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On the Instantaneous Polarographic Current

I. Automatic Recording of Selected Parts of the Current-time Curve of the Individual Mercury Drop

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A method of measuring the instantaneous polarographic current within an accuracy of $\pm$ 0.2 per cent is described. The apparatus includes a polarograph, a recording potentiometer and a device with the double purpose of knocking off the mercury drops and of periodically connecting the recording pen.

In polarography calculations are usually based, not on the instantaneous diffusion current, but on a mean value, evaluated in some way. This seems satisfactory for analytical purposes, but it is a serious drawback in theoretical studies. A method which gives the instantaneous current must, however, also have great advantages in analytical work. The correct evaluation of a polarographic curve is often very difficult and for practical reasons the recording instrument is damped. However the damping often conceals small polarographic waves and thus the sensitivity is reduced. Furthermore Lingane [1] has pointed out that the damping of the polarographic current results in a registered mean current; the deviation from the theoretical current depends on the degree of damping. In analytical work there is also a tendency to use shorter drop times in order to get smoother curves, but the gain in simplicity of evaluation is lost on account of interference from other sources.

In an earlier communication [2] Wåhlin has given a short description of an apparatus which makes it possible to measure a selected part of the diffusion-time curve. The present paper describes the apparatus fully and gives some tests of its performance.

List of Symbols used

C = concentration of depolarizer, millimoles liter^{-1}
D = diffusion constant, cm^2 sec^{-1}
$\bar{i}$ = mean diffusion current, microamperes

i_τ = instantaneous current, microamperes
i_t = instantaneous current immediately before the drop falls
K = a constant in eqn. (1)
n = number of faradays of electricity required per mole of electrode reaction
m = rate of flow of mercury from the capillary, mg sec^{-1}
τ = age of drop, sec
t = τ_{max}, sec
h = the distance between the upper and lower mercury surface (cm).

APPLICATIONS

The characteristic features of our apparatus make it suitable for measurements of the following types.

1. Checking the revised Ilkovic equations

The measurements on which the polarographic theory is based are mostly done with the mean diffusion current method. It would be more logical and closer to facts to use the instantaneous polarographic current for checking the modified Ilkovic equation[3,4]. Several investigators are of the opinion that the formula is as follows:

$$i_\tau = 709\ nD^{\frac{1}{2}}Cm^{2/3}\tau^{1/6} + KnDC(m\tau)^{1/3} \tag{1}$$

The mean diffusion current is derived from eqn. (1) and is only valid if eqn. (1) is correct

$$\bar{i} = 607\ nD^{\frac{1}{2}}Cm^{2/3}t^{1/6} + \frac{3}{4}KnDCm^{1/3}t^{1/3} \tag{2}$$

However the theoretical value of the constant K is still discussed in the literature[3-6], and furthermore Hans *et al.*[7] do not consider K a constant, but a function of τ and t. Sufficiently accurate measurements of i_τ are still very rare and therefore it is natural that values of the constant K as different as 17 and 39 may be found in the literature. Precision measurements of the instantaneous current are only given by Hans, Henne and Meurer [7], Taylor, Smith and Cooter [8], and Khalafalla [9]. The lack of data is due to the difficulty of making measurements of the complete course of the instantaneous current/time curve, owing to the discontinuity of the polarographic current obtained when the mercury drop falls and the rapid increase of current during the first second after the formation of a new drop.

Oscillographic measurements are of course quick enough, but the accuracy is only around ± 2 % which means that the second term of eqn. (1) can only be determined within approximately ± 20 %. Some research has also been done with undamped galvanometers. These instruments are, however, very delicate, and according to Strehlow [10] the results obtained are subject to certain limitations.

The fact that the polarographic current during the life-time of an individual mercury drop is approximately proportional to $\tau^{1/6}$ means that while the age of the drop increases from 0 to 1 second the current increase is 76 units, but from 4.0 to 5.0 seconds the increment is only 3.5 units. A polarograph cannot record this complete curve with its sharp discontinuity when the drop falls, but records instead some kind of "damped" curve, which is sometimes undesirable. Especially at long drop times the conventional polarograph gives curves with big oscillations and it is doubtful whether these curves have any relation to the true polarographic current.

Accurate measurements of the later parts of the current-time curve can be used for investigating the symbol K. Our method is well adapted for supplying such data and furthermore the measurements can be made very quickly.

2. Analytical precision polarography

For analytical polarography it may seem satisfactory to measure the mean diffusion current, but experience in this field has shown that correct evaluation of the curves requires a skilled analyst. As mentioned above the curves obtained with our apparatus are undamped and still very easy to evaluate (Fig. 1)

When prewave compensation is used on conventional polarographs, the results are not very accurate because of the big oscillations. With the present method straight lines are obtained, and the results are much more reproducible.

3. Extending the lower limit in analytical polarography

When determining micro quantities of depolarizer with the mean current method the diffusion controlled part of the measured current is only a minor constituent beside the main component, the condenser current. This restricts the possibility of determining very small quantities of depolarizer with any reasonable degree of accuracy. As the diffusion current increases with the

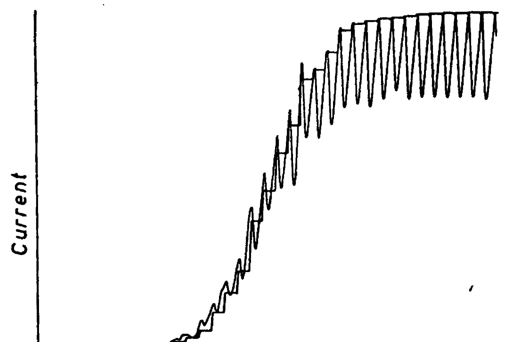

Fig. 1. Polarograms obtained in the conventional way (lower curve) and with the apparatus described in the text (upper curve).

age of the drop, while the condenser current decreases, the most favourable conditions for determining small diffusion currents occur immediately before the drop falls. Thus, if the instantaneous current is measured in this way the accuracy is increased and the lower limit of detection is depressed.

APPARATUS

1) *Capillary.* Length: 253 mm, drop time: 5.2 seconds in 0.1 M potassium chloride solution at a mercury pressure of 60 cm and at 0.90 volts *vs* the silver anode. The capillary was made from Pyrex glass rod [11].

2) *Polarographic vessel* including de-aerating tube and a tube to keep the oxygen out by blowing nitrogen gas over the surface. The nitrogen was purified by passing it over activated copper absorbed on diatomaceous earth according to Meyer and Ronge [12]. In this way the partial pressure of the oxygen was reduced to less than 3×10^{-4} mm of mercury.

3) *Anode,* a silver sheet of 8 cm^2. This anode proved to be much more convenient to handle than the conventional calomel electrode [13,14].

4) *Hammer for knocking off the mercury drops* at predetermined intervals. The hammer was actuated by an electromagnet [15] and the intervals were timed with an accuracy of ± 0.01 seconds by a rotating cam.

5) *Disconnector and interval selector for balancing motor.* The intervals were timed in the same way as above with the exception that the circuit could be also connected for longer periods. The cams were both attached to the same shaft, driven by a constant speed electric motor.

6) *Potentiometer recorder,* Speedomax Type G, Model S, Leeds and Northrup Comp. USA. The essential part of the recorder for this application is a phase sensitive balancing motor, which moves the pen to its correct position.

7) *Polarograph,* both an electronic polarograph, LKB Type 3266 B LKB-produkter, Fabriks AB, Sweden, and a Heyrovsky type polarograph, Polarograph 38, F. Leybold Nachfolger, Germany. Both types contain damping capacitors, which were disconnected in order to obtain the correct value of the polarographic current.

OPERATING PRINCIPLES

Fig. 2 illustrates the construction of the apparatus schematically and Fig. 1 shows a typical current/voltage curve. The operating principle of the apparatus is as follows:

The mercury drop is knocked off by the hammer for example every 5.02 seconds. The current is recorded while the age of the drop increases from *e.g.*, 4.5 to 5.0 seconds. Immediately before the drop falls the balancing motor circuit is broken and so the pen rests in the 5.0 second position until the next drop is 4.5 seconds old, and the same process is then repeated. In this way it is possible to record accurately the instantaneous value of the diffusion current (not the mean diffusion current), as a mean value from a suitable number of drops.

Especially at long drop times, the i/V curves of this apparatus will be smooth and easily evaluated. During the periods when the polarographic curve is not being recorded calibrated resistors may be connected in place of the polarographic cell, and the resulting current can be measured. This provides calibration of the polarograph.

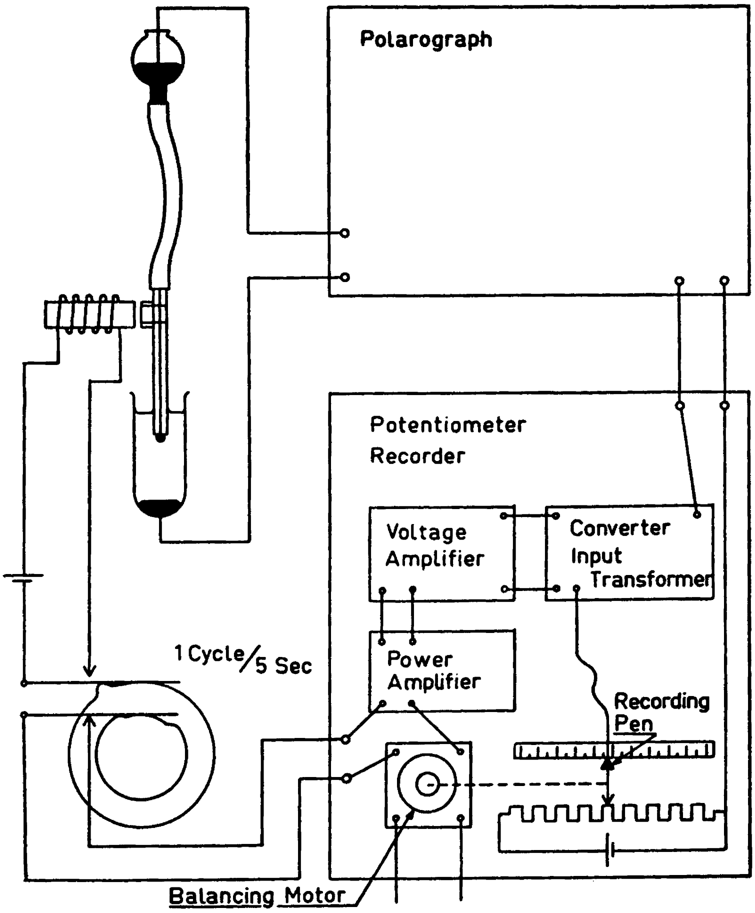

Fig. 2. Diagram of the assembly used in the experiments.

TESTS

1. It is essential to prove that the apparatus really records the true current. The following experiments were carried out in order to demonstrate that the recording pen always moves to its correct position.

A deaerated cadmium solution in potassium chloride was polarographed at constant voltage (—0.90 volts *vs* the silver anode). The mercury drops were knocked off every 5.0 seconds and the recorder was first connected during the whole drop life a) in Fig. 3. At b) the recorder was disconnected at a pen position corresponding to 4.7 seconds. As the timer had been adjusted to have the pen connected between 2.0—2.2 seconds, the pen moved downwards a small distance every time it was connected and reached its final position after about 4 drops. Then the paper was wound back and the pen was placed in a position

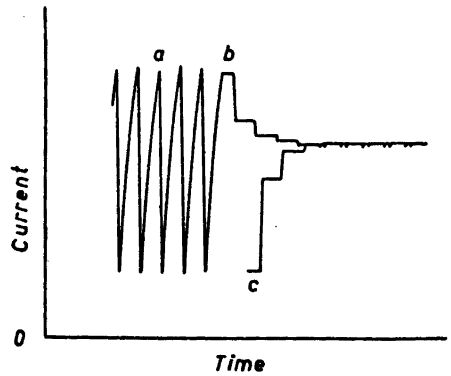

Fig. 3. Precision polarogram obtained at a constant potential. For explanation of a) b) and c) see p. 939.

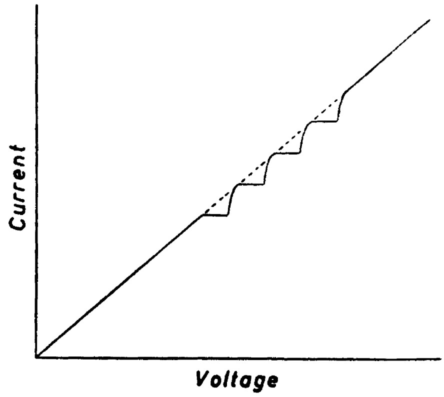

Fig. 4. Current-voltage diagram showing the ability of the apparatus to give a definite current for the short period of operation of the recorder.

corresponding to $\tau = 0.9$ sec, c) in Fig. 3. When connected, the pen now moved up to the same final value as before. This experiment proves that the apparatus records a definite current value corresponding to every value of τ during the drop life independently of the initial pen position.

2. In order to check the ability of the apparatus to record the true instantaneous current the following experiment was carried out. The polarographic cell was replaced by a resistor, and the voltage was increased at constant rate beginning at 0 volt. Under these conditions the recorded current should be a straight line. (Fig. 4). At the beginning the recorder was connected registering a straight line. Then the timer was started making the recorder to be connected and disconnected at predetermined intervals. Fig. 4 shows that when connected only 0.5 sec of a 5.0 sec period the pen moves to a position that coincides with the straight line. Of course this is only true when the i/V curve is not too steep, but the experiment shows that the apparatus is quick enough for the present investigation.

3. All revised formulae suggested for the polarographic current agree on one point, *viz.* the proportionality between current and concentration of depolarizer. All precision measurements up to now have proved this to be true within very close limits [16]. It was therefore considered important to use this well-known fact as a method of testing the apparatus. The following experiments were carried out: The timer was adjusted to give the undamped, instantaneous current after about 4.0 seconds. Drop time 5.2 sec. The cadmium concentration was varied according to Table 1. Background solution was 0.1 molar potassium chloride and 0.009 % gelatine. The height of the mercury reservoir was 60 cm above the capillary orifice and the temperature was 25.0 ± 0.1 °C.

Table 1 shows that our measurements of i_τ/C are constant within ±0.24 %, which lies within the experimental errors.

Table 1. The linear correlation between the diffusion current and the depolarizer concentration.

mM Cd	μA	μA$_{corr}$	μA$_{corr}$ / mM Cd
0.000	0.041	0.000	—
0.892	7.410	7.369	8.261
1.115	9.240	9.199	8.250
1.337	11.08	11.04	8.257
1.783	14.78	14.74	8.267
2.229	18.44	18.40	8.255
2.786	23.11	23.07	8.280

Mean value: μA$_{corr}$ / mM Cd = 8.26 ± 0.02.

4. In order to get a comparison between the polarographic current obtained from an electronic and from a non-electronic polarograph a polarogram was taken from the same solution with Polarograph LKB and Leybold Polarograph 38. The result is shown in Table 2. Under LKB is listed the instantaneous current obtained with the electronic polarograph and under LEYBOLD the same is given for the non-electronic instrument. The symbol Δ % is the percentage deviation of the current from the calculated mean value. As can be seen, the difference never exceeds 0.2 %.

Table 2. Comparison between currents obtained with an electronic and a non-electronic polarograph.

Sec	μA		Δ %
	LKB	LEYBOLD	
3.12	10.570	10.542	0.13
3.47	10.806	10.767	0.09
3.82	11.031	11.006	0.02
4.16	11.245	11.205	0.18

m = 2.024 mg Hg pr sec. h = 70 cm.
C = 1.315 mmoles/l. T = 25 °C.

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