A Titrimetric Method for Total Phosphoric Anhydride[1]

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THE method of analysis herein described was developed as a joint effort by several individuals working, more or less independently, in at least three departments of the Procter and Gamble Company Chemical Division. It has been tested in a dozen or more of our control laboratories, from several of which useful suggestions for its modification and improvement have been received. Under such circumstances it seems preferable to present it as a group effort without attempting to assign credit to any individual.

No claim is made for its fundamental originality. Its underlying principle has been known and recognized for at least 70 years. The failure of earlier investigators to achieve a satisfactory degree of success may be ascribed entirely to their lack of an instrument which has become commonplace in every analytical laboratory within the past 15 to 20 years. By this is meant the convenient and accurate pH meter, using glass and calomel electrodes.

Historical

Analytical chemical literature for nearly three-quarters of a century has been replete with references to the behavior of orthophosphoric acid H_3PO_4, during its titration in dilute aqueous solution with standard alkali hydroxide. Thompson (1), in 1883, pointed out that it (orthophosphoric acid) "is an example of another polybasic acid which may be titrated in steps, although not with entire satisfaction." Practically every analytical textbook devotes some space to this intriguing problem, which has developed more into an effort to determine total P_2O_5, by measurement of the acidity between the neutralization equivalents of the first and second hydrogens, than the original purpose of titrating the acid itself. Treadwell-Hall (2) treats the subject in a manner which is quite typical. This discussion is quoted from the 4th Edition (1915) but the most recent 9th Edition (1942) has little to add to observations made 27 years earlier.

> "NaH_2PO_4 reacts acid toward phenolphthalein and neutral toward methyl orange, while Na_2HPO_4 is neutral toward the former indicator and basic toward the latter. Therefore, on titrating free phosphoric acid with alkali the following reactions will take place:
>
> I. $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$. (Methyl Orange)
>
> II. $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$. (Phenolphthalein)
>
> The second reaction is not sharp, because pure Na_2HPO_4 is dissociated to a slight extent so that it becomes alkaline to phenolphthalein. . . . To prevent this hydrolysis, the titration is best effected in a cold, concentrated solution containing sodium chloride."

It may be pointed out that if the reactions expressed in I and II can be performed with titrimetric precision and to the exact equivalence indicated, in the absence of interfering ions, the titration difference is a measure of the phosphoric acid present in the system and $NaOH \Bumpeq P_2O_5/2$. A typical electrometric titration curve (3) of phosphoric acid will show these relationships quite clearly (Figure 1).

Note the essential equivalence of the titration to the first inflection point with that of the titration from the first to the second inflection point. Titration of the third hydrogen is beyond the working range of the laboratory pH meter using glass and calomel electrodes.

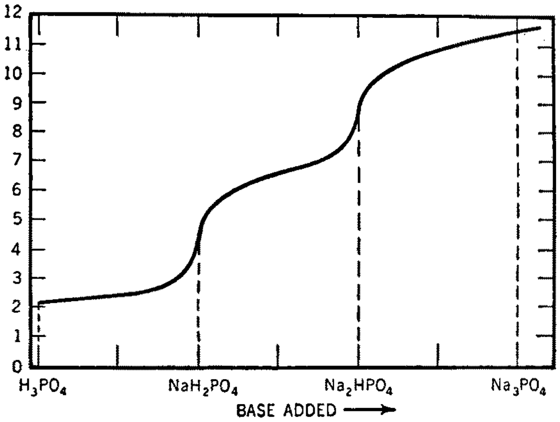

FIG. 1. Titration of orthophosphoric acid with sodium hydroxide (1 g. H_3PO_4/100 ml. solution; glass electrode with high pH correction).

Of necessity, nearly all of the earlier work on this problem was done with the aid of indicators. Much ingenuity has been displayed in their choice and use. Sutton (4), in 1935, summed up the situation at that time as follows:

> "Many attempts have been made to utilize these reactions for the accurate determination of P_2O_5 . . . but, so far as my experience goes, without adequate success."

Nevertheless, Kolthoff and Stenger (5), in 1942, prescribed conditions for this titration within a claimed probable error of 0.5% for the lower endpoint and 1% for the upper endpoint. Bromocresol green or methyl orange, with suitable reference solutions, may be employed at the lower endpoint; phenolphthalein and enough salt to half saturate the solution are used in titration to the upper endpoint. Alternatively thymolphthalein may be employed without the addition of salt.

Theoretical Considerations

Numerous investigators have determined the dissociation constants for the three acid hydrogens of H_3PO_4 with a fair amount of disagreement as would be expected. Quimby, in 1947, reviewing "Chemistry of the Sodium Phosphates" (6), discusses the available data briefly but lists about a dozen references. Although "quite a variety of dissociation constants can be found for H_3PO_4" the only ones cited are those of Harned and Owen (7), viz., "7.516×10^{-3} and 6.226×10^{-8} for the first and second hydrogens, respectively, at 25°C. The value for the third hydrogen is probably near 2×10^{-13} (8)." Kolthoff and Stenger (9), in 1942, using dissociation or ionization constants of unidentified source, calculated the pH

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[1] Presented at the 27th annual fall meeting, American Oil Chemists' Society, Chicago, Ill., Nov. 2-4, 1953.

values corresponding to neutralization of the first two acid hydrogens as 4.4 and 9.6, respectively. They point out that the older "concentration constants" were employed; had they used the "activity products," given elsewhere in their text, somewhat higher pH values would have been obtained.

While these theoretical values confirm the region in which these neutralizations must be effected, they are not a practical guide to actual titrations under laboratory conditions, using the glass and calomel electrode system. The figure for the lower endpoint is in close agreement with that obtained in practice but that for the upper endpoint seems considerably higher than that found in the present investigation.

Present Work

In connection with some other investigations conducted in our laboratories in 1946, a potentiometric titration was made on pure monosodium dihydrogen orthophosphate, NaH_2PO_4, extending the curve in both directions by use of standard acid and base solutions. In order to fix the pH values of the lower and upper inflection points more precisely than by the usual method of inspection, resort was had to differential plotting. If ΔpH is the change in pH produced by a small addition, Δ T, of either acid or base, then the ratio ΔpH/ΔT will pass through a maximum at a point of inflection on a curve obtained by plotting, as a positive ordinate, all values of ΔpH/ΔT, without regard for sign, against the pH of the solution as abscissa. The resulting curve is shown in Figure 2. Note that the maxima for ΔpH/ΔT occur at pH values of 4.2 and 8.7, which mark the inflection points corresponding to formation of NaH_2PO_4 and Na_2HPO_4, respectively. It is probable that variations of concentration and temperature will affect the pH location of these maxima, and their employment as fixed points will require fair maintenance of constancy for these variables.

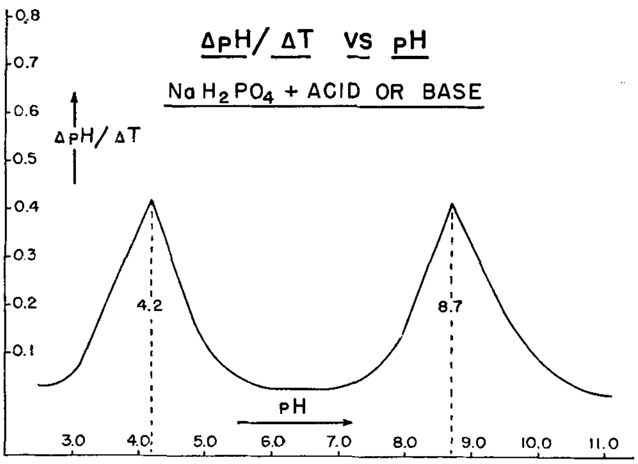

Fig. 2

These values were confirmed by titration curves obtained by the same method on a sample of sodium tripolyphosphate, $Na_5P_3O_{10}$, after preliminary hydrolysis to orthophosphate by boiling in acid aqueous solution. It should be emphasized that these curves, and the inflection points determined from them, were made from data obtained by use of a single pH meter.

In 1949, O. T. Quimby, in an unpublished technical report, suggested that total P_2O_5 could be determined in mixtures of sodium phosphates and in phosphate built synthetic detergents, by acid hydrolysis to the orthophosphate form followed by potentiometric titration between the inflection points at about pH 4 and pH 9. He called this proposed method the "two endpoint method," a terminology which has been accepted and is used throughout the Procter and Gamble Company. Acknowledgment was made to previous work by van Wazer (10), who had reported success with this method in the analysis of condensed phosphates.

By coincidence, at almost the same time and entirely independently, experiments had been initiated in another department, utilizing the same two endpoint principle, but titrating to the 4.2 and 8.7 pH values previously determined by differential plotting of potentiometric titration data. Over a period of several months, results were accumulated which justified the incorporation of this method in our Standard Analytical Methods for Control and Cost Accounting. With a few minor modifications the two endpoint method has been in daily use by all of our control laboratories as well as by the analytical laboratories serving our research, development, and products research organizations for a period of nearly three years. It should be emphasized that in the Procter and Gamble Company it is now a standard method subject to check and audit by regular submission of cooperative samples upon which a single analysis only is made and reported.

One of the modifications is a slight change in pH of the endpoints. A recent comparison in 13 of our control laboratories, using three samples of commercial condensed sodium phosphate, has shown the advisability of a change from the 4.2 and 8.7 pH values to 4.3 and 8.8. The spread, or difference in pH through which the titration is performed, remains 4.5 however. In obtaining the revised values, three different types of pH meter were used. Each was adjusted to 4.0 pH by use of a standard buffer and corrections were made for deviations from 7.0 to 10.0 pH buffers. For each 0.1 pH unit, in the region under examination, an average ΔpH/ΔT was calculated across the board. Only one individual laboratory exceeded 0.2 pH from the mean pH value of the maxima, and that was 0.3 in a total of 78 maxima computed.

Total P_2O_5—Two Endpoint Method

Principle: All of the phosphate present is converted, by acid hydrolysis, to the ortho form and titrated between pH 4.3 and 8.8. $NaOH \Bumpeq P_2O_5/2$.

Applicable to any species of alkali metal phosphates free from interfering ions. May be used for analysis of soap and synthetic detergent builders if the sample is properly prepared.

A. Apparatus

1. Electrometric titration apparatus, equipped with glass and calomel electrodes. Any standard pH meter, capable of performing titrations accurate to ±0.1 pH, is suitable.
2. Gas burners, preferably of the chimney or Argand type.
3. Muffle furnace, with suitable pyrometer and controls for maintaining temperatures up to 550°C.
4. Evaporating dish or large crucible, of porcelain or silica.
5. Motor stirrer, air or electric.
6. Beaker, 400 ml.

B. Reagents

1. Standard NaOH, 0.5 or 1.0 N, carbonate free. Prepare and standardize accurately as described in A.O.C.S. Method H 12-52.
2. Concentrated NaOH solution, approx. 50% by weight, carbonate free. A more dilute solution may be used. NaOH solutions must be protected from carbon dioxide contamination.
3. Concentrated HCl, sp. gr. 1.19, reagent grade.
4. Mixed indicator (Optional)
    - (a) 32 ml. methyl orange—0.05% in water.
    - (b) 32 ml. phenolphthalein—0.50% in 50% alcohol.
    - (c) 8 ml. thymol blue—0.04% in water.
    - (d) 4 ml. methylene blue—0.10% in water.
    - (e) 24 ml. alcohol—95% No. 3A or No. 30.

The individual components are stable indefinitely. The mixed indicator should be prepared at least weekly.

In practice 3 ml. of this mixed indicator are used in a final volume of approximately 250 ml. of solution to be titrated. The lower endpoint is taken as the first change from gray to a definite green; the upper endpoint is the change from pink to a bright purple.

C. Procedure

PREPARATION OF SAMPLE

a) *Commercial sodium or potassium phosphates* need no special preparation except solution in distilled water. Weigh a portion of the well mixed sample to the nearest 0.001 g., transfer directly to a 400-ml. beaker, and dissolve in about 100 ml. distilled water. Neutralize to litmus paper with conc. HCl and add 10 ml. excess. The optimum size of sample is given by the formula:

$$\text{Grams sample} = \frac{280 \times N}{\%\ P_2O_5 \text{ expected}}$$

N = normality of NaOH to be used in titration

b) *Soap products* may be analyzed by using the filtrate from the SiO_2 determination. Use care not to exceed the sample weight prescribed above. Alternatively the sample may be prepared as described in the paragraph to follow.

c) *Built synthetic products* may be analyzed by using the alcohol insoluble portion, but the following procedure is more rapid and quite as accurate. Weigh a sample, of size chosen by the formula above (but do not exceed 10 g.) to the nearest 0.001 g. Place sample in a porcelain or silica evaporating dish, or large crucible, and ignite gently over a low gas burner until most of the volatile combustible matter is burned off. Transfer to a muffle, operated at not over 550°C., for 10 to 15 minutes. The ignited residue need not be free from carbon and usually is of a grayish color. Cool and add cautiously 10 ml. conc. HCl. Evaporate to dryness, take up with 50 ml. distilled water, 10 ml. conc. HCl, and transfer to a 400 ml. beaker.

OPERATION

1. Each solution in a 400-ml. beaker, prepared as described above, should have a volume of about 100 ml. and contain an excess of at least 10 ml. conc. HCl. Cover with a watch glass and boil gently for 30 minutes. Cool to room temperature (20°-30°C.).

2. Dilute to 200-ml. volume, place on electrometric titration stand and neutralize to 4.3 pH. Most of the neutralization may be made with 50% NaOH solution, but final adjustment should be made with the standard NaOH to be used in titration (0.5 or 1.0 N). Cool again, if necessary, to maintain temperature below 30°C. Now titrate carefully to the 8.8 pH upper endpoint recording the titration between endpoints as "T."

NOTE: The mixed indicator may be used for this titration but with some small sacrifice of accuracy. If the samples have been prepared by the ignition method, they must be filtered and the paper washed thoroughly, after the acid hydrolysis, as particles of carbon obscure the visual endpoint. The color changes can be checked by comparison with pH meter readings to acquire familiarity with the exact shade required. For greatest accuracy, titration with a pH meter is recommended.

D. Calculations

$$\%\text{Total } P_2O_5 = \frac{T \times N \times 7.098}{\text{Weight of sample}}$$

INTERFERENCES

Heavy metals, such as Fe, Al, Ca, Mg, etc., which will precipitate, either as insoluble phosphates or hydroxides, before the upper endpoint is reached, of course will interfere. Interference also occurs if borates, sulfites, carbonates, or other buffering materials are present. The last two and much of the borate will be expelled during the acid hydrolysis boil. NH_4, or other weak bases also will interfere. The most common interference is from silicic acid. Experiment and experience in analysis of spray-dried synthetics, have shown that unless the ratio of % SiO_2/% P_2O_5 approaches or exceeds 0.2, the interference by silicates will be so slight that it may be neglected. Larger amounts must be dehydrated and removed by filtration during preparation of the sample. (See Tables I and II).

TABLE I

Effect of SiO_2 on % P_2O_5. (% SiO_2 = 4.0)

	SiO_2 Present	SiO_2 Removed
Synthetic A.		
Lab.		
1	25.77	25.77
2	25.76	25.83
3	25.84	25.84
4	25.88	25.95
5	26.00	26.14
6	25.69	26.26
7	26.01	26.01
8	25.69	25.77
9	25.48	25.74
Average	25.79	25.92
High	26.01	26.26
Low	25.48	25.74
Spread	0.53	0.52
Ratio % SiO_2/% P_2O_5 = 0.155		
Synthetic B.		
Lab.		
1	28.46	28.39
2	28.53	28.46
3	28.39	28.60
4	28.72	28.65
5	28.84	29.13
6	28.53	29.39
7	28.86	28.86
8	28.68	28.53
9	28.53	29.39
Average	28.62	28.82
High	28.86	29.39
Low	28.39	28.39
Spread	0.47	1.00
Ratio % SiO_2/% P_2O_5 = 0.139		

TABLE II

Effect of SiO_2 on % P_2O_5—Aqueous Mixtures of Sodium Silicate and Na_2HPO_4

% Apparent P_2O_5 No Treatment	Acid Hydrolyzed	Ratio % SiO_2/%P_2O_5
49.98*	50.13*	0.0
50.55	50.84	0.1
50.87	51.27	0.2
52.77	53.24	0.5
53.41	56.41	1.0

* Theoretical percentage = 49.99.

Results Obtainable

As previously stated, this method with titration between 4.2 and 8.7 pH has been in daily use in Procter and Gamble Company laboratories for nearly three years. It has been used on all of the types of materials indicated, especially in the analysis of phosphate built synthetic detergents. Tables III and IV show some of the results achieved. These are all single determinations in different laboratories with different apparatus, reagents and analysts. The standard deviation on samples of built synthetics, in the range

TABLE III

Cooperative Analyses of Built Synthetic Detergent

% Apparent Total P_2O_5					
Lab.	Molybdate	2 EP.	Lab.	Molybdate	2 EP.
1	26.85	27.19	7	27.46	27.11
2	27.99	27.62	8	27.30	28.10
3	27.33	27.63	9	27.15	27.11
4	27.93	26.97	10	27.40	27.53
5	27.15	27.25	11	27.31	27.29
6	27.15	27.04	12	27.20	28.00
Average Molybdate		27.35	Average 2 EP		27.40
High Molybdate		27.99	High 2 EP		28.10
Low Molybdate		26.85	Low 2 EP		26.97
Spread Molybdate		1.14	Spread 2 EP		1.13
Standard Dev		0.33	Standard Dev		0.39

TABLE IV

Cooperative Analyses of Built Synthetic Detergent

% Total P_2O_5—Two Endpoint Method			
Lab.		Lab.	
1	26.57	7	26.26
2	26.41	8	26.48
3	26.41	9	26.33
4	26.55	10	26.33
5	26.69	11	26.75
6	26.71	12	26.39
		13	26.36

Average..........26.48

High..........26.75; low 26.26; spread 0.49

Standard deviation: $\sqrt{\frac{\Sigma d^2}{n-1}} = 0.16$.

Accepted standard deviation for two endpoint method = 0.32.

from 25 to 30% total P_2O_5, has been found to be 0.32 *vs.* 0.60 by the method employing alkalimetric titration of the washed yellow phosphomolybdate precipitate, which was the procedure previously in operation. The two endpoint method offers a substantial reduction in the time required for analysis. From the best estimates obtained it is believed that a 50% reduction in elapsed time may be realized, with an even greater saving in the personal attention required.

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[Received October 21, 1953]

Report of the Referee Board 1953-1954

FOR the year ending May 31, 1954, 41 Referee Chemists were appointed. Thirty-five were renewals, and 26 were given certificates on cottonseed, oil cake and meal, and fatty oils. Thirteen held restricted certificates either from choice of application or by the discretion of the Board. The chemists are located in 12 states and 25 cities and represent 21 different laboratory organizations.

During the 1953-54 period the Board saw fit to suspend one chemist on the basis of factual information that his results were not of an accuracy expected of Referee Chemists.

The matter of qualifications, specifically educational, again arose during the period. It was the consensus of the Referee Board (not unanimous) that an active member could qualify without the possession of a degree in chemistry or chemical engineering from an accredited college or university. The matter was referred to the Governing Board by your chairman. It was the consensus of the Governing Board that the Referee Board could not require an active member to possess said college degree under Article V, Section 5, of the constitution and by-laws. Two chemists with many years of experience were certified as a result of this decision.

The 1953-54 Referee Board, cognizant of factors that will necessitate the replacement of some veteran members of the Board, feel duty-bound to offer some recommendations for the guidance of future Boards, *viz.:*

1. The Board urges a revision of Article V, Section 5, of the constitution and by-laws. This qualification should be written in a manner so clear that only one interpretation is possible. The 1953-54 Board feels that the possession of a degree in chemistry or chemical engineering from an accredited college or university should be a basic requirement for Referee certification.

2. The laboratory of a new applicant should be inspected by a member of the Referee Board or by two qualified members of the Society before certification is granted. The possession of approved equipment is very essential.

3. New applicants should be personally interviewed by the Referee Board or a Board member to ascertain his or her fitness for certification. Attendance at the spring meeting of the Society by prospective applicants would facilitate this phase.

The Referee Board urges prospective applicants to participate in the Smalley check sample program. Performance on the check samples has a considerable bearing on our decisions.

R. R. KING
G. CONNER HENRY
A. S. RICHARDSON
PROCTER THOMSON
R. W. BATES,
chairman

Addenda

IN passing, your chairman would like to pay tribute, on behalf of the Society, to a veteran member of the Referee Board, who has indicated his intention of retiring from active participation in the Board's activities.

Dr. Richardson has served on the Referee Board for 23 years, most of this service has been as chairman. The amount of energy, patience, and time he has expended in this important Society activity has been tremendous. The Society is deeply grateful for his efforts and truly wishes him well.

R. W. BATES