the fact that requirements are being thrust upon us that are far in excess of those applied to other industries with similar hazards. Refineries have no such rules, natural gas plants have no such rules, nor do dry cleaners or butane dealers or tank trucks or railroads. I think a solvent plant is safer than many filling stations where gasoline may be dispersed by a cigar-smoking attendant to a customer who has no hesitation about lighting a cigarette or flipping a cigarette butt out of the car window, where an automatic cut-off nozzle is used that frequently sloshes gasoline on the ground near a tank truck unloading gasoline. Cars and people in unlimited number go in and out of the danger area at will.

In view of the foregoing, it might be said, in closing, that these requirements seem unnecessary and unjust. Particular objection is taken to the use of such words and phrases as: "competent personnel experienced in . . . hazards of flammable liquids," "adequately curbed and drained," "adequate system," "properly detached," "approved," and "properly located."

Each of these words and phrases may have a different meaning to each person who reads them. And objection is made to the distrust evidenced in the proposed schedule where a mechanical policeman is set to watching the operator with another mechanical policeman watching the mechanical policeman.

Furthermore objection is made to the setting up of the N.B.F.U. pamphlets as rules with the only exceptions being those where adequate requirements are set aside in favor of other more-than-adequate requirements. In at least one case the requirements of the N.B.F.U. are doubled in this schedule.

My final thought is that the solvent-extraction industry should not be burdened with requirements far greater than those imposed on other industries with similar hazards.

The Determination of Pyrophosphate in Commercial Triphosphate

HERMAN J. WEISER JR., The Procter and Gamble Company, Cincinnati, Ohio

ONE OF THE MOST SERIOUS NEEDS in the field of phosphate chemistry has been for a direct, accurate method of determining pyrophosphate in the presence of large amounts of triphosphate. Good methods have been published for ortho- (10) and triphosphate (17), but a procedure for pyrophosphate in commercial triphosphate was needed. Two procedures involving zinc precipitation have been published. The first (1, 2, 5) involves precipitation of the zinc pyrophosphate at pH 3.8 and separation of the precipitate by filtration, followed by ignition and weighing of the precipitate. This is based on the earlier work of Britzke and Dragunov (3). In the second method (15) both pyro- and triphosphate are precipitated as zinc salts; and after drying and weighing, the precipitate is analyzed for zinc. Solution of simultaneous equations gives values for both pyro- and triphosphate. The first method has given good estimates of the pyrophosphate content of some samples despite radiochemical data (12), showing that it may be contaminated with a significant amount of triphosphate. When the pyrophosphate content is less than 10%, there is often no precipitation (12) unless extra pyrophosphate is added (2). As the authors of the second method point out (15), the zinc determination must give very accurate values, or it will adversely affect the pyro- and triphosphate results.

The earliest direct method of determining pyrophosphate was by x-ray diffraction (14, 9). Of course, this method can only be applied to solid samples, and all the pyrophosphate must be crystalline. A method involving the isotope dilution technique (13) also is specific for pyrophosphate. This method requires equipment to carry out the radiochemical counting and an elapsed time of one to three days to complete a determination.

Probably one of the earliest attempts to separate the individual phosphate species by ion exchange chromatography was carried out by the author (16) in 1950–51. The approach was empirical, yielding a separation of ortho- and trimetaphosphate from pyro- and triphosphate. The mathematical approach of Beukenkamp, Reiman, and Lindenbaum (4) proved more fruitful, and they have devised a procedure for separating not only these four species from each other but also the tetrameta- and tetraphosphate (8, 11). Paper chromatography has also been applied successfully to the separation and determination of the phosphate species (7). Both of these procedures have the important advantage of separating the various phosphate species from each other before hydrolyzing the individual components to orthophosphate and determining the amount present by an accurate colorimetric procedure. Since the ion exchange procedure appeared to be capable of greater accuracy by virtue of the larger amount of sample handled, it was applied to the analysis of commercial triphosphate.

DEVELOPMENT OF THE METHOD

Elution Curve. Commercial triphosphate normally contains 5 to 15% pyrophosphate and 85 to 95% triphosphate (17). Because of the great difference in the amounts of these two species it was necessary to modify the elution procedure of Peters and Rieman (11) to insure their quantitative separation. In addition, it was found that the acid eluant of Higgins and Baldwin (6) provided such a superior separation of ortho- and pyrophosphate that it was incorporated into the method. In fact, the separation was so good that it was necessary to add KCl to the eluant and change to eluant No. 2 before the end of the fraction so that the fractions would not be too widely separated. No evidence was obtained

to indicate that this eluant caused hydrolysis of the condensed phosphates.

A typical elution curve of a mixture of commercial triphosphate composition is shown in Figure 1. The curve was prepared by collecting 9.18 ml. fractions (this was the volume delivered by a commercial siphon collector having a nominal volume of 10 ml.). Each fraction was hydrolyzed, and the phosphate content was determined by the procedure described below. This procedure should be carried out with each new batch of resin to determine the proper volume of each eluant to be collected.

It should be noted that the trimetaphosphate fraction will contain tetrametaphosphate and some higher polyphosphates if they are present. In normal commercial triphosphate negligible amounts of these compounds will be present. As Peters and Rieman (11) point out, the highly polymerized molecules of Graham's salt are tenaciously held by the resin and must be hydrolyzed with hot acid before they can be removed.

Colorimetric Orthophosphate. In attempting to use the vanadomolybdate colorimetric procedure of Rieman and co-workers (4), it was found that the

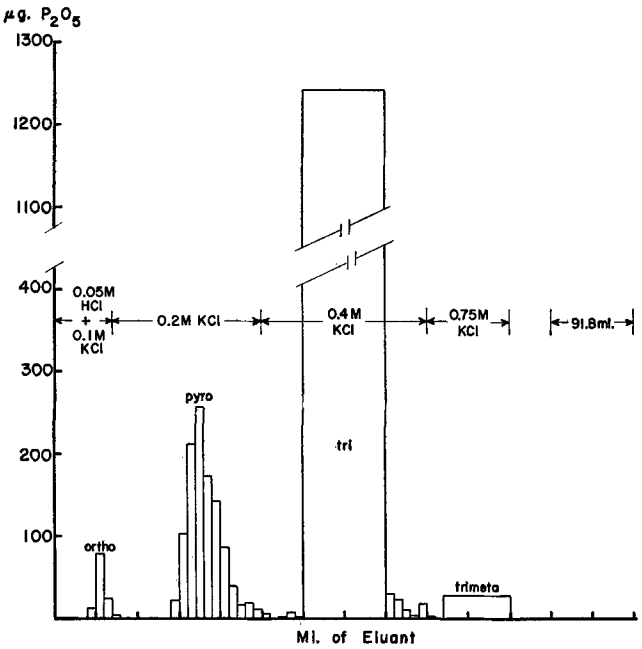

FIG. 1. Elution curve.

results obtained were always high. When the eluants were passed through the resin containing no phosphate sample, positive phosphate values were obtained. Because of this and to obtain a more sensitive method the Martin and Doty (10) procedure was adapted to the need. The splitting of the reagent into two portions, 8 N sulfuric acid and 10% ammonium molybdate, was successfully used in the analysis of paper chromatograms (7). It was found to be equally satisfactory here.

Experimental

Apparatus. The chromatographic set-up is shown in Figure 2. The capillary tubing controls the rate of flow through the column and relieves the operator of the tedious task of controlling the flow rate by adjusting the lower stopcock. The over-all distance between the bottom of the column and the liquid level in the funnel or the length of the capillary may have to be adjusted slightly for a particular column and packing to get the desired flow rate. A colorimeter with 13-mm. square cuvettes was used for the colorimetric determination.

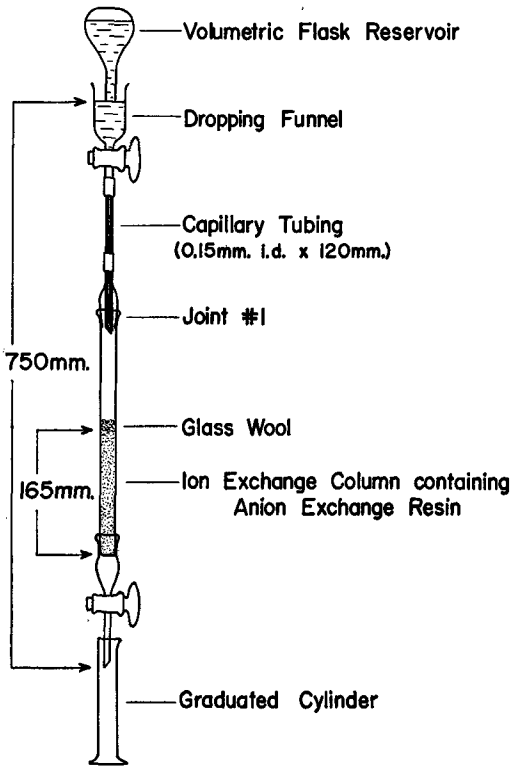

FIG. 2. Chromatographic apparatus.

Eluants. The eluants used were: No. 1—0.05 M hydrochloric acid, 0.1 M potassium chloride; No. 2—0.2 M potassium chloride; No. 3—0.4 M potassium chloride; and No. 4—0.75 M potassium chloride. Eluants 2, 3, and 4 were buffered at pH 5.0 by addition of 5 ml. of buffer stock solution to each 500 ml. of solution. The stock solution was prepared by dissolving 25.5 g. of anhydrous, A.C.S. grade sodium acetate, and 11.9 ml. of A.C.S. grade glacial acetic acid in enough distilled water to give 500 ml. solution. About five milligrams of mercuric iodide were added to each eluant solution to prevent mold growth.

Solutions. 10% Neutral Molybdate: dissolve 100 g. of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, A.C.S. reagent, in enough water to make 1 liter of solution; store in a brown bottle.

Methanol-Sulfuric Acid: add 20 ml. of conc. sulfuric acid (A.C.S. reagent) slowly with good stirring to 980 ml. methanol (A.C.S. reagent).

Stock Stannous Chloride: dissolve 10 g. of A.C.S. reagent stannous chloride dihydrate in 25 ml. of A.C.S. reagent conc. hydrochloric acid; prepare a fresh solution every two weeks and store in a brown bottle.

Dilute Stannous Chloride: add 0.5 ml. of stock stannous chloride to 100 ml. of 1 N sulfuric acid; prepare a fresh solution each day.

Preparation of Chromatographic Column. Lot number 3604–37 of Dowex 1-X10, 100–200 mesh anion ex-

change resin was used in this work. Soak the resin overnight in distilled water. Rinse the resin several times by decantation. Slurry enough resin into the column to give a resin height of 16.5 cm. Prepare the column for use by passing 500 ml. of eluant No. 2 through it. The same treatment is given all columns after use to prepare them for the next sample.

Elution Procedure. Dissolve 2.500 ± 0.001 g. of commercial triphosphate in water and dilute to 500 ml. Remove the top of the column at joint No. 1 and allow the liquid to flow out of the column until the surface of the liquid is 1 mm. above the top of the resin. Place a 100-ml. graduated cylinder under the column. Transfer a 5-ml. aliquot of the sample solution to the top of the resin. Open the stopcock and allow the liquid to flow from the column until the surface of the liquid is 1 mm. above the top of the resin. Add 5 ml. of eluant No. 1. Repeat this addition procedure with two more 5-ml. portions of eluant No. 1. Place the top on the column, and fill the dropping funnel and volumetric flask with eluant No. 1. Allow the eluant to flow through the column at 1.3 to 1.7 ml. per minute. When 65 ml. have been collected in the graduated cylinder, remove the remainder of eluant No. 1 from the dropping funnel and fill with eluant No. 2 and invert a 250-ml. volumetric flask of eluant No. 2 in the reservoir. When a total of 90 ml. have been collected, change receivers and place a 250-ml. graduated cylinder under the column. The 100-ml. graduated cylinder contains the orthophosphate fraction.

Collect 155 ml. of eluant No. 2. This is the pyrophosphate fraction. Change to eluant No. 3, and collect 190 ml. This is the triphosphate fraction. Change to eluant No. 4, and collect 100 ml. (in a volumetric flask) to get the trimetaphosphate.

Hydrolysis of Eluates. Transfer the orthophosphate fraction to a 100-ml. volumetric flask, and dilute to the mark with distilled water. Transfer a 20-ml. aliquot to a 20 x 200-mm. test tube. Dilute the pyrophosphate fraction to 200 ml., and transfer a 20-ml. aliquot to a test tube. Dilute the triphosphate fraction to 250 ml., and after thorough mixing dilute 50 ml. of this solution to 200 ml. Transfer a 10-ml. aliquot of the final solution to a test tube. After mixing the trimetaphosphate fraction, transfer a 20-ml. aliquot to a test tube. Place 10 ml. of distilled water in another test tube to be used as a blank.

Add 5 ml. of 8 N H_2SO_4 to each test tube. Place the test tubes in a boiling water bath and allow to hydrolyze 45 min. Remove the test tubes from the water bath, and let them cool to room temperature. Dilute each sample to 25 ml. (a scratch on the side of the test tube) with distilled water.

Colorimetric Determination of P_2O_5 in Eluate. Add to each test tube 25 ml. of a 1:1 (by volume) benzene-isobutanol mixture from an automatic pipette. Add 5 ml. of 10% neutral molybdate solution, stopper the tube with a rubber stopper, and shake vigorously for 15 seconds. Allow the layers to separate and transfer a 10-ml. aliquot of the upper layer to a 50-ml. glass-stoppered volumetric flask. (A pipetting bulb or water aspirator should be used for filling the pipette.) Rinse the pipette three times with methanol-sulfuric acid solution. Dilute the sample to about 40 ml. with methanol-sulfuric acid. Add 1 ml. of dilute stannous chloride solution, and swirl immediately. Dilute to the mark with methanol:sulfuric acid, and mix thoroughly. Transfer the blank and sample solutions to colorimeter cuvettes, and determine the absorbance at 630 mμ between 10 and 30 min. after the stannous chloride was added.

A calibration curve should be prepared beforehand, covering the range from 0 to 300 micrograms of P_2O_5.

Calculations. The general equation for calculating the percentage of a particular phosphate in the sample is as follows:

$$\% \text{ Phosphate} = \frac{\mu g\ P_2O_5 \text{ in aliquot} \times 10^{-6} \times \text{fraction dilution} \times \text{factor} \times 100}{\text{sample weight placed on column}}$$

The factor is the equivalent weight of the particular phosphate divided by the equivalent weight of P_2O_5. When applied to pyrophosphate, using the procedure given, the following equation is obtained:

$$\% Na_4P_2O_7 = \frac{\mu g\ P_2O_5 \text{ in aliquot} \times 10^{-6} \times 200/20 \times 1.873 \times 100}{\text{sample weight} \times 5/500}$$

$$= \mu g\ P_2O_5 \text{ in aliquot} \times 0.07492$$

Discussion

Accuracy of the Method. The accuracy of the method was tested by preparing two simulated commercial triphosphate samples by weighing known amounts of the pure individual phosphates. Six aliquots of each sample were chromatographed. Although the method was primarily set up to determine pyrophosphate, it was only a little more work to determine all of the components. The results obtained are summarized in Table I. Sample I is an "average" commercial triphosphate composition while sample II contains about the maximum amounts of the minor ingredients normally expected. The results indicate that very good pyrophosphate values are obtained and that the other three components can be determined with reasonable accuracy.

TABLE I
Determination of Phosphates in Known Mixtures

Sample	Compound	% Taken	Average % Found
I	Na_2HPO_4	1.03	0.96
	$Na_4P_2O_7$	8.25	8.08
	$Na_5P_3O_{10}$	89.3	88.2
	$Na_3P_3O_9$	1.40	1.33
II	Na_2HPO_4	1.50	1.39
	$Na_4P_2O_7$	10.0	9.75
	$Na_5P_3O_{10}$	85.0	84.7
	$Na_3P_3O_9$	3.50	3.39

The reproducibility of the method was determined by analyzing duplicate aliquots of three different weighings of a single commercial triphosphate sample. The results obtained are presented in Table II. The values obtained show good agreement with the standard deviations obtained by other methods, and the pyrophosphate value is a great improvement over previous methods.

In further testing the applicability of the proce-

TABLE II
Reproducibility Data

Compound	Mean	Range	Standard Deviation
Na_2HPO_4	0.19	0.14– 0.24	0.05
$Na_4P_2O_7$	7.64	7.53– 7.79	0.10
$Na_5P_3O_{10}$	88.6	87.7 –89.6	0.62
$Na_3P_3O_9$	0.38	0.32– 0.50	0.06

dure to commercial samples, two retained samples which had been analyzed by a different procedure (17) were run again. The results obtained are presented in Table III. The data show that although

TABLE III

Effect of Aging on Commercial Triphosphate

Sample	Method	Date of Analysis	% Na_2HPO_4	% $Na_4P_2O_7$	% $Na_5P_3O_{10}$	% $Na_3P_3O_9$
I	(a)	1952	0.40	3.7	95.4	0.63
	(b)	1956	0.55	14.4	82.9	0.56
	(a)	1956	0.79	14.2	84.4	0.25
II	(a)	1952	0.26	4.5	90.0	3.50
	(b)	1956	0.73	15.0	80.4	1.22
	(a)	1956	0.95	17.2	80.8	0.75

(a) See reference (17).
(b) Present chromatographic method.

only minor changes took place in the ortho- and trimetaphosphate content, approximately 10% of the triphosphate was converted to pyrophosphate in three and one-half years of standing in closed containers. The change was confirmed by re-running the samples by the same method used in 1952 (17). The data clearly indicate that in commercial triphosphate a direct conversion of triphosphate to pyrophosphate takes place at room temperature.

Pyrophosphate alone can be determined in about four hours elapsed time and all four components in about eight hours.

Application to Detergents. This method can be applied to triphosphate built synthetic detergents if an alcohol separation is used to remove the alcohol-insoluble portion (17). If the original sample is chosen to contain 2.5 g. of phosphate, the ion exchange procedure can be used as described except for changing the "sample weight" in the calculations. If a large portion of the triphosphate has hydrolyzed to pyrophosphate, it may be necessary to change the dilution of these fractions to get maximum sensitivity.

REFERENCES

1. Bell, R. N., Analytical Chemistry, *19*, 97 (1947).
2. Bell, R. N., Wreath, A. L., and Curless, W. T., *Ibid.*, *24*, 1997 (1952).
3. Britzke, E. V., and Dragunov, S. S., J. Chem. Ind. (Moscow), *4*, 29 (1927).
4. Buekenkamp, J., Rieman, W., and Lindenbaum, S., Anal. Chem., *26*, 505 (1954).
5. Cale, W. R., Can. Chem. Process Inds., *32*, 741 (1948).
6. Higgins, C., and Baldwin, W., Anal. Chem., *27*, 1780 (1955).
7. Karl-Kroupa, E., *Ibid.*, *28*, 1091 (1956).
8. Lindenbaum, S., Peters, T. V., and Rieman, W., Anal. Chim. Acta, *11*, 530 (1954).
9. Mabis, A. J., and Quimby, O. T., Anal. Chem., *25*, 1814 (1953).
10. Martin, J. B., and Doty, D. M., *Ibid.*, *21*, 965 (1949).
11. Peters, T. V., and Rieman, W., Anal. Chim. Acta, *14*, 131 (1956).
12. Quimby, O. T., J. Phys. Chem., *58*, 603 (1954).
13. Quimby, O. T., Mabis, A. J., and Lampe, H. W., Anal. Chem., *26*, 661 (1954).
14. Raistrick, B., Roy. Coll. Sci. J., *19*, 9 (1949).
15. Raistrick, B., Harris, F. J., and Lowe, E. J., Analyst, *76*, 230 (1951).
16. Weiser, H. J., "Water-Soluble Sodium Phosphates," Ph.D. thesis, University of Cincinnati, 1951.
17. Weiser, H. J., Anal. Chem., *28*, 477 (1956).

[Received September 25, 1956]

Purification of Long-Chain Saturated Fatty Acids by Recrystallization of Their Molecular Compounds with Acetamide

FRANK C. MAGNE, ROBERT R. MOD, and EVALD L. SKAU, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

IT HAS RECENTLY been shown by means of binary freezing point diagrams that acetamide forms molecular compounds of the general formula $RCOOH \cdot H_2NCOCH_3$ with long-chain saturated and mono-unsaturated fatty acids (2, 3, 4, 5, 6). It has now been found that the molecular compounds of the saturated fatty acids can be purified by recrystallization from concentrated solutions in suitable organic solvents and that the acids, freed from their homologs, can be regenerated by extraction of the acetamide with water.

Materials

Stearic Acid I, f.p. 68.5°C.; Palmitic Acid I, f.p. 61.4°C.; Myristic Acid I, f.p. 53.3°C.; and Lauric Acid I, f.p. 43.2°C. were Eastman [2] products. Stearic Acid II and Myristic Acid II were commercial grades obtained from Armour and Company. The former was Neo-Fat 1-65 (f.p. 66.8°C., iodine value 2.9), having the approximate composition of 90% stearic acid, 6% palmitic acid, and 4% of oleic acid. The latter was Neo-Fat 13 (f.p. 49.9°C., iodine value 2.0), purported to consist approximately of 90% myristic acid, 4% lauric acid, 4% palmitic acid, and 2% unsaturated acids. Reagent grade acetamide was dried in a vacuum desiccator over phosphorus pentoxide. The acetone was purified by treating with potassium permanganate, drying over anhydrous potassium carbonate, and distilling. Freezing points were obtained by the thermostatic, sealed tube method (2).

Results and Discussion

Equimolecular proportions of acetamide and fatty acid, based on the neutralization equivalent of the original acid, were dissolved by warming with an organic solvent in a centrifugal filtration tube (9). The tube was then assembled immediately to prevent evaporation and allowed to cool slowly to about 25°C. or, if necessary to obtain a satisfactory yield of crystals, to 0°C. The mother liquor was then separated from the crystals by exhaustive centrifugation at about 225 times gravity. Fresh solvent was added to the crystals without removing them from the container, and the process was repeated for two more recrystallizations. The resulting crystals of the acid-acetamide molecular compound were stirred with successive portions of hot water to extract the major part of the acetamide. After cooling, the solidified

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[2] Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.