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Long-term Integration of Polarographic Currents and Its Analytical Application

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The integral readout technique was applied to the accurate determination of average polarographic currents. The long-term integration of polarographic currents provides a useful method of compensating residual currents and thus of increasing the sensitivity and accuracy of the d. c. polarographic analysis. The analytical utility of the proposed method was tested with cadmium, lead, and zinc ions in chloride solutions; these ions were found to be determined with reasonable accuracy even at concentrations as low as 10^{-6} M. Depolarizers at concentrations of the order of 10^{-4} M can be determined accurately in air-saturated solutions. The present method has the considerable merit that its sensitivity is not affected by the degree of reversibility of the electrode reaction. The integral technique was also applied successfully to the compensation of residual currents by the twin-cell system, in which a pair of dropping mercury electrodes is not necessarily synchronized.

Increase in sensitivity and accuracy is an urgent requirement to the instrumental methods of analysis. The recent development in the modified alternating current (a.c.) polarography, the radio-frequency polarography, and the anodic stripping voltammetry has made it possible to determine the depolarizers at concentrations as low as 10^{-8} M. Their absolute accuracy, however, is not very high, and the sensitivity is low when the electrode reaction is slow.

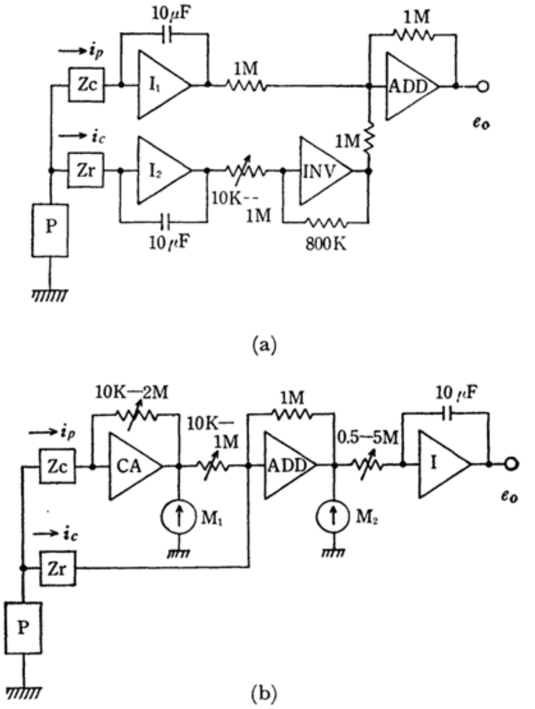
The diffusion current in the direct current (d.c.) polarography has the advantage of good reproducibility and high accuracy, when applied to the determination of depolarizers. In the conventional d.c. polarographic method, however, the measurement of diffusion currents at lower concentrations becomes increasingly difficult because of the large contribution of residual currents. Many attempts have been made to eliminate the residual current and to increase the signal-to-noise ratio; typical examples are the differential polarography, the derivative polarography,[1] and the tast polarography.[2] These methods generally require careful synchronization of a pair of dropping mercury electrodes (DME) or elaborate electronic instruments, and their practical usefulness is very much limited.

The application of integral readout methods is expected to be effective to overcome some of the above-mentioned difficulties and to increase the sensitivity and accuracy of the d.c. polarographic measurement. Booman *et al.* measured the charge transferred during a short period of electrolysis at solid electrodes by using a precision current integrator; they stated that a linear relation between the concentration and the charge transferred was obeyed to within 1%.[3] The integration of single sweep oscillopolarograms was proposed by Christie, Lauer, and Osteryoung.[4] Lauer and Osteryoung[5] reported that the integration of polargoraphic currents during a life of a single mercury drop is a suitable method for separation of capacitive and faradaic currents and for trace analysis.

The present paper deals with a new technique in which the polarographic current is integrated electronically over a long period of time (about 10 min) at a given electrode potential. The experimental results demonstrated the usefulness of the proposed technique for the elimination of residual currents and accurate measurement of average polarographic currents.

Experimental

Apparatus. The basic circuits of the apparatus used are shown in Fig. 1; both circuits (a) and (b) gave essentially the same results.



(a)

(b)

Fig. 1. Basic circuits of the plarographic current integrator with the residual current compensation: P, applying d. c. potentiometer; Z_c, polarographic cell; Z_r, variable resistance or a polarographic cell with supporting electrolyte solutions; I, integrator; ADD, adder; CA, current-to-voltage converter; INV, inverter; M, voltmeter. Chopper-stabilized operational amplifiers (Asia Seisakusho) were used in circuit (a), and solid-state differential operational amplifiers (Model 9814, Aiko Denki, Co., Ltd.) were used in circuit (b).

The principle of circuit (a) is similar to that of a linear bridge. The polarographic current, i_p, at a given electrode potential is integrated by the integrator, I_1, for a certain period of time (*e. g.*, about 10 min), while a constant current, i_c, is integrated by the other integrator, I_2; the sign and the magnitude of i_c are adjusted so that the output voltage of the inverter, INV, is opposite in its sign and exactly equal in its magnitude to the integrated value of the residual current at the given potential. The addition of both the signals from I_1 and INV by the adder, ADD, then eliminates the contribution of the residual current.

In circuit (b), the sign and the magnitude of the polarographic current, i_p, are changed by the current-to-voltage converter, CA; the residual current component is eliminated from the polarographic current by introducing a properly adjusted, constant current, i_c, to the summing point of the adder, ADD. The output signal of ADD is then integrated by the integrator, I, for a given period of time. In this circuit the adder, ADD, may be omitted by applying i_c directly to the summing point of the integrator, I.

The output voltage, e_o, of the apparatus was found to be strictly proportional to the input current over the wide range of current from a few nanoamperes to about 0.2 μA, the standard deviation of the slope being about 0.5%.

Cell and Reagents. The polarographic cell used was a glass beaker of a 100 cc capacity with a rubber stopper. The conventional DMEs of usual drop time and flow rate of mercury served as working electrodes. Either an internal mercury pool or an external saturated calomel electrode (SCE) was used as the counter electrode; the electric contact between the cell solution and the SCE was made by means of an agar bridge with a sintered glass tip.

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1) For example, D. J. Fisher, W. L. Belew and M. T. Kelley, "Polarography 1964," Vol. 1, ed. by Graham J. Hills, MacMillan, London (1966), p. 89.

2) K. Kronenberger, H. Strehlow and A. W. Elbel, *Leybold polarograph. Ber.*, **5**, 62 (1957) through L. Šerák, "Progress in Polarography," Vol. 2, ed. by P. Zuman and I. M. Kolthoff, Interscience Publishers, New York (1962), p. 546.

3) G. L. Booman, E. Morgan and A. L. Crittenden, *J. Am. Chem. Soc.*, **78**, 5533 (1956).

4) J. H. Christie, G. Lauer and R. A. Osteryoung, *J. Electrochem. Soc.*, **111**, 1420 (1964).

5) G. Lauer and R. A. Osteryoung, *Anal. Chem.*, **39**, 1866 (1967).

The solutions were prepared from redistilled water and analytical reagent grade chemicals. When the measurement was carried out with a deaerated solution, purified nitrogen gas was passed over the solution.

All measurements were made in a water thermostat of 25.0 ±0.1°C.

Results and Discussion

Theory. At a given constant potential in the diffusion current plateau the instantaneous polarographic current, $i_p(t)$, at time t during the growth of a spherical mercury drop is given by

$$i_p(t) = k_1nCD^{1/2}m^{2/3}t^{1/6} + k_2\sigma m^{2/3}t^{-1/3} \qquad (1)$$

where k_1 and k_2 are constants, σ is the surface charge density at the given potential, and the other symbols have their usual meaning. Integration of Eq. (1) then gives the charge, $Q(t_d)$, transferred during the growth of a single mercury drop with a drop time of t_d,[5)]

$$Q(t_d) = \frac{6}{7}k_1nCD^{1/2}m^{2/3}t_d^{7/6} + \frac{3}{2}k_2\sigma m^{2/3}t_d^{2/3} \qquad (2)$$

Multiplying Eq. (2) by θ/t_d we obtain the following equation representing the charge, $Q(\theta)$, transferred during the period of time of θ ($\theta \gg t_d$),

$$Q(\theta) = (\bar{i}_d + \bar{i}_r)\theta \qquad (3)$$

$$\bar{i}_d = \frac{6}{7}k_1nCD^{1/2}m^{2/3}t_d^{1/6}$$

$$\bar{i}_r = \frac{3}{2}k_2\sigma m^{2/3}t_d^{-1/3}$$

where $\bar{i}_d$ and $\bar{i}_r$ are the average diffusion current and the average charging current, respectively, over the drop life.

The output voltage, e_o, of the present apparatus, being proportional to $Q(\theta)$, is expected to give the average diffusion current when the contribution of the charging current is properly eliminated.

Compensation of Residual Currents. The long-term integration of polarographic currents almost completely eliminates the oscillation due to the periodical renewal of the mercury drop; this makes it possible to compensate the residual current by applying a constant current, i_c, in the way as described before.

The most important factor which determines the accuracy of the present method, when the method is applied to trace analysis, is the constancy of residual currents. Let us consider for example the determination of 1×10^{-6} M of cadmium in a 1 M potassium chloride solution. At the DME used, the residual current at −0.85 V *vs.* SCE in the deaerated supporting electrolyte solution was about 6×10^{-8} A when a SCE was used as an external counter electorde, and it was about ten times larger than the diffusion current of cadmium. Therefore, only 1% fluctuation in the residual current will result in an error of about 10% in the determination of cadmium.

The magnitude and constancy of residual currents in a deaerated potassium chloride solution were very much affected by the nature of the counter electrode and also by the purity of mercury of the DME. The residual current with an internal mercury pool was several times greater than that with the external SCE, and it increased gradually during the measurement, probably because of the dissolution of mercury. The increase in the residual current with an internal mercury pool was more remarkable in solutions saturated with air. When the external SCE was used, the residual current fluctuated slightly for a short period of time, but it reached a reasonably constant value after 1/2 to 1 hr. Therefore, the use of an external counter electrode such as a SCE is strongly recommended for trace analysis. The mercury of high purity should be used for the DME, because a slight contamination of mercury seems to increase the magnitude and instability of residual currents.

The complete compensation of residual currents, as shown in Fig. 2 (curve 1), was achieved by the careful adjustment of the magnitude of applying constant current, i_c. The differential polarography technique with a twin-cell system was also successful for compensating residual currents. The long-term integration method, when applied to the twin-cell system, has the advantage that it obviates the complication of synchronizing the two DME's. By using the twin-cell system, the residual current of an air-saturated potassium chloride solution with an external SCE was perfectly eliminated over the wide potential range from zero to −1.4 V, when the adjustment had been made at the potential of −0.85 V. The twin-cell technique seems to have another possibility of determining accurately the concentration of major component if a solution of a known concentration is used as the reference.

Relationship between the Output Voltage and the Concentration. The output voltage *vs.* concentration relationship was examined with cadmium, lead, and zinc ions in 1 M chloride solutions over the concentration range of 10^{-6}—10^{-3} M according to the following procedure. The constant current, i_c, necessary to compensate the residual current was determined first with the supporting electrolyte solution of a given volume. A known amount of the concentrated solution of the depolarizer was then added successively to the supporting electrolyte solution from a precision micro-syringe; the total volume of the added solution was always less than 1% of the initial volume of supporting electrolyte solution. When deaerated solutions were subjected to analysis, the purified nitrogen gas was bubbled through the solution for about 10 min after each addition of the depolarizer solution.

In each case, the output voltage of the apparatus increased linearly with the time of integration as shown in Fig. 2, and the output voltage, $e_o(\theta)$, at a given time of integration (*e. g.* $\theta=640$ sec) was found to be perfectly proportional to the concentration of the depolarizer except for the deviation at the lowest concentrations. Figure 3 shows a typical example of the $e_o(\theta)$ *vs.* C (concentration) relationship. The significant deviation from the linearity at very low concentrations ($C<3\times10^{-6}$ M) is thought to be due to the adsorption of depolarizer on glass surfaces of the cell.

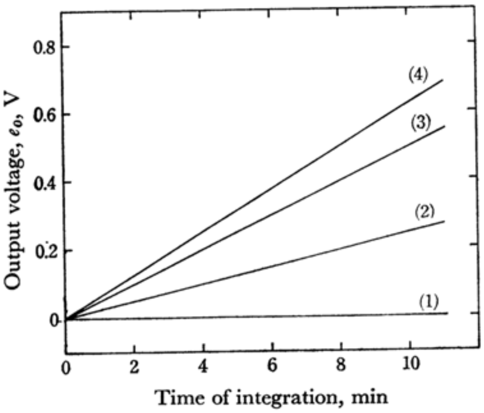

Fig. 2. Relation between the output voltage, e_o, and the time of intergration in deaerated 1 M KCl solutions with an external SCE: (1) 1 M KCl, (2) 4×10^{-5} M Cd(II) + 1 M KCl, (3) 8×10^{-5} M Cd(II) + 1 M KCl, (4) 1×10^{-4} M Cd(II) + 1 M KCl. The residual current was compensated by applying constant current, i_c.

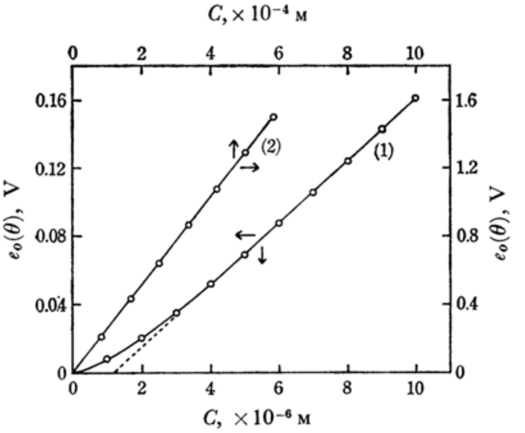

Fig. 3. Relationship between the output voltage, $e_o(\theta)$, at $\theta=640$ sec and the concentration, C, of cadmium ions in deaerated 1 M KCl solutions with an external SCE: (1) concentration range of 1×10^{-6}—1×10^{-5} M, (2) concentration range of 1×10^{4}—6×10^{-4} M. The residual current was compensated by applying constant current, i_c. The $e_o(\theta)$ values for (1) and (2) are not calibrated for the sensitivity of the apparatus.

TABLE 1. STANDARD DEVIATION, s_b, FOR THE SLOPE, b, OF THE $e_o(\theta)$ *vs.* C RELATIONSHIP

System	Concn. range	$(s_b/b)\times100$
Cd(II) in deaerated 1 M KCl at −0.85 V *vs.* SCE	$(1-10)\times10^{-6}$ M	1.83
	$(2-10)\times10^{-5}$ M	0.544
	$(1-6\ )\times10^{-4}$ M	0.484
Cd(II) in air-saturated 1 M KCl at −0.85 V *vs.* SCE	$(1-7\ )\times10^{-4}$ M	0.458
Pb(II) in deaerated 1 M KCl contg. 0.01 N HCl and 5×10^{-6} M LEO at −0.65 V *vs.* SCE	$(1-14)\times10^{-6}$ M	0.219
	$(2-14)\times10^{-5}$ M	0.578
Zn(II) in deaerated 1 M KCl contg. 2×10^{-6} M LEO at −1.20 V *vs.* SCE	$(2-14)\times10^{-6}$ M	0.560

LEO: polyoxyethylene lauryl ether.

The accuracy of the present method, when the method was applied to the determination of cadmium, lead, and zinc ions in chloride solutions, is demonstrated in Table 1 in terms of the quantity, $(s_b/b)\times100$, where b is the slope of the $e_o(\theta)$ *vs.* C relationship and s_b the standard deviation of the slope.

Conclusion. The present study shows that the long-term integration of polarographic currents provides a very useful method of determining depolarizers in solutions with a relatively large but constant background. With this technique the diffusion current as small as one tenth of the residual current can be measured with reasonably high accuracy. The application of the twin-cell system to the present method seems to be very promising for compensating the residual current and for determining the major component. The present method, when compared with the conventional a.c. polarography, has similar sensitivity but higher accuracy; the method also has the advantage that its sensitivity is not affected by the degree of reversibility of the electrode reaction. From the standpoint of theoretical application, the long-term integration technique will provide a useful method of measuring the true average current at the DME. The accuracy of measurements may be increased by the use of a digital readout equipment.

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