Pen Writing Polarograph with Direct Current Amplifier.

— Study of *p*-Nitrosodiethylaniline —

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Introduction

It is twenty-six years since polarography was born. There have been many studies of this subject especially in recent years as J. J. Lingane reported in Analytical Chemistry.(1), (2) Excited by the industrial use, the polarographic apparatus has gained remarkable progress and is ready for the new application. According to the progress of the apparatus, it is just now going to break new ground in polarography. The present authors feel keenly the importance of instrumentation for the above-mentioned considerations.

One of the eminent developments is the invention of a pen-writing device without photographic paper. It has been studied chiefly in U. S. A.,(1), (2) but to our disappointment, the structure of those devices has not been described in full.

Two of the present authors—S. Kikuchi and Y. Sakaguchi—employed the direct current amplifier and its recorder for silver potentiometric studies of photographic fog inhibitors,(3), (4), (5) while S. Kikuchi and K. Honda were studying the polarography for the research of the electrolytic preparation of diethylparamine from *p*-nitrosodiethylaniline.(6) The former is known as the developer of color photography.

Here we have combined both techniques, and have obtained excellent polarograms. We have compared the polarograms of *p*-nitrosodiethylaniline obtained with this recorder and those of ordinary photographic apparatus. We should like to report as follows, because we had satisfying results. We wish to write at this opportunity that the second and more improved apparatus is being made now.

Instrumentation

Direct Current Amplifier for Polarograph.—There are two systems which record the small potential difference, as a rule. The one is the recording potentiometer system, and the representative is Sargent visual recording polarograph(1) with Brown Electronik potentiometer recorder. The merits of this system are to keep good equilibrium notwithstanding the variation of voltage of alternating lines and to record with rectangular coordinates in a chart and so to have good reliance. On the other hand its defects are that half-period of the potentiometer is too long as it needs several seconds to cover all the range and the price is considerably expensive—this is an important problem in Japan.

The other is the direct current amplifier and recorder system and the representative is Polaro Analyzer(1) of Rutherford Instrument Co. The merit of this system is that half-period of recorder is within one second. This allows us to use it not only in the industial application, but also for theoretical studies. Among other instruments, this is very cheap, the predominant merit for us. The defects of this system are the use of the direct current amplifier for this purpose is very difficult, and especially difficult, in Japan, because of the bad quality of the electric line in Japan, and that it records with curved coordinates. Considering all these conditions, we adopted the latter.

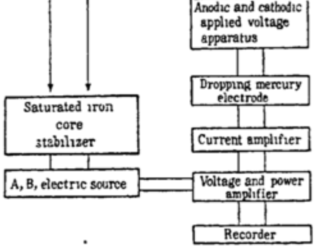

Fig. 1.—Block diagram of pen-writing polarograph with direct current amplifier.

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(1) J. J. Lingane, *Anal. Chem.* **21**, 45 (1949).

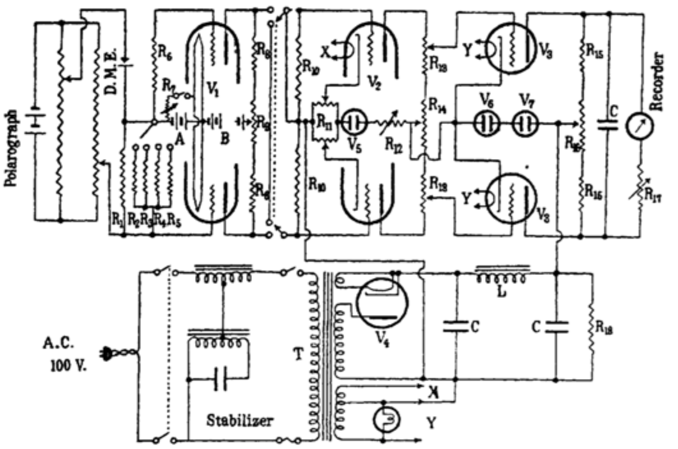
(2) J. J. Lingane, *ibid*, **23**, 86 (1951).

(3) S. Kikuchi and Y. Sakaguchi, *J. Soc. Sci. Phot. Japan*, **12**, No. 4, 3 (1950).

(4) S, Kikuchi & Y. Sakaguchi, *ibid*., **13**, No. 4, 6 (1951).

(5) S. Kikuchi & Y. Sakaguchi, "Seisan Kenkyu" published by Tokyo Univ. **3**, No. 4, 161, (1951).

(6) S. Kikuchi and K. Honda, *ibid*., **2**, No. 6, 267 (1950).



R_1	1	MΩ	R_{13}	50	KΩ V. R.	V_5	VRA 60/80
R_2	1.5	KΩ	R_{14}	20	KΩ V. R.	V_6	VRB 135/60
R_3	2	KΩ	R_{15}	10	KΩ	V_7	VRA 140/50
R_4	3	KΩ	R_{16}	2	KΩ V. R.	A	two of 1.5 volts dry battery (special unit one)
R_5	5	KΩ	R_{17}	5	KΩ V. R.		
R_6	3	KΩ	R_{18}	1	MΩ	B	67.5 v. piled dry battery
R_7	10	Ω variable resistor	C	4	μF oil filled condenser		
R_8	30	KΩ	L	10	H 80 mA.	T	secondary 350 v. 70 mA. 6.3 v. × 2 5 v. for 40 watts
R_9	5	KΩ V. R.	V_1	UZ30MC			
R_{10}	3	MΩ	V_2	US6SL7GT			
R_{11}	100	Ω V. R.	V_3	UY76		D. M. E.	dropping mercury electrode
R_{12}	600	Ω V. R.	V_4	KX80HK			

Every resistors are for 1 watt.

Fig. 2.—Circuit of the amplifier.

Then the amplifier is the main point of this report. The mechanism of this system is shown in Fig. 1 as the block diagram.

When the polarographic current I flows on the resistance R—1.5 KΩ∼5 KΩ, the potential drop is IR which is amplified so as one can get the polarograms on the recording milliammeter. Suitable voltage amplification degree and power amplification degree to drive the recorder are possessive functions of course. The circuit of this amplifier is shown in Fig. 2.

Balanced type UZ 30 MC preamplifier with dry batteries was made to recover the shortage of amplification degree of main amplifier which had been made to potentiometric titrations. Its voltage gain was about 6 times. The main amplifier based on the balanced bridge of 6SL7GT and two of UY76 was a eliminator system and its voltage gain was about forty times, in other words it needed 400 mv. for a full swing of the recorder.

Stability of the amplifier was obtained by the next three methods. The first was the customary saturated iron core type stabilizer; the second was "μ balanced circuit"⑺ which was composed of R_{11}, V_5, and R_{12} in 6SL7GT's circuit; the third was stabilo-volt tubes of V_6 and V_7 in UY 76's circuit. The "μ balanced circuit" is as follows,

$$\mu = (-\mathrm{d}E_p/\mathrm{d}E_g)_{I_p}$$

where, μ is amplification factor, I_p is plate current E_p is plate voltage, and E_g is grid voltage. Controlling that $-\mathrm{d}E_p/\mathrm{d}E_g$ is equal to μ of the tube, one gets the constancy of plate current. It is that $1/\mu$ of $\mathrm{d}E_p$ is negatively fed back to the grid. The stabilo-volt tube is used for taking formulated ratio. If it is fed back to slightly excess, it is possible for one to avoid the variation of emission of

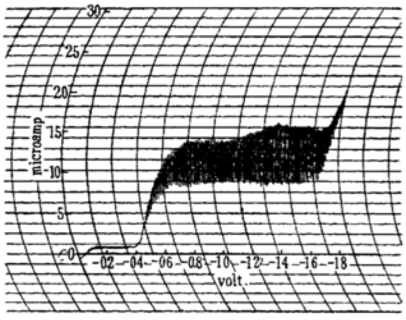


Fig. 3.—Micro-ampere and voltage graduation of the co-ordinates with the example of the polarogram by the amplifying method.

⑺ G. P. Harnwell and S. N. Van Voorhis, *Rev. Sci. Instruments*, **5**, 244 (1934).

filament. Thus, the movement of zero-point of this direct current amplifier was within 1% between 90 and 110 volts of alternating lines.

Having combined pre-amplifier, main amplifier, and recorder, the micro-ampere and voltage graduation was shown in Fig. 3 where in-put resistance was 2KΩ.

Its stability was a function of A dry battery, which was able to be employed about five hours. The movement of zero-point was 3% of full range in fifteen minutes. B battery was not changed. The total error of this recording system was within 5%. The amplification degree was adjusted by R_2, R_3, R_4, R_5, and R_{17}: and zero-point was adjusted by R_9 and R_{14} roughly, and by R_{16} finely. The main amplifier was originally a voltage amplifier, then the potential difference of anode pool electrode *vs.* calomel electrode was recorded with this amplifier. The graduation in the chart on this case was as shown in Fig. 4.

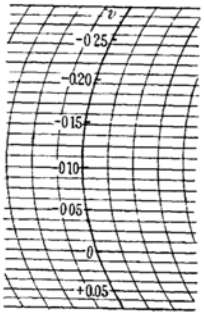


Fig. 4.—Voltage graduation of the anode potential *vs.* S. C. E.

There were four combinations of electric source, stabilizer, and main amplifier. Only one or two of them were suitable for good recording; then the combination was changed occasionally by inspection. The apparatus was not electrically grounded.

Recorder.—It was a direct current 2 milliamp. recorder and its inside resistance was 6000 Ω and its half-period was within one second. It had twelve chart speeds, but we used usually that of 20 mm./min. The effective width of the chart was twelve cm. and its length was 20 m., and it was moved with a clock. This recorder was made by Yokogawa Electric Works, Japan, in 1951.

Experimental

As described before, *p*-nitrosodiethylaniline was studied polarographically, using both our new pen-writing apparatus and ordinary photographic apparatus. The aim is to test the faculty of this new apparatus by comparing the data gained from both apparatuses and so to contribute to the study of electrolytic reduction of *p*-nitrosodiethylaniline.

(a) **Preparation.**—*p*-Nitrosodiethylaniline investigated here, was synthetized from diethylaniline and sodium nitrite,(8) and further recrystallized twice as dark green needles from methanol. Its m. p. was 84.5~85°C. This compound was dissolved in ethanol to the concentration of $5\cdot10^{-3}$ mol/l. as the stock solution. On the other hand, Sφrensen's citrate-HCl, citrate-NaOH, borate-HCl, and borate-NaOH buffer solutions were prepared, which, were added to the stock solution with the ratio of 4:1~40:1 to make up the proper concentration of test solution. The electrolysis was carried out with the anode of mercury pool at the constant temperature of 20°C. in the liquid paraffin bath. The potential of the anode was measured with potentiometer or amplifying recorder referring to the saturated KCl calomel electrode after each electrolysis. The drop time of capillary was 5.7 sec. per drop and the value of $m^{2/3}t^{1/6}$ was found to be 1.8 $\text{mg.}^{2/3}\,\text{sec.}^{-1/2}$ in water with no applied potential. To remove oxygen from the solution, nitrogen was bubbled. As for the photographic polarograms, they were recorded using Yanagimoto's pre-war type polarograph.

(b) **Results.**—*p*-Nitrosodiethylaniline gives only one typical reduction wave and its limiting current is very clear. The values of the half-wave potentials of this in buffered ethanol solution *vs.* various *p*H values, and also the values of the wave heights in the same solution at the concentration of 10^{-3} *M.*/l., are tabulated in Table 1. In this table, the half-wave potentials obtained by amplifying method which adopts the inserted resistance of 2 KΩ, and those of photographic are compared. The wave-heights in the table are measured from the polarograms by the former.

Table 1

Comparison of Half-wave Potential *vs.* *p*H by Both Methods. Concentration of the sample is 10^{-3} *M.*/l.

*p*H	$E_{1/2}$ v. (v. s. c.)		Wave height, microamp.
	pen-writing	photographic	pen-writing
1.93	+0.124		
3.36		+0.053	
4.16	−0.008	−0.031	6.9
5.98	−0.128	−0.229	6.6
7.93	−0.272	−0.287	6.0
9.91	−0.583	−0.598	6.1
11.7	−0.559		7.2

Inspecting this table, the differences between the $E_{1/2}$ of both methods are about 10 mv. with one exception. The present authors think that possible fluctuation of $E_{1/2}$ which often appears in the irreversible system of such organic compounds, can actually make this difference negligible, and consequently the potential drop by the

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(8) Kopp, *Ber.*, 8, 621 (1875).

inserted resistance which is $2 \cdot 10^3 \Omega \times 6 \cdot 10^{-6}$ amp. $=12$ mv. in this case, becomes not very important.

Now going back to the standpoint of polarographic study, it is concluded that the reduction mechanism would be the same in the whole pH range because of the similar wave form and the character of each polarogram. The half-wave potential of this compound is more positive than those of other nitro compounds and so it shows that this compound is very easily reducible. This corresponds to the results of the former investigation about electrolytic reduction.(6) Especially, in the solution of pH value 1, the reduction proceeds with no applied potential.

The relation between the $E_{1/2}$ and pH shows their complete linearity over the whole pH range with one exception which seems to be the experimental error. The increase of $E_{1/2}$ per unit pH value is about 75 mv.

The relation of concentration and wave height at the pH 9.91, in the case of using the amplifying method is shown in Table 2. It shows their linearity generally, between the range of 2.5×10^{-4} and 3×10^{-3} M./l.. From this result, it is proved that this pen-writing apparatus can be used especially for quick quantitative analysis.

Table 2

Relation between Concentration and Wave-height ($p\mathrm{H}=9.91$)

Concentration, M/l.	Wave-height, micro amp.
2.5×10^{-4}	1.88
5×10^{-4}	3.13
1×10^{-3}	6.72
2×10^{-3}	10.0
3×10^{-3}	15.6

Summary

A new type of polarographic apparatus which utilizes the amplifying method and recorder is described. And its faculty is studied by comparing it with usual photographic apparatus. At the same time, p-nitrosodiethylaniline is studied polarographically and the comparison of both apparatuses is achieved through that study.

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