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Direct Reading Concentration-meter. The Use of Differential Technique in the Polarographic Analysis

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By connecting the differentiator (double-pole double-throw rotating switch) with the ordinary polarographic apparatus, the current voltage curve is differentiated with regard to potential.

Properly selecting the applied voltage, the concentration of the reducible ion can be measured indifferently to other substances present together.

The concentration-meter was constructed and used for the direct-reading of the concentratin of zinc in the presence of much copper, cadmium, etc. and the satisfactory result was obtained.

INTRODUCTION

Previously, Professor Ishibashi and the author reported on the new device for self-recording the differential polarogram with one dropping electrode.[1] Heyrovsky[2] and other workers already reported on the method for differentiating the ordinary polarographic current-voltage curve using two dropping electrodes, but this method is not quite practical owing to the difficulty of synchronizing the dropping rate of the two electrodes. Lévèque and Roth[3] succeeded in getting the differential curves with one dropping electrode using a condenser in series with the recording galvanometer. In this method, however, the applied potential must be continuously increased and when the increasing of potential is once stopped, the differential current also stops.

The authors' method is very similar to Kalousek's polarograph of discontinuous applied potential[4] ; the rotating-current-alternator is inserted in series with the circuit of polarograph to apply alternately two potentials, which are different by ΔE, to the cell, thus effecting the flowing of the corresponding currents through the galvanometer in the reverse directions to each other. If the rotation velocity of the alternator is raised so high that the galvanometer cannot follow by its inertia to the changing of connection, the differential current with one dropping mercury electrode can be obtained at any applied potential (whereas the ordinary

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polarogram is obtained without changing its circuit when the rotation of alternator is stopped).

The studies on the differntial polarogram obtained through this method and the discussion on the electrode reaction were already reported by the author[5]. This paper is a report on the concentration-meter which is one of the applications of this differential technique.

INSTRUMENTATION

The apparatus is shown in Fig. 1 and the circuit is shown in Fig. 2, in which R_1 is a potentiometer with 200 divisions on its scale, whose resistance is 600 ohms ; R_2 is five unvariable resistances whose values are from left to right, 15, 15, 30, 30 and 510 ohms and their terminals are all connected with switch ΔE. R_3 is 200 ohms variohm used for radio. V is a voltmeter with a full scale of 3 volts, G is a microammeter with a full scale of 5 microamperes, B is a dry cell of 3 volts and S is its switch. D is a rotating-current-alternator, in other words, a differentiator which is a cylindrical double-pole double-throw switch and is rotated by a motor. The minimum permissible rotation velocity is ca. 1000 r.p.m. in case of use of an ordinary microammeter or galvanometer and 5 percent fluctuation in the velocity has no influence on the result. As seen from Fig 2, when the alternator is stopped

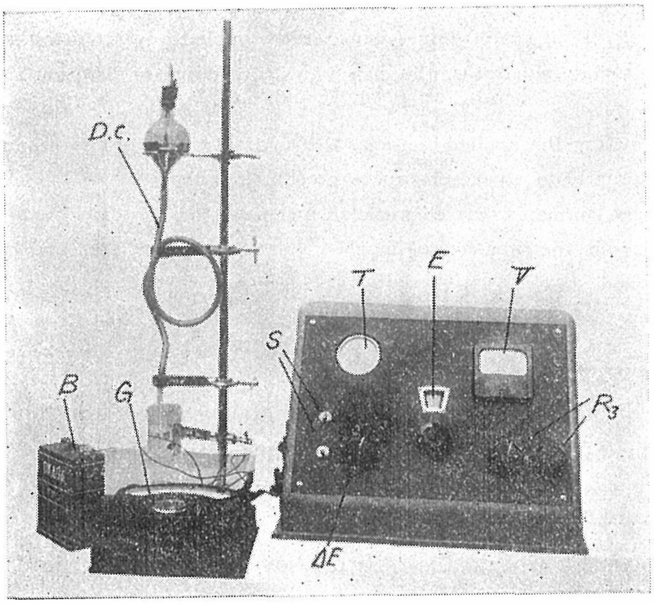

Fig. 1. Concentration-meter.
B : dry battery, D.C. : dropping electrode, V : voltmeter,
E : potentiometer, ΔE : switch of selecting ΔE,
G : microammeter, T : tachometer, S : switch.

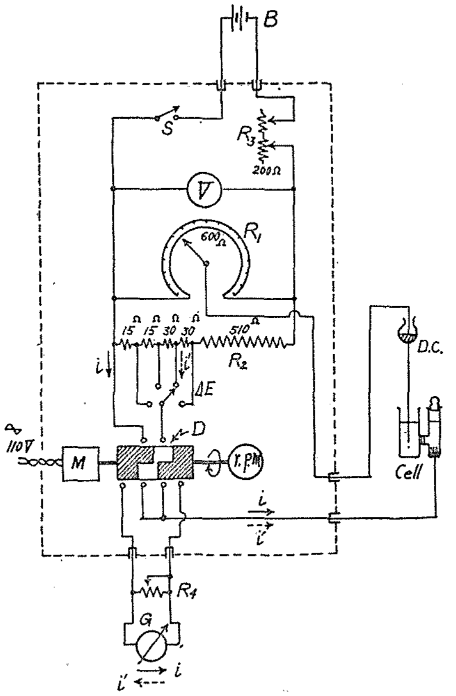

Fig 2. Circuit of the concentration-meter.

and the voltmeter is so adjusted as to indicate 2.000 volts using the variohm R_3, the potential E which is indicated on the scale division of the potentiometer is applied to the cell. When the alternator is half rotated, however, the applied potential decreases to $E-\Delta E$. Here, ΔE is properly selected as 50, 100, 200 or 300 millivolts according to the switch connection. Since the electrolytic currents i and i' corresponding to the applied potential E and $E-\Delta E$ respectively, flow through the galvanometer in reverse directions to each other, the galvanometer can be adjusted to indicate $\Delta i = i - i'$ at the proper rotation of the alternator. Thus the differential polarogram can be obtained by recording Δi which corresponds to E, changing with the movement of potentiometer contact. As a result of fundamental studies, it has been found that the potential at the maximum of the differential polarogram is in good agreement with the ordinary half-wave potential when the mean value of the applied potential $E-\Delta E/2$ is read on the differential polarogram. In addition, it was also found that the peak current in the differential polarogram of zinc ion in ammoniacal solution is proportional to its concentration. Therefore, the concentration of zinc ion in solution can be directly read through this apparatus.

EXPERIMENTAL

The H type cell was used as an electrolytic cell and one of the chambers is equipped with a saturated calomel electrode or is connected by a salt bridge with it. The sample solution of zinc ion in 1N-ammonium hydroxide and ammonium chloride is put into another chamber, the switch S is switched on and E and ⊿E are properly adjusted in order that $E - ⊿E/2 = E_{1/2} = -1.3$ volts is kept (in case of the differential polarography, ⊿E should be taken as small as possible, but it is advisable in this concentration-meter that ⊿E should be selected so large as to make the peak flat —see Fig. 3— which was recorded dy the ordinary polarographic apparatus with the differentiator) and to prevent the fluctuation of the peak cur-

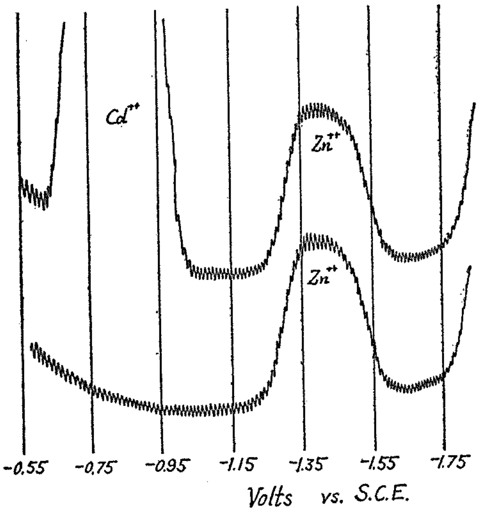

Fig. 3 Differential polarogram obtained with the ordinary polarographic apparatus and the rotating-current-alternator.
Curve 1 : Zinc in ammoniacal solution (⊿E=200 millivolts).
Curve 2 : Same as curve 1, but much cadmium is present together.

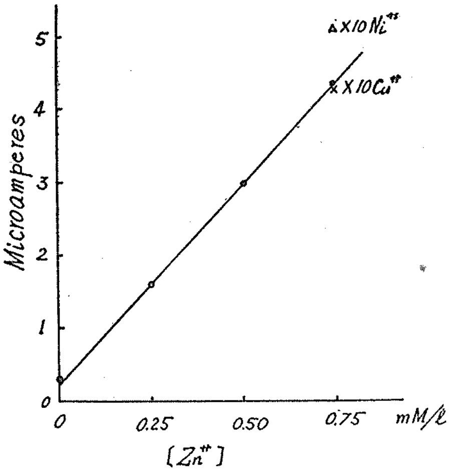

Fig. 4. Differential currents of increasing zinc ion concentrations.
E=−1.4 volts vs. S.C.E., ⊿E=200 millivolts.

rent even if there if a small fluctuation in the electrode potential. The current-alternator is rotated and the dropping electrode is inserted to the cell. Through this procedure the concentration of zinc ion is indicated by the microammeter (or galvanometer). The results obtained are shown in Fig. 4 and Table 1. It was observed that the concentration of zinc ion was measured indifferently with the presence of ten times ammount of copper or cadmium ion etc., so the zinc content in brass was conveniently determined through this apparatus; the brass was dissolved with aqua regia in the usual way and the solution was concentrated to the syrupy state occasionally adding concentrated hydrochloric acid and diluted to the definite volume. The aliquot portion of the solution was taken out and to this was added the same volume of 2N-ammonium hydroxide and ammonium chloride solution which contained 0.02 percent gelatine. This final solution was tested as the sample electrolytic solution. As is mentioned above, the determination of zinc ion is not influenced by the presence of ten times amount of the former-discharging substances such as copper or cadmium etc. (see Fig 3) only if the concentration of such ions is less than one-fiftieth of that of ammonium ion as in the case of ordinary polarographic analysis. However, a large quantity of nickel interferes to some extent the determination of zinc when ΔE is greater than 200 millivolts.

Table 1. Results obtained on the determination of zinc by the concentration-meter.
ΔE=200 mV, E=−1.4 Volt vs. S.C.E.

Zinc concentration	Other reducible ions present	Observed differential curreut
mM/*l*-NH_4OH,NH_4Cl	mM/*l*	μA
0.0	none	0.28
0.25	none	1.54
0.50	none	2.98
0.75	none	4.32
0.75	Cu : 5.0	4.29
0.75	Cu : 7.5	4.30
0.75	Cu : 7.5	4.32
0.75	Ni : 0.5	4.33
0.75	Ni : 7.5	5.21

100.3 mg Brass*/*l* NH_4OH,NH_4Cl	Observed differential current A	Zinc found %
0.57 mM−Zn/*l* (37.3 mg−Zn/*l*)	3.36 ± 0.07	37.2 ± 0.8

* By the gravimetric analysis, this brass contains 37.2%−Zn, 59.0%−Cu, 1.71%−Sn and trace of Pb etc.

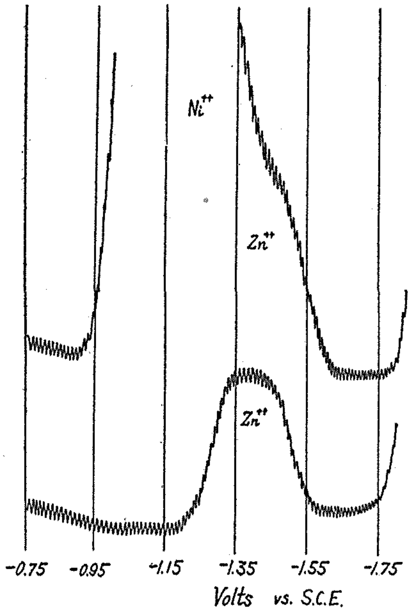

Fig. 5. Differential polarogram of zinc (ΔE=200mV).
Curve 1: in the absence of nickel.
Curve 2: in the presence of nickel.

SUMMARY

The possibility was studied of applying the technique of the differential polarography with the rotating-current-alternator to the concetration-meter and good results were obtained in the determination of zinc through this method. For example, the zinc in copper base alloy was determined by direct reading without any separation of the copper, etc. It was found that only the presence of a large quantity of nickel interfered with the zinc determination.

Studies are now being performed on the possibility of the determination of other metals through this apparatus. The concentration of other metals than zinc, such as copper, cadmium, etc. ought to be indicated only by taking applied voltage E properly. As has already been reported⁵⁾, however, the differential current obtained with this rotating-currentalternator is often different from the differential curve of the ordinary polarogram and this effect is now under research.

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