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THE DETERMINATION OF CADMIUM
AS CADMIUM PYROPHOSPHATE

Thesis for the Degree of M. S.
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George Jacob Atchison
1941



**THE DETERMINATION OF CADMIUM AS
CADMIUM PYROPHOSPHATE**

by

GEORGE JACOB ATCHISON

A THESIS

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INTRODUCTION

The well known method of determining magnesium as the pyrophosphate by igniting the precipitated magnesium ammonium phosphate has been applied to the determination of cadmium but without a large measure of success. The determination is time consuming and due to the solubility of the cadmium ammonium phosphate in both acidic and basic solutions the results obtained are usually low. As a consequence the method has never been popular.

The accepted procedures specify that the precipitation is to be made in a neutral or faintly acid solution, however none of the previous investigators has determined the influence of the hydrogen-ion concentration on the precipitation. The object of this investigation, therefore, was to find the effect of changing pH, to determine the optimum pH for the precipitation, and to study the precipitation of cadmium with diammonium hydrogen phosphate in solutions of controlled pH.

HISTORICAL

Austin (1) in 1899 investigated the double phosphate method of precipitation and applied it to zinc, beryllium and cadmium. She made the precipitation by adding hydrogen sodium ammonium phosphate to the hot solution containing the metal and then heating until the precipitate became crystalline. Results obtained for cadmium were good when the precipitation was made in the presence of ten per cent of ammonium chloride with a standing time of about sixteen hours before filtration.

Dakin (2) reported in 1900 that the presence of large amounts of ammonium chloride were unnecessary for accurate results. He also advocated the use of diammonium phosphate instead of the sodium compound as eliminating the error due to the presence of sodium in the precipitate. Another of Dakin's modifications was the precipitation of the cadmium ammonium phosphate from a cold rather than a hot solution since he found that hot precipitation gave a product of deficient ammonia content.

Miller and Page (3) a year later verified Dakin's method of cold precipitation and stipulated that for accurate results the precipitation should take place in a cold, neutral solution with a large excess of diammonium phosphate and an overnight standing period before filtration. Winkler (4) reported in 1921 that

the presence of more than five grams of ammonium chloride in one hundred milliliters of solution produced low results, and gave the ideal concentration of ammonium chloride as being two grams per one hundred milliliters of solution.

None of the investigators gave equations for the reactions between the cadmium and the precipitating reagent. Willard & Furman (5) in their book "Elementary Quantitative Analysis" state that "cadmium is precipitated first as simple phosphate which later becomes the crystalline double salt." The expected equations for the reactions are:



EXPERIMENTAL

A stock solution was prepared by dissolving 62.8 grams of C.P. $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ and ten milliliters of concentrated C.P. hydrochloric acid in distilled water and making up to roughly seven liters. This solution was then used as a source of standard cadmium content.

To determine the cadmium content of the stock solution twenty-five milliliter portions were standardized by two methods, (a) by electrolytic deposition of the cadmium upon platinum, and (b) as cadmium sulfate. For the electrolytic determination the samples were treated according to the cyanide method of Beilstein and Jawein (6) as given by Hillebrand and Lundell. Platinum gauze was used for the anode and for the cathode and the solutions were tested for complete deposition after electrolysis using hydrogen sulfide gas. For the determination as cadmium sulfate the samples were evaporated in platinum crucibles with an excess of sulfuric acid and the excess acid carefully fumed off using a nickel radiator. The residue was then ignited in an electric muffle furnace by gradually raising the temperature to five hundred degrees Centigrade and weighed as cadmium sulfate. The residue was dissolved in a small volume of water, carefully evaporated and ignited and this procedure continued until constant weights were obtained. Table I shows the results obtained by the two described

methods for samples from a pipette found to deliver 24.94 milliliters.

TABLE I
Standardization of the Cadmium Solution

g. Cd / 24.94 ml. soln.	
As CdSO ₄	Electrolytic Deposition
0.1035	0.1038
0.1037	0.1039
0.1035	0.1036
0.1037	0.1036
0.1036	0.1036
0.1038	0.1036
0.1036	
0.1037	

The value 0.1036 grams was used as the cadmium content of the 24.94 milliliter sample.

The cadmium sample was added to a buffer solution containing, for pH values below 7, varying volumes of approximately 1N ammonium acetate and approximately 1N acetic acid such that their sum was equal to twenty milliliters and the solution then diluted to roughly ninety milliliters using distilled water. The cadmium was then precipitated by adding ten milliliters of a 15 per cent solution of diammonium hydrogen phosphate drop by drop from a pipette with constant stirring to

the cold solution. For pH values above 7 approximately 1N ammonium hydroxide and approximately 1N ammonium chloride were used to buffer the solutions. In the case of the high pH values, that is, above 9 the ammonium hydroxide used was 6N.

All of the buffer solutions used for this work were tested with standard cadmium solution and found to give no precipitate under the range of conditions used.

The samples were allowed to stand overnight after precipitation and were then filtered through weighed Gooch crucibles, washed free of chlorides with a one per cent solution of the precipitating reagent and finally three small portions of a sixty per cent alcohol solution. The precipitates were then carefully ignited using first Bunsen burners and gradually increasing the flame until the final ignitions were made with Meker burners.

The results obtained, however, at the beginning of this work when low pH values were used showed such large errors that a standing period of about forty-eight hours between precipitation and filtration was tried and the samples were placed in an ice chest with a temperature of about 10° C. This treatment was followed for all samples while the effect of pH was being studied. Later after the optimum pH range was determined other standing periods were studied.

The amount of cadmium was calculated on the basis of the ignition of the precipitate to cadmium pyrophosphate.

The pH values of the samples were determined using the undiluted filtrates and a hydrogen electrode set-up using a normal calomel half-cell without a salt bridge. A student's type potentiometer was used for the voltage measurements. The set-up was checked periodically against .05 M potassium acid phthalate solution which has a pH of 3.97 and was further checked several times during the course of the work by using a glass electrode to verify the results given with the hydrogen electrode set-up.

During the first part of this work several of the filtrates were made up to a volume of two hundred and fifty milliliters in volumetric flasks, thoroughly mixed and the amount of cadmium determined on ten milliliter portions using the dithiazone color method of Leininger and Armstrong (7). The results obtained were in good agreement with the cadmium error found in the pyrophosphate determination. Table II gives the results obtained.

TABLE II

Cd Found in Filtrate Using Dithiazone

Cd taken	Cd found as $\text{Cd}_2\text{P}_2\text{O}_7$	Error	Cd found in filtrate using dithiazone
0.1036	0.1029	-0.0007	0.0006
0.1036	0.1030	-0.0006	0.0006
0.1036	0.1029	-0.0007	0.0006
0.1036	0.1027	-0.0009	0.0007

The effect of the pH of the solution upon the precipitation of the cadmium ammonium phosphate is shown in Table III.

TABLE III

Effect of pH Upon Precipitation of Cadmium Ammonium Phosphate

No.	Cd taken	Cd found	Error mgms. Cd	pH
1	0.1036	0.0981	-5.5	5.4
2	0.1036	0.0977	-5.9	5.4
3	0.1036	0.1025	-1.1	6.0
4	0.1036	0.1018	-1.8	6.0
5	0.1036	0.1031	-0.5	6.5
6	0.1036	0.1029	-0.7	6.5
7	0.1036	0.1033	-0.3	6.8
8	0.1036	0.1033	-0.3	6.8
9	0.1036	0.1033	-0.3	7.0
10	0.1036	0.1034	-0.2	7.0
11	0.1036	0.1033	-0.3	7.2
12	0.1036	0.1034	-0.2	7.2
13	0.1036	0.1034	-0.2	7.4
14	0.1036	0.1031	-0.5	7.4
15	0.1036	0.1035	-0.1	7.4
16	0.1036	0.1033	-0.3	7.4
17	0.1036	0.1036	0.0	7.5
18	0.1036	0.1035	-0.1	7.5
19	0.1036	0.1036	0.0	7.6

TABLE III
cont.

Effect of pH Upon Precipitation of Cadmium
Ammonium Phosphate

No.	Cd taken	Cd found	Error mgms. Cd	pH
20	0.1036	0.1035	-0.1	7.6
21	0.1036	0.1033	-0.3	7.6
22	0.1036	0.1031	-0.5	7.6
23	0.1036	0.1036	0.0	7.7
24	0.1036	0.1037	+0.1	7.7
25	0.1036	0.1032	-0.4	7.9
26	0.1036	0.1034	-0.2	7.9
27	0.1036	0.1036	0.0	7.9
28	0.1036	0.1039	+0.3	8.0
29	0.1036	0.1038	+0.2	8.0
30	0.1036	0.1037	+0.1	8.0
31	0.1036	0.1038	+0.2	8.0
32	0.1036	0.1038	+0.2	8.0
33	0.1036	0.1032	-0.4	8.2
34	0.1036	0.1036	0.0	8.2
35	0.1036	0.1033	-0.3	8.3
36	0.1036	0.1034	-0.2	8.3
37	0.1036	0.1029	-0.7	8.5
38	0.1036	0.1029	-0.7	8.5
39	0.1036	0.1032	-0.4	8.5
40	0.1036	0.1032	-0.4	8.5
41	0.1036	0.1029	-0.7	8.6

TABLE III
cont.

Effect of pH Upon Precipitation of Cadmium
Ammonium Phosphate

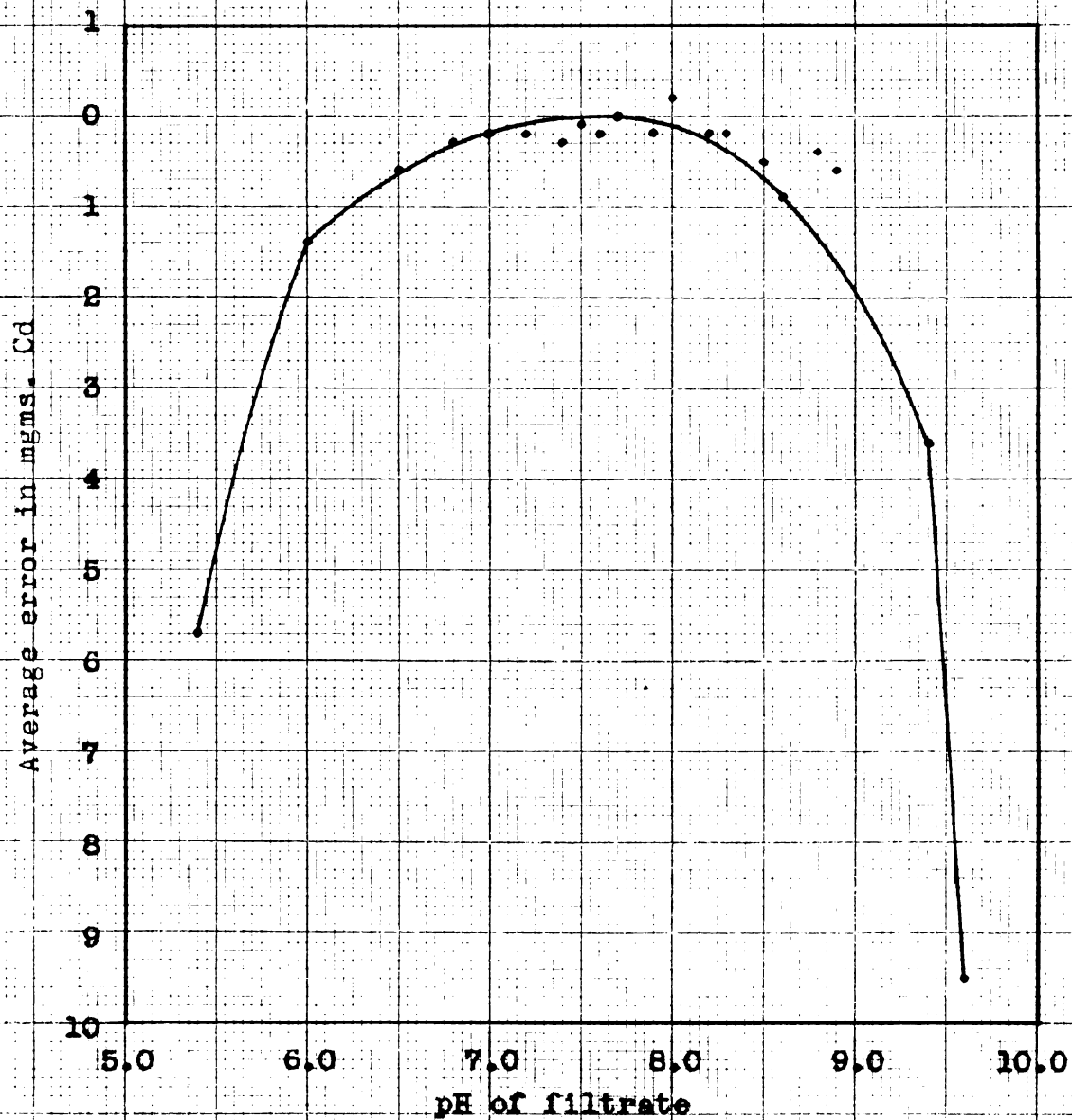
No.	Cd taken	Cd found	Error mgms. Cd	pH
42	0.1036	0.1025	-1.1	8.6
43	0.1036	0.1032	-0.4	8.8
44	0.1036	0.1032	-0.4	8.8
45	0.1036	0.1031	-0.5	8.9
46	0.1036	0.1028	-0.8	8.9
47	0.1036	0.1006	-3.0	9.4
48	0.1036	0.0993	-4.3	9.4
49	0.1036	0.0940	-9.6	9.6
50	0.1036	0.0941	-9.5	9.6

A study of this table shows that the best pH range for the precipitation to take place lies between pH values 7.0 and 8.3. Below a pH of 7 the results are consistently low and above a value of 8.3 the error increases rapidly.

In figure 1 the average error in milligrams of cadmium has been plotted against pH values of the undiluted filtrates. The results although not as consistent as it was hoped do show that the proper range for the determination is between pH 7 and pH 8.3. The optimum pH as obtained from the curve is at a pH of 7.7.

Very little difficulty was encountered due to the residues of cadmium pyrophosphate turning dark colored during the ignition period. Occasionally if the Bunsen flames were raised too rapidly the residues became light

Figure 1



grey in color but in no case did they turn black or dark grey. Most residues remained pure white throughout the ignition.

After the optimum pH range was determined the following five factors were studied separately:

(1) temperature between precipitation and filtration,
(2) standing time between precipitation and filtration,
(3) various amounts of precipitating reagent, (4) various amounts of ammonium chloride, and (5) efficiency of alcohol wash solution. The error in terms of milligrams of cadmium was determined for each of these factors as follows:

1. The results obtained for samples at 10° - 12° C. and at room temperature are given in Table IV. The samples used were all pipetted from the same pipette used for standardizing the stock solution and the solutions were buffered with one gram of ammonium chloride, four milliliters of filtered dilute ammonium hydroxide (one volume of 6N to five volumes of water) and the precipitating reagent. A standing period of forty-eight hours was allowed between precipitation and filtration. The 10° - 12° C. temperatures were obtained by using an ice chest.

TABLE IV
Effect of Temperature

Number	10° - 12° C.		Room Temp.	
	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate
1	-0.2	7.8	-0.1	7.8
2	-0.2	7.8	-0.2	7.8
3	-0.1	7.8	-0.1	7.8
4	+0.2	7.8	+0.1	7.8
5	+0.2	7.8	+0.1	7.8

It is apparent that the results are not improved by the use of an ice chest for the digestion period.

2. The effect of standing time between precipitation and filtration of the cadmium ammonium phosphate is shown in Table V. In each case the samples were delivered from the standardization pipette and buffered as described above. All determinations were carried out at room temperatures. No definite trend is indicated in any of the three standing periods studied.

TABLE V
Effect of Standing Between Precipitation and Filtration

No.	16 hrs.		24 hrs.		48 hrs.	
	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate
1	0.0	7.7	-0.1	7.7	-0.1	7.7
2	-0.2	7.7	-0.2	7.7	-0.2	7.7
3	-0.2	7.7	0.0	7.7	0.0	7.7
4	-0.2	7.7	+0.1	7.7	+0.1	7.7

Standing periods of less than sixteen hours were not tried since the most convenient working arrangement was to make the precipitation in the late afternoon and filter the precipitate the next morning. Winkler (5) however, reports that a standing period of two hours might be sufficient if one is pressed for time and if the corrections given by him are applied.

3. In Table VI the results of using various amounts of the precipitating reagent are shown. All determinations were made at room temperature with a twenty-four hour standing period allowed between precipitation and filtration. A 15 per cent solution of diammonium hydrogen phosphate was used as the precipitating reagent. The samples were buffered as described before.

TABLE VI

Effect of Various Amounts of Precipitating Reagent

No.	10 ml.		20 ml.		30 ml.	
	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate
1	0.0	7.8	-0.1	8.0	0.0	8.1
2	0.0	7.8	0.0	8.0	+0.1	8.1
3	-0.1	7.8	-0.2	8.0	+0.1	8.1
4	-0.2	7.8	+0.1	8.0	+0.1	8.1

4. The data obtained from a study of the effect of various amounts of ammonium chloride are presented in Table VII. The samples were all buffered as before with the exception of the amount of ammonium chloride which was

one, five and ten grams. The precipitates were allowed to stand twenty-four hours at room temperature before filtration.

TABLE VII

Effect of Various Amounts of Ammonium Chloride

No.	1g. NH_4Cl		5g. NH_4Cl		10g. NH_4Cl	
	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate	Error in mgm. Cd	pH of filtrate
1	+0.1	8.0	-0.1	7.5	-7.0	7.2
2	+0.1	8.0	+0.2	7.5	-6.9	7.2
3	0.0	8.0	-0.2	7.5	-7.1	7.2
4	+0.1	8.0	-0.2	7.5	-6.5	7.2

When ten grams of ammonium chloride were used the error was very large showing that for best results the ammonium chloride concentration of the one hundred milliliters of solution should be kept to not over five grams.

5. To determine if all of the diammonium hydrogen phosphate from the one per cent wash solution was being removed by the alcohol wash the following determination was carried out. After the precipitate had been transferred from the beaker to the Gooch mat it was washed with two one milliliter portions of alcohol. The Gooch funnel was then thoroughly washed with distilled water so as to remove any diammonium hydrogen phosphate wash solution adhering to the funnel. Then five milliliters of alcohol wash solution was used to wash the precipitate and this alcohol was caught in a clean test tube,

transferred to a weighed twenty-five milliliter beaker and evaporated to dryness on the steambath. The results given in Table VIII indicate that the alcohol wash solution as used for this determination removes all of the diammonium hydrogen phosphate adhering to the precipitate.

TABLE VIII

Residue From Alcohol Wash Solution

Number	Mgm. residue
1	0.0
2	0.0
3	0.0
4	0.0

The next step in this work was the working out of a simple, easy method of adjusting the pH of the sample so as to have it within the permissible range. This was accomplished by using the indicator phenol red which changes color at pH 6.9 as determined with a hydrogen electrode and adding ammonium hydroxide until the color change is noticed and then five drops in excess. Table IX contains the data obtained when the following procedure was used. One gram of ammonium chloride was dissolved in sixty milliliters of distilled water in a one hundred and fifty milliliter beaker. Samples of the standard cadmium solution were added using the original standardization pipette. Two drops of phenol red indicator were added producing a yellow

colored solution. Filtered ammonium hydroxide (one volume of 6N to five volumes of water) was added from a burette until the color changed from yellow to pink and then five drops in excess. The cadmium was then precipitated by adding ten milliliters of a 15 per cent diammonium hydrogen phosphate solution drop by drop from a pipette with constant stirring. The precipitate was allowed to stand sixteen hours at room temperature and then filtered through a weighed Gooch crucible. The precipitate was washed free of chlorides using a one per cent solution of the precipitating reagent and finally with three small portions of a 60 per cent alcohol solution. The precipitate was then ignited as described in the first part of this work. This method of adjusting the pH of the solution produced satisfactory results as the data in Table IX indicates.

TABLE IX

Test of pH Adjusting Procedure

Cd taken	Cd found	Error mgm. Cd	pH of filtrate
0.1036	0.1036	0.0	7.7
0.1036	0.1037	+0.1	7.7
0.1036	0.1037	+0.1	7.7
0.1036	0.1036	0.0	7.7
0.1036	0.1034	-0.2	7.7
0.1036	0.1034	-0.2	7.7

The procedure was also checked using varying amounts of cadmium sample and produced satisfactory results for quantities of cadmium greater than 0.04 gram. For samples of less than 0.04 gram the error is negative and very large while for samples of more than 0.2 gram the error is positive but not excessive as the data of Table X shows.

TABLE X

Results Using Varying Quantities of Cadmium

Cd taken	Cd found	Error in mgm. Cd	Percentage error
0.0208	0.0198	-1.0	-4.80
0.0208	0.0202	-0.6	-2.88
0.0208	0.0198	-1.0	-4.80
0.0208	0.0200	-0.8	-3.84
0.0415	0.0418	+0.3	+0.72
0.0415	0.0412	-0.3	-0.72
0.1036	0.1036	0.0	0.00
0.1036	0.1037	+0.1	+0.09
0.1036	0.1037	+0.1	+0.09
0.1036	0.1036	0.0	0.00
0.1036	0.1034	-0.2	-0.18
0.1036	0.1034	-0.2	-0.18
0.2075	0.2072	-0.3	-0.14
0.2075	0.2073	-0.2	-0.09
0.4151	0.4156	+0.5	+0.12

TABLE X
cont.

Results Using Varying Quantities of Cadmium

Cd taken	Cd found	Error in mgm. Cd	Percentage error
0.4151	0.4162	+1.1	+0.26
0.5187	0.5195	+0.8	+0.15
0.5187	0.5202	+1.5	+0.28

Several samples were run in which the volume of solution was varied and gave the results shown in Table XI.

TABLE XI

Effect of Varying Volumes of Solution

Error in mgm. Cd		
Total Vol. 100 ml.	Total Vol. 200 ml.	Total Vol. 300 ml.
0.0	-0.4	-0.8
+0.1	-0.4	-0.7
+0.1	-0.3	-0.8
0.0		
-0.2		
-0.2		

From the results given in Table XI it is evident that the volume of the solution containing the cadmium must be kept small for best results.

A series of unknown samples prepared by two other workers in the laboratory were run using the phenol red method of adjusting the pH and gave the results

tabulated in Table XII.

TABLE XII

Unknown Samples

Grms. Cd taken	Grms. Cd found	Error in mgm. Cd	Percentage error
0.0400	0.0398	-0.2	-0.50
0.0600	0.0598	-0.2	-0.33
0.0999	0.0998	-0.1	-0.10
0.0999	0.0999	0.0	0.00
0.1399	0.1404	+0.5	+0.36
0.2001	0.2000	-0.1	-0.05
0.2598	0.2601	+0.3	+0.11
0.2997	0.3002	+0.5	+0.15
0.3000	0.2995	-0.5	-0.16
0.3397	0.3406	+0.9	+0.26
0.3996	0.4004	+0.8	+0.20
0.4003	0.3996	-0.7	-0.17

The samples for which a positive error was obtained were prepared by one worker in the laboratory and the samples for which a negative error was obtained were prepared by another worker in the laboratory.

The errors were not excessive, however, for any sample and the method for determining cadmium produced acceptable results.

The directions for determining cadmium by this method are as follows:

The solution containing not more than 0.3 gram and not less than 0.04 gram cadmium and no interfering substances should have a volume of approximately 75 milliliters. Add one gram of ammonium chloride and two drops of phenol red indicator thus producing a yellow colored solution. Add from a burette filtered ammonium hydroxide (one volume of 6N to five volumes of water) until the color of the solution changes from yellow to pink, then add five drops in excess. Precipitate the cadmium by adding a 15 per cent solution of diammonium hydrogen phosphate drop by drop and with constant stirring until five milliliters have been added. Allow the precipitated cadmium ammonium phosphate to settle slightly and test for complete precipitation. When the cadmium is completely precipitated add an excess of ten milliliters of the precipitating reagent drop by drop and with constant stirring. The volume of the solution at this point should not be greater than 100 milliliters.

Allow the precipitate to stand overnight and then filter through a weighed Gooch crucible. Transfer the precipitate to the Gooch crucible and wash with a 1 per cent solution of diammonium hydrogen phosphate until no test for chloride is obtained. Remove any adhering wash solution using three two milliliter portions of a 60 per cent ethyl alcohol solution.

Carefully dry the residues in the Gooch crucible using the smallest Bunsen flame possible. Gradually increase the flame so that at the end of about four hours a full Bunsen flame is being used. If the residue begins to turn grey in color the flame must be increased more slowly. Continue the ignition for one hour with a full Bunsen flame and finally ignite for one hour with a Meker burner. Cool and weigh the Gooch crucible and ignite for one-half hour with a Meker burner, continuing this procedure until constant weights are obtained. The cadmium pyrophosphate residue will be pure white in color.

SUMMARY

A method of determining cadmium as cadmium pyrophosphate by precipitating cadmium ammonium phosphate from a solution of controlled pH is described. Fairly satisfactory results may be obtained for the precipitation of cadmium ammonium phosphate over a pH range of 7.0 to 8.3 for amounts of cadmium from 0.04 gram to 0.3 gram. The proper pH is indicated by the color change of phenol red from yellow to pink. Below a pH of 6.5 and above a pH of 8.5 the results obtained are much too low. A concentration of ammonium chloride between one and five grams per 100 milliliters has no detrimental effect.

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