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CO-PRECIPITATION OF MANGANESE WITH CALCIUM PHOSPHATE

A thesis, presented to the Department of
Chemistry of Union College, in partial ful-
fillment of the requirements for the Degree
of Bachelor of Science in Chemistry, by

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Approved by

J. D. Porter

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INTRODUCTION

This investigation was undertaken to study, in a preliminary way, the effect of precipitating tricalcium phosphate in the presence of manganous salts.

Certain facts in relation to manganese deficiency in the diet of fowls, giving rise to perosis, makes the problem of interest in view of the work carried out at the Agricultural Experiment Station at Colorado State College.(3). It has been known for a long time that a diet high in calcium produces perosis which can be corrected by peritoneal injection of manganese.(1). C. D. Caskey and L. C. Norris (2) have found that in the presence of large amounts of calcium and phosphate, perosis can be induced even when the manganese is considerably increased in the diet. It is known that tricalcium phosphate dissolves in the upper intestinal tract and precipitates again in the lower tract.(3). This suggests that in precipitating, the tricalcium phosphate removes the manganese either in a solid solution, in chemical combination, or by some form of co-precipitation.(4). These possibilities can be investigated by phase rule studies.(5).

Some work has been done by H. S. Wilgus and A. R. Patton (3) in vitro in the removal of manganese with tricalcium phosphate and ferric chloride solutions.

EXPERIMENTAL

The tricalcium phosphate available was a commercial product. It was thought that an analysis of this product should be carried out to be sure of its composition.

The standard procedure of removing the calcium by precipitating as calcium oxalate and then titrating with a standard solution of potassium permanganate was used.(6). In this process it was found that boiling the solution with H_2SO_4 previous to titration hastened solution, but if filter paper were used to collect the calcium oxalate, the permanganate solution apparently oxidized some of this paper at this high temperature as high results were obtained. When Gooch crucibles were substituted for filter paper, consistent results were obtained.

In determining the phosphate the filtrate from the calcium oxalate precipitation was treated with magnesia mixture and made alkaline with ammonium hydroxide solution.(7). The precipitate, $MgNH_4PO_4 \cdot 6H_2O$, was ignited in a porcelain crucible to $Mg_2P_2O_7$ and weighed as such. The results were not consistent. In the presence of the oxalate, the magnesium ammonium phosphate apparently removed a considerable amount of oxalate. The ignited precipitate had a dark gray appearance and was matted together.

In connection with the ignition of the crucibles to constant weight, an interesting experience came up. The cooling of the crucibles in the desiccator requires some time and it was thought that by setting the desiccator at an open window, the process could be hastened. The weight of the crucibles could not be made to check. Some typical results are given. The crucibles were heated over a Meeker Burner for fifteen minutes and cooled for forty-five minutes between successive weighings.

	<u>Crucible</u> <u>1</u>	<u>Crucible</u> <u>2</u>	<u>Crucible</u> <u>3</u>
Weight	20.4238 gm.	20.4232 gm.	20.4232 gm.
	20.7906 gm.	20.7897 gm.	20.7909 gm.
	20.7548 gm.	20.7905 gm.	20.7917 gm.

When the desiccator is placed in the room and the cooling period extended to one hour, successive weighings agree within .0002 - .0003 gm.

The explanation of the discrepancy in the first case is, I believe, undercooling of the crucible below the room temperature, with the result that water condenses on the crucible.

In order to be sure that the analytical procedure was reliable, it was decided to analyze a solution containing known amounts of calcium and phosphate in the same proportion as in tricalcium phosphate.

Calcium carbonate was obtained pure, as Icelandspar and a weighed amount dissolved in hydrochloric acid. A known amount of calcium could easily be obtained by measuring out a volume of this solution.

The phosphate solution was obtained by diluting phosphoric acid and was standardized as follows. A standard solution of hydrochloric acid was prepared and a solution of sodium hydroxide standardized against this. The phosphoric acid was then titrated with this sodium hydroxide solution. (7). The first hydrogen is removed at the methyl orange end point and the second at the phenolphthalein end point.

Twenty-five cubic centimeters of the calcium chloride solution containing .2967 gms. and 25 cubic centimeters of phosphoric acid solution containing .3261 gms of phosphate were mixed for analysis. The calcium was determined as previously described. The phosphate was first precipitated as ammonium phosphomolybdate (7) then redissolved and precipitated as magnesium ammonium phosphate and weighed as the pyrophosphate.

The analysis gave the following satisfactory results:

	<u>1</u>	<u>2</u>
Ca present	.2967 gm.	.2967 gm.
Ca found	.2970	.2976
PO ₄ present	.3261	.3261
PO ₄ found	.3274	.3263

The same procedure was followed in analyzing the commercial sample of tricalcium phosphate. The sample was dried at 120° centigrade for a period of three hours. The loss on ignition was also determined on the dried sample. The analysis gave the following results.

	<u>1</u>	<u>2</u>
CaO found	45.71%	45.83%
P ₂ O ₅ found	44.47%	44.30%
Loss on ignition	8.34%	8.37%
Calc. for Ca ₃ (PO ₄) ₂		
CaO	54.22%	
P ₂ O ₅	45.82%	

Evidently the commercial sample is heavily contaminated with other calcium phosphates.(9).

In order to prepare the pure tricalcium phosphate, considerable time is required (10), so we proceeded to precipitate the calcium phosphate in the presence of a manganous salt from a solution containing known amounts of calcium chloride and phosphoric acid. A solution of MnCl₂ was used as a source of manganese.

PH FOR COMPLETE PRECIPITATION OF CALCIUM PHOSPHATE

A preliminary experiment was undertaken to determine the PH at which all of the calcium was precipitated from a solution of calcium and phosphate ions.

Fifty cubic centimeters of phosphoric acid solution containing .3261 gms. of phosphate (PO₄) and 50 cubic centimeters of

calcium chloride solution containing .2967 gms. of calcium were mixed and the PH taken using the Beckman PH meter. The PH was found to be 1.12.

It might be well to point out that certain precautions are necessary in the use of the Beckman PH meter to obtain reproducible results. The calomel electrode should be made up with extreme care and only a small amount of calomel should be deposited on top of the mercury. If too large a quantity is used, the mercury and calomel will tend to mix and the readings will drift. A little practice in making up the cell and in the operation should be undertaken before attempting readings on unknown solutions. A package of Kleenex (absorbent tissue paper) affords a good neutral material to clean the electrodes after rinsing with distilled water.

The PH of the above solution was changed by the addition of tenth normal ammonium hydroxide solution and the PH was measured at intervals. A small sample of the filtrate was tested for calcium after each PH determination. A solution of ammonium oxalate was used as a test solution. The results are as follows:

PH of Solution	Ca Test	PH of Solution	Ca Test
8.73	+	8.30	+
9.10	+	9.12	+
9.32	+	9.00	+
9.48	+	9.32	+
9.28	-	9.45	-

In Table 1, the first four determinations were carried out consecutively. The solution was left standing for two days and then the PH was determined. A drop in the PH was noticed and a negative test for calcium was obtained.

In Table 2, the first two determinations were carried out consecutively. The solution was left standing for one day and

then the PH was determined. A drop in the PH was noticed and a positive test for calcium was obtained. The PH was then raised to 9.32 and a positive test was still obtained for calcium. More ammonium hydroxide was added and the solution left standing for another day. Then the PH was determined and found to be 9.45 with a negative test for calcium.

These data show the fall in PH on standing which was noticed by H.T.S. Britton.(11). They show furthermore that calcium phosphate is not at once completely precipitated even at a PH above 9.

PRECIPITATION OF MANGANOUS HYDROXIDE

An experiment was undertaken to determine the PH at which manganous hydroxide is precipitated. Fifty cubic centimeters of 0.1N (tenth normal) manganous chloride solution was titrated with 0.1N (tenth normal) ammonium hydroxide solution. The results are tabulated.

<u>CC NH₄OH</u> <u>Added</u>	<u>PH</u> <u>of Solution</u>	<u>CC NH₄OH</u> <u>Added</u>	<u>PH</u> <u>of Solution</u>
0.00	6.56	12.32	8.64
0.07	7.83	22.32	8.80
0.12	7.99	27.32	8.93
0.22	8.10	32.32	9.03
0.34	8.19	37.32	9.13
0.43	8.05*	42.32	9.22
2.32	8.30	50.00	9.40
7.32	8.51	55.00	9.43

*First turbidity appeared.

A plot of these data is given on Curve #1. It was noticed that the manganous hydroxide readily oxidized to the higher valence and became colloidal on standing ten or twelve hours.

PRECIPITATION OF MANGANOUS PHOSPHATE

Twenty-five cubic centimeters of 0.1N manganous chloride and 25 cubic centimeters of 0.1N phosphoric acid were mixed and titrated together with 0.1N ammonium hydroxide solution. The results are as follows:

Run #1

<u>CC NH₄OH Added</u>	<u>PH of Solution</u>
0.00	2.00
2.00	2.23
4.00	2.73
6.00	5.13*

*First turbidity appeared.

Run #2

<u>CC NH₄OH Added</u>	<u>PH of Solution</u>	<u>CC NH₄OH Added</u>	<u>PH of Solution</u>
0.00	1.98	8.00	4.95
2.00	2.21	10.00	4.81
4.00	2.76	12.00	5.08
4.50	3.06	14.00	5.75
5.00	3.83	20.00	8.72
5.50	4.90	25.00	9.02
6.00	5.15*	30.00	9.18

*First turbidity appeared.

These results are plotted on Curve #1.

At this point, it was thought that precipitating manganous ion with phosphate ion in the presence of ammonium hydroxide might form the manganese ammonium phosphate ($MnNH_4PO_4$). The precipitate was washed free of the filtrate containing ammonium hydroxide and tested in the usual way with sodium hydroxide for ammonia. The test was positive.

With this information in mind, a solution of 25 cubic centimeters of 0.1N manganous chloride solution and 25 cubic

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centimeters of 0.1N phosphoric acid solution were titrated with 0.1N sodium hydroxide. The results are tabulated.

<u>CC NaOH Added</u>	<u>PH of Solution</u>	<u>CC NaOH Added</u>	<u>PH of Solution</u>
0.00	1.89	23.00	5.35
3.00	2.10	25.00	5.89
6.00	2.46	27.00	6.90
9.00	4.30	29.00	9.40
11.00	5.18*	31.00	10.20
13.00	4.88	33.00	10.65
15.00	4.70	35.00	10.85
17.00	4.78	37.00	10.99
19.00	4.90	39.00	11.00
21.00	5.20		

*First turbidity appeared.

These data are plotted in Curve #2.

This curve does not differ significantly from that for the corresponding titration with NH_4OH except that the final PH is higher due to the strong base

PRECIPITATION OF CALCIUM PHOSPHATE

Twenty-five cubic centimeters of 0.1N calcium chloride solution and 25 cubic centimeters of 0.1N phosphoric acid solution were titrated together with 0.1N ammonium hydroxide solution. The original solution was made up to 300 cubic centimeters. The results follow:

<u>CC NH_4OH Added</u>	<u>PH of Solution</u>	<u>CC NH_4OH Added</u>	<u>PH of Solution</u>
0.00	1.88	28.00	4.49
1.00	1.89	30.00	5.42
2.00	1.90	32.00	5.72*
3.00	1.94	36.00	5.82
4.00	1.96	40.00	5.49
6.00	2.01	45.00	5.65
11.00	2.11	50.00	5.71
16.00	2.39	60.00	6.78
23.00	2.75	70.00	8.66

*First turbidity appeared.

These data are plotted in Curve #1.

As compared with manganese phosphate, calcium phosphate begins to precipitate at a somewhat higher PH.

PRECIPITATION OF PHOSPHATES FROM SOLUTIONS
CONTAINING CALCIUM AND MANGANESE

A solution containing calcium and bivalent manganese in the ratio of three equivalents to one was titrated with 0.1N sodium hydroxide. Twenty-five cubic centimeters of 0.1N manganous chloride, 75 cubic centimeters of 0.1N calcium chloride, and 100 cubic centimeters of 0.1N phosphoric acid were used. The data follows:

<u>CC NaOH Added</u>	<u>PH of Solution</u>	<u>CC NaOH Added</u>	<u>PH of Solution</u>
0.00	1.78	97.00	7.35
10.00	1.95	100.00	7.91
20.00	2.18	102.00	8.42
30.00	2.60	104.00	9.00
40.00	4.88	106.00	9.50
42.00	5.18*	108.00	9.90
44.50	5.28	110.00	10.22
50.00	5.38	112.00	10.42
55.00	5.46	114.00	10.58
60.00	5.53	116.00	10.65
65.00	5.66	118.00	10.76
70.00	5.75	120.00	10.85
75.00	5.92	125.00	11.00
80.00	6.09	130.00	11.11
85.00	6.32	131.00	11.11
90.00	6.62		
95.00	7.02		

*First turbidity appeared.

The data are plotted in Curve #3.

The curve shows only one break corresponding to the beginning of the precipitation of the manganese.

In the next part of our investigation, calcium phosphate is to be precipitated in the presence of manganous ion and we propose to use various ratios of manganese to calcium.

The filtrate required for manganese to determine if the manganese was removed from the solution by the calcium phosphate.

Two simple tests were available, the lead dioxide test and the sodium bismuthate test.(8). These tests simply depend on the oxidizing of the manganous ion to the permanganate. The sensitivity of the sodium bismuthate test is given as .000005 gm. in 50 cubic centimeters of solution. Chloride ion interferes with the sodium bismuthate test.

Known concentrations of manganous ion in the presence of calcium and phosphate ion were tested with lead dioxide using a blank control. The results were satisfactory.

The PH of a solution containing 25 cubic centimeters of 0.1N manganous chloride solution and 25 cubic centimeters of 0.1N phosphoric acid solution was varied by the addition of 0.1N sodium hydroxide solution. The amount of 0.1N sodium hydroxide required to bring the PH to about seven was read from graph #2.

The data follows:

<u>PH</u> <u>of Solution</u>	<u>Test for Mn</u> <u>in Filtrate</u> ⁺⁺
6.95	+
7.55	+
7.95	+
9.08	+
9.80	+
9.80	- Standing overnight

On Page 7 it was shown that manganese phosphate begins to precipitate at a PH5.1-5.2. The above data supplements the previous findings.

The PH of a solution containing calcium and manganese in the ratio of three to one of manganese was now raised using 0.1N sodium hydroxide solution. The solution contained 25 cubic centimeters of 0.1N manganous chloride solution, 75 cubic

centimeters of calcium chloride solution, and 100 cubic centimeters of 0.1N phosphoric acid solution. The lead dioxide test was used to test for manganese in the filtrate. The results are as follows:

<u>PH</u> <u>of Solution</u>	<u>Test for Mn</u> ⁺⁺ <u>in Filtrate</u>
7.12	+
7.78	+
8.18	+
8.61	+

From the above data, it can be seen that manganese is not removed completely from solution by the precipitating of calcium phosphate at a dilution of three to one.

The previous tests of the filtrates for manganese were carried out using the lead dioxide test. Since the manganese concentration was to be decreased considerably, it was thought that the sodium bismuthate test should be used to confirm the lead dioxide test. We also had in mind carrying out some quantitative determinations of manganese and it was thought that the sodium bismuthate offered the best possibilities for accuracy and speed.(7). Since the chloride ion interferes with the quantitative and qualitative test using the sodium bismuthate method, nitrate solutions were now used.

A solution of the following concentrations was made up and 10 cubic centimeters used for tests.

Mn	2.5 X10 ⁻⁶ n
Ca	2.5 X10 ⁻⁴ n
PO ₄	3 X10 ⁻⁴ n

Positive tests for Mn using the lead dioxide and sodium bismuthate tests were obtained.

Solutions containing a greater ratio of calcium to manganese were now prepared.

Twenty-five cubic centimeters of 0.1N calcium nitrate solution, 30 cubic centimeters of 0.1N phosphoric acid, and 2.7 cubic centimeters of 0.1N manganous nitrate solution were mixed and the PH of the solution varied by adding 0.1N sodium hydroxide solution. The ratio of calcium to manganese was about ten to one. The lead dioxide and sodium bismuthate tests for Mn were positive as follows:

<u>PH</u> <u>of Solution</u>	<u>Test for</u> <u>Mn⁺⁺</u>
7.1	+
7.8	+
9.2	+

A solution containing 50 cubic centimeters of 0.1N calcium nitrate, 115 cubic centimeters of 0.1N phosphoric acid solution, and 1.23 cubic centimeters of 0.1N manganous nitrate solution was used and the PH changed by the addition of 0.1N sodium hydroxide solution. At a PH of 7.02 we obtained a negative test for manganese. The ratio of calcium to manganese was about forty to one. The original sample before the sodium hydroxide solution was added, gave a positive test, showing that we had not exceeded the sensitivity of the test.

CONCLUSIONS AND COMMENTS

From graph #1 it is seen that calcium and manganese phosphate begin to precipitate at very nearly the same PH. However, it has been shown that the PH for manganese must be raised to 9.80 and for calcium to 9.50 before a negative test for these ions can be obtained using the tests as described above.

It was thought that even though calcium and manganese phosphate evidently are precipitating together above a PH of 5.72, as shown from Curves #1 and #3, the calcium phosphate could remove manganese from solution by one of the methods previously mentioned.

This means that the concentration of manganese in solutions of PHs higher than 5.72 in the presence of calcium and phosphate ions should be less than that at the same PH with manganous and phosphate ions alone, if the initial concentrations of the manganese was the same in both cases.

This point of view could explain the inability for absorption of manganese to take place in the intestines in the proper manner with a diet high in calcium phosphate.

Our experiment shows that calcium does remove manganese at a PH near 7 when the ratio of calcium to manganese is high. We chose this particular PH because the intestinal tract, although alkaline, is not far from a PH of 7.

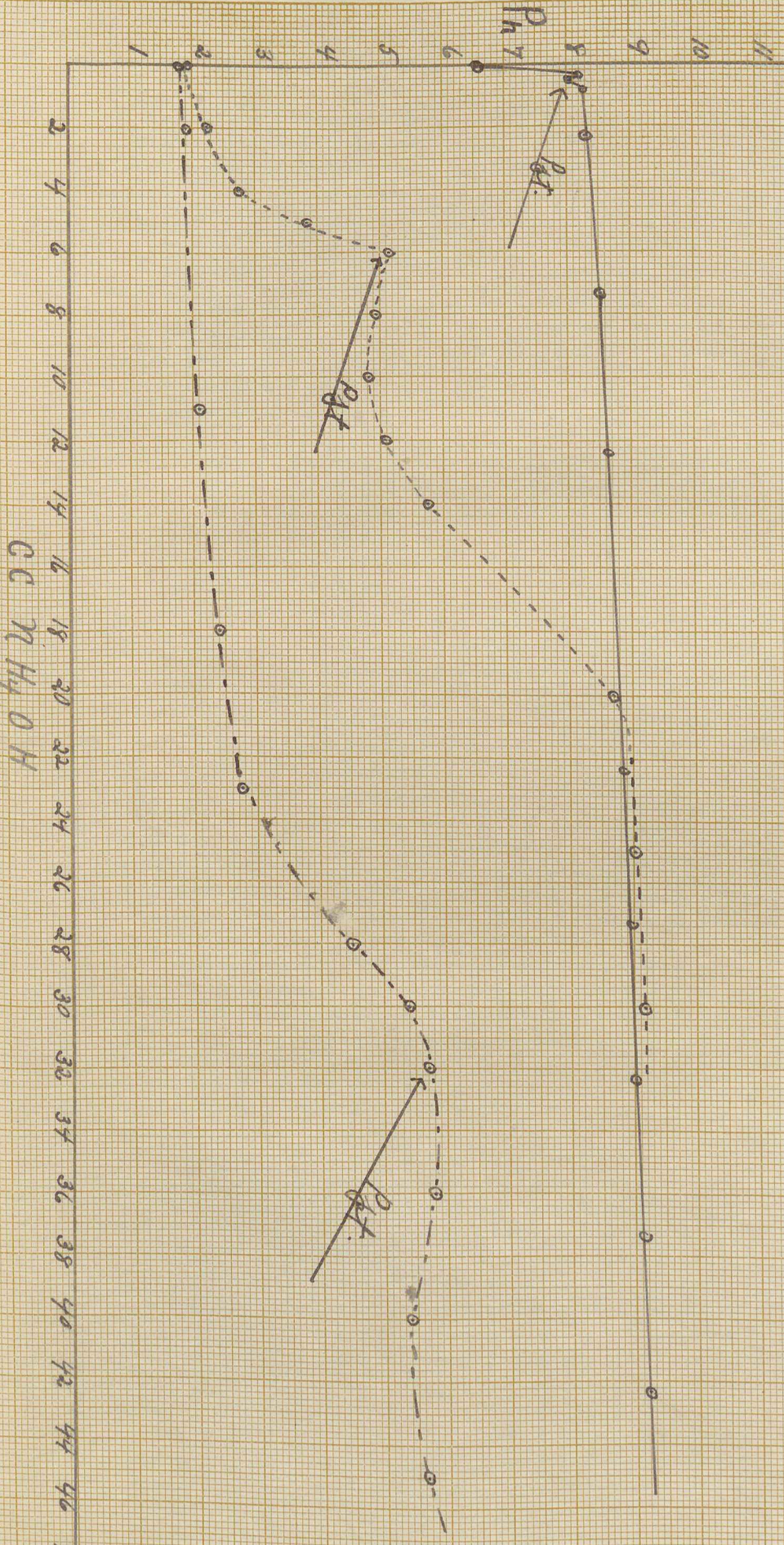
In view of these findings, the problem of determining some quantitative measurements for phase rule studies was to be undertaken but time did not permit.

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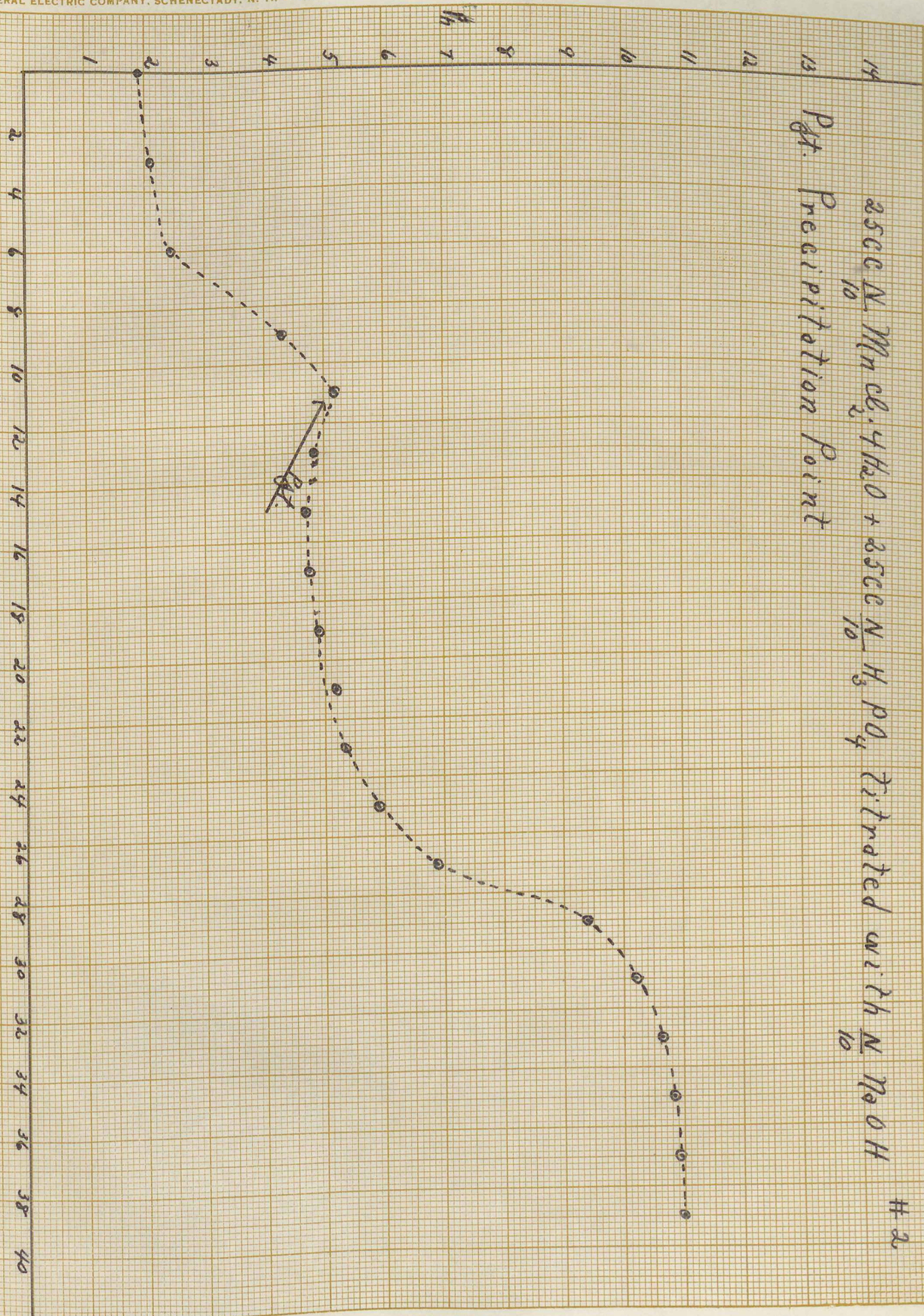
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_____ 500cc $\frac{N}{10}$ $MnCl_2 \cdot 4H_2O$ Titrated with $\frac{N}{10}$ NH_4OH
 - - - - - 250cc $\frac{N}{10}$ $MnCl_2 \cdot 4H_2O$ + 250cc $\frac{N}{10}$ H_3PO_4 Titrated with $\frac{N}{10}$ NH_4OH
 - - - - - 250cc $\frac{N}{10}$ $CaCl_2$ + 250cc $\frac{N}{10}$ H_3PO_4 Titrated with $\frac{N}{10}$ NH_4OH
 Ppt Precipitation Point



25cc $\frac{N}{10}$ $MnCl_2 \cdot 4H_2O$ + 25cc $\frac{N}{10}$ H_3PO_4 Titrated with $\frac{N}{10}$ $NaOH$ #2
Ppt. Precipitation Point



CC NaOH

#3
 250 cc $\frac{N}{10}$ $MnCl_2$ + 750 cc $\frac{N}{10}$ $CaCl_2$ + 100 cc $\frac{N}{10}$ H_3PO_4
 titrated with $\frac{N}{10}$ $NaOH$
 Ppt = Precipitation Point

