59. Morizo Ishidate, Takashi Isshiki, Yasushi Mashiko, and Noboru Hosoya :

Derivative Polarography. I. A New Circuit for Derivative Polarography.

(Pharmaceutical Institute, Medical Faculty, University of Tokyo, and Pharmaceutical Institute, Engineering Faculty, Nippon University)*

Semerano and Riccoboni⁽¹⁾ in 1942 reported a circuit for differential polarography which was suggested to be able to determine a small amount of substance in the presence of a large amount of the reducible interfering substances. Heyrovsky⁽²⁾ devised a circuit for obtaining derivative polarogram, in 1946, which was very similar to Semerano-Riccoboni's circuit. These methods are very convenient to analyse impurities in medical or biochemical reagents and the mixture of some polarographically active substances such as mineral water, reaction products, food, and others. A pair of dropping mercury electrodes, as nearly identical in characteristics as possible, is necessary for these techniques when the dropping mercury electrode is necessary as an indicating electrode. It is well known that the characteristic of the dropping mercury electrode is represented by $m^{2/3}t^{1/6}$. The value of m is influenced by such factors predicted by Poiseuille equation as effective pressure on the dropping mercury, radius and the length of the electrode capillary, etc. The value of t is inversely proportional to the effective pressure for a given electrode capillary. Though the characteristics of the given two electrode capillaries may, therefore, be unified by adjusting the effective pressure on each dropping mercury, some device is necessary for the synchronization of the drop life of each electrode. On the other hand, the Reveque and Roth derivative technique is of interest in the sense that this technique uses only one electrode capillary, but this technique has also the unavoidable recording lag on its principle. Hereupon, a technique for the derivative polarography was studied in our laboratory as shown in Fig. 1, which is similar to Müler's oscillographic technique.

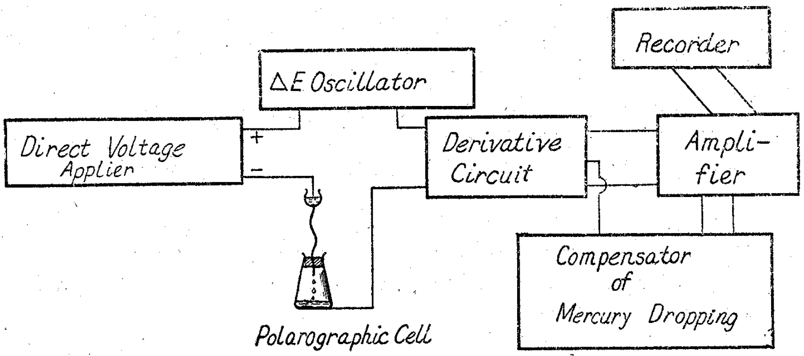


Fig. 1. Block Diagram of the Derivative Technique

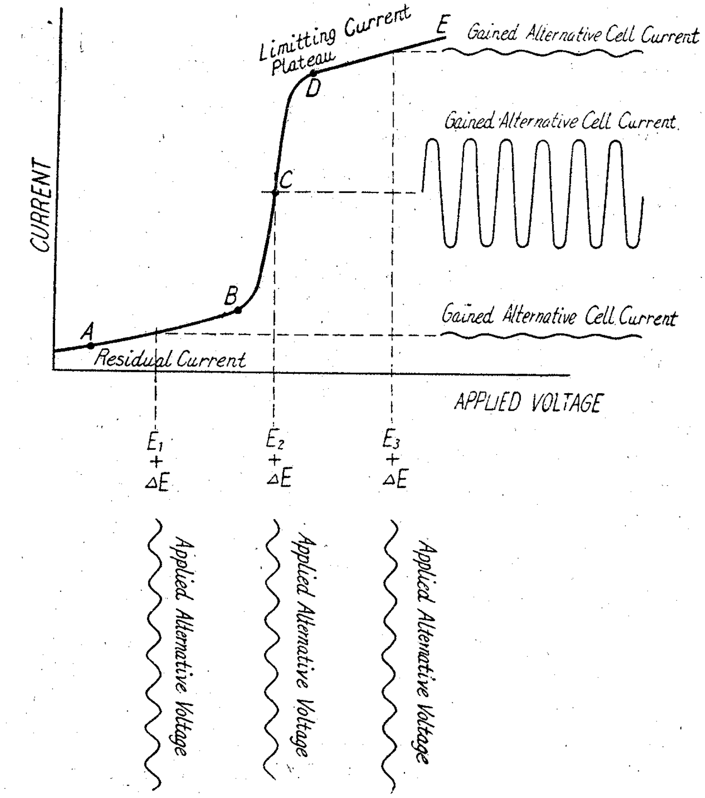
Principle The principle of our technique is indicated in Fig. 2 and $AECDE$ is an ordinary polarographic wave. When the small alternative voltage, which falls within the differential applied voltage (ΔE) of Heyrovsky derivative technique, is superimposed on the ordinary, directly applied voltage on the micro-electrode, the cell current contains the same alternative current which falls in the differential current (Δ^{i}) against ΔE indicated by Heyrovsky. When velocity of the reaction on the micro-electrode surface is sufficiently rapid as compared with the frequency of the applied alternative voltage, the alternative cell current is very small at E_1 and E_3, and it attains the largest value at the half-wave potential of E_2, as shown in Fig. 2. Therefore, if only this alternative

---

* Hongo, Tokyo (石館守三, 一色 孝, 益子 安, 細谷 昇).

1) G. S. Semerano, L. Riccoboni : Gazz. chim. ital., **72**, 297 (1942).

2) J. Heyrovsky : Chem. Listy, **40**, 22 (1946); Analyst, **72**, 229 (1947).



alternative

Fig. 2.

Principle of this Technique

cell current may be picked up and measured, this value may indicate the derivative one. Many kinds of circuits may be considered for this purpose, but we adapted the following circuit which will be described in the next chapter. In any case, these circuits differ only in such ways that they would pick up alternative cell current and measure its value, otherwise they have no difference in the principle.

Instrument of this Technique—The detailed diagram of the instrument for this technique is shown in Fig. 3, which is divided into six parts.

(I) Direct voltage applier.

Part one contains one battery (B_1), one variable resistance, and a finely variable resistance. The direct voltage can be applied to the cell when selector switch (S_{w_2}) is placed on MEAS. The applied voltage can be changed by R_2, and the span voltage range is adjusted by R_1 as an ordinary potentiometer does.

(II) Oscillator for $\varDelta E$.

This oscillator for $\varDelta E$ is constituted with a transformer T_1 (a heater-transformer—output : 5 V—for radio) and a voltage divider. From this circuit, 1 mV which is applied to the cell as the differential alternative $\varDelta E$, is taken up at both extremities of R_{41} when the switch S_{w_1} is placed on 1 mV.

(III) Derivative circuit.

T_2 is a derivative circuit in this instrument. When the pulse current is raised in cell circuit, T_2 picks up only alternative part of its pulse and alternative power in the secondary coil is applied to the amplifier (Part IV) as a signal of the derivative current.

(IV) Amplifier.

At first the signal from the secondary coil of T_2 is amplified by two parallel 6 SJ 7, and again by two parallel 6C6. Then the gain of the second stage is sent to part (V) for the measurement of its value.

(V) Recorder.

This recorder is a kind of vacuum tube voltmeter. The sensitivity of galvanometer (G) is adjusted by R_{28} and protected from the pulse of the mercury dropping by great capacitance condenser C_{16}. R_{23} serves to balance this bridge circuit and to adjust the zero point of the galvanometer deflection. When the in-put circuit of this recorder catches the signal through C_{11} and C_{12}, the alternative signal from amplifier is commuted to direct current by two rectifiers, M_1 and M_2. Then this rectified direct voltage biases the grid potential of one triod of 6 SN 7. By the biased grid potential the balance of this bridge is broken and the galvanometer is deflected according to the alternatively effective current of the cell circuit.

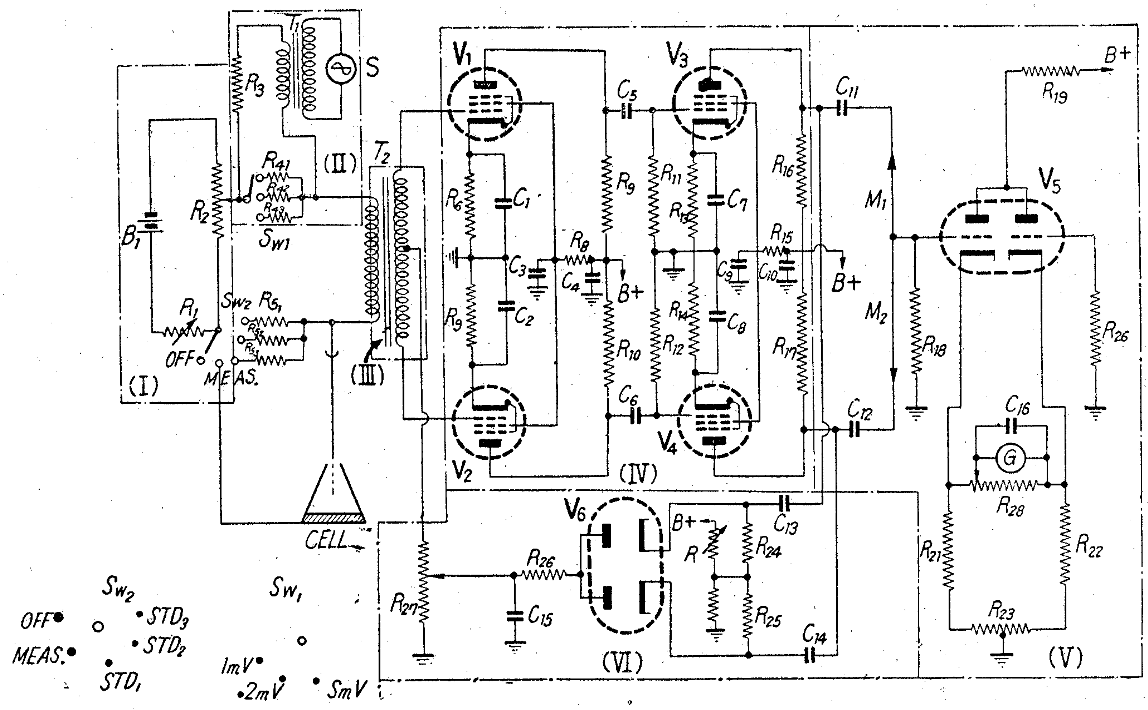


Fig. 3. Detailed Diagram of the Circuit

Part (I)—Direct voltage applier; Part (II)—Oscillator for ΔE; Part (III)—Derivative circuit (High impedance transformer); Part (IV)—Amplifier; Part (V)—Recorder; Part (VI)—Mercury dropping compensator.

V_1, V_2 ··········6 SJ 7; V_3, V_4 ··········6C6; V_5 ·········6 SN 7; V_7 ··········6H6

R_1	200 Ω	C_1, C_2, C_7, C_8	100 μF (25 V)
R_2	100 Ω	C_3, C_4, C_9, C_{10}	8 μF
R_3	10 KΩ	C_5, C_6, C_{11}, C_{12}, C_{13}, C_{14}	0.5 μF
R_{41}	2 Ω	C_{15}	0.1 μF
R_{42}	4 Ω	C_{16}	1000 μF
R_{43}	10 Ω	T_1	Power trans. (output 5 V)
R_{51}, R_{52}, R_{53}	Standard resistance	T_2	In-put trans. (low frequency)
R_6, R_7, R_{13}, R_{14}	1.5 KΩ		pr. 10^5 Ω (at 1 Kc)
R_8, R_{11}, R_{12}, R_{15}, R_{18}, R_{20}	500 KΩ		Se, 10^6 Ω
R_9, R_{10}, R_{16}, R_{17}, R_{19}	250 KΩ	B_1	2~4 V Battery
R_{21}, R_{22}, R_{30}	5 KΩ	B_+	250~300 V-D. C.
R_{23}, R_{28}	V. R. 10 KΩ	S	Electric source
R_{24}, R_{25}	20 KΩ		50 c/o 110 V (commercial voltage)
R_{26}	100 KΩ	S_{w_1}, S_{w_2}	Switch
R_{27}	V. R. 1 Ω	M_1, M_2	Metal rectifier
R_{29}	V. R. 50 KΩ	G	Micro-ammeter full scale 50 μA

(VI) Mercury dropping compensator.

At the instant when dropping of microelectrode begins, the big change in cell current is suddenly raised in the cell circuit. This sudden change of the current is picked up by T_2 and appears as a large noisy deflection of the galvanometer which cannot pass through C_{16}. When such noisy current is picked up by T_2, 6H6 in part (VI) catches only this noise-gain of the amplifier and commutes this noise to the negative potential against the cathode potential of two 6 SJ 7 in the first stage, then sends back to the middle point of the secondary coil of T_2 and cuts off the amplification of the part (III) for some time. This interval of the cut-off and the gained negative potential is adjusted by R_{27} and C_{15}. This part protects the galvanometer from the overscale deflection and the vacuum tube system of this instrument from the instability by great noisy signal.

Application of this Technique to several Metal Ions—After the proper galvanometer sensibility is selected by using R_{23} at some STD position of selector switch S_{w_2}, then the selector switch is replaced on MEAS. The oxygen in the cell solution (HCl–0.2 M/L. KCl buffer solution, pH 2.2) is eliminated by bubbling oxygen-free nitrogen, then the galvanometer deflection is plotted against the direct applied voltage. This curve shown in Fig. 4 is the derivative polarogram of this empty solution.

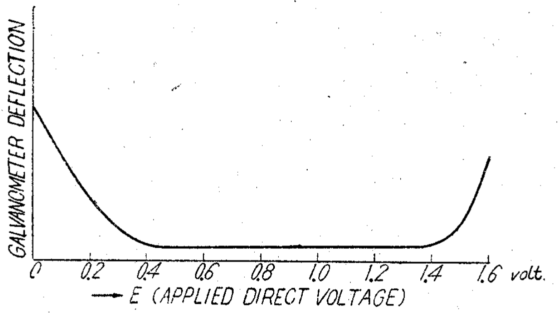


Fig. 4.

Derivative Current–Voltage Curve of the Empty Solution (HCl–0.2 M KCl Buffer Solution : pH 2.2) Internal Mercury Pool as Anode.

Then Cd^{++} and Zn^{++} of about $10^{-3} M$ are added to this cell solution, and the oxygen is removed again from this solution by bubbling nitrogen through and the deflection is plotted as above procedure. This derivative polarogram is shown Fig. 5.

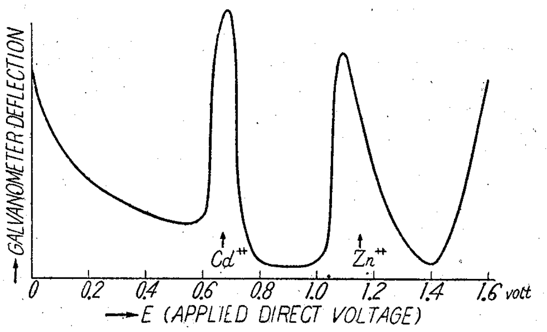


Fig. 5.

$10^{-3} M$ Cd^{+++} and Zn^{++} in HCl–0.2 N. KCl Buffer Solution (pH 2.2)

Fig. 6 shows the derivative polarogram for Sb^{+++}, Pb^{++}, Cd^{++}, and Zn^{++} in 0.1 N KCl solution.

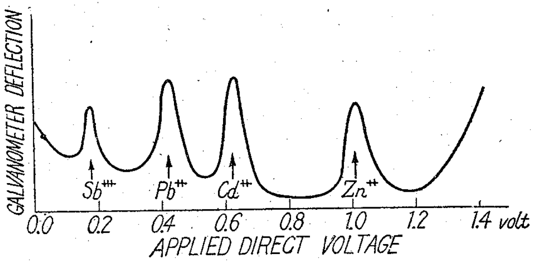


Fig. 6.

Sb^{+++}, Pb^{++}, Cd^{++} and Zn^{++} in 0.1 N KCl Solution (slightly acidic tylose was added)

From the data obtained it was proved that each maximum appeared practically at the same points of the half-wave potential of the ion and the shape of these curves were about symmetrical. But we could not determine theoretically whether the shape was the true derivative of the ordinary polarogram or not, because the applied voltage to the electrolysis contains the relatively high, frequent alternative one. In any case, this technique might be considered to have applicability for the biochemical and medical purposes or the rapid analysis of the mixture of the polarographically active substances. The application of this technique to the determination of several metal ions or of other substances will be discussed quantitatively in the following paper of this series.

The authors are indebted to Toa-Dempa Inc., and Yanagimoto Co. Ltd. for supplying materials, and wish to acknowledge kind assistance from Mr. Tada and others in this Laboratory.

Summary

In a single dropping mercury electrode cell, the derivative polarogram was obtained by a new circuit which was able to measure the alternative current of the pulse-cell current obtained by the superimposition of the small alternative applied-voltage on the ordinary direct one. It was not possible to determine theoretically whether the shape of this derivative polarogram is the true one, but the maximum of the curves appeared practically at the same points of the half-wave potentials concerning several cations.

(Received June 18, 1954)