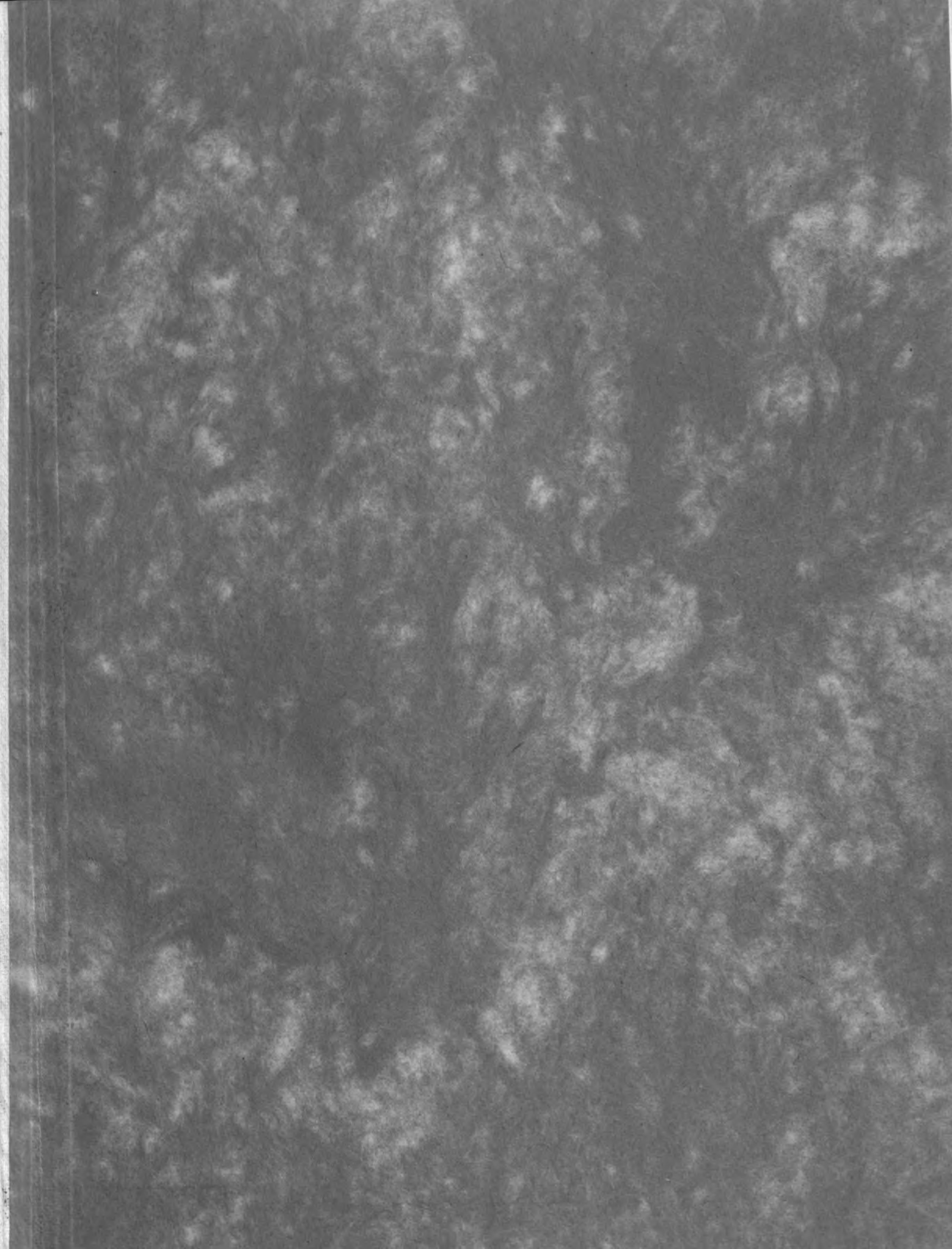
THE POTENTIOMETRIC TITRATION OF P-AMINO PHENOL, MONO METHYL P-AMINO PHENOL SULPHATE, P-PHENYLENE DIAMINE, PYROGALLIC ACID, AND GLYCIN WITH CERIC SULPHATE

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

Lawrence E. White

1939



THE POTENTIOMETRIC TITRATION OF P-AMINO PHENOL, MONO METHYL P-AMINO PHENOL SULPHATE, P-PHENYLENE DIAMINE, PYROGALLIC ACID, AND GLYCIN WITH CERIC SULPHATE.

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To

DWIGHT TARBELL EWING

Whose tactfulness in applying human psychology to difficult problems has made my search for knowledge a pleasure and not a task.

The use of cerium salts in volumetric analysis has been very extensively investigated by H.H. Willard (1) and by N.H. Furman (2). The reports of these workers as found in their publications include the study of many oxidation reduction reactions for both inorganic and organic substances. In this laboratory it has been found by Ewing and Wilson (3) that cerium in the four valent state is a satisfactory oxidant for reduced uranium solutions. The methods of using ceric sulphate and the double salt ceric ammonium sulphate as standard oxidizing agents have recently been classified under the general heading of cerate oxidimetry. The titrations are usually carried out in a sulphuric acid or hydrochloric acid medium.

This report has as its purpose the further development of the use of ceric sulphate for titrating the following substances: P-amino phenol hydrochloride, p-phenylene diamine, mono methyl p-amino phenol sulphate, pyrogallic acid, and glycin. The p-amino phenol hydrochloride was found to be oxidized in an acid solution by the ceric sulphate according to the following equation

$$2Ce(SO_4)_2 + HOC_6H_4NH_2HCl \rightarrow OC_6H_4NHHCl + Ce_2(SO_4)_3 + H_2SO_4$$

or

$$2Ce^{++++} + HOC_6H_4NH_2HCl \rightarrow OC_6H_4NHHCl + 2H + 2\,Ce^{+++}.$$

Solutions and Materials. The ceric sulphate solution used in this investigation was made up according to the method outlined by Willard and Furman (4). Ceric ammonium sulphate purchased from O.T. Coffelt was used in making the ceric sulphate solution. The ceric sulphate solution was standardized by electrometrically titrating it against hot solutions of weighed amounts of sodium oxalate (5), and was found to be exactly .0694 normal. The sodium oxalate was procured from the United States Bureau of Standards.

The p-amino phenol hydrochloride, p-phenylene diamine, mono methyl p-amino phenol sulphate, pyrogallic acid, and glycin was a commercial product of the Eastman Kodak Co.

Apparatus. The titration cell consisted of a 150 ml. beaker, a normal calomel electrode as a reference electrode, a bright platinum electrode, and a mechanical stirrer. The reagent was added to the cell by means of a carefully calibrated burette that read to one tenth of a ml.

The e.m.f. of the titration cell was determined by a Leeds and Northrup student type potentiometer that read to one-half a millivolt.

Experimental Procedure.

A. The titration of p-amino phenol hydrochloride.

A 0. 1200 g. sample of p-amino phenol hydrochloride was accurately weighed and dissolved in 50 ml. of water or dilute sulphuric acid solution and was then titrated immediately with the ceric sulphate solution. The procedure used in titrating the p-amino phenol solution was similar to that used in any other potentiometric titration. The ceric sulphate solution was added rapidly at first and as the end point was approached the solution was added more slowly. After each addition of ceric sulphate time was allowed for the system to come to equilibrium before a reading was made upon the potentiometer. The results of six consecutive titrations are given in table one.

TABLE ONE

Titration No.	Wt. of p-amino phenol	Ml. H_2SO_4 Sp. Gr. 1.83	Ml. of $Ce(SO_4)_2$ (.0694N)	Eq. Wt. of p-amino phenol (from data)	Valence change of p-amino phenol
1.	.1200	5	23.78	72.72	2.001
2.	.1200	5	23.80	72.68	2.002
3.	.1200	5	23.79	72.68	2.002
4.	.1200	0	23.81	72.64	2.003
5.	.1200	0	23.78	72.72	2.001
6.	.1200	0	23.80	72.68	2.002

(Volume of solution at the beginning of titration 50 ml.)

In table two the results of the voltage readings of the titration cell are given for a typical titration of .1200 g. of p-amino phenol with the .0694 N ceric sulphate. The results are also given in graphical form in graph I.

TABLE TWO.

Ml. of $Ce(SO_4)_2$	0	20	23	23.5	23.7	23.75	23.80	26
Voltage	.320	.481	.516	.524	.540	.550	.803	.950

(The volume of the p-amino phenol hydrochloride solution at the beginning of the titration was 50 ml. and it contained 5 ml. of sulphuric acid Sp. Gr. 1.83.)

The Reverse Titration. In addition to the above procedure reverse titrations were made as follows: A weighed amount of p-amino phenol hydrochloride was dissolved in boiled distilled water and carefully made up to 250 ml. in a volumetric flask. This solution was then used in titrating a definite volume of standard ceric sulphate solution. Table 3 gives the results of titration where a definite amount of ceric sulphate was titrated with p-amino phenol hydrochloride solutions.

TABLE 3

Titration No.	P-amino phenol hydrochloride ml.	P-amino phenol hydrochloride g/l. of sol.	$Ce(SO_4)_2$ ml.	Eq. Wt of p-amino phenol hydrochloride	Valence change
1	20.95	6	25	72.46	2.009
2	20.97	6	25	72.55	2.005
3	10.50	12	25	72.63	2.003
4	10.48	12	25	72.50	2.007
5	7.00	18	25	72.63	2.003
6	7.00	18	25	72.63	2.003

(The volume of the solution in titrating beaker at the beginning of titration 50 ml.)

The results of a typical titration of 25 ml. of standard ceric sulphate solution with a solution containing 6 g. of p-amino phenol hydrochloride per liter is given in table 4 and are given graphically in graph 2.

TABLE 4

Ml. of p-amino phenol hydrochloride	0	15	20	20.5	20.8	20.9	20.95	22
Voltage	1.199	1.091	1.032	1.023	1.002	.988	.549	.446

The titration beaker contained 25 ml. of $Ce(SO_4)_2$ and 25 ml. of H_2O at the beginning of the titration.

The Use of Diphenyl Amine Sodium Sulphonate Indicator.

A .01 molar solution of diphenyl amine sodium sulphonate was prepared according to a method outlined by Ralph E.

Oesper (6), ("Newer Methods of Volumetric Analysis." D. Van Nostrand Co. Inc., 1938, p. 33). A solution of p-amino phenol was prepared in a manner similar to that used in the electro-metric titration using 1.5 g. of p-amino phenol hydrochloride in 250 ml. of solution. This was titrated against 25 ml. of standard ceric sulphate to which 2 drops of the dyphenyl amine sodium sulphanate had been added as an internal indicator. The reverse titration was also made using 25 ml. of p-amino phenol hydrochloride solution with 2 drops of the diphenyl amine sodium sulphanate indicator and the ceric sulphate was used as the reagent. The results of these titrations are given in table five.

TABLE 5(a)

$Ce(SO_4)_2$ ml.	P-amino phenol hydrochloride ml.	P-amino phenol hydrochloride theoretical
25	21.1	21.03
25	21.07	21.03
25	21.1	21.03

5(b)

P-amino phenol hydrochloride ml.	$Ce(SO_4)_2$ ml.	$Ce(SO_4)_2$ theoretical
25	29.75	29.72
25	29.77	29.72
25	29.77	29.72

Experimental Procedure.

B. The titration of p-phenyene diamine, mono methyl p-amino phenol sulphate, pyrogallic acid, and glycin.

These substances are classified together in this report because of the similarity in the method of procedure. A weighed amount of each substance was dissolved in boiled distilled water and carefully made up to 250 ml. In the particular case of glycin 5 ml. of sulphuric acid Sp. Gr. 1.83 was added before making up to volume in order to increase the solubility of the glycin. The solutions were made up one at a time and immediately after one was made up it was titrated against a definite volume of standard ceric sulphate solution. At least three titrations were made with each concentration of solution and the individual titrations checked with each other within .05 ml. in each case. Three different concentrations of

reagents were used. The results of these titrations are given in table 6. The results in each case are the average of three titrations.

TABLE 6

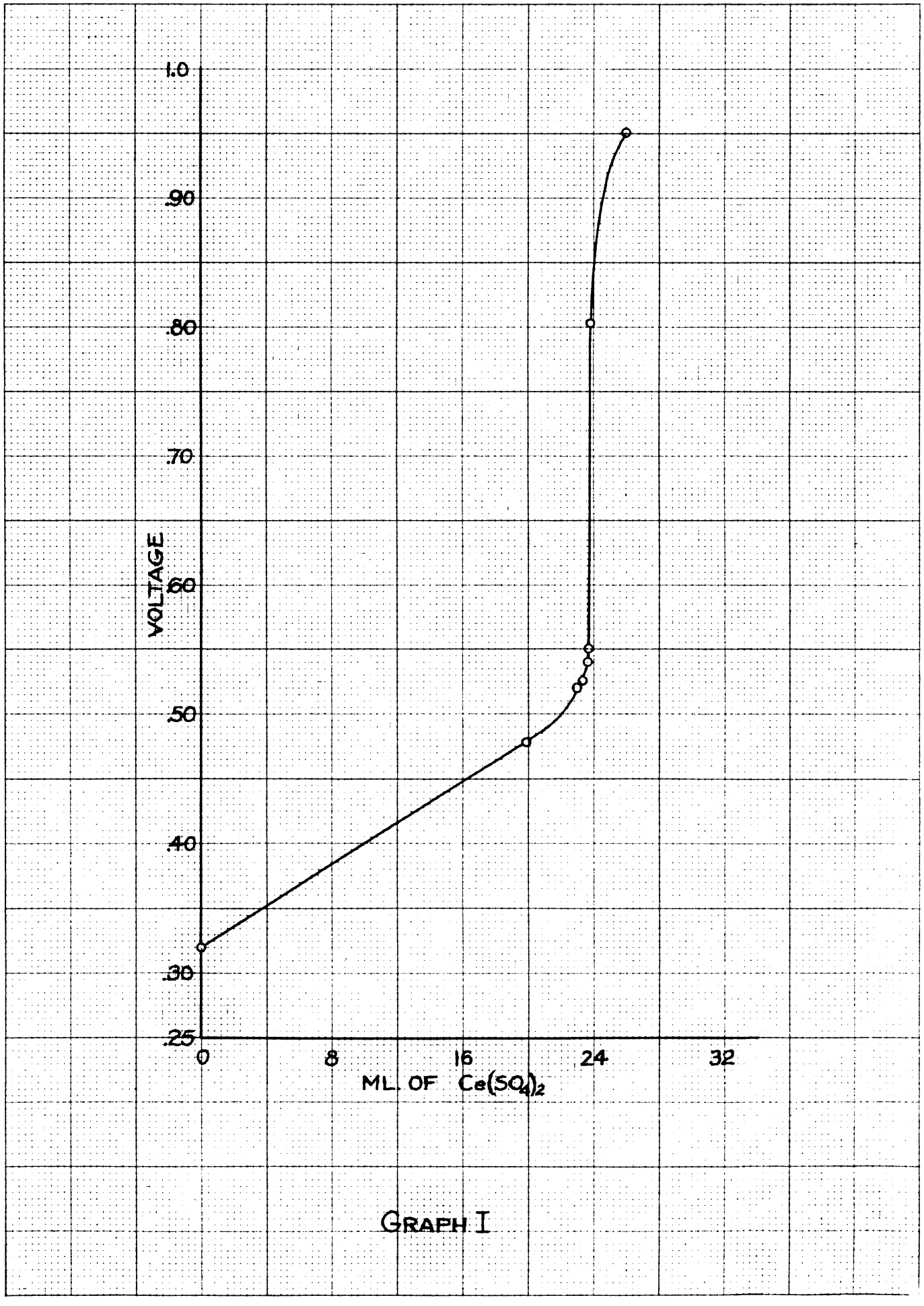
Reagent	Reagent g/250 ml. (a)	Reagent ml. (b)	$Ce(SO_4)_2$ ml.	a.b
Mono methyl p-amino phenol sulphate	1.5	22.90	25	34.35
	3.0	11.45	25	34.35
	4.5	7.65	25	34.42
Pyrogallic acid.	.5	19.80	25	9.90
	1.0	9.92	25	9.92
	1.5	6.62	25	9.93
P-phenylene diamine	1.5	27.62	25	41.43
	3.0	13.80	25	41.40
	4.5	9.20	25	41.40
Glycin	1.0	15.95	25	15.95
	1.5	10.62	25	15.93
	3.0	5.33	25	15.99

In table 7 the results of the voltage reading of the titration cell are given for typical titrations of the above substances containing 1.5 g/250 ml. of material and titrated against 25 ml. of .0694N ceric sulphate

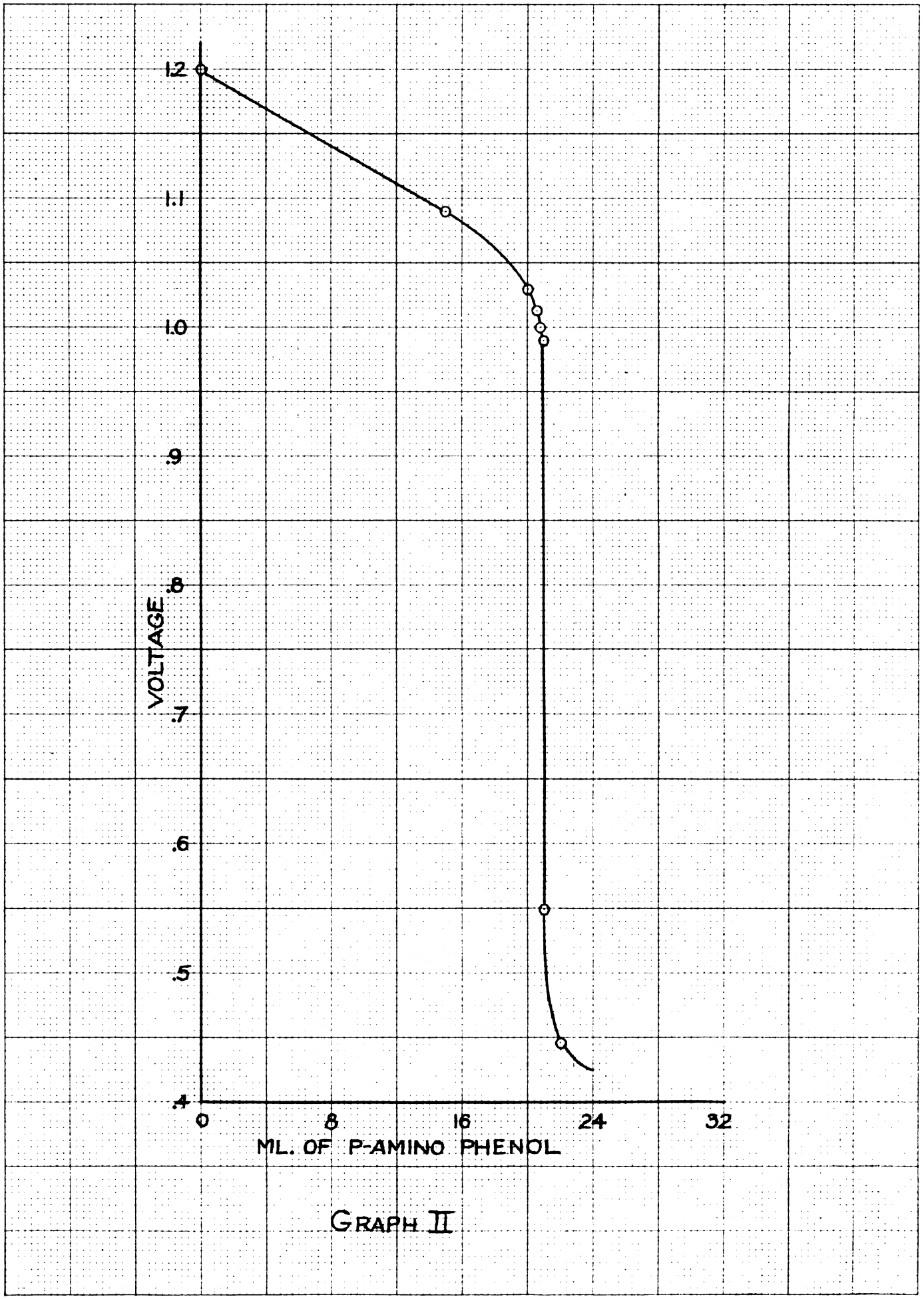
solution in 25 ml. of water. These results are also given in graphical form. Graph 3 is the titration curve obtained from titrating 25 ml. of ceric sulphate with p-phenylene diamine solution containing 1.5g/250 ml. of p-phenylene diamine; graph 4 is the titration curve obtained under similar conditions with mono methyl p-amino phenol sulphate; graph 5 is the titration curve obtained with pyrogallic acid; and lastly graph 6 is the titration curve obtained with glycin.

TABLE 7

Ml of p-phenylene diamine	0	20	27	27.5	27.58	27.62	30
Voltage	1.201	1.084	1.021	.993	.974	.502	.430
Ml. of mono methyl p-amino phenol sulphate	0	20	22.5	22.8	22.85	22.90	25
Voltage	1.203	1.075	1.044	1.031	.993	.494	.435
Ml. of pyrogallic acid	0	6	6.5	6.58	6.62	7	10
Voltage	1.097	1.080	1.045	1.005	.257	.244	.220
Ml. of glycin	0	5	10	10.5	10.57	10.62	12
Voltage	1.095	1.077	1.034	1.008	.985	.453	.408



GRAPH I



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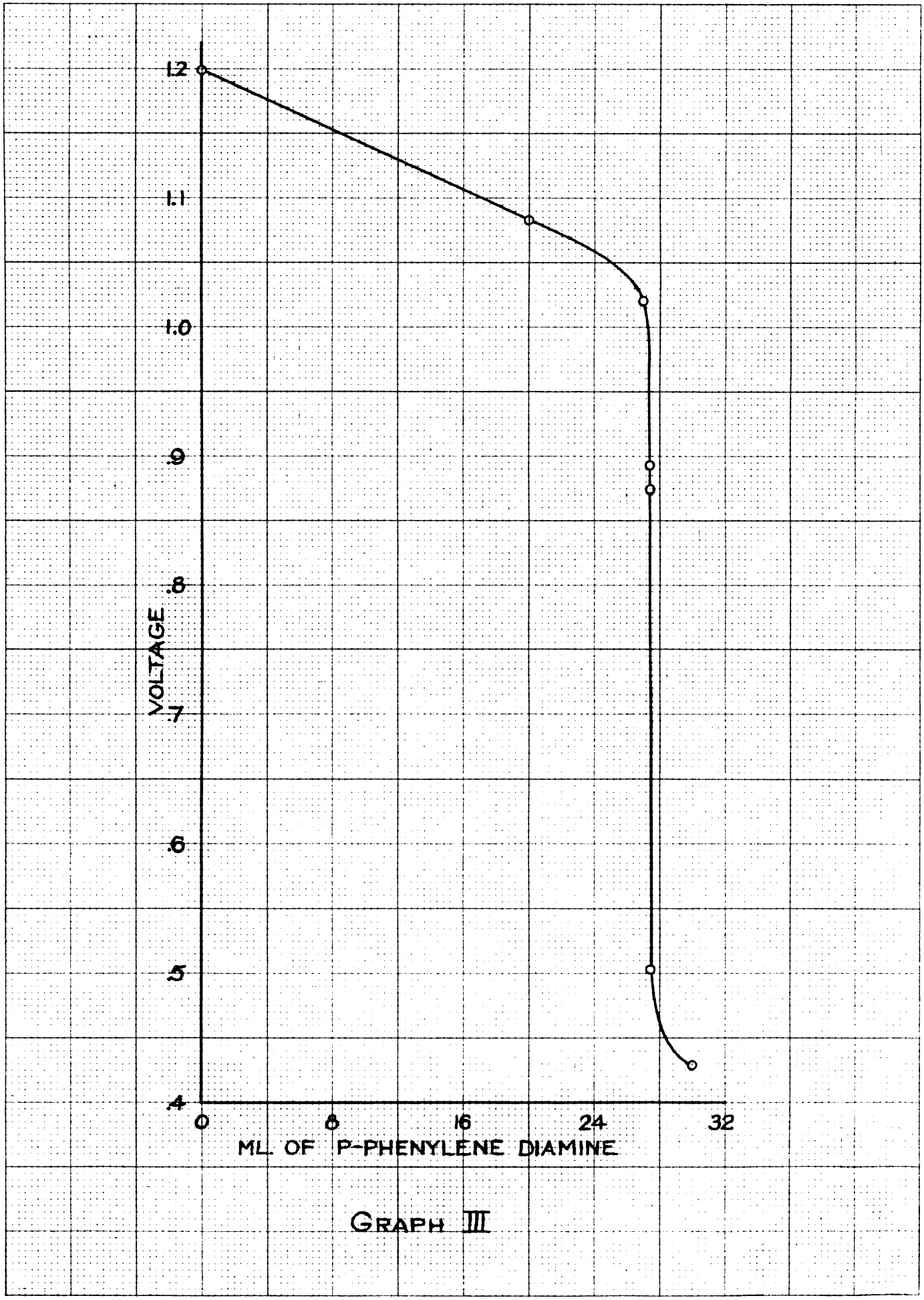

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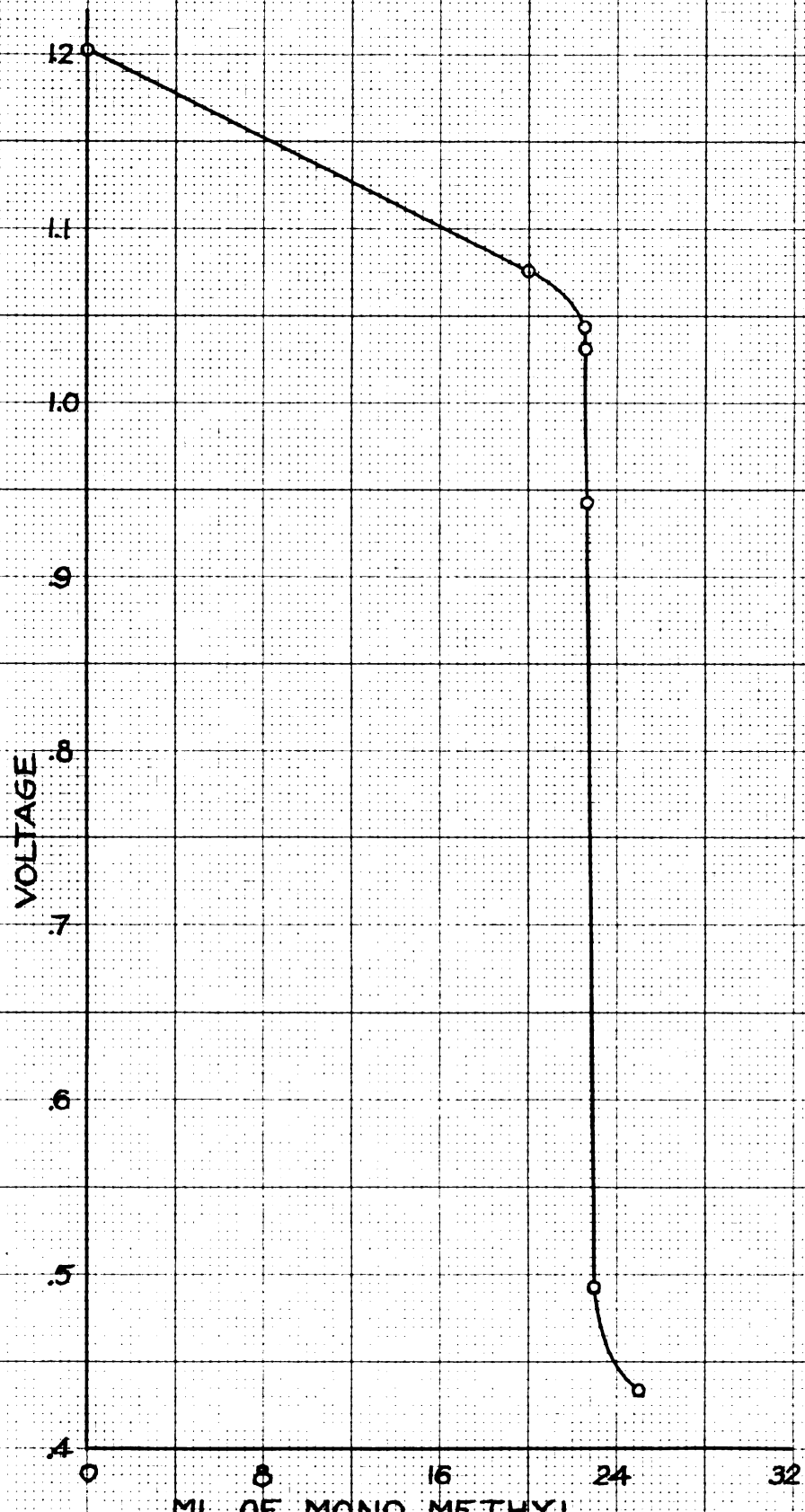

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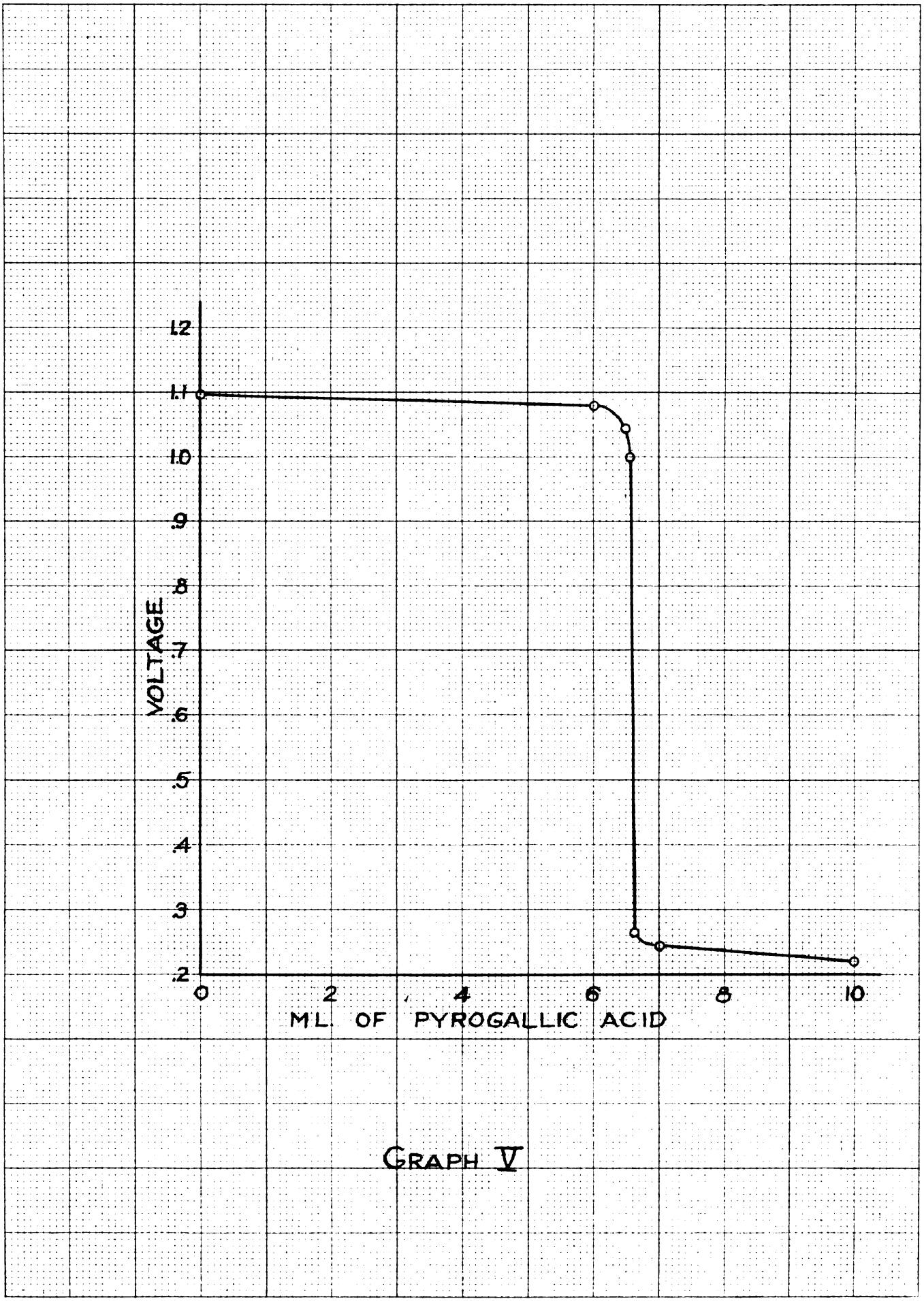
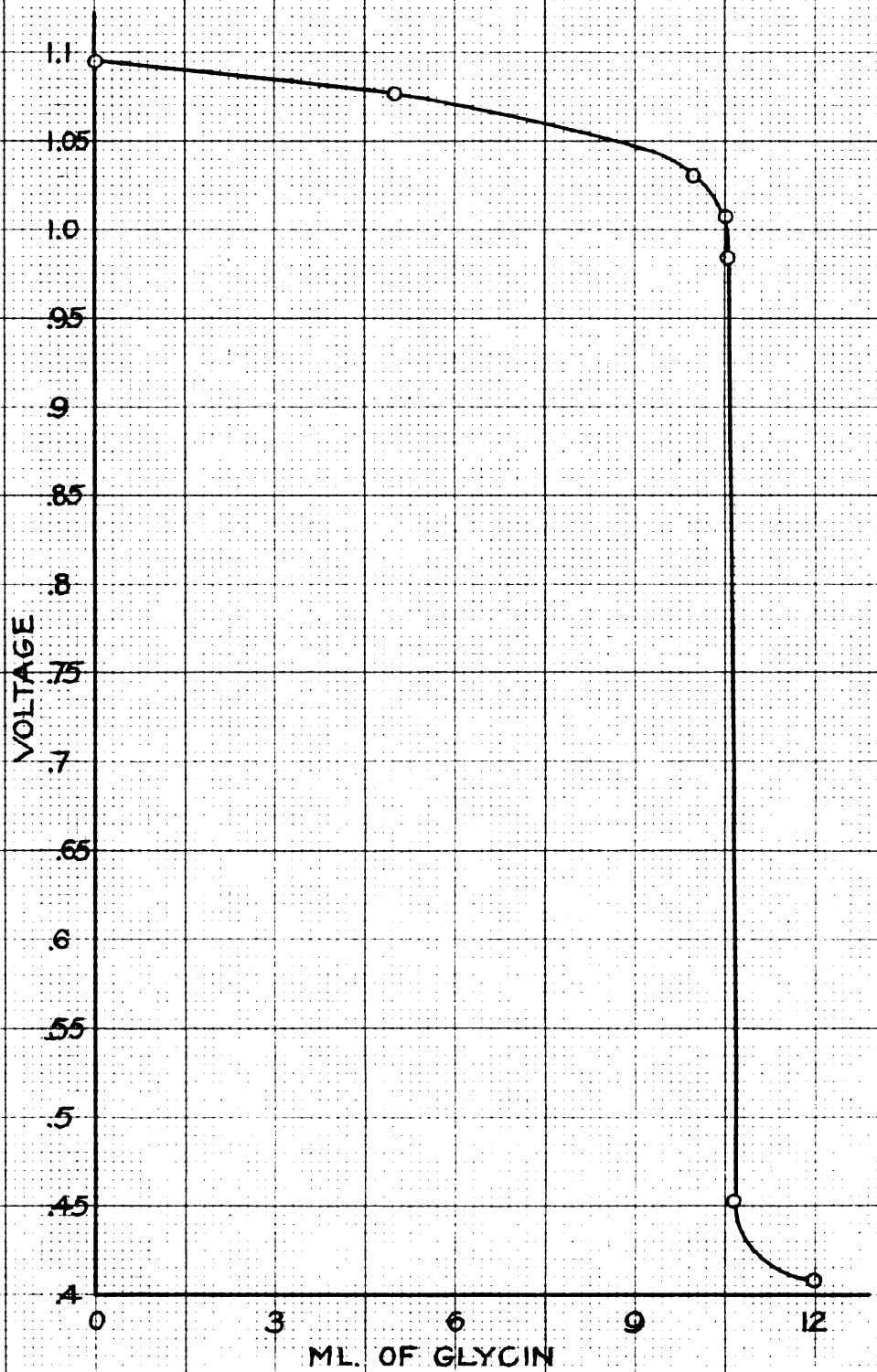


GRAPH V



GRAPH VI

Discussion of Results: In the case of the titration of p-amino phenol hydrochloride with ceric sulphate the initial E.M.F. of the p-amino phenol hydrochloride was between 250 and 300 millivolts. This was gradually increased to 500 millivolts as the ceric sulphate was added, then a jump of 400 millivolts was caused by the addition of a single drop of the reagent ceric sulphate. The potential after each addition of reagent came to equilibrium quickly and there was a good warning of the end point.

The break in potential at the end point was decreased 50 millivolts by the addition of 5 ml. of sulphuric acid Sp. Gr. 1.83. This is in agreement with the theory advanced by G. Frederick Smith and C.A. Getz (7), which states that ceric sulphate becomes a weaker oxidizing agent as the sulphuric acid concentration is increased. If more than 5 ml. of sulphuric was per 50 ml. of solution the end point was hard to distinguish. The break in potential was decreased and there was also a tendency for the potential to drift near the end point.

The p-amino phenol hydrochloride solution at the beginning of the titration was colorless. The color of the solution at the end point was light yellow due to

the oxidized p-amino phenol solution and was not due to the yellow color of the ceric sulphate solution entirely. The color at the end point was not very deep and caused no interference with the color change of the indicator.

The diphenyl amine sodium sulphate indicator changed color when approximately .05 ml. more of the reagent was used than the calculated theoretical amount. This is the amount of the reagent necessary to cause the indicator to change color. The color change of the indicator was easily distinguishable in the light yellow color of the solution.

As the curves indicate all of the titrations of ceric sulphate with p-phenylene diamine, mono methyl p-amino phenol sulphate, pyrogallic acid, and glycin are similar. There was a good break in potential at the end point of the reaction in each case. The pyrogallic acid gave the largest jump in potential of any of the substances titrated, being approximately .750 millivolts when .05 ml. of the reagent was added at the end point. The glycin gave the smallest break in potential, giving a break of .450 millivolts for .05 ml. of glycin at the end point. This is sufficient to distinguish the end point and a good curve is produced by this titration. A good warning

was given of the end points in every case.

Of the substances titrated against ceric sulphate in this report the p-amino phenol hydrochloride and the mono methyl p-amino phenol sulphate came to equilibrium faster than the other three substances p-phenylene, pyrogallic acid, and glycin.

An attempt was made to titrate ceric sulphate with pyrocatechin and chlorohydroquinone electrometrically but the voltage of the titration cell came to equilibrium so slowly that it was impossible to make these titrations.

Summary. (1) P-amino phenol hydrochloride is oxidized quantitatively by a solution of ceric sulphate.
(2) When p-amino phenol is oxidized by ceric sulphate the valence change of the p-amino phenol is 2.
(3) A good indicator for determining the end point of the reaction between p-amino phenol and ceric sulphate is diphenyl amine sodium sulphonate.
(4) The concentration of a solution of p-phenylene diamine, mono methyl p-amino phenol sulphate, pyrogallic acid, or glycin may be determined by electrometrically titrating it against standard ceric sulphate solution.

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