carbon) is the only solid electrode to give a completely reproducible surface. Until recently graphite had been used as an electrode material only in technical electrochemistry [2]. It was first used as an indicator electrode in volt-amperometry by Lord and Rogers [3, 4]. They employed 1/8 or 3/16 rods, for spectral analysis grade, and pencil rods of medium hardness, coated with axiezon wax. The reproducibility of the limiting current at a rotating electrode was found to be 1.9%.

Graphite electrodes were further used in volt-amperometry [5-12], amperometric titrations [13, 14], oscillographic [15] and alternating current polarography [16], chronopotentiometry [11, 17], and potentiometric titrations [18]. There have also been papers on the use of carbon paste as a material for electrodes [19, 20].

Graphite rods of spectral and ultraspectral purity have been used for electrode preparation [4, 10, 11]. Our investigations have shown that the purity of spectral graphite (10^{-3}-10^{-6}% of impurities is not reflected in the results of polarography of supporting electrolytes. The use of pencil rods is not recommended, except for special purposes, since the composition and quality of these rods are not sufficiently standardized.

In all the papers listed above, the end of the electrode was used as the working surface of a graphite indicator electrode. The sides were insulated by sealing wax, ceresin wax, paraffin, resin, adhesive BF-2, etc. The electrodes used were 0.6 cm in diameter and 10-12 cm long. The resistance of such a rod was comparable with that of a platinum electrode 0.5 mm in diameter and 5 mm long (0.3 and 0.1 Ω respectively).

Impregnation of the electrode with certain materials considerably increased the reproducibility of the results and made it possible to obtain a considerably smaller residual current, so that the sensitivity was increased.

Gaylor, Conrad, and Landerl [7] tested a large number of impregnants; they concluded that their actions differed and also depended on the solubility of the impregnant in the medium used.

All the authors [7, 10, 11] explained the ability of the impregnants to reduce the residual (capacity) current in terms of filling up of the graphite pores and the formation of a more compact surface. In achieving this the impregnants hardly reduced the value of the Faraday current.

The means of renewing the electrode surface is very important, but the conditions for renewal have not yet been standardized. Lord and Rogers [4] renewed the surface by breaking off the end of the electrode, while other authors used sawing and scraping the surface with emery paper* [7, 9, 11]. Morris and Schempf [10] constructed an instrument for cutting off the end of the electrode. Electrode renewal sometimes caused changes in the size and quality of the surface (nonuniformity of structure), which affected the consistency of the results. Our observations showed that differences in surface purity produced by cutting with a file resulted in differences in capacity current. Development of the surface could also affect the reproducibility of results because of the phenomenon of potential-limiting adsorption [21].

In order to reduce the capacity current it was necessary to reduce the true area of the electrode surface; this could be achieved, not only by impregnation, but also by smoothing the surface. Working with a graphite electrode, we removed a thin film of graphite, about 1.5 mm thick, from the end with very fine emery paper. The surface was then polished with filter paper, and residual dust was washed off with distilled water. By using a sufficiently uniform emery paper, it was possible to reduce the residual current, at zero potential relative to a mercurous iodide electrode, to 10^{-7} A. On the other hand, when the surface had been filed, the residual current often exceeded 5 μA.

Hence it followed that the capacity current i_c depended on the true surface of the electrode, while the diffusion current was mainly determined by the geometrical area of the surface. This has been expressed by the equation [21]:

$$i_d = K_1 \cdot D \cdot A \cdot C,$$

from which it is clear that the diffusion current is proportional to the diffusion coefficient D of the material acting over a definite area A to the electrode surface.

In order to obtain reproducible results, it was also necessary to select electrodes which had a strictly uniform diameter over their whole length.

It follows from the above that the ratio i_d/i_c could be reduced by impregnating the electrode, by polishing the surface, or by using both methods.

Both stationary and rotating graphite electrodes have been used for polarographic investigations. A flowing liquid with a fixed electrode has also been used. Gaylor noted [7] that stirring impaired the reproducibility of the results (the relative error increased to 10%), but considerably increased the diffusion current and hence improved the sensitivity of polarographic determination.

Cells for use with graphite electrodes do not differ from normal polarographic cells for use with solid electrodes [4, 10, 11].

One of the main advantages of the graphite electrode is the wide range of potential over which it can be used for polarography. According to Lord and Rogers [4], and this has been confirmed by our own work, the potential range for a nonimpregnated graphite electrode, in an acid medium (0.1 N HCl), extended from $\varphi_{\text{anode}} = 1.12$ V to $\varphi_{\text{cathode}} = -0.32$ V, while in an alkaline medium (0.1 N NaOH), it extended from $\varphi_{\text{anode}} = 0.7$ V to $\varphi_{\text{cathode}} = -0.34$ V. According to the literature [7], impregnating the electrode extended the polarization range in the negative region to −1.3 V† in a medium of 0.1 N KCl.

These authors [7] attached great interest to the wave for reduction of dissolved oxygen at negative voltages (−0.41 to −0.7 V with 0.05 M KCl as supporting electrolyte). According to our data for a platinum elec-

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* The layer removed was normally 1.5-10 mm thick.

† This potential was referred to a saturated calomel electrode.

trode with the same supporting electrolyte, the oxygen reduction wave could be observed at potentials from +0.7 to +0.15 V (relative to a mercurous iodide electrode), depending on the acidity of the electrolyte. Thus the higher overvoltage for oxygen reduction at a graphite electrode is an advantage as compared with a platinum electrode. With an unimpregnated electrode the reduction wave of oxygen was generally unobservable, but an increase in cathode current began at a potential of 0.2 V (relative to a mercurous iodide electrode).

Methods of impregnating electrodes have been described by various authors [7, 10, 11]. It is essential that the air filling the rod should be completely removed from the graphite pores. The presence of air in the pores of unimpregnated graphite obviously accounts for differences in the polarization limits, in the negative region, of impregnated and unimpregnated graphite electrodes. Both types of electrode are similar in other respects (polarization limits in the positive potential region are the same), so that, in our view, unimpregnated graphite rods with polished surfaces can be recommended, since they are easier to prepare. Moreover, an impregnant may affect the quality of an electrode and give an unsteady Faraday current at high positive potentials; we observed this experimentally, and it has been noted by other authors [12].

Most of the published work on the use of graphite electrodes refers to the polarographic method of investigating a large number of inorganic and organic substances. The greatest interest attaches to reactions involving the oxidation of organic substances at a graphite electrode. In most cases it has been possible to obtain reproducible waves for oxidation or reduction. Lord and Rogers [4] investigated by polarography the systems: quinone-hydroquinone-quinhydrone; aniline; o-, p-, and m-toluidines; phenylenediamine. Gaylor and Elving [5] investigated compounds of the phenolic type; phenol, dimethylphenol, and hydroquinone. Gaylor, Konrad, and Landerl [7] investigated the behavior of catechol, resorcinol, phenol, butylaminophenol, phenylenediamine, dibutylphenylenediamine, and oxalic acid. They proposed a method for the direct polarographic determination of dibutylphenylenediamine and butylaminophenol in ligroine. They made a comparison of the behavior of these substances at platinum and dropping mercury electrodes [7, 9]. The good reproducibility of the results for organic substances has been explained by some authors as due to the formation of a film of polymerized free radicals at the electrode where the substance is being oxidized [10, 11].

Inorganic substances, whose behavior has been investigated, include the ions of iron [4, 9], cerium [9],uranyl [9], lead [7], oxygen [7], and permanganate [4]. Detailed investigations have been made of mercury [9], silver [9, 10], and copper [9, 10]. The waves of inorganic substances, which were reduced at the electrode but not precipitated on it, were found to be poorly defined. However, the ions of ferri- and ferro-cyanide gave well defined limiting current plateaus. The reversibility of this system was studied by Morris and Schempf [10]. It was interesting to record the peaks of substances deposited on the electrode as the result of electrochemical reactions. Brainina and Kiva [15] used the oscillographic method to record the peaks of cadmium, copper, and nickel with an impregnated graphite electrode.

We investigated the problem of determining microquantities of mercury with an unimpregnated graphite electrode by the method of inverse polarography.

Novak [12] used a graphite electrode for determining sulfur dioxide and hydrogen sulfide in technical gases (0.01-10%). They developed a design of cell for the continuous measurement of the gas concentration in a solution 0.5 M in H_2SO_4 and 0.02 M in $CuSO_4$.

It would be noted that the best polarographic results were obtained after the electrode had been polarized for some time at a potential normally equal to the half-wave potential of the substance to be investigated.

Various authors have studied the effects on the reproducibility of voltage-current curves of the following factors: polarization rate, acidity of solution [4, 5], ionic strength and concentration, polarization voltage, and change in temperature [4, 5, 10].

Interesting results can be obtained if I – t curves are investigated by the linear diffusion method, proposed by Lingane and Kolthoff; for example, the equation

$$I_t = n \cdot F \cdot C \cdot A \sqrt{\frac{D}{\pi t}}$$

can be used to calculate the area of an electrode [10, 19].

Consideable interest attaches to the work of Elvin and his colleagues on chronopotentiometry at a graphite electrode [11, 17].

The constant of chronopotentiometric measurements was obtained with a precision of 3%, when the concentration of the substance investigated was 10^{-3}-10^{-4} M. In many cases the results of chronopotentiometric measurements were more reproducible than those of voltage-current measurements.

The most obvious advantages of the graphite electrode have been found in work on amperometric titration. Thus, Smith, Jamieson, and Elving [13] used graphite electrodes for the direct amperometric titration of potassium tetraphenylborate in aqueous solution. Under the same conditions tetraphenylborate gave no oxidation wave at a platinum electrode, but with graphite there were well defined oxidation waves at potentials of +0.3 and +0.9 V (relative to a sodium chloride-calomel electrode).

We have titrated small amounts of uranium with EDTA at +1.3 V and also at +0.2 V (both relative to a mercurous iodide electrode), without removal of dissolved oxygen [14].

Bercik and Hladky [18] used a graphite electrode for the potentiometric titration of weak organic bases. The authors noted that, after activation with permanganate, the electrode could be used instead of a glass electrode to measure the acidity of a solution. This use of the graphite electrode deserves a more detailed investigation.

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