

Recent Developments in Polarography

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Zusammenfassung

Zu den letzten Fortschritten auf dem Gebiete der Polarographie gehört auch die Entwicklung neuer Instrumente, insbesondere von Kathodenstrahl- und Wechselstrompolarographen. Die «square wave»- und «pulse»-Polarographen gehören zu der letzteren Klasse von Instrumenten. Die Prinzipien dieser Geräte und ihre Vorzüge gegenüber den gebräuchlichen Gleichstrompolarographen werden beschrieben. Diese neuen Apparate haben den Anwendungsbereich der Polarographie in der analy-

tischen Chemie beträchtlich erweitert, insbesondere bei der Bestimmung von Spurenelementen. Mehrere typische Verwendungsarten werden aufgeführt.

Die coulometrische Analyse ist eine weitere in der analytischen Chemie wichtige elektrochemische Methode. Es werden für ihre Ausführung geeignete Apparate und einige typische analytische Anwendungsmöglichkeiten beschrieben.

1. Introduction

The conventional method of polarographic analysis is based upon the application of a slowly increasing applied voltage to the electrodes of an electrolysis cell containing the sample solution and the recording of the resultant current-voltage curve. The cathode consists of small reproducible drops of mercury forming at the end of a fine-bore capillary, whilst the anode is either an unpolarised pool of mercury or a standard reference electrode. The current-voltage curves consist of steps caused by the reduction of electro-reducible ions in solution. Each increase in current is governed entirely by the diffusion of a particular ionic species from the bulk of the solution to the cathode surface and the diffusion current, as measured by the height of the step, is proportional to concentration. The technique is generally applicable to the determination of concentrations of reducible ions in the range from 10^{-2} to 2×10^{-5} M.

The limitations of conventional polarography in analysis can be summarised as follows:

- (1) The determination of concentrations smaller than about 10^{-5} M is impossible because of the interference of a current referred to as the condenser current. This latter current may be as much as $0.2 \mu\text{A}$ and is due to the charging of the double layer of ions that form a capacitor on the growing surface of the drop.
- (2) The resolution between two steps is not very satisfactory unless the halfwave potentials are separated by approximately 200 mv.
- (3) Serious interference can result from a large step caused by the previous reduction of a major reducible constituent in the sample solution. In some cases it is possible to eliminate this type of difficulty by adding a supporting electrolyte to the sample solution which preferentially forms a stable complex with the major constituent and removes the step to a more negative potential.

Developments in polarography in the past decade have been directed mainly towards the improvement of the sensitivity and resolution of the technique, and the various aspects are considered in this paper.

2. Alternating Current Polarography

2.1. Instrumentation

BREYER and co-workers^{1,2} developed an A.C. technique employing a small sinusoidal alternating potential of low frequency superposed on the direct potential applied to the dropping mercury electrode. The resulting alternating component of the cell current was measured and its magnitude found to be dependent on reaction rates, being much greater for substances reversibly

reduced than for those irreversibly reduced at the dropping mercury electrode. This method produced derivative polarograms which possessed several advantages over the steps in conventional polarography:

- (1) The peaks for two substances were resolved when they were separated by only 40 mv. This represents a considerable improvement in resolution.
- (2) The effects of previous reductions were of far less importance. For instance small amounts of less noble ions could be determined in the presence of greater concentrations of nobler substances.
- (3) The removal of oxygen from solutions before recording polarograms proved less important, because the reduction of oxygen is irreversible and no interfering peak is produced.

However, a serious disadvantage in this technique arose from the occurrence of an alternating current component associated with the double layer capacity of the mercury-solution interface. This component can be considered analogous to the condenser current in conventional polarography. BREYER and co-workers were unable to eliminate this interference and in consequence the sensitivity of this technique was no better than that obtained by conventional polarography.

The interfering capacity current has been eliminated in the *square wave polarograph* developed at Harwell by Dr. G. C. BARKER and his co-workers.^{3,4,5} In this method a small alternating square wave voltage (≤ 30 mv) of 225 cycle/second is superposed on the normal slowly changing D.C. voltage, and the amplitude of the resulting A.C. component of the cell current is measured shortly before each change in sign of the alternating voltage. In this way an almost perfect separation of the faradaic current and the capacity current is achieved. Variations of applied voltage and current with time are shown in Figure 1. It will be seen that the diffusion current never decays to zero in the interval between successive voltage changes, but in the same time interval the capacity current decays exponentially with time and decreases to a negligible value sometime before the next change in applied voltage. The A.C. component of the cell current is recorded by the instrument at a time when the capacity current has decayed to zero and it is thereby governed by diffusion at the dropping mercury electrode. This polarograph possesses all the advantages inherent in the A.C. method together with high sensitivity.

With the square wave polarograph it is possible to determine reversibly-reduced metallic ions, such as Pb and Cd in chloride solutions, in the molar concentration range from 10^{-4} to 10^{-7} and even less in favourable cases.

³ G. C. BARKER and I. JENKINS, *Analyst* 77 (1952) 685.

⁴ G. C. BARKER and D. R. COCKBAIN, *Atomic Energy Research Establishment, Report C/R 1404* (1954), H. M. S. O.

⁵ D. R. COCKBAIN, *Atomic Energy Research Establishment, Report EL/R 1528* (1954), H. M. S. O.

¹ B. BREYER and F. GUTMAN, *Australian J. Sci. Research* 3 (1950) 558.

² B. BREYER, F. GUTMAN and S. HACOBIAN, *ibid.* 3 (1950) 567.

This instrument is at least 200 times more sensitive than conventional polarography. It is, however, less satisfactory for the determination of elements that are irreversibly reduced at the dropping mercury electrode. In inorganic polarography it is frequently possible to overcome this difficulty by a suitable choice of supporting electrolyte and this can best be illustrated by the case of nickel. This element is irreversibly reduced from a chloride base solution and small amounts cannot be determined. In a cyanide base solution, however, the nickel ions are complexed to form nickel cyanide complex ions which are reversibly reduced at the dropping mercury electrode. An alkaline cyanide base solution is consequently extremely satisfactory for the determination of trace amounts of nickel.

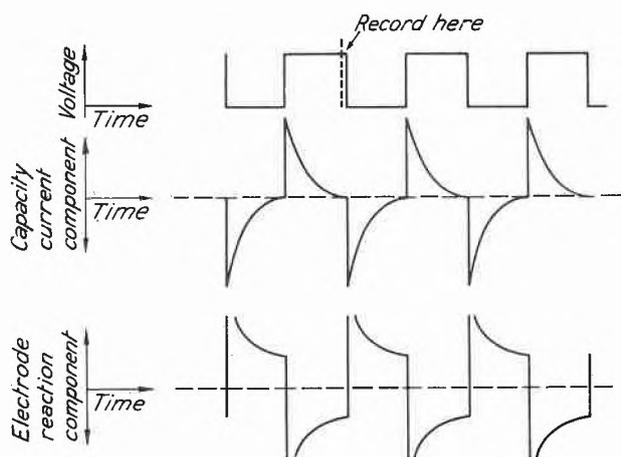


Fig. 1. Square wave voltage and current wave forms

The resolving power of the square wave polarograph compares very favourably with the earlier A.C. method and can best be assessed from results obtained for the determination of Cd and In in a 1.0 M KCl solution. The halfwave potentials for the cadmium and indium steps in this solution are -0.642 v and -0.597 v relative to the saturated calomel electrode respectively. For a mixture of cadmium and indium in equal concentrations ($20 \mu\text{g}$ per ml) the degree of separation is such that both peaks are measurable. When the cadmium to indium ratio is 10:1 the indium peak can be detected as a swelling at the base of the cadmium peak and it is possible to make an approximate estimate of the indium concentration. These results illustrate that the square wave polarograph will resolve peaks separated by only 45 mv, which is a great improvement on the 200 mv required for separations in conventional polarography.

The effect of previous reductions is very much less in square wave polarography than in conventional polarography because of the derivative type of polarogram produced. The square wave polarograph is able to produce a peak for a substance which is quite unaffected by the previous reduction of a major constituent when the ratio of concentrations is 1 to 20,000. The current from

the reduction of ferric ions does not interfere with peaks for copper, lead and tin in a chloride supporting electrolyte and this instrument has been used to determine these constituents in steels for ratios of copper, lead and tin to ferric ion of 1 to 5000, 1 to 1000 and 1 to 20,000 respectively. The negligible interference from major constituents improves the directness and simplicity with which analyses can now be carried out. Very little pre-treatment of the sample solution is generally required; this is in direct contrast with conventional polarography in which the prior chemical separation of interfering constituents is often needed.

In the use of the square wave polarograph the importance of the care of the capillary cannot be overstressed, particularly as the instrument is more critical to variations in drop time, and because the diffusion current is measured at a prescribed time in the drop life. A drop time in the range from 4 to 7 seconds is recommended. In determining the highest sensitivities attainable with this instrument, Dr. G.C. BARKER found that the maximum sensitivity was not limited by the noise level of the electronic circuits, but by the instability of a response occurring from solution entering the tip of the capillary of the dropping mercury electrode. This capillary response varied slightly from drop to drop and caused the noise level of the polarograph to be as much as four times more than that attributable to noise in the electronic circuits. One fairly satisfactory solution of the capillary response problem makes use of the fact that the capillary response current usually decays more rapidly after a sudden change of potential than the faradaic current associated with an electrode reaction. Hence the ratio of desired signal to undesired signal can be improved by extending the time scale. To obtain a significant improvement in performance it is necessary to reduce the frequency from the normal value of 225 c/s to about 10 c/s. However, such a frequency is inconveniently low from a design point of view and it is more convenient to replace the square wave voltage by a series of pulses of relatively long duration, each of which occurs at a predetermined time in the droplife. A new polarograph, known as the *Pulse Polarograph*, is based on this pulse technique.⁶ In this instrument one long pulse is applied in the life of each mercury drop. The duration of the pulse is 40 milliseconds and is of much longer duration than the 2.2 millisecond half cycle of the square wave voltage used in the square wave polarograph. In favourable circumstances reversibly-reduced ions can be detected with the pulse polarograph at concentrations down to about 10^{-8} M and irreversibly-reduced ions can be detected at concentrations close to 10^{-7} M.

Differences in the behaviour of the pulse and square wave polarographs can be conveniently grouped under two headings, those arising from the difference in the

⁶ G.C. BARKER and A.W. GARDNER, *Atomic Energy Research Establishment, Report C/R 2297* (1958). To be published.

electronic circuits and those arising from the chemical effects of the longer pulse.

Electronic Effects.—The pulse polarograph is four times more sensitive than the square wave polarograph for reversible reductions. This increased sensitivity is obtained entirely by an improved electronic circuit, since the current which is actually measured is smaller due to the longer decay. The improved sensitivity can only be used if the output of the amplifier is smoothed by a condenser to reduce the noise level. This in turn is only possible because the capillary response has been allowed to die away completely, so that the remaining noise is truly random. The smoothing required depends on the sensitivity of the instrument, according to the following values:

For maximum sensitivity, integration over the average of 9 drops is used.

For maximum $\div 2$, integration over the average of 3 drops is employed, and

for maximum $\div 8$ and lower, no integration is needed.

The use of integration makes the response of the instrument rather sluggish and slow sweep speeds must be employed e. g. for a 9 drop integration the slow sweep speed of 1 volt per 50 minutes is used. As a consequence, analyses using the pulse polarograph at maximum sensitivity are slower than those customarily carried out on the square wave polarograph (S.W.P.). At lower sensitivities, comparable with those often used on the S.W.P., faster speeds can be employed and the pulse polarograph is then no slower than the S.W.P. in this respect.

The longer interval between the first application of the pulse and the time of measurement of the current allows the double layer capacity charging current to decay more completely in the pulse polarograph, or conversely allows base solutions of higher resistance to be used in the cell. The use of lower concentrations of supporting electrolytes is an advantage in trace analyses, since the need for the purification of electrolytes is thereby decreased. Also, since the capillary response is allowed to die away more completely in the pulse polarograph than in the S.W.P., the background at negative potentials is better at equal sensitivities.

Chemical Effects.—The chemical effects arise from the fact that the pulse polarograph is much more sensitive to irreversible reductions than the S.W.P. This increased sensitivity is obviously an advantage in some cases, but in using the polarograph for elements which are reversible reduced, it is invariably a disadvantage because interfering reductions become more important. The irreversible reductions of oxygen and organic matter constitute a problem in analysis. In the case of oxygen a large broad reduction peak appears in the range -0.2 to -0.3 v, if the solution is not properly degassed. Efficient degassing of the solution is not difficult to achieve, but it takes time and contributes to the slowness with

which solutions can be analysed. If a solution containing oxygen is allowed to stand in contact with mercury for sometime, hydrogen peroxide is formed and gives a reduction peak. For this reason it is advisable to de-aerate all solutions immediately they are transferred to the cell. Organic species, which are irreversibly reduced, produce a greater response on the pulse polarograph and they must therefore be completely destroyed prior to the analysis of solutions for inorganic constituents.

Another aspect of the pulse polarograph, as distinct from the S.W.P., is its ability to produce a conventional type of polarographic step, and because of this it is potentially more suited to the continuous analytical control of process solutions. In operation the dropping mercury electrode is held for most of the time at a fixed potential with respect to the anode, but at a certain time in the life of each mercury drop a polarising pulse changes the drop potential for 40 milliseconds to a value that gradually is made more and more negative. The size of this voltage pulse is increased from zero amplitude to a value of about 1 volt. The resultant step is almost the same shape as a normal conventional polarograph step except in the following aspects:

- (1) The limiting current does not vary with drop time, as in conventional polarography, because the current is measured at a fixed time in the life of the drop.
- (2) There is an appreciable increase in step height relative to residual current, a 7-fold gain in ratio of limiting current to residual current being obtained. This arises because the concentration gradient is much higher in the pulse polarograph than in the conventional polarograph.

The performance of the pulse polarograph has been compared with that of the S.W.P. and the findings are summarised under various headings, as follows:

- (1) Sensitivity—the pulse polarograph is 4 times more sensitive for reversible reactions and 20 times more sensitive for irreversible reactions.
- (2) Sweep rate—generally more rapid sweep rates can be used with the S.W.P. and slightly less time is therefore used in recording polarograms.
- (3) Oxygen interference—this is less troublesome with the S.W.P. and less time is required for degassing each solution.
- (4) Organic matter—there is less interference from reducible organic material with the S.W.P., whereas adsorbed material gives less difficulty with the pulse polarograph.
- (5) Supporting electrolyte—the pulse polarograph is able to use supporting electrolytes at least 10 times more dilute than those necessary for the S.W.P. Interferences caused by impurities in the supporting electrolyte are thereby reduced.
- (6) Resolution—the resolution with the pulse polarograph is only slightly inferior to that obtainable with the S.W.P.

The pulse polarograph is an electronic instrument using a total of 60 valves and is therefore of the same complexity as the present model of the S. W. P. On the whole it is a more satisfactory instrument, but the preliminary chemistry must be planned with more care than is necessary for the S. W. P. and analyses generally take slightly longer to complete.

2.2. Analytical Applications

Many useful applications have already been developed for the S. W. P. in the analysis of such materials as metallurgical alloys, waters, trade effluents, foodstuffs, fertilisers, minerals and various miscellaneous materials. In many cases only small sample weights are required and the chemical treatment consists in dissolving the sample and adding the base electrolyte. In all cases, however, a considerable improvement over conventional polarography is obtained. The advantages of square wave polarography are brought out in metallurgical analysis. In the analysis of steels and copper-base alloys, for example, several constituents can be determined directly in the presence of the major constituents and this is a major improvement over the practice in conventional polarography which generally requires separation of the main constituents from solution.^{7,8} The constituents that can be determined with advantage by this instrument include lead, cadmium, nickel, zinc, tin and chromium. The determination of lead is often required in metallurgical analysis and a chloride base solution is generally employed. Tin unfortunately gives a step in this base solution which interferes with the lead step, but by using a molar phosphoric acid solution in conjunction with the S. W. P. better conditions have been developed for the direct determination of lead.⁹ The reduction of tin is so irreversible in this solution that it is possible to determine lead directly in the presence of a 1000-fold excess of tin. The phosphoric acid supporting electrolyte is recommended for the determination of minor alloying amounts of lead in tin, copper and aluminium base alloys and in steels.

The high sensitivity of A. C. polarographs is extremely valuable in the analysis of effluents for the presence of metallic impurities. In atomic energy work the S. W. P. has proved useful for the examination of effluents for trace amounts of uranium. The most sensitive peak for uranium is obtained from a molar perchloric acid solution, when concentrations down to 0.1 μg per ml of final solution can be determined. The procedure for effluents simply consists in evaporating a suitable aliquot to fumes of perchloric acid in the presence of nitric acid to destroy any organic matter in the solution. Equally, the high sensitivity attainable with the S. W. P. is very valuable for measuring the rate of uptake by aqueous solutions of corrosion products from steel

loops.¹⁰ In some experiments with loops at Harwell only 2 ml aliquots of solution were available for analysis, so as to avoid replenishments of water, and by analysing for iron, chromium, nickel and manganese some information could be obtained on corrosion rates. Both iron and chromium could be determined simultaneously down to concentrations of 1 p.p.m. and detected at levels of 0.2 p.p.m. The nickel and manganese could be determined down to 0.4 and 2 p.p.m. respectively, whilst the lowest levels of detection for these two constituents amounted to 0.06 and 0.4 p.p.m. respectively.

3. Cathode Ray Polarography

The cathode ray oscilloscope is extremely useful for recording electrical effects because of its high speed of response and it has now been incorporated in a commercially available instrument for recording current-voltage curves. RANDES^{11,12} first described the principles of linear sweep cathode ray polarography and for analytical work this technique is the most satisfactory of the various oscillographic methods so far developed. A linear voltage sweep, which starts at a predetermined time in the life of the mercury drop, is applied to the electrodes of the polarographic cell and the variation of the cell current during the sweep is displayed on the screen of a cathode ray tube. Since the early work, improved designs have been described and a commercial instrument is produced by Southern Instruments Ltd. to a design first reported by DAVIS and SEABORN.¹³ This instrument is intended for use with drop times of the mercury cathode of about 7 seconds and the voltage sweep takes place in the last 2 seconds of the drop life. On this basis a number of polarographic steps can be recorded and measured in a fraction of the time required in conventional polarography. Increased sensitivity is also achieved by virtue of the particular diffusion conditions at the mercury drop resulting from the extremely rapid sweep of potential. Normally reducible ions can be detected at concentrations down to about 5×10^{-7} M when the electrode reaction involves 2 electrons. The instrument has a derivative circuit giving very high resolution and this is useful for the determination of a minor constituent in the presence of a more readily reducible major constituent. Unfortunately, however, there is a considerable loss in sensitivity on the derivative circuit so that the highest degree of sensitivity and resolution are not attained simultaneously. Even so, this useful and inexpensive instrument is now used for routine analysis in many laboratories.

As in conventional polarography, the sensitivity is limited by the inconstancy of the non-faradaic residual

¹⁰ D. J. FERRETT and G. W. C. MILNER, *Proceedings of the First International Conference on the «Peaceful Uses of Atomic Energy»*, United Nations, 1956, Vol. IX, p. 436.

¹¹ J. E. B. RANDES and L. AIREY, *Analyst* 72 (1947) 301.

¹² J. E. B. RANDES, *Trans. Faraday Soc.* 44 (1948) 334.

¹³ H. M. DAVIS and J. E. SEABORN, *Electronic Eng.* 25 (1953) 314.

⁷ D. J. FERRETT and G. W. C. MILNER, *Analyst* 80 (1955) 132.

⁸ D. J. FERRETT and G. W. C. MILNER, *ibid.* 81 (1956) 193.

⁹ G. W. C. MILNER and L. J. SLEE, *ibid.* 82 (1957) 139.

current associated with the charging of the surface of the expanding mercury drop and it is adversely affected by the large variations of this non-faradaic current during the voltage sweep. The amplitude of the voltage sweep is about 0.5 volts and there is no possibility of greatly improving the ratio of faradaic to non-faradaic current by changing the duration or amplitude of the voltage sweep. The steps obtained in oscillographic polarography are somewhat inferior in shape to those obtained by most other polarographic methods. The steps produced by reversible and irreversible reductions are very asymmetric, the faradaic current decreasing slowly as the potential becomes more negative than the potential at which the current is largest. In analytical work this asymmetry is unimportant when the solution contains only one reducible ion, and also when several reducible species are present the asymmetry does not matter if the halfwave potentials are well separated, since the starting potential can be changed for the determination of each ion. However, when the halfwave potential values are not greatly different errors clearly can occur when attempting to measure the height of a step which is superimposed on the tail of an earlier step. In such cases the errors would be smaller if the steps had the same shape as the peaks of a first derivative polarogram. Suggestions have recently been made by Dr. G. C. BARKER¹⁴ for overcoming this type of difficulty by converting the asymmetric current peaks into flat-topped steps similar to those observed in conventional polarography. This change of wave shape can be effected very readily by passing a current proportional to the faradaic current through an electrical 'shaping' circuit which is the electrical analogue of linear diffusion in a semi-infinite medium. The voltage appearing across this circuit, after appropriate amplification is displayed on the screen of the cathode ray tube.

For removing the interferences of non-faradaic currents DAVIS and SEABORN¹⁵ have recently developed an improved single sweep oscillographic polarograph

¹⁴ G. C. BARKER, *Proceedings of the Second International Conference on Polarography*, Cambridge 1959.

¹⁵ H. M. DAVIS and J. E. SEABORN, *Proceedings of the Second International Conference on Polarography*, Cambridge 1959.

which can be used with twin cells containing synchronised dropping mercury electrodes. If one cell contains supporting electrolyte only, a polarogram largely unaffected by the non-faradaic charging current can be obtained with this instrument by displaying on the screen of the cathode ray tube a voltage proportional to the difference between the cell currents when the voltage sweep is applied to both cells. This twin cell method clearly can give a significant gain in sensitivity but it is important that both sweep start potentials are identical. Another important advantage of this technique is that it can be used for 'Comparative Polarography'. This is the special case of high precision differential polarography in which one cell contains an accurately known standard solution of the ionic species under determination, the concentration in this reference solution being near to the concentration of the particular constituent in the sample solution. The following design requirements have been satisfied in this instrument:

- (1) The stability of the measuring circuit must be such that very small differences (e.g. 1 in 10^4 or less) between the cell currents can be measured with precision.
- (2) It must be possible to equalise the true sweep start potentials, i. e. taking pool potential variations into account, and maintain equality during the course of a determination.
- (3) The dropping mercury cathode surfaces must be renewed simultaneously.
- (4) The rates of growth of the drop surfaces must be identical.

For requirement (3) the most satisfactory method of separating the drops simultaneously was to produce a violent lateral acceleration of the capillaries and to arrest them after they had travelled only a few capillary diameters. Requirement (4) was satisfied by using two adjacent sections of equal length from a piece of capillary tubing. These were gravity fed with mercury from reservoirs capable of independent adjustment.

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