Notes On The Determination Of Phosphates In Soap

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Introduction

The recent utilization of complex phosphates such as tetrasodium pyrophosphate (1) (2) and sodium hexametaphosphate (2) by the soap industry has rendered the present A.O.C.S. method for phosphate inadequate. The method is satisfactory when all the phosphate is present in the "ortho" form. Pyrophosphate and other complex phosphates are not precipitated or incompletely precipitated, depending upon the conditions of the analysis. When these complex phosphates are present it is necessary to hydrolyze them by boiling in acid solution before precipitating with ammonium molybdate.

After the sample has been boiled in acid solution, all phosphate present will be in the "ortho" form and the total P_2O_5 may be determined. If only one form of phosphate was originally present in the sample its percentage can readily be calculated from the total P_2O_5. In the case of mixtures of phosphates, additional suitable methods will be required to estimate the percentage of each type for definitive analysis.

The gravimetric technique involving ultimate weighing as magnesium pyrophosphate, described in the A.O.C.S. method, requires so long a time for completion that it is not entirely suitable for control purposes. Volumetric procedures based on the titration of the precipitated phosphomolybdate have been commonly employed in the fertilizer industry and should be suitable for the estimation of phosphates in soap. The purpose of the present paper is to present and discuss briefly certain points of general interest developed during the study of the latter procedure for this determination. The study has been limited to pyrophosphate since this is the form of complex phosphate commonly encountered in soap products.

Hydrolysis of Pyrophosphate

Since the precipitation of phosphate with ammonium molybdate is complete for the orthophosphate only, it is necessary to convert the pyrophosphate to that form by hydrolysis. The reaction may be represented by the following equation:

$$H_4P_2O_7 + H_2O \rightarrow 2\ H_3PO_4$$

Gerber and Miles (3) state that the hydration may be accomplished by diluting the phosphate solution to 100 ml., adding 7 ml. of concentrated nitric acid, and then boiling steadily for 15 minutes. Identical portions of a solution of tetrasodium pyrophosphate were taken, one boiled steadily for 15 minutes, the other for 1 hour. The phosphate was determined by the volumetric procedure as described later. The results were identical, 94.4 and 94.2 mg. $Na_4P_2O_7$, respectively, indicating that boiling in excess of 15 minutes did not hydrolyze more pyrophosphate. Evidence that 15 minutes steady boiling is sufficient for the complete hydration is given in Table I. The solution was prepared so that the 25 ml. which were used for analysis would contain 99.8 mg. tetrasodium pyrophosphate. The results by four analysts were all in good agreement with this value.

TABLE I
Hydrolysis and Determination of $Na_4P_2O_7$ in Solution

Time of Boiling: 15 minutes.
$Na_4P_2O_7$ Taken for Analysis — 99.8 milligrams.
Milligrams of $Na_4P_2O_7$ Found by Analyst

	No. 1	No. 2	No. 3	No. 4
	100.6	101.3	99.8	101.0
	100.5	100.7	100.2	101.2
	100.1	100.8	100.5	100.1
	100.4	101.2	100.1	100.3
Average —	100.4	101.0	100.2	100.7

That steady boiling is necessary for complete hydration is indicated by the data given in Table II. Instead of boiling for 15 minutes, solutions of varying concentrations were heated on a steam bath for one hour. In all cases the results were low and erratic.

TABLE II
Incomplete Hydrolysis of $Na_4P_2O_7$ Solutions When Heated One Hour on Steam Bath

Solution	No. 1		No. 2		No. 3		No. 4	
$Na_4P_2O_7$ Milligrams.	97.8		95.0		91.0		85.9	
	Found	Dev.	Found	Dev.	Found	Dev.	Found	Dev.
	97.4	— 0.4	90.0	— 5.0	79.5	—11.5	81.8	— 4.1
	80.3	—17.5	75.8	—19.2	56.5	—34.5	53.9	—32.0

Volumetric Method

The volumetric method of Pemberton (4), in which the washed ammonium phosphomolybdate precipitate is dissolved in a measured volume of sodium hydroxide of known concentration, and the excess titrated with standardized acid, is much less time-consuming than the gravimetric method and, therefore, more applicable for control purposes. It is essential for this method that all the ammonium phosphomolybdate be collected and that it be washed free of acid. A 1% potassium nitrate solution is preferred for washing the precipitate free of acid. The Shimer tube (5), which is extensively used in phosphate determination in the fertilizer field, has been found to be of great value in effecting these operations. The reproducibility of results by eleven control analysts each operating on four different solutions containing to them unknown quantities of tetrasodium pyrophosphate is shown in Table III. The analysts were instructed to hydrolyze the pyrophosphate by boiling for 15 minutes with concentrated nitric acid (5 ml. in a volume of 50 ml.). The actual analysis of each solution was established by taking the average of four analyses, very carefully performed, in duplicate, by each of two skilled research analysts. None of the results of the latter differed from the average by more than 0.3 mg. Further, these agreed closely with those calculated from the weights of phosphate used in preparing the solutions.

With one exception in the 44 determinations in Table III, performed by the eleven control analysts, no error was greater than 1.5% while the greatest average deviation for any one solution was 0.8 mg. in a total of 97.8 mg. or 0.8%.

TABLE III

Reproducibility of Results on $Na_4P_2O_7$ Solutions

Solution —	No. 1		No. 2		No. 3		No. 4	
$Na_4P_2O_7$ Taken								
Milligrams	97.8		95.0		91.0		85.9	
Analyst	**Found**	**Dev.**	**Found**	**Dev.**	**Found**	**Dev.**	**Found**	**Dev.**
No. 1	99.0	+ 1.2	95.4	+ 0.4	91.2	+ 0.2	86.8	+ 0.9
No. 2	97.8	0.0	94.3	— 0.7	91.0	0.0	86.3	+ 0.4
No. 3	98.5	+ 0.7	95.5	+ 0.5	91.3	+ 0.3	87.2	+ 1.3
No. 4	99.1	+ 1.3	94.6	— 0.4	90.9	— 0.1	86.1	+ 0.2
No. 5	97.9	+ 0.1	93.8	— 1.2	90.4	— 0.6	85.1	— 0.8
No. 6	98.5	+ 0.7	95.2	+ 0.2	90.8	— 0.2	86.6	+ 0.7
No. 7	97.2	— 0.6	94.9	— 0.1	91.4	+ 0.4	83.3	— 2.6
No. 8	99.1	+ 1.3	95.1	+ 0.1	91.2	+ 0.2	86.5	+ 0.6
No. 9	97.6	— 0.2	95.0	0.0	90.9	— 0.1	86.0	+ 0.1
No. 10	97.2	— 0.6	94.5	— 0.5	90.6	— 0.4	85.1	— 0.8
No. 11	98.5	+ 0.7	94.8	— 0.2	90.8	— 0.2	86.3	+ 0.4
Average	98.2	0.7	94.8	0.4	91.0	0.3	85.9	0.8

Effect of Silicate

Any silicate in phosphated products must be removed by acidification followed by dehydration to silica and subsequent separation by filtration. Two solutions of tetrasodium pyrophosphate were prepared, one containing 99.8 mg. per 25 ml., the other 89.8 mg. per 25 ml. Twenty-five ml. portions of these solutions were added to 0.9 g. of a silicated soap containing no phosphate. Two samples of each of these combinations were given to four analysts with instructions to evaporate the solution, ash the soap, dehydrate the silicate by adding 5 ml. of concentrated hydrochloric acid and evaporating to dryness on a steam bath, hydrolyze, filter the dehydrated silica from the solution, and subsequently estimate the phosphate. The results are given in Table IV.

TABLE IV

Determination of Pyrophosphate in Presence of Silicate and Soap
25 ml. of solution of $Na_4P_2O_7$ added to 0.9 g. soap.

Solution evaporated on Steam Bath.
Determinations made by four analysts.

	Milligrams of $Na_4P_2O_7$			
Added to Soap	**Found by Analysts**			
	1	2	3	4
99.8	100.1	100.1	99.4	99.8
	100.1	100.1	99.5	
89.8	89.1	89.9	90.4	89.8
	89.3	90.4	90.0	89.8

It will be noted that the results are in good agreement both among themselves and with the amount of tetrasodium pyrophosphate added.

Similar combinations were treated in exactly the same manner except that the silicate was dehydrated on an electric hot plate. The results are tabulated in Table V.

TABLE V

Effect on Phosphate Determination Caused by Dehydrating Silicate on Electric Hot Plate

	Milligrams of $Na_4P_2O_7$	
Added to Soap	**Found**	**In Silica Residue**
99.8	99.5	1.3
	97.5	3.2
89.8	85.2	3.2
	87.8	2.5

The results are considerably lower than those tabulated in Table IV. The silica residues from these determinations were decomposed with hydrofluoric acid and analyzed for phosphate. The quantities found are also tabulated in Table V. It will be seen that the silica must not be heated excessively and preferably should be dehydrated on a steam bath, in order to avoid occlusion of the phosphate by the silica. The dehydration of the silica may be done rapidly at a higher temperature, provided the silicon is evolved as silicon fluoride, the excess hydrofluoric acid eliminated, and the phosphatic residue combined with the bulk of the phosphate.

Details of Method

Since the method of the A.O.C.S. for phosphate in soap is inadequate for the complex phosphates, and since the volumetric method has decided advantages in its favor, the details of the method applied to this present work are given as a basis for further discussion and possibly for cooperative work by the laboratories interested in this problem.

A quantity of soap containing approximately 0.050 grams of phosphorus pentoxide is weighed into a platinum dish or pyrex beaker, heated at low temperature, until the soap is carbonized and smoking ceases. The dish or beaker and contents are cooled, 5 ml. of concentrated hydrochloric acid are added, and evaporated to dryness on a steam bath. Forty ml. of water and 5 ml. of concentrated nitric acid are added, then boiled steadily for 15 minutes and filtered. The filtrate is diluted to 125 ml., neutralized with 1:4 ammonium hydroxide, and acidified with 5 ml. concentrated nitric acid. The solution is heated to exactly 60°C., and 50 ml. of freshly filtered ammonium molybdate solution are added slowly with stirring. The solution is digested on a hot water bath for 15 minutes at a temperature not exceeding 65°C.

The supernatant liquid is filtered with suction through a paper mat in a Shimer filter tube. The precipitated ammonium phosphomolybdate is washed twice by decantation with 30 ml. portions of 1% potassium nitrate solution and then transferred to the filter where it is again washed with 3 portions of the solution. The precipitate and filter mat are transferred to a beaker and the tube washed with water until the volume is about 100 ml. Forty ml. of 0.5 N sodium hydroxide are added from a burette and the solution thoroughly stirred. After standing 5 minutes the solution is titrated with 0.5 N hydrochloric acid using 3 drops of 0.5% phenolphthalein indicator solution. The phosphorus pentoxide content is equivalent to the volume of the sodium hydroxide minus the volume of the hydrochloric acid used. The commonly accepted ratio of 23 molecules of sodium hydroxide to one molecule of ammonium phosphomolybdate has been employed in the calculation of the phosphorus pentoxide content of all solutions, phosphate and soap mixtures and phosphated soaps in the present work, hence 1 ml. of normal solution of sodium hydroxide reacts with a quantity of yellow precipitate containing an equivalent of 0.00309 g of P_2O_5. Thus

$$\text{Milligrams of } P_2O_5 = (AN - BN')\ 1.545$$

where A is volume in ml. and N the normality of the sodium hydroxide and B the volume and N' the normality of the acid.

Reproducibility of Results:

The reproducibility of results of analyses of phosphated soaps when analyzed by the method described is indicated by the results for four different samples of soap given in Table VI.

TABLE VI

Percentage $Na_4P_2O_7$ in Phosphated Soap

Soap Sample	No. 1	No. 2	No. 3	No. 4
	% $Na_4P_2O_7$			
Analyst 1	9.40	9.44	9.51	9.63
Analyst 2	9.34	9.40	9.46	9.55
	9.40	9.43	9.50	9.63
Analyst 3	9.45	9.51	9.57	9.70
	9.36	9.57	9.67	9.73
Average —	9.39	9.47	9.54	9.65
Max. Dev. from Average	+0.06	+0.10	+0.13	+0.10

The greatest deviation in any one set of results from the average is 0.13% at a 10% level of the tetrasodium pyrophosphate which indicates that the reproducibility of the method is about 1.5%.

Summary

1. Complex phosphates as tetrasodium pyrophosphate and sodium hexametaphosphate in soap are not

completely precipitated with ammonium molybdate when treated in the manner described by the present A.O.C.S. method for phosphate. Phosphates of this type are hydrolyzed to the "ortho" form when boiled steadily for 15 minutes in a nitric acid solution.

2. Silicates interfere with the determination by occluding phosphates if during dehydration they are heated at too high a temperature.

3. The volumetric method for the estimation of phosphate is more rapid than the gravimetric method, and yields results which are reliable and reproducible to within 1.5%.

4. The method will determine total P_2O_5 but will not differentiate between the different types of phosphate. It is convenient where only one type of phosphate is present. For mixtures of phosphates additional specific analyses must be employed.

REFERENCES:

1. Cobbs, Soap, 14, No. 11, 24 (1938).
2. Gillet, Soap, 15, No. 1, 24 (1939).
3. Gerber and Miles, Ind. Eng. Chem., Anal. Ed. 10, 519, 1938.
4. Pemberton, Chem. News, 46, 4 (1882); J. Am. Chem. Soc., 16, 278 (1894). See also Methods of Analysis of the Ass'n. of Off. Agric. Chem., 3 ed., 16, (1930); Hildebrand and Lundell, Applied Inorganic Analysis, 567, (1929); Scott's Standard Methods of Analysis, 697 (1939).
5. Shimer, Chem., Eng. 6, 197 (1907); J. Am. Chem. Soc., 27, 287 (1909).

The Pharmacology of Soaps

The Irritant Action of Refined Oil Soaps on Human Skin

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THIS laboratory undertook sometime ago the study of the irritant action of soaps on human skin. The first papers ([1]), dealing with the irritant action of soaps made from single fatty acids and single alkyl sulfates, were presented at the Atlanta meeting of the American Pharmaceutical Association (August 1939), and are to be published in the Journal of that organization. The same method of application of the soaps, as described in these earlier reports, has been used in this subsequent work on soaps of refined oils.

Sources of Refined Oils

The refined oils, sweet almond, castor, corn, linseed, palm, palm kernel (denatured), peanut, poppyseed, rapeseed, sesame, and soya were obtained from Eimer and Amend, New York. Cocoa butter, coconut, cod liver, cottonseed and olive oils were secured from the School of Pharmacy, W.R.U. Raisin seed oil was supplied by the California Products Co., Fresno, Calif. Avocado pear oil was purchased from the Mefford Chemical Co., Los Angeles, Calif. Beef suet was purchased from a meat market and the fat rendered.

TABLE I.
THE PHYSICAL-CHEMICAL PROPERTIES OF 5% SOAP SOLUTIONS OF SINGLE REFINED OILS

	State of 5% Soap Solution		pH at 28°C.	
Refined Oil	Na	K	Na	K
Almond	L	L	10.3	10.1
Avocado pear	L	L	9.3	9.4
Beef suet	G	G	10.5	10.7
Castor	L	L	9.5	9.7
Cocoa butter	G	G	10.8	11.1
Cocoanut	L	L	10.2	10.4
Cod liver	L	L	10.0	10.4
Corn	L	L	10.1	10.4
Cottonseed	L	L	10.0	10.5
Linseed	L	L	10.3	10.3
Olive	L	L	10.2	10.4
Palm	G	G	gel (too thick)	10.5
Palm kernel	L	L	10.3	10.4
Peanut	L	L	10.1	10.5
Poppyseed	L	L	10.0	10.3
Raisin seed	L	L	9.3	9.5
Rape seed	L	L	10.3	10.5
Sesame	L	L	10.3	10.5
Soya bean	L	L	10.3	10.4

L = Clear liquid G = Gel

The Preparation of Soaps of Refined Oils

The U.S.P. XI methods were used for the determination of the saponification value and the preparation of free fatty acids of the oils.

The following method was used for the preparation of the neutral soaps. Approximately 150 grams of an oil, accurately weighed, was added to one liter of 95% alcohol in a two-liter pyrex flask connected to a reflux condenser. The calculated amount of 6N NaOH was added to the boiling alcohol-oil mixture, and the whole allowed to reflux for one hour. At this point the mixture was tested for the completeness of saponification and for excess alkali. The saponification was considered complete when the soap from 5 cc. of the hot mixture produced a clear solution with 50 cc. of hot distilled H_2O. The soap formed was considered a neutral soap when 5 cc. of the hot mixture diluted with 50 cc. of previously neutralized alcohol, containing phenolphthalein, produced a pink color which was discharged by one drop of 0.05N HCl. The soap was dried in a pyrex flask at the temperature of a boiling water bath under the vacuum produced by a water aspirator. The soap, after it had reached a gel state due to the distillation of the alcohol, was transferred to a press which made ribbons of the soap approximately 0.5 mm. in thickness and 5 mm. in width. The soap was then dried for 5 hours under the above conditions. The potassium soaps were made in a similar manner. Some physical and chemical properties of the 5% soap solutions of the oils are given in Table I.

Skin Results of Soaps of Refined Oils

The results on human skin of the 5% solutions of neutral soap prepared from the refined oils are listed in Table II.

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