60. Takashi Isshiki, Yasushi Mashiko, and Shigeru Tsukagoshi: Derivative Polarography. II. Derivative Polarography of Cadmium, Antimony, and Lead Ions.

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In the previous paper[1], the circuit for the derivative polarography was chiefly discussed. The following investigation was undertaken in order to test the relation between the maximum current in the derivative polarogram and the concentration of the cell solution, and others. The instrument manufactured by Yanagimoto Co., Ltd. according to the previous report[1] was used in this investigation. The main part of this derivative polarograph is shown schematically in Fig. 1, where both alternative current and direct one are applied together in series, and ΔE corresponding to the alternative span voltage was adjusted to 1 mV in the following measurements.

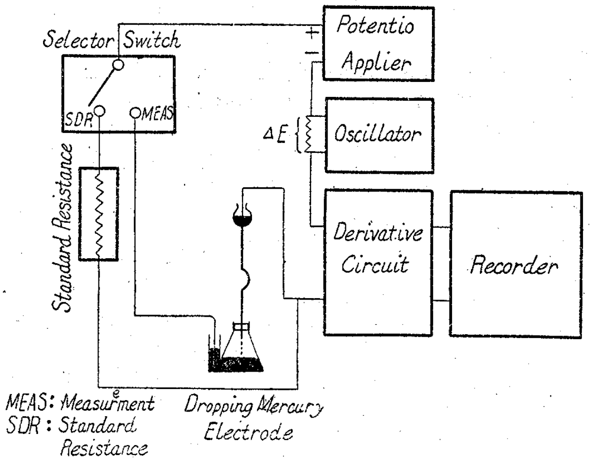

Fig. 1. Scheme of the Derivative Polarograph

The sensitivity of the galvanometer was adjusted as follows: When 2 kΩ of resistance was inserted as the standard it was so regulated that the fluctuation came to 20 μA using the sensitivity dial. Thus, the instrument is ready for experiment by placing the selector switch on *MEAS* (measurement). In this connection, plot of the galvanometer deflection against various standard resistances in the same sensitivity, is shown in Fig. 2.

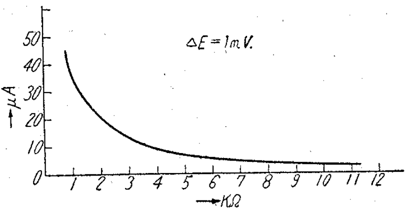

Fig. 2. Curve of the Galvanometer Reading against the Standard Resistances

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Experimental

Solvent—Aqueous 0.2 N HCl as supporting electrolyte.
Standard Solution—0.1 M $Cd(NO_3)_2$, 4.38×10^{-2} M $SbCl_3$, and 3.02×10^{-2} M $Pb(NO_3)_2$.
Pipet—0.0305 cc./drop.
Capillary Constant—At a mercury level of 320 mm. (mg./sec. in distd. water) = 2.03; t (sec./drop

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* Hongo, Tokyo (一色 孝, 益子 安, 塚越 茂).
[1] Ishidate, Isshiki, Mashiko, Hosoya: This Bulletin, **2**, 259 (1954).

in $0.2\,N$ HCl solution at 0 volt of applied voltage) $=3.07$; thus $m^{2/3}.t^{1/6}=1.93$.

Procedure—The electrolysis cell was an ordinary one and 20 cc. of the aqueous supporting electrolyte was taken into the cell. This cell was kept at 25° ± 0.2° by immersing in a constant temperature bath and oxygen-free hydrogen was bubbled in for about 15 minutes. Then the ordinary polarogram was recorded and the derivative one was plotted against the applied voltage. Further experiments were carried out in the same way by adding these standard solutions dropwise into the same supporting electrolyte.

Results

When no standard solution was added to the aqueous supporting electrolyte, namely, when the empty solution was examined, the derivative polarogram was obtained as shown in Fig. 3. Repeating the same operations every time when each drop of the standard solution was added to, the results obtained for Cd^{++}, Sb^{+++}, and Pb^{++} are summarized in Figs. 4, 5, and 6, and in Tables I, II, and III.

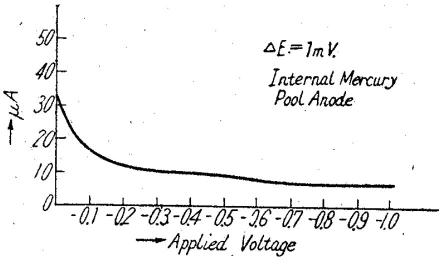

Fig. 3.

Derivative Curve of Empty Solution (20 cc. of $0.2\,N$ HCl)

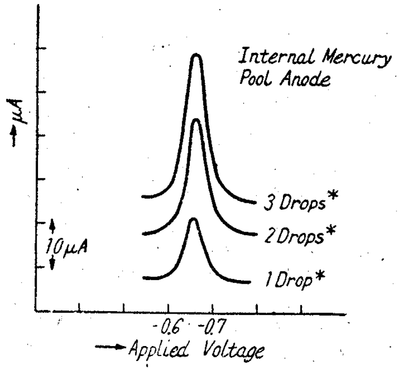

Fig. 4.

Derivative Curve of Cd^{++}

$\Delta E=1$ mV

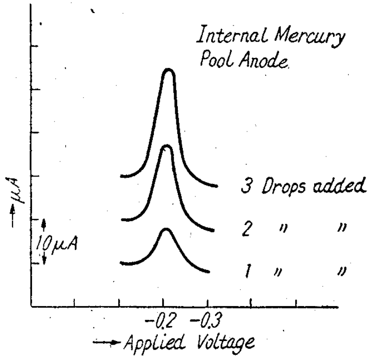

Fig. 5.

Derivative Curve of Sb^{+++}

$\Delta E=1$ mV

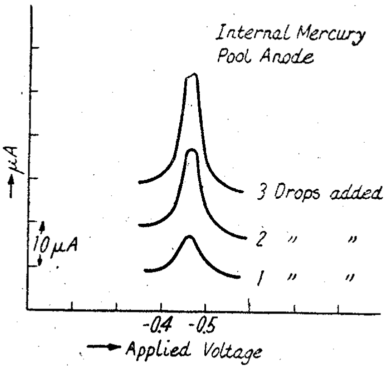

Fig. 6.

Derivative Curve of Pb^{++}

$\Delta E=1$ mV

* These number of drops indicate those of the standard solution added to 20 cc. of $0.2\,N$ aq. HCl solution.

TABLE I. Cd^{++}

No. of drops*	$C\,(M)\,10^{-4}$	I_{max} (μA)	$E_{1/2}$ (V)	E_{max} (V)
1	1.5_2	14.8	−0.68	−0.67
2	3.1_3	25.2	−0.68	−0.67
3	4.8_7	32.8	−0.68	−0.67

* These figures indicate the number of drops of the standard solution [$0.1\,M$ $Cd(NO_3)_2$] added to 20 cc. of $0.2\,N$ aq. HCl soln.

C : Concentration (calculated from the diffusion current).

I_{max} : Maximum reading of derivative curve.

$E_{1/2}$: Half-wave potential } vs. Mercury pool anode.
E_{max} : Potential at I_{max}

TABLE II. Sb^{+++}

No. of drops*	$C\,(M)\,10^{-4}$	I_{max} (μA)	$E_{1/2}$ (V)	E_{max} (V)
1	0.6_7	9.1	−0.21	−0.21
2	1.4_8	18.0	−0.21	−0.21
3	1.9_5	27.0	−0.21	−0.21

* These figures indicate the number of drops of the standard solution [$4.36\times10^{-2}\,M$ $SbCl_3$] added to 20 cc. of $0.2\,N$ aq. HCl soln.

TABLE III. Pb^{++}

No. of drops*	$C\ (M.)\ 10^{-4}$	I_{max} (μA)	$E_{1/2}$ (V)	E_{max} (V)
1	0.4_6	9.1	−0.47	−0.47
2	0.9_2	20.0	−0.47	−0.47
3	1.4_5	26.6	−0.47	−0.47

* These figures indicate the number of drops of the standard solution [$3.02\times10^{-2}\,M\ Pb(NO_3)_2$] added to 20 cc. of $0.2\,N$ aq. HCl soln.

The current at the maximum of the derivative curve (I_{max}) was measured according to the drawing shown in Fig. 7, and the concentrations of the final cell solution were calculated from the diffusion current in the ordinary polarogram.

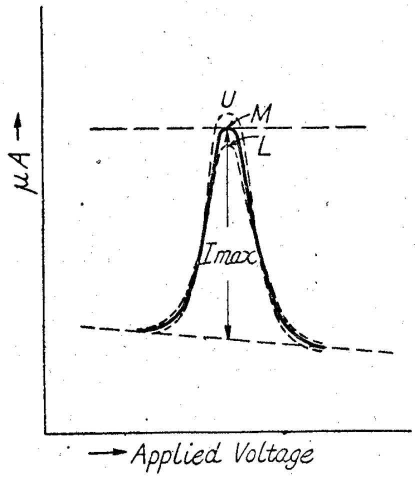

Fig. 7.
Drawing Methode for Measuring I_{max}

U : Upper limit of the galvanometer oscillation
M : Average
L : Lower limit

It is clear that the half-wave potential ($E_{1/2}$) and the potential at the maximum current of the derivative curves (E_{max}) are practically identical and the shapes of the derivative curves are almost symmetrical and the wave height of derivative curve is not strictly linear function of the concentration tested in spite of the fact that wave height in the ordinary polarogram is linear.

In our laboratory, commercial alternative current was not stable for the accurate measurement, so the voltage- and current-stabilizers were used during the experiments.

Summary

The derivative polarograms of Cd^{++}, Sb^{+++}, and Pb^{++} were obtained using a new circuit reported previously1). From these results it is clear that the potential at the maximum current of each derivative curve corresponds to the half-wave potential of each ion, and the maximum current of each derivative curve is not strictly linear function of the concentration.

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