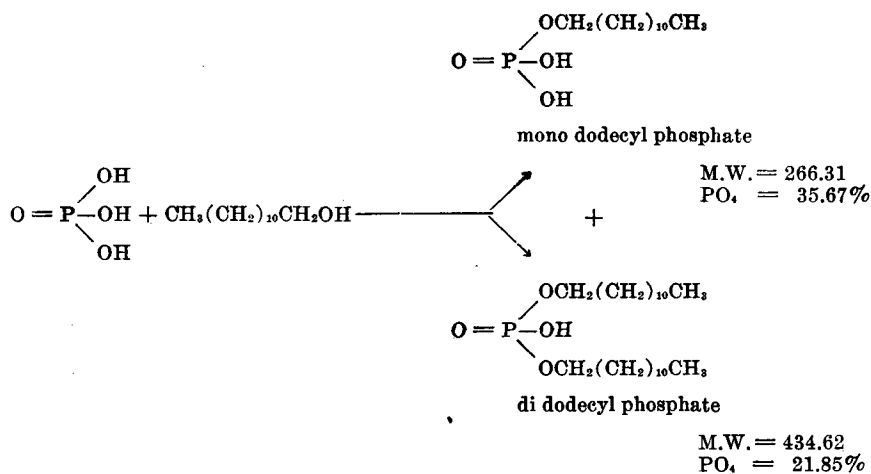# The Estimation of Mono and Di Alkyl Phosphate in the Presence of Phosphoric Acid and Alcohol

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THE commercial utility of fatty esters of phosphoric acid is often dependent upon the relative amounts of the mono and di substituted constituents present. When a fatty alcohol such as dodecyl is reacted with phosphoric acid or phosphorous pentoxide, the product is usually a mixture of mono dodecyl phosphate and di dodecyl phosphate (1,4,6) along with unreacted dodecyl alcohol and free phosphoric acid or phosphorous pentoxide. If P_2O_5 is used, water is added at the end of the reaction to decompose any excess P_2O_5. For this reason water may also appear in the product and further complicate the analyses. An incidental amount of inorganic matter is sometimes present as an impurity in such a quantity as to necessitate consideration. Such a mixture can be reasonably well characterized by a determination of total phosphate, free phosphoric acid, and free fatty alcohol. In spite of the nature of the mixture it is not necessary, nor is it desirable to resort to potentiometric methods (8) or fractional precipitations. After these three items have been determined by the simple methods described below, it is possible to calculate the relative amount of mono and di dodecyl phosphate. If water and ash are present they must also be individually determined and considered in the final calculation.

If in the syntheses of these commercial products the esterification is carried out under such conditions that no tri alkyl phosphate is formed, the reaction may be represented as:

content of the mixed esters is then known and the amounts of each substituent can be calculated after correcting for ash, water, and free alcohol.

Total phosphate is determined by the ammonium molybdate method after wet combustion of the sample by means of a mixture of nitric and perchloric acids. Nitro-perchloric was first used for the digestion of organic matter by Kahane (7) when he employed it for determining sulfur in rubber. Wolesenky (10) later describes an improvement of this method. It was largely through the efforts of G. Frederick Smith that perchloric acid became a popular agent for analytical purposes. It was widely applied to digestions of various types of materials and was extensively used for analysis of fats and oils in our laboratory (5). Only by close adherence to the following procedure are the hazards completely removed and the accuracy maintained.

Procedure for Total PO₄

Weigh out 2-3 grams of the sample, dissolve in ethyl alcohol and transfer the whole to a 200-ml. volumetric flask. Fill up to the mark with alcohol and mix thoroughly. Pipette out a 2.0-ml. aliquot into a 250-ml. wide mouth Erlenmeyer flask. Place the flask on the steam bath until the alcohol is completely volatilized. Cool the flask and add 30 ml. of a 75/25 mixture of nitric-perchloric acid and swirl vigorously for several minutes. Place the flask on a hotplate and heat gradually. When the reaction starts, as indicated by a vigorous boiling of the liquid,

mono dodecyl phosphate

M.W. = 266.31
PO₄ = 35.67%

di dodecyl phosphate

M.W. = 434.62
PO₄ = 21.85%

Because of the wide difference in PO₄ content of the two esters it is evident that one could easily calculate the amounts of each component if the amount of combined PO₄ were known. The method is therefore based upon this principle. The free phosphate (which is present as H_3PO_4) is subtracted from the total phosphate to give the combined phosphate. The PO₄

remove the flask from the hotplate until the reaction has subsided. The flask is then returned to the hotplate and swirled often during the remainder of the oxidation which should take about 10 minutes. At no time should the sample be left unattended on the hotplate. No danger of explosion is involved if the above precautions are followed and the sample size

does not exceed one gram. The end of the reaction is reached when no oil remains in the flask and the contents are completely homogeneous. It is desirable to continue the digestion until the volume within the flask is reduced to about 3 ml. Transfer the residue quantitatively to a 400-ml. beaker, add 10 ml. of concentrated nitric acid and about 200 ml. of water. Heat the resulting solution to 45° and add 50 ml. of warm ammonium molybdate reagent (4). The solution is then stirred until the yellow precipitate forms. The beaker is then allowed to stand in a warm place for 4 hours, or until precipitation is complete. Filter off the precipitate by pouring the contents of the flask through a filter prepared by building up a $\frac{1}{8}''$ layer of asbestos on a perforated porcelain disk placed in the bottom of a glass adapter. The precipitate is washed 10 times with small portions of 1% nitric acid and then with 1% ammonium nitrate until free from acidity (about 10 times). Transfer the entire contents of the adapter (the precipitate, the asbestos, and the perforated disk) to a 400-ml. beaker by inserting a stirring rod in the bottom of the adapter and punching out the perforated disk. Wash off any adhering precipitate with a stream from the wash bottle. Add 30 ml. of standard N/10 NaOH to the beaker and stir until all the yellow precipitate is dissolved. Let stand for a few minutes and then titrate the excess NaOH with standard N/10 nitric acid using phenolphthalein indicator.

Calculation:

$$\% \ PO_4 = \frac{\text{ml. N/10 NaOH consumed} \times .0004133 \times 100}{\text{Wt. of aliquot sample}}$$

Free phosphoric is determined by extracting the sample dissolved in petroleum ether three times with saturated salt solution. The three combined extracts are then filtered and titrated.

Procedure for Free Phosphoric Acid

Dissolve 1-2 grams of the sample in 250 ml. of petroleum ether and transfer to a separatory funnel. Add 50 ml. of saturated sodium chloride solution and shake. Allow the layers to separate and draw off the bottom layer. Repeat this operation twice more and combine all three salt solution extracts. The addition of a little octyl alcohol aids in suppressing emulsification which causes some of the oily portion to appear in the salt solution layer. Disregard any slight amount of emulsified oil in the combined salt extracts because all oil is removed in the next step. Filter the combined extracts through a filter paper moistened with saturated salt solution. The oily portion remains on top of the paper and the filtrate contains the free phosphoric acid. Wash the paper once with more salt solution and titrate the combined filtrates with standard N/10 NaOH using phenolphthalein indicator.

Calculation:

$$\frac{\text{ml. N/10 NaOH} \times .0049 \times 100}{\text{Wt. of sample}} = \% \ \text{free} \ H_3PO_4$$

$$\% \ \text{free} \ PO_4 = \% \ \text{free} \ H_3PO_4 \times .969$$

Free dodecyl alcohol is obtained by determining the free hydroxyl content by the method of Ogg, Porter, and Willits (9). This involves acetylizing with a solution of 1 volume of acetic anhydride in 3 volumes of pyridine.

Procedure for Free Dodecyl Alcohol

Weigh accurately into a 24/40 100-ml. round flask about 2 grams of sample. Measure into the flask, by means of a micro burette, 5 ml. of acetic anhydride in pyridine 1:3. Moisten the stopper with pyridine and press the stopper firmly in place. Place the stoppered flask on the steam bath for 45 minutes, then remove from the bath and add 10 ml. of water, shake and let stand for 5 minutes longer. Add 10 ml. of neutral n-butanol and titrate with standard N/1 NaOH using phenolphthalein (Titration A).

To correct for the free acidity of the sample run a blank through the same procedure but omit the anhydride solution and substitute 5 ml. of pyridine. Instead of using exactly the same weight of sample as before, weigh accurately about 5 grams and from the titration obtained calculate the volume of N/1 NaOH required to neutralize the free acidity of the sample used to obtain titration A. Call this Volume B.

Run a blank determination on the 5 ml. of the acetic anhydride-pyridine acetylating solution (Titration C).

Calculation:

$$\frac{[(C+B)-A].017 \times 100}{\text{Wt. of sample}} = \% \ OH$$

$$\% \ \text{Dodecyl alcohol} = \% \ OH \times 10.96$$

Water is determined by the method of Alexander (2) which consists of measuring the water in a Hercules Trap after it is separated from the sample by azeotropic distillation.

Procedure for Water

Weigh out 10 grams of sample into a 500-ml. round bottom flask and add 200 ml. of methylene chloride. Between the flask and the reflux condenser attach a Hercules trap. Heat the flask by means of a bath until the methylene chloride begins to boil. Continue the refluxing for about one hour, then cool and, by means of the graduations on the trap, read the amount of water collected.

Calculation:

$$\frac{\text{ml. water} \times 100}{\text{Wt. of sample}} = \% \ \text{water}$$

Ash is determined in the usual manner by igniting a five-gram sample in a silica dish.

Integration of Results

With the above information at hand sufficient data is available to calculate the amounts of mono and di dodecyl phosphate in the mixture. Since all contaminating constituents are thus determined, the amount of phosphate esters is obtained by difference. Phosphate present as a combination of mono and di derivatives is then compared to the theoretical PO_4 content of each of the pure derivatives. The relative amount of each ester is then estimated as shown in the following calculation:

Let a = % Combined PO_4 (total PO_4—free PO_4)
    b = % Ash
    c = % Water
    d = % Free dodecyl alcohol
    e = % Free H_3PO_4
35.67 = Theoretical % PO_4 in mono dodecyl phosphate
21.85 = Theoretical % PO_4 in di dodecyl phosphate
    f = % Total mono and di dodecyl phosphate

I. Then f $= 100 - (b+c+d+e)$

Let g $= \%PO_4$ in total mono and di dodecyl phosphate

II. Then g $= \dfrac{a \times 100}{f}$

Let X $= \%$ di dodecyl phosphate

III. Then X $= \dfrac{35.67-g}{35.67-21.85} \times 100$

Let Y $= \%$ mono dodecyl phosphate

IV. Then Y $= 100-X$

However X and Y are both based on the total amounts of mono and di esters but since there are only f $\%$ of such compounds, X and Y must be multiplied by .01 f to give percentages based on the original sample.

Example:

By determination a $= 17.04\%$ (combined PO_4)
                b $=$ .90% (ash)
                c $=$ 0.00% (water)
                d $= 25.5$ % (free dodecyl alcohol)
                e $= 1.51\%$ (free H_3PO_4)

I. $100-(b+c+d+e) = f$

    Substituting f $= 100 - (0.90 + 0.00 + 25.50 + 1.51)$
                   f $= 72.09$

II. $\dfrac{a \times 100}{f} = g$

        g $= \dfrac{17.04 \times 100}{72.09}$

        g $= 23.64$

III.   X $= \dfrac{35.67-g}{35.67-21.85} \times 100$

        X $= 87.05$ ($\%$ di dodecyl phosphate based on phosphate esters alone)

IV.   Y $= 100-X$

        Y $= 100-87.05$

        Y $= 12.95$ ($\%$ mono dodecyl phosphate based on phosphate esters alone)

$87.05 \times .01 \times 72.09 = 62.75$ di dodecyl phosphate based on original sample

$12.95 \times .01 \times 72.09 = 9.34$ mono dodecyl phosphate based on original sample

Analysis:

          1.51% free H_3PO_4
          25.50% free dodecyl alcohol
          0.00% water
          .90% ash
          62.75% di dodecyl phosphate
          9.34% mono dodecyl phosphate

    Total 100.00%

The same method applies for other fatty phosphates providing the proper factors are applied in equation III.

Summary

A method is presented for the determination of mono and di alkyl phosphates in the presence of the contaminants usually present when the sample is prepared by the reaction of P_2O_5 or H_3PO_4 on fatty alcohol. Total PO_4, free H_3PO_4, hydroxyl, ash, and water are determined by simple methods and the percentage of mono and di esters are calculated therefrom.

REFERENCES

1. Adler, H., and Woodstock, W. H., Chem. Industries, 51, 516-21, 557 (1942).
2. Alexander, H. B., Ind. Eng. Chem., Anal. Ed., 8, 314 (1936).
3. Furman, N. H., "Scott's Standard Methods of Chemical Analysis," 5th ed., vol. 1, p. 697, D. Van Nostrand Co., Inc., 250 Fourth Ave., New York (1939).
4. Harley, V., J. Pharm. Chem., 20, 160-7 (1934).
5. Heineman, H. C., Celanese Corporation of America, Cumberland, Maryland, private communication.
6. Hochwalt, C. A., Lum, J. H., Malowan, J. E., and Dyer, C. P., Ind. Eng. Chem., 34, 20-5 (1942).
7. Kahane, E., Ann. Chim. Analyt., 9 (ii), 261-264 (1927); Brit. Chem. Abstracts B., 823 (1927).
8. Kumler, W. D., and Eiler, J. J., J. Am. Chem. Soc., 65, 2355 (1943).
9. Ogg, C. L., Porter, W. L., and Willits, C. O., Ind. Eng. Chem., Anal. Ed., 17, 394 (1945).
10. Wolesensky, Edward, "Perchloric Acid," 3rd ed., vol. 1, G. Frederick Smith Chem. Co., 867 McKinley Ave., Columbus, Ohio (1934).

Polymer Formation From Natural and Synthetic Drying Oils

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General

THE natural triglyceryl esters of importance in polymer chemistry are predominantly the esters of the octadecadienoic and octadectrienoic isomers characteristic of linseed and tung oils, respectively. The polymerized vegetable oils sold commercially for use in various phases of the protective and decorative coatings industries (paints, varnishes, lacquers, printing inks, linoleum, binding agents, etc.) are not *high* polymers. The maximum polymeric form found in such oils has been the tetramer, and the average form would be approximately that of the dimer; however, the final utility of these oils in coatings depends in some measure on their ability to form high polymers.

When such drying oils are spread out in thin films and allowed to "dry" or otherwise processed to form gels the products are in a large degree insoluble and infusible and relatively chemically resistant. Their examination is subject to the same limitations as is that of the polyesters, which are now clearly recognized as high polymers. It should be noted, however, that the resultant poly-films or gels contain varying amounts of smaller molecular species interspersed therein. It is probably this characteristic which has resulted in the colloidal approach to the problem by some workers in the field. The view now generally held is that the colloidal phenomena are a secondary problem, and result from the formation of a polymeric phase (1).

The vegetable oils are a relatively cheap source of raw material, so that their total yearly product value possibly does not approach that of the synthetic