THE DETERMINATION OF PHOSPHATES IN BOILER SALINES

A Thesis

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TABLE OF CONTENTS

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INTRODUCTION

The colorimetric determination of phosphates, as used at present, is a rapid method for the estimation of phosphates between certain limits. The method is used in boiler plants to control the addition of trisodium phosphate to prevent boiler embrittlement. The method is used at Virginia Polytechnic Institute for the same purpose. The procedure for the colorimetric determination in this study was recommended to the local power plant by the Permutit Company as was also the method for checking the colorimetric method. Both procedures were modified in the course of the investigation.

One of the aims of this work was to find out the accuracy of the above mentioned colorimetric method as well as the limits in range of the method as given. It was also intended to attempt to improve the accuracy or the rapidity of the method without affecting the utility, and thereby increase the range of use for the method.

The use of the method in other analyses, where a rapid but fairly accurate phosphate determination is needed, was also kept in mind. If the accuracy and the limits of the method of analysis were known, its use in other analyses might be predicted. If greater accuracy could be secured without taking more time, this would be desirable in the boiler plant operation to give closer control over phosphate addition.

Work was done on color standards. Good standards would eliminate many runs. These runs are made to find the exact phosphate content. The limits only are found in the boiler plant phosphate analysis. Standards would give the exact phosphate content. This would allow better control of phosphate addition.

HISTORICAL

Taylor and Miller(19) in 1914 first suggested the possibility of the use of the blue color resulting from the partial reduction of the complex phosphomolybdates in a colorimetric determination of the phosphates in a solution. They showed that the depth of color was proportional to the amount of phosphates present. They did not however work out a method for such an analysis.

Wu(20) in 1920 did some work on phosphomolybdic acid and the reduced complexes and indicated the method for analysis. Deniges(7) (8) in 1920-1921 worked out what he called the coerula-molybdate method, due to the blue color, for determining phosphates colorimetrically. This was modified slightly by Florentin(13) in 1921 to the method used by Atkins(2) in 1923 in this country for the determination of phosphates in soil extracts. Some work on glass color standards to replace the standard solutions and save time was done by Chapman(6) in 1931 when the method was coming into some use for rapid determinations.

Bell and Doisey(3) in 1920 applied the Deniges method but used different reagents and changed the procedure for the analysis of phosphates in urine and blood. The Bell and Doisey method was modified by Briggs(5) in 1922 using hydroquinone as the reducing agent. Benedict and Theis(4) in 1924 worked out a method using sodium bisulphite and hydroquinone which gave a good color comparison. Fiske and Subbarow(12) in 1925 found that 1, 2, 4 amino napthol sulphonic acid gave a better color than the quinone.

These methods were studied in 1926 by Parker and Fudge(16), who found that Deniges' method which used stannous chloride as a reducing agent,

was more sensitive but that Fiske and Subbarow's method, altho only one fifth as sensitive, was useful in phosphate concentrations over one part per million. Farber and Youngsburg(14) studied Deniges' method in 1931 and found it quite useful and accurate in plain water analysis.

Yoe(21) lists in his "Photometric Chemical Analysis" the Briggs modification of the Bell and Doisey, the Fiske and Subbarrow method, and the Benedict and Theis method as standard photometric methods in particular reference to blood analysis for phosphates.

Kolthoff(15) in 1917 found that SiO_2 above 25 to 30 mg. per liter interfered with the regular phosphate determination. Scarritt(18) in 1930 worked out a procedure whereby the colorimetric method could be used in boiler water analysis even though the silicates were present in some quantity. Another possible source of error in this determination, as pointed out by Denis(10) in 1922, is the fading of the blue color. This fading is caused by large amounts of oxalates and citrates in the solution.

Parr and Straub(17) evolved a theory for the embrittling action of caustic and dissolved salts on the metal of boilers. In 1927 they worked out a method for the prevention of embrittlement. This method, which has been in use for some years, includes the use of trisodium phosphate. This method is usually used when Zeolite softened waters are the source of the "make up" boiler water.

THEORETICAL

The determination of the phosphate ion by colorimetric comparison is done by reducing the complex molybdic acids forming on adding ammonium molybdate to phosphate solutions. The solution must be acid to nitric acid and the molybdate must be in excess. The reduced ion imparts a blue color which is intensified the greater the amount of phosphate present. Standards, which were run along with the sample, gave better checks. The same time and temperature when read caused the better results. Sodium sulphite is added because of its basic nature to partially neutralize the acid and to give a better color.

Wu(19) in 1920 and Deniges (9) in 1928 worked on the ammonium phosphomolybdate complex compounds. Wu found two phosphomolybdic acids, one with one P_2O_5 to eighteen MoO_3 and one with one P_2O_5 to twenty four MoO_3 of the type $3H_2O.P_2O_5.24MoO_359H_2O$. The unreduced compound he gave on the order of $3(NH_4)_2P_2O_5.$ 18 $MoO_3.11H_2O$(yellow). On reduction he got two compounds that might be responsible for the blue color:- $3(NH_4)_2O.P_2O_5.22MoO_3.$ $2MoO_3.H_2O$ blue crystals $3(NH_4)_2O.P_2O_5.16MoO_3.Mo_2O_5.H_2O$ deep violet crystals.

Deniges got from adding H_3PO_4 to partially reduced H_2MoO_4 a sapphire blue compound $(4MoO_3.MoO_3).H_3PO_4.H_2O$. He also heated $(NH_4)_3PO_4.12MoO_3.$ $2HNO_3.H_2O.(NH_4)_3PO_4.12MoO_3$ which on reduction gave a blue compound.

There seems to be little doubt that there are several reduction products that give the blue color altho the exact composition of these complexes does not seem to be known. They seem to be formed in proportional

amounts at any one temperature and acidity but there can be no comparison at different conditions.

Before the blue color is developed, a green color is predominant. This green color has been used for the color comparison but it is less intense and therefore gives poorer results than the blue color that shows on addition of the sodium sulfite. This green color points to a partial reduction of the yellow crystals of phosphomolybdate and possibly a mixture of blue and yellow crystals in solution.

Trisodium phosphate is added to boiler waters particularly where the Zeolite water softening system has been used(10) to prevent boiler embrittlement, especially if chlorides are present. According to Parr and Straub this would offset the high concentration of caustic, that builds up in the crevices or around rivets, below that which is necessary to produce embrittlement. A phosphate content of over thirty four parts per million(PO_4) is recommended.

There are a number of selective reducing agents which may be used that will reduce phosmolybdic acid without affecting molybdic acid. This avoids the necessity of isolating the ammonium phosphomolybdate. Hydroxylamine, phenols and hydroquinone have been tried at different times with some success in this capacity. This reduction color is intensified by making the solution alkaline and the greenish shade is removed by the addition of sulfite.

Standards must be made for each determination since the blue color fades to a certain extent on standing. The hydroquinone itself becomes

colored on standing but this does not affect the use of the reagent. Stannous chloride was first used as a reducing agent and it gave more accurate results when the amount of (PO_4) was around one part per million (16).

EXPERIMENTAL

Two analytical procedures were used in this work. One as given by the Permutit company for colorimetrically determining phosphates, which is essentially the modified Bell and Doisey(9) method, the other the standard Association of Official Agricultural Chemists(1) volumetric method for determining phosphates in water. These two procedures are outlined below with the reagents used.

Colorimetric Determination of Phosphates.

Reagents:- (1) Molybdate Solution- 25 gms. of ammonium molybdate(if $(NH_4)6Mo7O_2.4H_2O$ use 26.6 gms.) in 300cc. H_2O,75cc. concentrated H_2SO_4 diluted to 200cc. with distilled water is added to the ammonium molybdate.

(2) Hydroquinone- 2 gms. of hydroquinone in 100cc. of distilled water. Add a drop of conc. H_2SO_4.

(3) Carbonate-Sulfite Solution- 200 gms. of sodium carbonate made up to 1000cc. with distilled water. 37.5 gms. of sodium sulfite made up to 250cc. with distilled water and the solutions mixed.(75 gms. if the sodium sulfite has water of crystallization.)

(4) Sulphuric Acid- 110cc. of conc. H_2SO_4 made up to 1000cc. with distilled water. This gives 4N. acid.

(5) Standard Phosphate Solution- Weigh accurately 0.4394 gms. potassium acid phosphate, KH_2PO_4(anhydrous). or 0.5682 gms. of K_2HPO_4, and dilute with distilled water to 1000cc. One cc. of this solution equals 0.1 milligram of Phosphorus or 0.306 milligrams of (PO_4).

Procedure:- 1-Sample the boiler blow off, filter, and allow to cool.

2-Take 25cc. of the sample and dilute to 50cc. in a 100cc. graduate.

3-Add 10cc. of the H_2SO_4 solution.

4-Add 5cc. of the ammonium molybdate solution.

5-Add 5cc. of the hydroquinone solution and allow to stand five minutes.

6-Add 15cc. of the carbonate sulphite solution.

7-Allow the solution to stand ten minutes and then compare it with the standards. Two standards are run along with the sample. They are made up to 50cc. with distilled water. #1 contains 4.8cc. of the standard phosphate solution. It gives an equivalent of 60 ppm. as (PO_4). #2 contains 2.4cc. of standard phosphate solution. It gives an equivalent of 30 ppm. as (PO_4). Both are treated with the same reagents as the sample. They are compared in 100cc. Nessler tubes. The sample should fall between the two if the correct amount of trisodium phosphate is being fed into the boiler.

Determination of Phosphates by Titration

In this method the phosphates are precipated by ammonium molybdate as ammonium phosphomolybdate. This precipitate is caught on filter paper, washed and either the precipitate or the paper and precipitate are transfered to a beaker containing a known quantity of sodium hydroxide. The amount of base used up in dissolving the ammonium phosphomolybdate is ascertained by back titration with sulphuric acid.

Solutions:- 1-Neutralizing Solution- One part of conc. HNO_3 to 4 parts of distilled water in a dropper bottle.

2-Precipitation Solution- 100 gms. of molybdic acid are dissolved in ammonium hydroxide (144cc. of strong ammonium hydroxide and 271cc. of water); this solution is then poured slowly and with constant stirring into the dilute nitric acid (489cc. of strong nitric acid and 1148cc. of water). This mixture must be aged for several days. 100cc. of this solution and 5cc. of conc. nitric acid gives the solution used for precipitation.

3-N/25 NaOH and N/10 H_2SO_4 and Phenol Red Indicator(1%).

Procedure:- 50cc. of the sample are taken and made neutral to methyl orange by adding the nitric acid from the dropper bottle. A small amount of ammonium nitrate is added to this solution and it is then placed in a water bath between 38c. and 65°C. 15 to 25cc. of the acid molybdate solution is then added and after shaking for several minutes, the solution is allowed to stand for 15 minutes.

The solution is then filtered on fine particle filter paper or with several thicknesses of regular filter paper using suction. The precipitate is redissolved with 5cc. of the sodium hydroxide or the filter and precipitate may be transfered to a beaker and the 50cc. of the known sodium hydroxide added. This is then back titrated with the sulphuric acid using Phenol Red(ph of 6.8 to 8.4) which changes from purple to a light orange. (Phenolphthalein may be used as the indicator here).

50cc. of the N/25 NaOH used equals 20cc. N/10 H_2So_4. This gives the

20. The mille equivalent of the PO_4 in this neutralization is $PO_4/23000$ or 95/23000. This gives .00414 grams per liter. A 50cc. sample causes multiplication by 2000 to convert to ppm. This gives the factor 8.28. This back titration shows the amount of PO_4 which reacted with the NaOH. The calculation used is then;

(20-ccs.H_2SO_4)times 8.28 gives the ppm PO_4.

Tests were run on solutions of various strengths to determine the limits and the accuracy of the method at these various points. Solutions of boiler water, boiler water with trisodium phosphate added, and solutions of a Bureau of Standards phosphate rock were used in this work. Various modifications in the procedure and in the reagents were tried for increased and decreased time necessary for the analysis. These modifications were then checked against the known strength solutions. Work was done to get some good color standards to eliminate the necessity of repeating runs due to the fading of the standards and solution on standing.

Several samples of the boiler water from the blow off at the Virginia Polytechnic Institute power plant were taken on different days and a number of analyses of these samples were run concurrently by the colorimetric and volumetric methods. These results are shown in the following tables.

TABLE 1

Colorimetric and Volumetric Results on Boiler Salines

Collected 9/21/38 (Sample #1)

PPM (PO_4)

Run Number	Colorimetric	Volumetric
1	3	6.6
2	5	6.6
3	6	4.13
4	3	--
average	4	5.8

TABLE 2

Colorimetric and Volumetric Results on Boiler Salines.

Collected 9/27/38 (Sample #2)

PPM (PO_4)

Run Number	Colorimetric	Volumetric
1	4	3.3
2	2.5	4.1
3	2.5	2.9
4	--	3.3
average	3	3.4

These percentages of phosphates were lower than should have been found if proper dosage of phosphate had been used. The plant must have depended more on the blow down to keep the amount of caustic low, than on the addition of trisodium phosphate. Therefore to get a solution nearer the concentration which should be encountered in testing boiler salines for phosphates, which should be between thirty and sixty parts per million, a solution was made up from a standard phosphate rock (U. S. Bureau of Standards, Standard Sample #56). This enabled a solution to be made up between the limits desired and also gave a check on the method of analysis. Some difficulty was encountered in dissolving the rock but the solution was made up by dissolving 0.1 gm. of the standard rock in aqua regia. This was then made up to a liter. All of the Hcl was removed by evaporation before this dilution.

TABLE 3

Colorimetric and Volumetric Results on Standard Phosphate Rock Solution.

PPM (PO_4)

Run Number	Colorimetric	Volumetric
1	42	44.3
2	43	45.1
3	44	44.3
4	43	45.1
average	43	44.7

The correct analysis of this sample as given by the Bureau of Standards would have been 41.9 ppm.(PO_4) on the 0.1 gm. sample taken exactly.

The fourth sample taken for analysis was made by adding trisodium phosphate to one of the boiler water samples taken for first analysis(Sample #2). A water with the same chemical nature as the boiler water was obtained, with phosphate added as would be encountered when checking for phosphate feed in usual practice. The trisodium phosphate was obtained from the power plant as the standard grade put out by the General Chemical Company for boiler water. The phosphate already in the water was taken into account and enough was added to give a water running between 30 and 60 ppm. phosphates.

The residue in the water, which is generally filtered off, was considered as a possible source of error. The samples were run in duplicate, one well mixed and the other filtered as usual.

TABLE 4

Colorimetric and Volumetric (Clear and Unfiltered) Results on Boiler Salines with Trisodium Phosphate Added.

	PPM (PO_4)		
	Colorimetric	Volumetric	
Run Number		Clear	Unfiltered
1	40	44.0	43.4
2	45	45.4	43.8
3	42	43.4	42.9
4	42	44.0	44.6
average	42	44.2	43.7

The fifth solution taken for analysis was made up by adding trysodium phosphate to some of the boiler water. The addition was calculated to give a solution with phosphate content which ran somewhere halfway between solutions one, two and four. This was done to establish the accuracy of the colorimetric method between these limits as well as to get a further comparison of the clear and unfiltered solution at a different concentration. This solution was run colorimetrically. The solution was also analyzed unfiltered and filtered, in the volumetric analysis.

TABLE 5

Colorimetric and Volumetric (Clear and Mixed) Results on Boiler Salines with Trisodium Phosphate Added.

	PPM (PO_4)		
	Colorimetric	Volumetric	
Run Number		Clear	Unfiltered
1	24	25.2	23.5
2	25	28.0	23.5
3	25	27.3	25.6
4	24	26.7	26.5
average	24.5	26.8	24.7

The sixth solution taken for analysis was made up by adding trisodium phosphate to sample number two of the boiler water. It was calculated

to give a solution with phosphates running higher than the sixty parts per million upper limit of the boiler salines. This was done to check the accuracy at higher concentrations and to establish an upper limit for the method of analysis as given in this procedure. This solution was also run colorimetrically and volumetrically in duplicate with both clear and unfiltered samples.

TABLE 6

Colorimetric and Volumetric (Clear and Unfiltered) Results on Boiler Salines with Trisodium Phosphate Added.

	PPM (PO_4)		
	Colorimetric	Volumetric	
Run Number		Clear	Unfiltered
1	63	59.1	59.4
2	63.6	63.6	69.4
3	64	70.2	60.3
4	64	67.7	66.9
average	63.6	65.1	64.0

The next step in this work was to try to improve the colorimetric phosphate determination. The method could be made more accurate. This would allow the method to be used for more of the gravimetric and volumetric analyses, which would be advantageous due to its greater speed. The method might be made to take less time yet and thus be of greater use as a rapid determination. Various hoped for improvements had to be tried and then each one had to be checked against a known strength solution for

accuracy.

It was found that keeping the solution for the colorimetric analysis in a water bath between 38°C. and 65°C. while the sulphuric acid, ammonium molybdate, and hydroquinone were being added would allow the time of standing between these steps to be cut in half.

TABLE 7

Colorimetric Results on Boiler Salines

Comparing the Original Analysis with the Modified Analysis

	PPM (PO_4)	
Solution	Original (Average)	Modified
1	4	5
3	43	43
4	42	43
5	24.5	23
6	63.6	64

Table 7 shows the results with the modified procedure. The modified procedure used the higher temperatures and the shorter time.

Good color standards with the same blue source of color and apparently permanent were made from the colorimetric solutions. These solutions were found to reach a stable state in their fading in less than forty eight hours and could then be used to make permanent standards by diluting to match standards made up to different strengths. Two samples of standard solution and one of boiler water were taken and checked against other standards every twenty four hours until no change was observed.

TABLE 8

Colorimetric Results on Boiler Saline and Standard Solutions

Over a Period of Time.

Time	Beginning	24 hrs.	48 hrs.	70 hrs.
#4 Boiler Water	43(ppm PO_4)	187	187	187
2.4 Standard	30	63	110	110
4.8 Standard	60	110	150	150

Ammonium molybdate solution made according to the A.O.A.C. method with 5ccs. of concentrated nitric acid added worked better than that given in the Permutit method made from ammonium molybdate rather than molybdic acid. A better comparison could be gotten in the colorimetric method in the more dilute strengths.

Table 9 was compiled from the average results from the first six tables. It shows the difference in results between the methods.

TABLE 9

Colorimetric and Volumetric Averages

Showing the Differences.

Solution	($PPM.PO_4$) Volumetric	Colorimetric	Difference
1	5.8	4	1.8
2	3.4	3	.4
3	44.7	43	1.7
4	44.2	42	2.2
5	26.8	24.5	2.3
6	65.1	63.6	1.5
average			1.6

DISCUSSION

The use of the Permutit volumetric procedure was modified to more closely agree with the A.O.A.C. method. Although the indicator, Phenol Red, and the temperatures from the Permutit method were found more satisfactory than those of the A.O.A.C. method. The Permutit method was designed for a more rapid method.

The first step in this work was to ascertain the accuracy of the colorimetric method compared with the standard methods such as the volumetric. Tables 1 and 2 show fairly close agreement between these two methods on samples of boiler saline running low in phosphates. These percentages were so low that solutions had to be made up other than the straight boiler saline to get phosphate analyses more like those which should be encountered in boiler plant analysis.

A solution made up by dissolving a Bureau of Standards Rock Sample gave a check on the volumetric method of analysis. This also gave a solution near the desired phosphate content. From table #3 the colorimetric and volumetric results may be seen to check fairly close. The volumetric ran slightly higher. They also check fairly closely the correct analysis as given by the Bureau of Standards which on exactly a 0.1 gm. sample should have been 41.9 ppm.(PO_4).

Some trouble was encountered in getting check results with the volumetric method as outlined by the Permutit company. One error was observed in the outline where the make up for solution #2 is given. The amount of chemicals which are listed totaled more than the 250cc. solution expected when they were mixed. The amount of ammonium nitrate is apparently

too large.

Taking the filter paper and transferring to a beaker was found to work better than trying to dissolve the precipitate from the paper. The paper in the solution gives a background for a better end point. Phenol Red as an indicator worked better with a clearer end point than Phenolpthalein. The best color in the colorimetric analysis seemed to occur in about five minutes after addition of the carbonate sulphite solution.

Table #4 showed that the colorimetric analysis ran slightly lower than the volumetric and that the unfiltered solution ran a little lower than the filtered solution. Comparison of the colorimetric with the volumetric analyses is shown in table #9. The ability to use the colorimetric method for closer analyses than those used in boiler saline analysis is clearly shown.

Tables #5 and #6 showed the same differences with the volumetric running higher than the colorimetric and the clear solution running higher than the unfiltered solutions. The methods checked about the same on table #5, the solution of intermediate strength, as on the other solutions. Table #6 showed more difference between runs. This indicated that the limit of the method as outlined in this procedure was being reached.

From table #9 a fairly constant difference between the colorimetric and volumetric analyses may be observed. A variance of one or two parts per million might be due to the standard phosphate solutions being slightly in error. The use of a different indicator was found to vary the results. The fact that the unfiltered solution of boiler saline ran consistantly

lower than the filtered solution in the volumetric analysis seems to indicate the reaction of some of the residue with some of the phosphoric acid. This results in less indicated phosphates for the mixed solution. Any acid salts might cause this result.

Considering the range of concentrations of phosphate taken, table #9 indicates close and uniform checks throughout the work. The colorimetric is generally used for boiler saline analysis only to see that the phosphates fall between certain limits. Finding the exact amount of phosphates required numerous runs until a standard was found which checked the sample. The sample had to be run each time due to the fading color on standing. The variance between the clear and unfiltered analyses and also between the volumetric and colorimetric analyses averaged less than two parts per million of phosphates as (PO_4) over the range of tests.

In attempting to improve the colorimetric method, various hoped for improvements had to be tried and then each one had to be checked against a known strength solution. It was observed in the volumetric analysis that the solution was kept at a temperature between 38°C. and 65°C. during the precipitation to get better and faster results. The temperature could not be allowed any higher or the silicates would precipitate. This might break the phosphomolybdate down to molybdic acid. This procedure was then tried on the colorimetric analysis. The solution was kept in a water bath from 38°C. to 65°C. while the sulphuric acid, ammonium molybdate, and hydroquinone were being added. The solution has a tendency to foam when the carbonate sulphite solution is added so this higher temperature should not

be maintained when that is added.

It was found, as hoped for, that the color developed more rapidly and that the time necessary between additions of the solutions could be reduced. On experimentation it was found that the time for the analysis could be lowered ten minutes, if carried out at this elevated temperature. Table #7 shows analyses of some previously analyzed solutions, when the shortened time and the higher temperatures were used.

Slightly lower temperatures are given in the A.O.A.C. method for the volumetric method (between forty and fifty degrees Centigrade) but no difficulty was encountered and good precipitation was obtained with the higher temperatures on the solutions used in this work.

It was observed that there was less change on standing in the color of the colorimetric solutions than expected. There is a fading at first and then the color deepens. It was observed that the boiler water solutions darkened more than the standard solutions on standing so that if much time is allowed to elapse before reading an error will arise.

Several Nessler tubes of both the boiler water and the standard solution in the blue colorimetric state were kept several months and after reaching an equilibrium seemed to be quite stable. This suggested a method for making color standards that would have exactly the same blue source as the samples. Table #7 shows the time necessary for the solutions to reach an equilibrium, which was between twenty four and forty eight hours. The boiler water reached an equilibrium quicker than the standard solutions.

No quantitative relationship could be observed between the final color

and the phosphate content and the time would be too great to make direct standards useful. Some of this solution which has reached an equilibrium must then be taken and diluted to match standards made fresh over the desired range. These could then be kept indefinitely for use against the sample. This eliminated the need to carry through standards each time and gave more accurate results. The exact standards to match could be found rather than just the limits as is done with the boiler salines.

A better comparison could be gotten in the colorimetric method in the more dilute strengths. The solutions in any case are too opaque to allow comparison by looking down through the Nessler tubes and the comparison must therefore be made from the side. The more dilute solutions give better comparison for this reason. Taking smaller numbers of ccs. of the sample, where accurate results are desired and the parts per million phosphates runs high, is recommended.

Parts per million of phosphate beyond the maximum and minimum limits of three and sixty five parts as found in this work seem to require variations in the reagents and procedure outlined to get the same results. These limits cover the range of phosphates which might be found in boiler salines. Other attempted improvements proved unsuccessful where the various reagents were tried combined.

CONCLUSIONS

1- The colorimetric phosphate determination on boiler salines may be run to two parts per million phosphates as (PO_4) if the phosphate content lies between three and sixty five parts per million. The five samples of boiler saline and boiler saline with various degrees of phosphate content added gave, in the authors opinion, very good checks between the colorimetric and volumetric analyses.

2- The colorimetric phosphate determination is an accurate determination if the phosphate (PO_4) content is below sixty five parts per million. This method could be more widely used than it is at present since the method takes less time than the other methods of analysis.

3- Keeping the solution, in the colorimetric phosphate determination, between forty and sixty degrees Centigrade during the precipitation will allow the color to develop in one half the time required at room temperature. This will allow the time for the analysis to be cut from approximately thirty to twenty minutes.

4- Stable color standards may be made from some of the colorimetric solution if some of the solution is allowed to reach a stable color. The solution will reach a stable color in from twenty-four to forty-eight hours and it may then be diluted to match freshly made standards. The standards may be kept indefinitely then for comparison. Standards made from the colorimetric solution will have the same shade of color as the solution.

5- There is work which could be done on the interfering substances in the local boiler salines which affect the analysis. The possibility of an

error in overloading in starting a boiler into operation with a constant phosphate dosage and much less salt present could be investigated. Work could be done to discover the exact complexes which cause the blue color used for comparison in the colorimetric method of analysis.

SUMMARY

This investigation showed that solutions could be analyzed about as accurately by the colorimetric method as by the standard volumetric method if the phosphate content lies between three and sixty parts per million (PO_4) in water solutions. The colorimetric method had to be varied to a longer procedure than the Permutit procedure for more accurate analyses but the method was still more rapid than the volumetric method.

Certain recommendations are given for making the colorimetric determination of phosphates even more rapid. The maintainance of a solution temperature of between forty and sixty Centigrade will allow the time of standing to be cut in half.

A method for making color standards using the same color as a standard as that which occurs in the sample is given. This does away with that part of the analysis which calls for the additional time, in more accurate work, where the exact standard to match must be found.

The colorimetric method for phosphate determination on the whole seems to be quite good and it should be used more generally than it is at present. The short time required for this method should recommend its use. Variations in the reagents and procedure seem to be necessary to go beyond the limits of three and sixty parts per million phosphates(PO_4).

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