Takashi Isshiki, Shigeru Tsukagoshi, and Eiichi Akita : A Simple Mercury Drop-time Regulator for Polarography.

(*Pharmaceutical Institute, Medical Faculty, University of Tokyo**)

Though the regulation of mercury drop-time is an indispensable problem in ploarographic study, particularly in differential polarography when more than one dropping electrode are employed, only a few mechanical devices for regulation have appeared in literature. Among them, the so-called Koryta and co-worker's clapper[1] seems to be well-known in general.

In connection with series of experiments[2,3] with derivative polarography, a necessity was felt for regulating the drop-time of mercury to a constant magnitude and this necessity was met by a new sipmle regulator shown in Fig. 1.

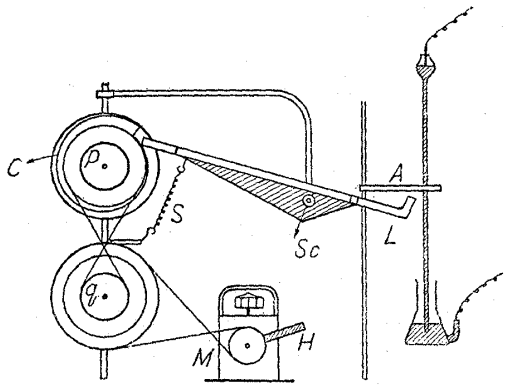


Fig. 1. Assembly for Regulating Mercury Drop-time

C : Cam
L : Lever
M : Synchronous Motor
A : Arm
S : Spring
S_c : Supporting Center
p, q : Pulley

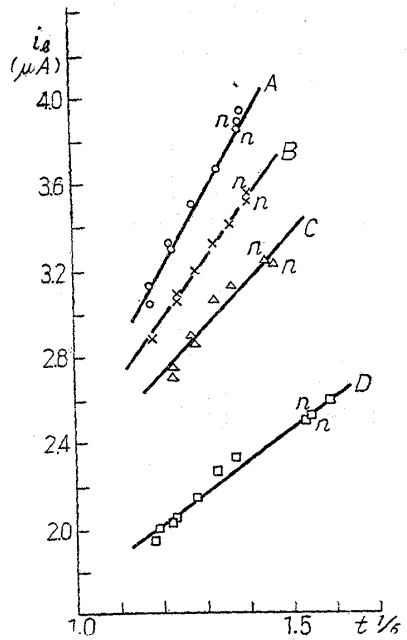


Fig. 2. Calibration Curve between i_l and $t^{1/6}$ (ca 0.75×10^{-3}M Cd^{++} in 0.19 N HCl soln.)

A : $m=1.07_1$ mg./sec. B : $m=0.94_6$ mg./sec.
C : $m=0.82_1$ mg./sec. D : $m=0.56_1$ mg./sec.
Dotts indicated by n are values for natural drops.
All other dotts indicate values for mechanical drops by clapping.

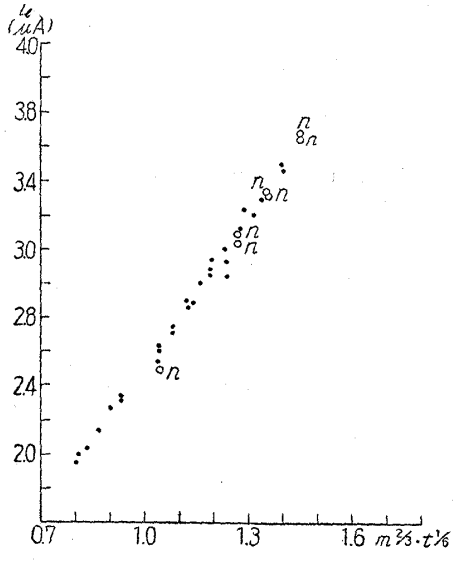


Fig. 3. Calibration Curve between i_l and $m^{2/3}\cdot t^{1/6}$ (The test solution is the same as in Fig. 2)

Dotts indicated by n are values for natural drops.

* Hongo, Tokyo (一色 孝, 塚越 茂, 秋田英一).

1) Koryta, Zuman : Chem. Listy, **46**, 389(1952).
2) M. Ishidate, T. Isshiki, Y. Mashiko, Hosoya : This Bulletin, **2**, 259(1954).
3) T. Isshiki, Y. Mashiko, S. Tsukagoshi : *Ibid.*, **2**, 263(1954).

The principle of this regulator is as follows. Mercury is forced to drop periodically by means of a gentle shock on the capillary electrode caused by collision against arm A of the lever L which is in periodic motion at optional regular intervals through the mechanical works of cam C and the synchronous motor M. This motion of the lever L, consequently, the drop-time of mercury, can be adjusted to an appropriate magnitude either by changing the ratios of pullies p and q, or by controlling the velocity of rotation of the synchronous motor with the hand brake H. It is necessary, before setting it in motion, to fix up the impact upon the capillary electrode to such an extent as sufficient to let mercury drops fall by force, but not strong enough to disturb the diffusion layer of cell solution. It may be easily accomplished by either stretching or loosening the spring S.

The test of the regulator was carried out by varying either drop time t at the constant value of m (m : weight of mercury flowing from the capillary per second) or m at the constant magnitude of t(=drop time).

From Figs. 2, 3, and 4, it is clear that the limiting current (i_l) is practically a linear function of both $t^{1/6}$ and the product $m^{2/3}t^{1/6}$. Some of the polarograms obtained actually by varying t are shown in Fig. 5.

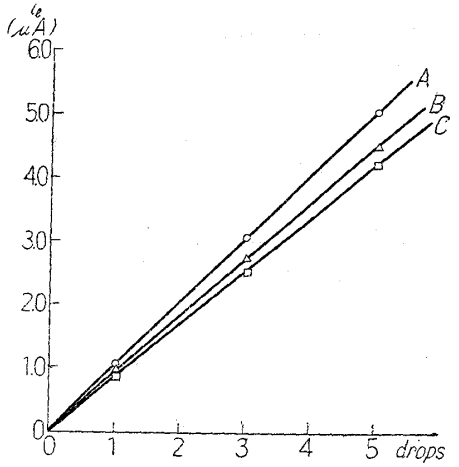
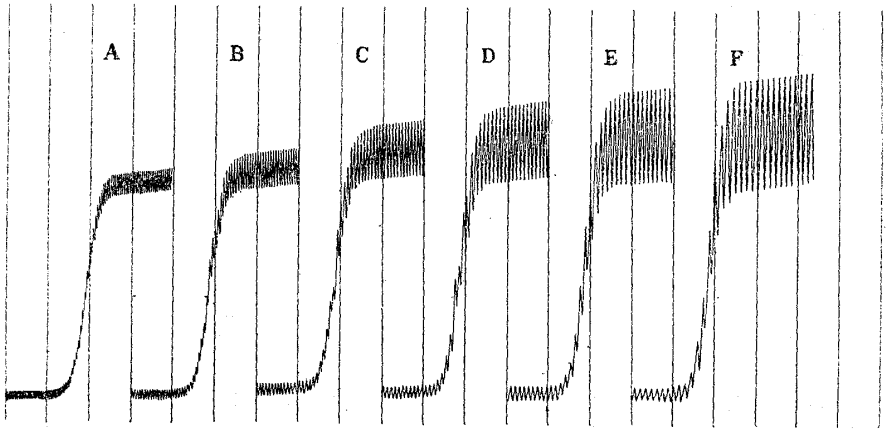


Fig. 4. i_l-Concentration Diagram

A : t=7.02 sec. (natural drop)
B : t=4.21 sec. (mechanical)
C : t=3.06 sec. (mechanical)

Figures on the abscissa : Mean drop numbers of ca. $4\times10^{-2}M/L$. $CdCl_2$ solution added to 5 cc. of 0.189 N HCl (each drop=0.03 cc.). Mercury pressure=585 mm. m=1.07 mg./sec.

Fig. 5. Polalograms obtained by varying t (The test solution is the same as in Fig. 2)



$m^{2/3}t^{1/6}$: A $\begin{cases}1.13_8\\2.89\end{cases}$ B $\begin{cases}1.19_0\\3.06\end{cases}$ C $\begin{cases}1.23_3\\3.21\end{cases}$ D $\begin{cases}1.27_2\\3.33\end{cases}$ E $\begin{cases}1.31_2\\3.41\end{cases}$ F $\begin{cases}1.35_0\\3.55\end{cases}$
i_d :

It may, therefore, be said that the limiting current is exactly diffusion controlled and the simple regulator has practical utility for polarographic purpose.

The authors wish to express their appreciation to Prof. M. Ishidate for his direction and advice. They also wish to thank Messrs. K. Tada and Y. Mashiko for kind assistance.

Experimental

Apparatus—Instruments: Polarograph improved in our Laboratory was used. The galvanometer was calibrated according to the method of Kolthoff and Lingane[4] and had the maximum sensitivity of 1.10×10^{-9} A/mm./m.

Capillary: A capillary having the constants indicated below was used.

Mercury Pressure (mm.)	m (mg./sec.)	Mercury Pressure (mm.)	m (mg./sec.)
585	1.07_1	446	0.82_1
517	0.94_6	310	0.56_1

All the m-values were measured in distilled water. The polarographic measurments were carried out at $25°\pm0.2°$.

Summary

A simple mercury drop-time regulator shown in Fig. 1 was assembled for polarographic study. It was clarified that this regulator did not disturb the diffusion layer of a cell solution and it had the practical utility for polarographic purpose.

(Received October 14, 1955)

4) Kolthoff, Lingane: "Polarography," Interscience Publishers, Inc., New York, 320(1952).