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Polarography

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POLAROGRAPHY

A SPECIAL STUDIES PROJECT

for

HONORS PROGRAM

H490

Honors Paper # 77

by

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POLAROGRAPHY

During the past semester this student has studied some applications of polarography in chemical analysis for his special studies in the Honors Program.

Jaroslav Heyrovsky invented the technique of polarography about 1920 at Charles University in Prague. With proper use one can obtain both qualitative and quantitative analyses of solutions of electrooxidizable or electroreducible substances at concentrations from 10^{-6} M to 10^{-2} M.[1]

The key part of a polarograph is the dropping mercury electrode. This consists of a fine bore capillary tube connected to a large reservoir of mercury. Each tiny drop which falls from the capillary has approximately the same surface area and takes about the same time to form and fall. The greatest advantage is that each drop is actually a new electrode, and there is consequently no change in the electrode with time nor any chance of poisoning. The dropping mercury electrode is usually the cathode of the cell, and a calomel reference electrode is used for the anode. These are attached

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[1] I. M. Kolthoff and James J. Lingane, Polarography (New York: Interscience Book Company, 1952), I, p. 345.

to a slide-wire potentiometer, as in Fig. 1, so that the potential between the electrodes can be varied at will.

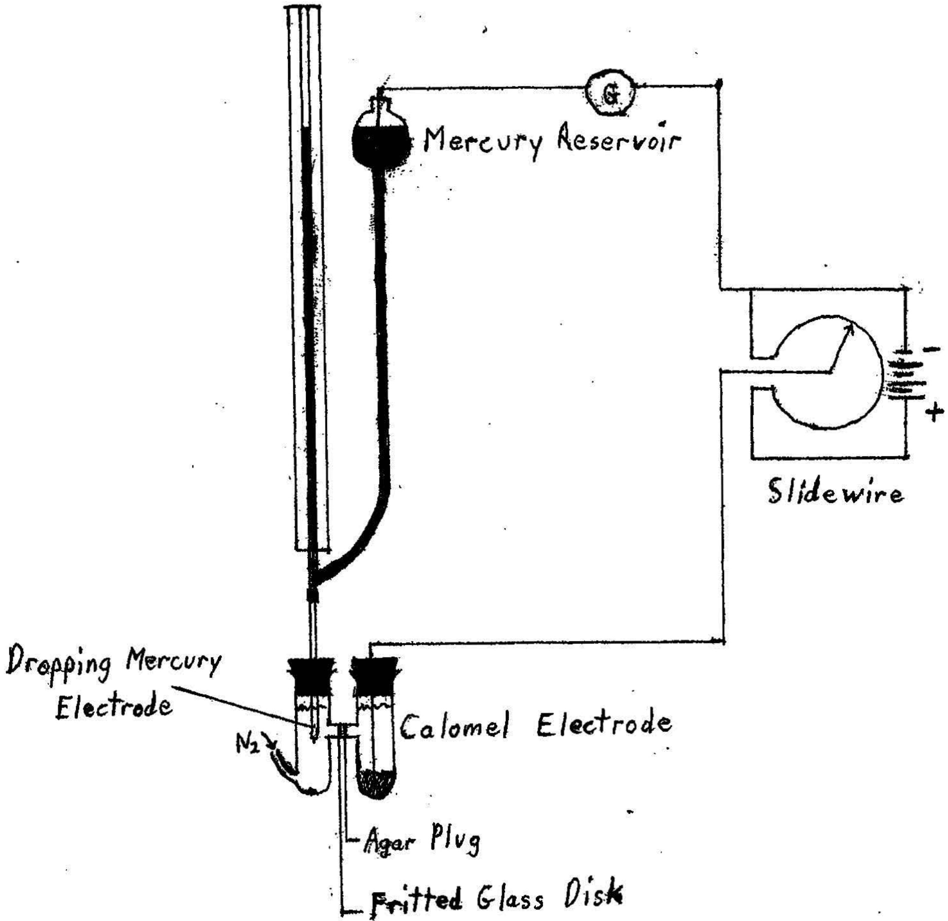

Fig. 1. Diagram of the polarograph

A substance can be reduced or oxidized only when it is brought to the electrode surface. There are three types of movement: migration, diffusion, and convection. Migration is caused by the attraction of unlike charges. The electrode sets up a potential gradient around it, and oppositely charged ions are attracted. This effect can be eliminated by adding an excess of some inert electrolyte. Convection is simply a stirring of the solution. It can be held to a minimum fairly easily. Diffusion is the movement of a substance from a region of higher concentration to one of lower concentration. As a substance is used up at the electrode surface, more will diffuse from surrounding areas. Thus the rate of reduction will be limited by the rate at which the substance can diffuse to the electrode.[2]

In polarography only the diffusion current is measured. The current is plotted against the voltage to obtain a curve. A typical curve will look something like Fig. 2. At more positive voltages, almost none of the substance is reduced, and only a small residual current is recorded. As the potential becomes more negative, the reaction rate slowly increases. At first there is only a slight increase in the current. As the negative potential increases, however, reduction takes place faster and faster; and the current soon reaches the limiting value determined by the diffusion rate.

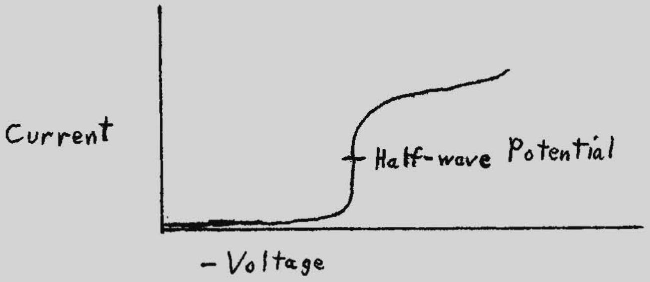

Fig. 2. Typical current-voltage curve

The potential at which the current has reached half

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[2] Charles N. Reilley and Donald T. Sawyer, Experiments for Instrumental Methods (New York: McGraw-Hill Book Company, Inc., 1961), p. 52.

this limiting value is called the half-wave potential. Each substance has a characteristic half-wave potential. Thus a qualitative determination can be made by measuring this potential and comparing it with known values.

Ilkovic developed this equation for ideal behavior:

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}$$

where i_d = average current in microamperes during the life of the drop

n = number of faradays of electricity required per mole of the reaction at the electrode

D = diffusion coefficient of the substance in the units $cm.^2/sec$

C = concentration in millimoles per liter

m = rate of flow of mercury in mg./sec

t = drop time in seconds, usually measured at the half-wave potential[3]

The current is thus directly proportional to the concentration. This fact can be used in quantitative analysis. One need only make comparisons with a solution of known concentration.

The first experiments were carried out with the manual polarograph. The following solutions were made in 0.2 M HCl:

I. 0.001 M Cd^{++}

II. 0.002 M Cd^{++}

III. 0.001 M Cd^{++} + 0.001 M Pb^{++}

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[3] Hobart H. Willard, Lynne L. Merrit Jr., and John A. Dean, *Instrumental Methods of Analysis* (New York: D. Van Nostrand Company, Inc., 1958), p. 528.

Fig. 3. Polarograms of Cadmium

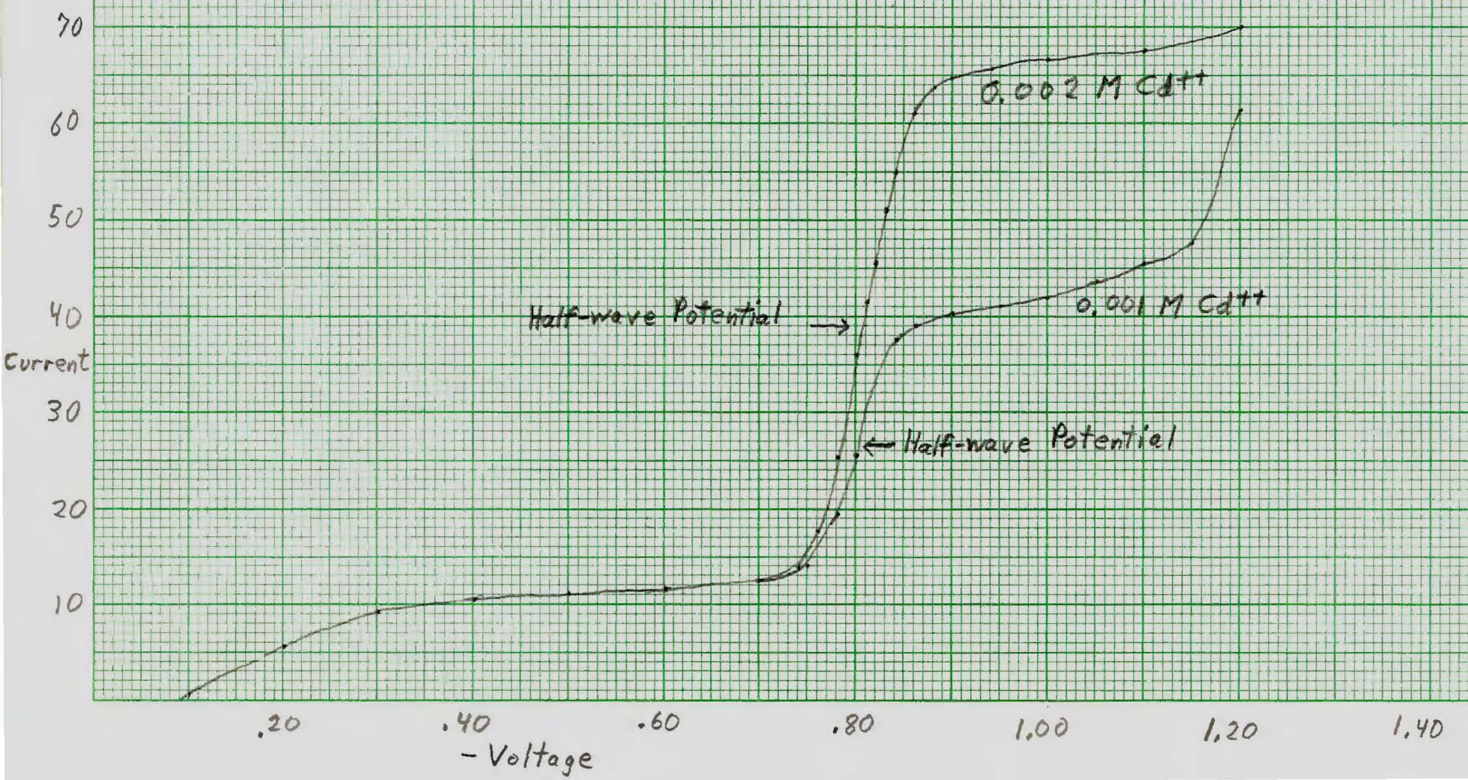
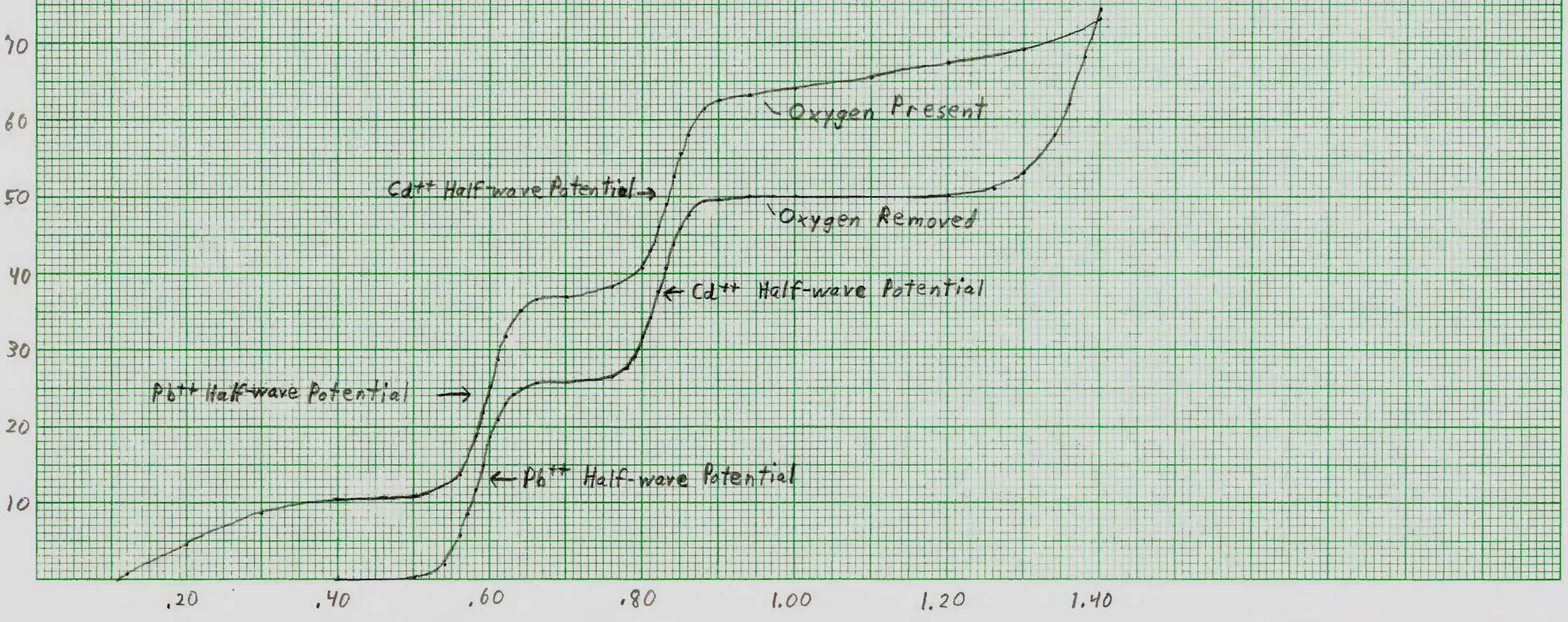


Fig. 4. Polarograms of Lead and Cadmium mixture



the cis and trans isomers of azobenzene and verify this on the recording polarograph. Studies have shown that in properly buffered solutions, the two isomers have the same half-wave potentials. However, in unbuffered solutions the trans isomer has a slightly higher half-wave potential.[4]

First 100 ml of a stock solution containing 0.4 g. of azobenzene in low boiling petroleum ether was prepared. This was left in the sunlight several days to insure an equilibrium mixture of the cis and trans isomers. Five ml of this solution was dried under reduced pressure, and the residue was dissolved in methanol. Five ml of 0.2 N NaOH was added, and the solution was diluted to 100 ml with water. This same preparation procedure was followed with later samples.

A polarogram of the standard solution is shown in Fig. 5. The cis isomer produced a sharp peak at -0.80 volts, and the trans had a half-wave potential of about -0.815 volts. Increasing amounts of Triton x-100 maximum suppressor were added in an attempt to eliminate the peak at -0.80 volts. These results are also shown on Fig. 5. The peak was reduced somewhat but not completely. It was decided to use only 3 drops, since larger amounts seemed to distort the trans curve.

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[4] Charles R. Castor and John H. Saylor, _J_. _Am_. _Chem_. _Soc_., _75_, 1428 (1953).

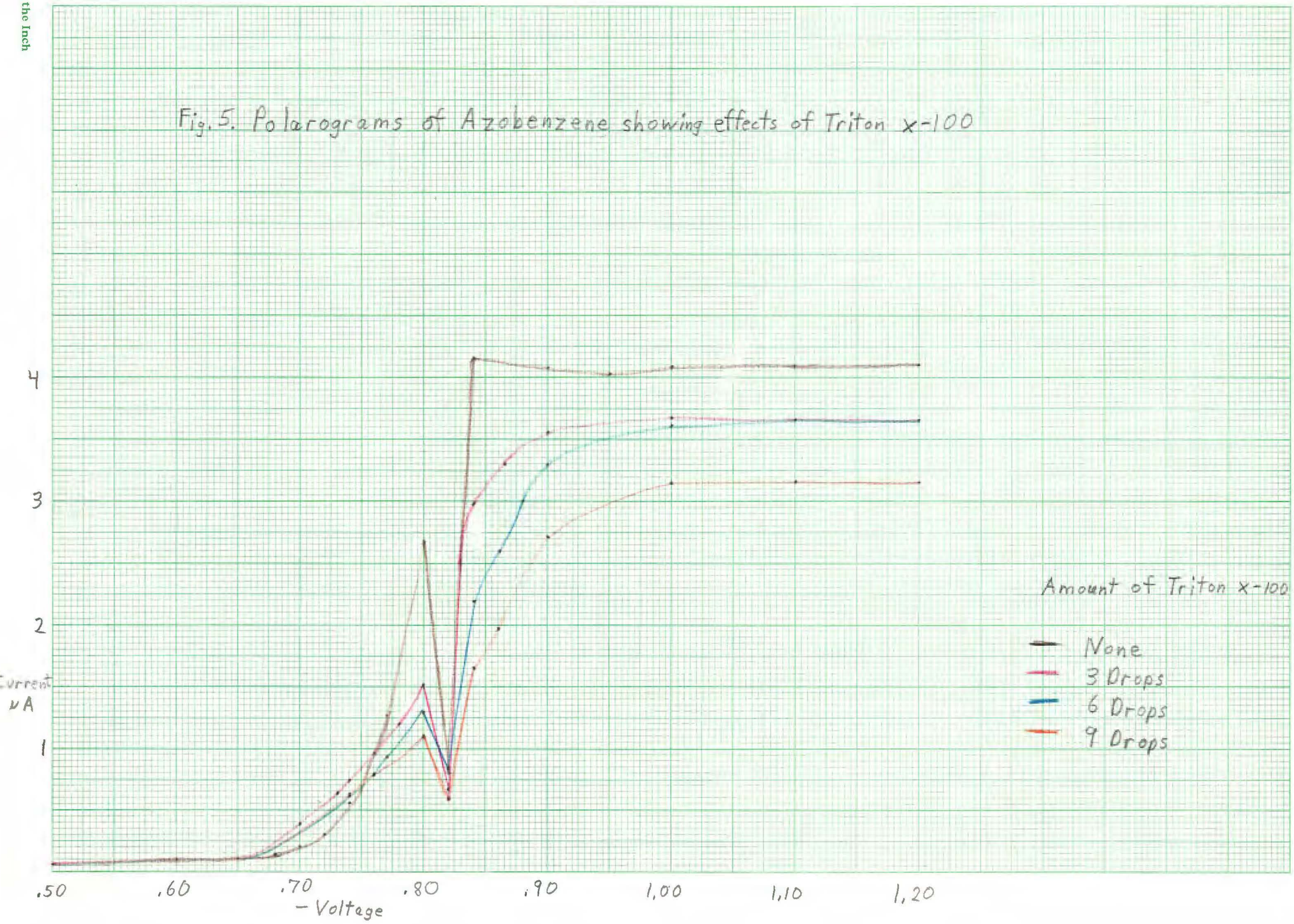


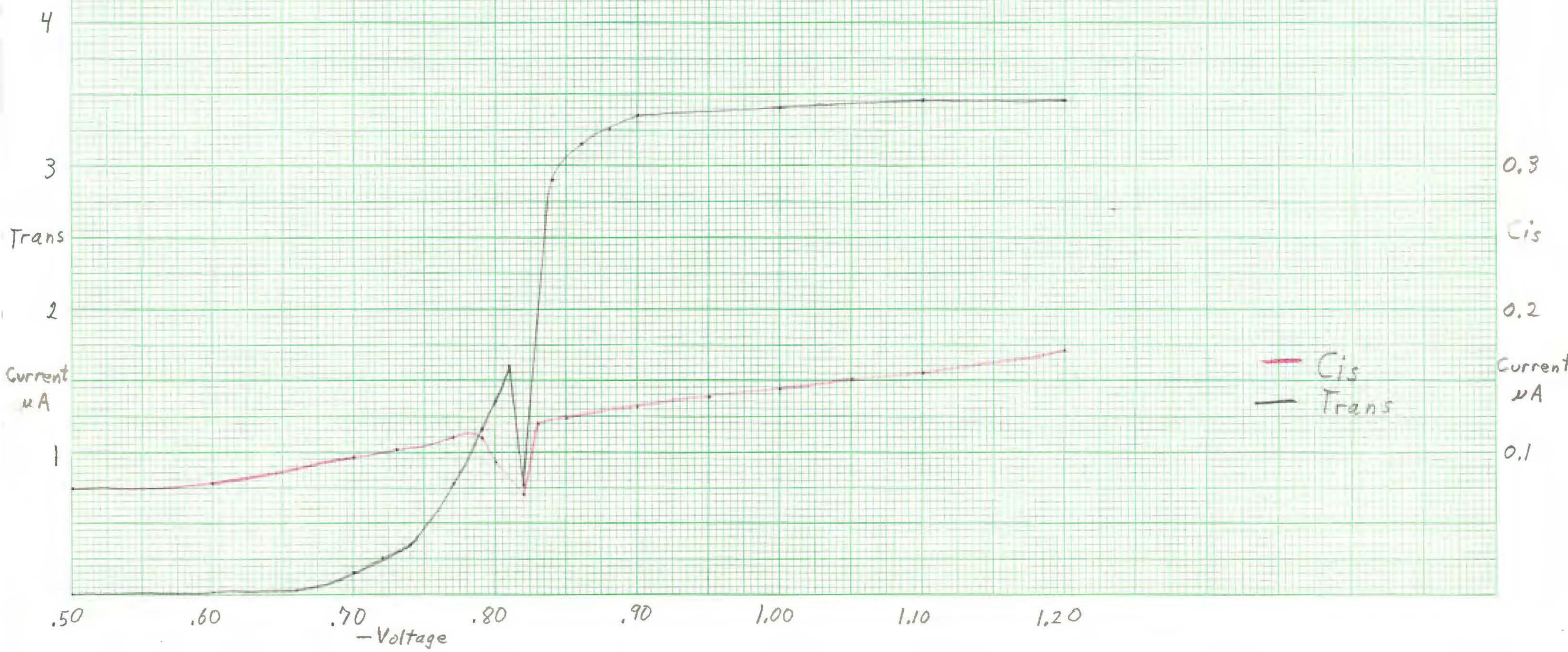
Fig. 5. Polarograms of Azobenzene showing effects of Triton x-100

Five ml of the stock azobenzene solution was placed in a 6-inch chromatographic column of alumina. The trans isomer was first passed through with petroleum ether. A mixture of methanol, ethyl ether, and petroleum ether was used to free the small amount of cis from the column. Both solutions were dried and prepared for analysis as before.

The cis and trans polarograms are shown in Fig. 6. The trans polarogram had less trans than the standard but about the same amount of cis as before. Since very little cis isomer was recovered from the column, the second polarogram was made at ten times normal sensitivity. A small amount of cis is evident as well as even less trans. These results seem to show that some of the cis was separated, but that most of it went through the column with the trans. One misleading factor may be that the polarograms were not run immediately. The dried isomers were placed in a relatively dark place for two days before being polarographed. This should have retarded change, but it may not have prevented it. Another indication that most the cis left the column with the trans is that very little cis was recovered, as noted above. To obtain a better separation, one would have to use a different packing material in the column and/or a different series of solvents.

Although his results have not been too consistent, the writer feels that he has benefited from this study.

Fig. 6. Polarograms of Cis and Trans Azobenzene



He has learned how to operate the polarograph and has gained some insight into its applications. The polarograph has already proved to be a valuable research tool for analytical chemists. New applications will quite likely be found in the not too distant future.

BIBLIOGRAPHY

Castor, Charles R., and John H. Saylor. J. Am. Chem. Soc., 1953, 75:1427-1429.

Kolthoff, I. M., and James J. Lingane. Polarography. 2 vols. New York: Interscience Book Company, 1952.

Reilley, Charles N., and Donald T. Sawyer. Experiments for Instrumental Methods. New York: McGraw-Hill Book Company, Inc., 1961.

Wawzonek, S., and J. D. Fredrickson. J. Am. Chem. Soc., 1955, 77:3985-3988.

Willard, Hobart H., Lynne L. Merrit Jr., and John A. Dean. Instrumental Methods of Analysis. New York: D. Van Nostrand Company, Inc., 1958.