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Measuring the Resistance of Polarographic Cell Circuits

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POLAROGRAPHIC circuit resistances can be measured accurately and conveniently by the use of an oscilloscope as the null point detector in a Wheatstone bridge arrangement.

Ordinarily, the polarographic half-wave voltage read from a *c.-v.* curve must be corrected for iR across the circuit in order to arrive at the characteristic half-wave potential of the test substance. The current, i, is readily obtained from the curve, while the measurement of the resistance R is more difficult. Ilkovič (*3*) introduced for the latter purpose the Kohlrausch method employing an alternating audible signal of unspecified frequency. Müller (*8*) prefers a method of approximation, stepwise increasing the applied e.m.f. to a high value and calculating R by means of Ohm's law. In this manner, the voltage lost by polarization at the dropping electrode becomes negligible. Elsewhere (*7*), he mentions a number of other methods. For instance, he utilizes the shift in half-wave potential of a given substance on a well-defined curve, resulting from variations in wave height, to calculate R by means of Ohm's law.

Furman and Bricker (*1*) measured R with a conductivity bridge containing an electron ray tube balancing device, at a frequency of 1000 cycles per second. It is claimed also that R may be determined in certain special cases from the slope d_E/d_i (*2*).

These methods are not very precise, and some of them are insufficient even for a reasonable estimate of the circuit resistance. Errors arise, for instance, whenever the E/i relationship is used to calculate R from small increments or differences in potential and current, the size of which may actually approach the limits of experimental error. In other cases, the resistance is determined at applied voltages far apart from the half-wave potential. This changes the drop time with a concurrent change in resistance (*3*).

Until recently, a precision of a 1 mv. per μa. in the half-wave potential or of 500 to 1000 ohms in the resistance has been considered adequate (*4, 5, 8*). Ilkovič's method is suited for this purpose, although it is somewhat cumbersome to use. However, caution must be exercised in more precise polarographic studies such as reported by Meites (*6*), who aims at half-wave potentials with a probable error of ±0.2 mv. at 2.5 μa.

For refined determinations like these, the bridge method can be improved considerably by introducing an oscilloscope as the null point detector. We have used a 5-inch DuMont 208B oscilloscope having a 10 mv. per inch deflection sensitivity (vertical amplifier), in combination with a Leeds and Northrup #4725 bridge. Equally satisfactory results were obtained with 3 inch oscilloscopic equipment, using an external amplifier to obtain the desired sensitivity. In operation, the polarographic circuit is made part of the bridge and a sine wave signal of the desired frequency is fed into the system. The bridge is then balanced, using the minimum vertical deflection of the oscilloscope beam as the null point. It is convenient to turn off the sweep (horizontal) amplifier of the oscilloscope during measurement.

With the above procedure, it is possible to measure polarographic circuit resistances with different cell arrangements with a precision of ±20 ohms. These visual measurements have the added advantage that they are not subject to the individual experimentor's sensitivity towards fluctuating sound signals of low amplitude and to noise in the laboratory. They are, therefore, obtained in a few minutes time. The data in Table I are typical for a set of resistance measurements over a frequency range of 150 to 1500 cycles per second. The minimum values determined have been adjusted to the average resistances in the life of the mercury drops by multiplying by 4/3, as usual. Table II exhibits results obtained in the same manner before and after the introduction of an "ohmite" resistance of 450 ohms into the circuits of two cells. In this case, the actually found minimal resistances are reported.

Table I. Resistance of a Polarographic Circuit Containing Dropping Electrode, Agar Bridge, and Saturated Calomel Electrode

(Test solution: 2 millimolar Cd ion in 0.1 *N* KCl solution, airfree. No maximum suppressor. Temp., 25 ± 0.1° C. Applied e.m.f.: − 0.600 v. versus S.C.E. Mass of mercury flow 1.47 mg./sec., drop time 5.30 sec. in circuit not connected to Wheatstone bridge. Amplitude of signal across dropping electrode–S.C.E. in all cases 0.8 v.)

Frequency of Signal, Cycles/Sec.	Resistance, Ohms	Drop Time, Sec.
150	1930	5.12
200	1830	5.22
400	1630	5.28
600	1570	5.30
1000	1560	5.28
1500	1550	5.28

The data show that at frequencies between 600 and 1500 cycles per second, the resistance measured is stable within ±20 ohms and that the drop time likewise is stable and unaffected as compared with the drop time determined under the same conditions of experiment but without the input of an alternating signal. Resistances of known magnitude are accurately indicated by the method when introduced in polarographic cell circuits. The significant deviations in drop time as well as resistance observed at frequencies lower than 400 cycles per second confirm the generally known fact that resistance values obtained with the Wheatstone bridge method become inaccurate at very low frequencies due to the polarization of the dropping mercury electrode by the signal fed into the system. In a separate series of measurements at a constant frequency of 1000 cycles per second both the drop time and the resistance remained constant when varying the amplitude of the signal between 0.5 and 1.2 v., measured across the dropping electrode and the saturated calomel electrode.

Table II. Recovery of Known Resistance Included in Circuit of Two Polarographic Cells

(Test solution: 2 millimolar Cd ion in 0.1 *N* KCl solution, airfree. No maximum suppressor. Applied e.m.f.: − 0.600 v. versus S.C.E. Added resistance 450 ohms. Amplitude of signal across dropping electrode-S.C.E. in all cases 0.8 v.)

Frequency of signal, cycles/sec.	150	200	400	600	1000	1500
Cell I						
Original resistance, ohms	[a]	730[b]	670	620	610	600
Drop time, sec.	4.15	4.30	4.44	4.43	4.43	4.47
Resistor added						
Resistance, ohms	...	...	1130	1070	1050	1030
Recovery, ohms	...	...	460	450	440	430
Cell II						
Original resistance, ohms	1300[a]	1060[b]	950	940	940	930
Drop time, sec.	4.62	4.78	4.90	4.87	4.86	4.86
Resistor added						
Resistance, ohms	...	1500	1380	1380	1380	1380
Recovery, ohms	...	440	430	440	440	450

[a] Difficult to measure due to irregularity of wave.
[b] Uncertain to ±30 ohms.

It was ascertained that the Leeds and Northrup bridge is satisfactory for measurements under the experimental conditions given. At higher frequencies and for still more precise *R* values, an impedance bridge would have to be used.

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