

### Literatur

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## Pulse Polarography

By

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### Introduction

FERRETT et al.<sup>4</sup> have shown that the square wave polarograph (S.W.P.) is the most sensitive of the instruments giving derivative polarograms. With the prototype of the commercially manufactured model\*, reversibly reduced and irreversibly reduced ions can be detected at concentration as low as approximately  $4 \cdot 10^{-8}$  M and  $10^{-6}$  M respectively. The noise level of the electronic circuits is not the limiting factor for this sensitivity, which is determined more by the instability of a response associated with the capillary<sup>1</sup>. To obtain an appreciable improvement in performance the square wave frequency must be reduced to about 10 c/s and this introduces design difficulties arising from the small number of square wave cycles within the strobe delay time of the polarograph ( $\sim 2$  sec).

This improvement in performance can also be obtained by discarding the square wave voltage and substituting polarizing pulses of  $\sim 1/25$  sec duration, each of which occurs at a definite time ( $\sim 2$  sec) after the fall of the preceding mercury drop.

The general principles of pulse polarography are discussed here, and the results obtained with pulse polarograph employing pulses of  $1/25$  sec duration are briefly described. This instrument is capable of detecting reversibly reduced and irreversibly reduced ions at concentrations down to about  $10^{-8}$  M and  $5 \cdot 10^{-8}$  M respectively. The instrument uses 58 valves and is only slightly simpler in design than the S.W.P.

### General Principles

In pulse polarography the current flowing through the polarographic cell has three important components:

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\* Mervyn Instruments, St. Johns Wood, Woking, England.

1. A background diffusion current connected with electrode reactions in progress at the D.M.E. (dropping mercury electrode) prior to the polarizing pulse.
2. A current, produced by the pulse, associated with the charging and discharging of the double-layer capacity of the D.M.E.
3. A current, produced by the pulse, connected with changes in rates of electrode reactions.

To obtain high sensitivity the shape of the polarogram must be completely independent of the first and second of these.

#### *Derivative Polarogram*

In this case the polarizing pulses are of constant amplitude (50 mv) and are superimposed on a slowly changing polarizing voltage. If the solution in the cell contains ions which are being reduced prior to the application of the polarizing pulse the background current resulting from this reduction will vary with time in the same manner as the diffusion current in D.C. polarography. If the application of the polarizing pulse results in a change in the rate of an electrode reaction then there will be a sudden change in the diffusion current. The *change in diffusion current* produced by the pulse will be termed the electrode reaction current. This current gradually decays with time during a pulse, but is always finite just before the end of the pulse. For a reversible reduction, the magnitude of this current (at a fixed time in the pulse duration) is greatest at a potential close to the normal half wave potential. The double-layer capacity changing current decays rapidly if the internal resistance of the cell is small.

The separation of the current components produced by the pulse from the background current, may, in principle, be achieved by the use of a high pass filter. In practice the imperfections of such filters at low frequencies necessitate the use of an unconventional dynamic filter. By measuring the current over the second half of the pulse life the capacity changing current may be eliminated. Selection of the desired information is made by a somewhat similar procedure to that used in square wave polarography<sup>3</sup>.

#### *Normal Polarogram*

The pulses, in this case, vary in amplitude from zero to 1 volt or more. Their amplitude is proportional to the elapsed time from the start of the sweep. They are superimposed on an adjustable polarizing voltage which is held constant during the recording of a polarogram, and their usual sign is such that they make the potential of the D.M.E. more negative. The cell current has the same three principal components listed above.

A normal polarogram produced in this unusual way shows the *change in diffusion current* produced by the pulse as a function of the

potential of the D.M.E. during the pulse. As only the change in current is measured, and the background current is eliminated by the dynamic filters, the polarogram is compensated for any reductions which are completely diffusion controlled at the starting potential. This compensation is fully automatic, thus interference from ions reduced at more positive potentials is avoided without introducing a derivative plot. Previously, only A.C. polarographs such as the S.W.P., giving derivative polarograms, have been able to operate satisfactorily in the presence of large amounts of interfering ions.

Since the elapsed time between the start of a pulse and the time interval over which the current is measured is much shorter than the drop time, the limiting value of the measured current change is appreciably larger than the limiting diffusion current in conventional polarography. This results in an increase in sensitivity of about 7 times, for a pulse length of 0.04 sec and a pulse delay time of 2 sec. An even greater gain in sensitivity can often be obtained if accurate compensation for the *change in residual current* produced by the pulse is provided.

#### *Minor Currents*

In addition to the current components already considered there are several minor currents, some of which tend to affect sensitivity adversely especially in normal pulse polarography.

*a) Residual Current.* When the potential of the D.M.E. is changed by the pulse, the residual current<sup>5</sup> associated with the expansion of the electrode also changes. This change in residual current is proportional to the charge which must be supplied to the double-layer capacity of the electrode at the start of the pulse to change the electrode potential, and so can be accurately neutralised by integrating the double-layer capacity charging current, taking a compensating current from the resulting voltage.

*b) Capillary Response.* This arises from a thin film of solution between the internal wall of the capillary and the mercury thread. This film enables the surface of the thread slowly to follow changes in drop potential, so that an abrupt change of electrode potential is always followed by a small current associated with the charging of the surface of the mercury thread produced by a reversible electrode reaction. The influence of this current is less pronounced in pulse polarography than in square wave polarography. The capillary response is generally proportional to a power of the pulse amplitude slightly greater than unity.

Compensation is provided by a current which is proportional to the pulse amplitude. The non-linear relation between pulse height and capillary response renders this compensation imperfect except over limited potential ranges, but, in practice, it is satisfactory even at the highest sensitivity on a normal pulse polarogram.

*c) Oscillatory Current.* This arises from the change in surface tension at the start of the pulse, which causes the drop to oscillate slightly. This oscillation will modulate the background current, and, if this is large, a small current may pass through the filter circuits. This current can be minimised by making the size of the drop small at the time of the pulse, and by keeping the pulse amplitude less than 0.2 to 0.3 volts.

*d) Organic Adsorption Current.* The current<sup>2</sup> associated with the adsorption or desorption of organic molecules on the surface of the D.M.E. always decays more rapidly than the electrode reaction current and thus has less influence on a derivative pulse polarogram than on a square wave polarogram. However, with high instrumental sensitivity it is desirable that the solution should contain little or no organic matter. Since this current does not normally vary linearly with pulse amplitude there is no completely satisfactory way of deriving a compensating current, although some compensation can be achieved with the aid of the capillary response compensation circuit.

### Typical Polarograms

The polarograms which have been obtained with the prototype instrument clearly indicate that its performance is fully up to the anticipated standard. Thus, normal polarograms at low sensitivity (e.g.  $10^{-3}$ — $10^{-4}$  M) are smooth curves (without electronic smoothing), with non-sloping, linear baselines and plateaux. Some exhibit small maxima, somewhat reduced by the addition of gelatine, the suppressor not influencing the height of the wave measured from baseline to plateau. Normal polarograms at high sensitivity (e.g.  $10^{-6}$ — $10^{-7}$  M) maintain the satisfactory shape and smoothness of the polarogram made at low sensitivity, while the maximum sensitivity of the instrument is such that a divalent ion at the  $10^{-7}$  M level produced a step with a height of about 30 mm. The fluctuations in the level of the baseline at this sensitivity do not exceed  $\pm 2$  mm with the maximum degree of electronic smoothing provided, and hence there is no difficulty in detecting reversibly-reduced and irreversibly-reduced ions at this concentration. The compensation of minor currents is entirely adequate to produce polarograms with flat baselines and plateaux at this sensitivity. The ability to yield normal polarograms of a satisfactory character for a low concentration of an ion in the presence of a large concentration of a more readily reducible ion has been tested with ferric-uranyl ion and copper-cadmium ion mixtures in concentration ratios of 1250:1 and  $10^4$ :1 respectively. The resulting polarograms lead to the conclusion that one part of uranyl ion in the presence of  $5 \cdot 10^3$  parts of ferric ion is readily detectable, while one part of cadmium ion in the presence of  $10^4$  parts of copper ion is also readily detectable.

Derivative polarograms show the same level of performance. There is the anticipated gain over the S.W.P. in sensitivity for irreversible reductions (resulting from the change in time scale). The ratio of the heights of derivative waves from the reductions of nickel (irreversible) and cadmium (reversible) is about 4 times larger with the pulse polarograph than with the S.W.P. The change in time scale also results in an improvement to the derivative polarograms from the reduction in capillary response. This gives a much flatter baseline than that obtained with the S.W.P. at the highest sensitivity, yielding polarograms which can be measured with greater ease and certainty.

In the absence of interfering ions reversibly reduced ions can often be detected with certainty at  $10^{-8}$  M, on a derivative polarogram, while irreversibly reduced ions can usually be detected at  $5 \cdot 10^{-8}$  M. The sensitivity of the pulse polarograph is thus appreciably higher than that of the S.W.P. particularly in the case irreversible reductions.

The pulse polarograph can be used with base solutions about 10 times more dilute than those used in square wave polarography and satisfactory polarograms have been obtained with solutions as dilute as 0.01 M KCl. Impurities in the base electrolyte are thus less important in pulse polarography than in square wave polarography.

In only one respect is the derivative circuit of the present instrument inferior to the S.W.P. in performance; minor constituents can only be detected in the presence of a major constituent that is reduced at a more positive potential when the concentration ratio is larger than  $10^{-4}$ , whereas the corresponding figure for the S.W.P.<sup>4</sup> is 5—10 times smaller.

### Summary

The application of a pulse technique to polarography results in a further improvement in polarographic performance, the new instrument being capable of detecting reversibly reduced species at concentrations as low as  $10^{-8}$  M, and irreversibly reduced species at  $5 \cdot 10^{-8}$  M. The new instrument also yields both derivative and normal polarograms of much improved types. We are indebted to Mr. R. J. Jacob of the Electronics Division, A.E.R.E., for invaluable assistance in the construction of the electronic equipment.

### References

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