Designation: D501 – 03 (Reapproved 2016)

Standard Test Methods of Sampling and Chemical Analysis of Alkaline Detergents[1]

This standard is issued under the fixed designation D501; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover procedures for the sampling and chemical analysis of inorganic alkaline detergents.

1.2 The procedures appear in the following order:

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D459 Terminology Relating to Soaps and Other Detergents

[1] These test methods are under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and are the direct responsibility of Subcommittee D12.12 on Analysis and Specifications of Soaps, Synthetics, Detergents and their Components.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

D1193 Specification for Reagent Water
E1 Specification for ASTM Liquid-in-Glass Thermometers
E70 Test Method for pH of Aqueous Solutions With the Glass Electrode

3. Terminology

3.1 *Definitions:*

3.1.1 *inorganic alkaline detergent*—a water soluble inorganic alkali or alkaline salt having detergent properties, but containing no soap or synthetics.

3.1.2 For definitions of other terms used in these test methods, refer to Terminology D459.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 The term "inorganic alkaline detergent" in these test methods is defined in accordance with Terminology D459.

4. Purity of Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

CAUSTIC SODA

5. Sampling

5.1 *Flake Caustic Soda*—Flake caustic soda shall be sampled by removing portions from various parts of the drum.

5.2 *Powdered Caustic Soda*—Powdered caustic soda shall be sampled by inserting a sampling tube through the contents of the drum in several places. The tube shall be dried by heating just before use.

5.3 *Fused Caustic Soda*—Fused caustic soda shall be sampled by taking chipped samples from the center and bottom of the drum and then mixing the gross sample in the approximate proportions in which the tops and bottoms occur in the drum.

5.4 *Precautions*—Caustic soda shall not be sampled in a moist atmosphere. In the case of fused caustic soda the portion taken for analysis shall have the surface layer of carbonate scraped off immediately before transferring to the weighing bottle. In all cases the sample shall be transferred to a thoroughly dried weighing bottle immediately after it is taken; the bottle shall be tightly stoppered at once.

TOTAL ALKALINITY AS SODIUM OXIDE (Na_2O)

6. Reagents

6.1 *Acid, Standard* (1.0 *N*)—Prepare and standardize a 1.0 *N* acid solution.

6.2 *Methyl Red Indicator Solution.*

7. Procedure

7.1 Weigh 10 g of the sample, dissolve in carbon dioxide (CO_2)-free water, wash into a 500-mL volumetric flask, and dilute to volume with CO_2-free water. Protect the solution from the air as much as possible. Pipet a one-fifth aliquot into a 400-mL beaker and determine sodium oxide (Na_2O) by titrating the sample against 1.0 *N* acid, using methyl red as the indicator.

8. Calculation

8.1 Calculate the total alkalinity as sodium oxide (Na_2O) as follows:

$$\text{Total alkalinity as } Na_2O, \% = (A \times 5 \times 3.1)/W \quad (1)$$

where:

A = millilitres of acid required for titration of the Na_2O in the sample, and
W = grams of sample used.

SODIUM HYDROXIDE (NaOH)

9. Reagents

9.1 *Acid, Standard* (1.0 *N*)—Prepare and standardize a 1.0 *N* acid solution.

9.2 *Barium Chloride, Neutral Solution* (100 g/L)—Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L. Make the solution neutral to phenolphthalein.

9.3 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 50 mL of ethyl alcohol and then mix with 50 mL of water.

10. Procedure

10.1 Determine the NaOH on a second one-fifth aliquot pipetted into a 250-mL Erlenmeyer flask. Add about 25 mL of $BaCl_2$ solution and titrate the sample with 1.0 *N* acid using phenolphthalein as the indicator.

11. Calculation

11.1 Calculate the percentage of sodium hydroxide (NaOH) as follows:

$$\text{NaOH}, \% = (B \times 5 \times 4.0)/C \quad (2)$$

where:

B = millilitres of acid necessary for titration of the NaOH in the sample, and
C = grams of sample used.

CARBONATE AS SODIUM CARBONATE (Na_2CO_3)

12. Calculation

12.1 Calculate the carbonate as sodium carbonate (Na_2CO_3) as follows:

$$Na_2CO_3, \% = [(A - B) \times 5 \times 5.3]/W \quad (3)$$

where:

A = millilitres of acid required for titration of the Na_2O in the sample,
B = millilitres of acid required for titration of the NaOH in the sample, and
W = grams of sample used.

NOTE 1—When more accurate results are desired, the evolution method for carbon dioxide as described in Sections 13 – 16 should be used.

CARBON DIOXIDE (CO_2) BY THE EVOLUTION METHOD

13. Apparatus

13.1 *Apparatus Assembly*—Place a 150-mL wide-neck extraction flask on a gauze over a burner. Fit the flask with a three-hole rubber stopper, one opening to carry a 25-cm reflux condenser, the second to carry a thistle tube with a two-way stopcock for the introduction of acid into the flask, and the third to carry a tube for the introduction of a continuous stream of carbon dioxide (CO_2)-free air into the flask. Draw out the ends of the thistle and air supply tubes to a small point, and place them in the stopper so that the points are very close to the bottom of the flask. Attach to the air supply tube, a U-tube containing soda-asbestos (Ascarite) so that the air admitted to the flask will be free from CO_2.

13.2 *Preparation of Absorption Train*—Attach to the top of the reflux condenser a train consisting of the following:

13.2.1 A U-tube containing granulated zinc for the removal of acid gases,

13.2.2 A drying tube containing magnesium perchlorate, anhydrous calcium sulfate (Drierite), or anhydrous calcium chloride,

13.2.3 A weighed U-tube containing soda-asbestos in the first half and the same drying agent in the second half as used in 13.2.2, and

13.2.4 A protective U-tube containing any of the above mentioned drying agents.

13.2.5 Attach the final tube to an aspirator.

14. Reagents

14.1 *Methyl Orange Indicator Solution* (1 g/L)—Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

14.2 *Sulfuric Acid* (2 + 9) —Mix 2 volumes of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) carefully with stirring into 9 volumes of water.

15. Procedure

15.1 Aspirate with a stream of carbon dioxide (CO_2)-free air at a rate of approximately 20 to 30 mL/min until the train is free from CO_2 as determined by no further change in weight greater than 0.3 mg in the U-tube.

15.2 Weigh 10 g of the sample to the nearest 0.01 g directly into the extraction flask, cover with 50 mL of freshly boiled water, add 2 drops of methyl orange solution, and close the apparatus with the train in place. Start the aspiration at a rate of 20 to 30 mL/min, and slowly add through the thistle tube sufficient H_2SO_4 (2 + 9) to neutralize the NaOH and a sufficient excess to ensure the final acidity of the mixture as indicated by the methyl orange. Always leave some acid in the thistle tube as an air seal. Heat gently and continue until the contents of the flask have boiled for 5 min; remove the source of heat, and continue aspirating until the flask has cooled, or for about 30 min.

15.3 Remove the U-tube containing soda-asbestos and weigh using a tared U-tube as a counterpoise. The increase in weight represents CO_2.

16. Calculation

16.1 From the increase in weight of the tube calculate the percentage of carbon dioxide (CO_2) as sodium carbonate (Na_2CO_3) as follows:

$$Na_2CO_3, \% = [(C \times 2.409)/W] \times 100 \quad (4)$$

where:

C = grams of CO_2, and
W = grams of sample used.

NOTE 2—This test method for the determination of Na_2CO_3 as CO_2 is to be preferred when a procedure more accurate than that described in Section 12 is required.

17. Sampling

17.1 Soda ash shall be sampled by removing portions from various parts of the container. Samples shall not be taken from those portions of the soda ash where caking is noticeable due to the absorption of moisture and carbon dioxide through the container. If the soda ash is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

MATTER VOLATILE AT 150 TO 155°C

18. Procedure

18.1 Place approximately 2 g of the sample in a tared weighing bottle and weigh to the nearest 0.1 mg. Remove the stopper and dry in an oven at 150 to 155°C for 1 h. Replace the stopper and allow to cool to room temperature in a desiccator containing no desiccant and reweigh.

19. Calculation

19.1 Calculate the percentage of volatile matter as follows:

$$\text{Volatile matter, } \% = (L/W) \times 100 \quad (5)$$

where:

L = grams loss in weight, and
W = grams of sample used.

TOTAL ALKALINITY AS SODIUM CARBONATE (Na_2CO_3)

20. Reagents

20.1 *Methyl Orange Indicator Solution* (1 g/L)—Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

20.2 *Hydrochloric Acid, Standard* (0.5 *N*)—Prepare and standardize 0.5 *N* hydrochloric acid (HCl).

21. Procedure

21.1 Transfer approximately 1.2 g of sample into a tared weighing bottle. Weigh to the nearest 0.1 mg, protecting the sample at all times, as much as possible, from moisture in the air during weighing. Dissolve the sample in about 50 mL of water in a 400-mL beaker and add 2 drops of methyl orange indicator solution. Run in, while stirring, 0.5 *N* HCl until 1 drop establishes the first appearance of a pink color in the solution. Remove the beaker, heat to boiling, and boil for 1min to remove most of the CO_2. Cool and finish the titration to the first appearance of a pink color in the solution.

22. Calculation

22.1 Calculate the total alkalinity as sodium carbonate (Na_2CO_3) as follows:

$$\text{Total alkalinity, } \% = (AN \times 5.3)/W \quad (6)$$

where:

A = millilitres of HCl required for titration of the sample,
N = normality of the HCl, and
W = grams of sample used.

SODIUM BICARBONATE ($NaHCO_3$)

23. Reagents

23.1 *Silver Nitrate Solution* (100 g/L)—Dissolve 100 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L. Prepare this solution fresh before use.

23.2 *Sodium Hydroxide, Standard Solution* (1.0 *N*)—Prepare and standardize a 1.0 *N* sodium hydroxide (NaOH) solution.

24. Procedure

24.1 Weigh 8.4 g of the sample to the nearest 0.05 g and transfer to a 250-mL beaker. Dissolve in 100 mL of water, and titrate with 1.0 *N* NaOH solution until a drop of the test solution added to a drop of $AgNO_3$ solution on a spot plate gives a dark color instantly.

25. Calculation

25.1 Calculate the percentage of sodium bicarbonate ($NaHCO_3$) as follows:

$$NaHCO_3, \% = \text{mL of 1.0 } N \text{ NaOH solution} \quad (7)$$

Calculate the percentage of sodium carbonate (Na_2CO_3) as follows:

$$Na_2CO_3, \% = A - (NaHCO_3, \% \times 0.6309) \quad (8)$$

where:

A = total alkalinity as Na_2CO_3, in percent.

NOTE 3—For referee purposes, or when more accurate results are required than are yielded by the procedure described in Section 25, the method described in Section 28 shall be used.

SODIUM BICARBONATE ($NaHCO_3$) BY POTENTIOMETRIC TITRATION

26. Reagents

26.1 *Barium Chloride, Neutral Solution* (122 g/L)—Dissolve 122 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L. Make the solution neutral to phenolphthalein.

26.2 *Hydrochloric Acid, Standard* (0.1 *N*)—Prepare and standardize 0.1 *N* hydrochloric acid (HCl).

26.3 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* sodium hydroxide (NaOH) solution.

27. Procedure

27.1 Weigh approximately 10 g of the sample to the nearest 1 mg. Transfer to a 250-mL volumetric flask and dissolve in freshly boiled, cooled water. Dilute to the mark, mix thoroughly, and transfer, by means of a pipet, a 50-mL aliquot of the solution of a 250-mL beaker.

27.2 Add 5.0 mL of 0.1 *N* NaOH solution from a pipet or buret; then add 50 mL of neutral $BaCl_2$ solution. Introduce the

electrodes of a glass-electrode pH meter (Note 4) and mix continuously by means of a mechanical stirrer. Titrate with 0.1 *N* HCl without undue delay, in order to minimize absorption of CO_2 from the atmosphere. When the pH begins to change, record the readings at intervals of 0.1 mL of HCl.

27.3 In an identical manner carry out a blank determination (Note 5) on 10 g of bicarbonate-free sodium carbonate (Na_2CO_3) prepared by igniting another portion of the same sample overnight at 200°C.

27.4 Plot the pH values *versus* millilitres of 0.1 *N* HCl for both the sample and the blank on the same paper. The volume of HCl represented by the difference between the points of inflection of the two curves is equivalent to the sodium bicarbonate content of the sample.

NOTE 4—Careful standardization of the pH meter with standard buffers is not necessary. Instruments as specified in Test Method E70 are satisfactory.

NOTE 5—The blank correction is required since appreciable amounts of NaOH are occluded in the precipitated $BaCO_3$. It is imperative that identical quantities of NaOH be used for both sample and blank, since the blank correction is related directly but not linearly to the quantity of excess NaOH present when the $BaCO_3$ is precipitated. The correction varies sufficiently with different reagents so that it should be measured for each determination unless its constancy has been established.

28. Calculation

28.1 Calculate the percentage of sodium bicarbonate ($NaHCO_3$) as follows:

$$NaHCO_3, \% \left[(A - B)N \times 8.4\right]/W \quad (9)$$

where:

A = millilitres of HCl required for titration of blank,
B = millilitres of HCl required for titration of sample,
N = normality of the HCl, and
W = grams of sample in the aliquot.

MATTER INSOLUBLE IN WATER

29. Procedure

29.1 Dissolve 20 g of the sample, weighed to the nearest 0.1 g, in 300 mL of water in a 400-mL beaker. Filter through a previously prepared, dried, and weighed Gooch or fritted-glass crucible. Wash the residue free of alkali with water and dry in an oven at 100°C.

30. Calculation

30.1 Calculate the percentage of matter insoluble in water as follows:

$$\text{Matter insoluble in water, \%} = \text{grams of residue} \times 5 \quad (10)$$

APPARENT DENSITY

31. Procedure

31.1 Weigh 30 g of the sample and transfer to a 100-mL graduate. Rotate the graduate until the sample flows freely and then, taking great care to avoid jarring, level the surface of the sample, and read the volume.

32. Calculation

32.1 Calculate the apparent density as follows:

$$A = 30/V \quad (11)$$

$$\text{Apparent density, lb/ft}^3 = A \times 62.4$$

where:

A = apparent specific gravity, and
V = millilitres of sample.

MODIFIED SODA (SESQUICARBONATE TYPE)

33. Sampling

33.1 The sample of modified soda (sesquicarbonate type) shall be selected as described in Section 17 for the sampling of soda ash.

TOTAL ALKALINITY AS SODIUM OXIDE (Na_2O)

34. Reagents

34.1 *Methyl Red Indicator Solution.*

34.2 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* sodium hydroxide (NaOH) solution.

34.3 *Sulfuric Acid* (1.0 *N*)—Prepare and standardize 1.0 *N* sulfuric acid (H_2SO_4).

35. Procedure

35.1 Weigh 3.1 g of the sample and dissolve in about 100 mL of water in a 500-mL Erlenmeyer flask. Add 4 drops of methyl red indicator solution and enough 1.0 *N* H_2SO_4 to reach the end point plus approximately 1 mL in excess. Place a small funnel in the neck of the flask and boil for 5 min to expel CO_2. The solution should still be acid after boiling. Rinse down the sides of the flask and back-titrate with 0.1 *N* NaOH solution.

36. Calculation

36.1 Calculate the total alkalinity as sodium oxide (Na_2O) as follows:

$$\text{Total alkalinity as } Na_2O, \text{ percent} = A - (B/10) \quad (12)$$

where:

A = millilitres of H_2SO_4 required for titration of the sample, and
B = millilitres of NaOH solution required for titration of the excess H_2SO_4.

SODIUM BICARBONATE ($NaHCO_3$) AND SODIUM CARBONATE (Na_2CO_3)

37. Reagents

37.1 *Silver Nitrate Solution* (100 g/L)—Dissolve 100 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L. Prepare the solution fresh before use.

37.2 *Sodium Hydroxide Solution* (1.0 *N*)—Prepare and standardize a 1.0 *N* sodium hydroxide (NaOH) solution.

38. Procedure

38.1 Weigh 8.4 g of the sample and dissolve in about 100 mL of water in a 250-mL beaker. Titrate the sample with 1.0 *N* NaOH solution until a drop of the solution added to a drop of $AgNO_3$ solution on a spot plate gives a dark color instantly.

39. Calculation

39.1 Calculate the percentage of sodium bicarbonate ($NaHCO_3$) as follows:

$$NaHCO_3, \% = \text{mL of } 1.0\ N \text{ NaOH solution} \quad (13)$$

39.2 Calculate the percentage of sodium carbonate (Na_2CO_3) as follows:

$$Na_2CO_3, \% = [X - (Y \times 0.3690)]1.7097 \quad (14)$$

where:

X = percentage of sodium oxide (Na_2O) (Section 35), and
Y = percentage of $NaHCO_3$.

MATTER INSOLUBLE IN WATER

40. Procedure

40.1 Determine the matter insoluble in water in accordance with the procedure described in Section 29.

SODIUM BICARBONATE

41. Sampling

41.1 Unless caking is noticeable, sodium bicarbonate shall be sampled by removing portions from various parts of the container. If the sodium bicarbonate is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

SODIUM BICARBONATE ($NaHCO_3$), SODIUM CARBONATE (Na_2CO_3), AND FREE MOISTURE

42. Summary of Test Method

42.1 Sodium bicarbonate is thermally decomposed in a special apparatus, and the carbon dioxide evolved is absorbed and weighed. The reaction is as follows:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \quad (15)$$

The loss in weight of the sample is determined, and the content of $NaHCO_3$ and free water are calculated from these values. The Na_2CO_3 content is estimated by difference, the result representing the sum of the Na_2CO_3 content and the minor nonvolatile impurities.

43. Apparatus

43.1 The apparatus shall be assembled as shown in Fig. 1 and shall consist of the following:

43.1.1 *Electric Furnace,* split-type, approximately 33 cm in length, with an opening 3.5 cm in diameter, and with a power requirement of approximately 750 W.

43.1.2 *Variable Transformer,* having an adequate capacity to supply the full rated power of the furnace, and capable of reducing the input voltage so that the temperature of the furnace can be maintained continuously at any value between 95 and 275°C.

43.1.3 *Decomposition Tube,* of heat-resistant glass, having an over-all length of 53 cm, of which 38 cm is 30 mm in outside diameter and the remaining 15 cm is 10 mm in outside diameter, and having a side arm 10 mm in outside diameter attached at a point 5 cm from the large end of the tube.

43.1.4 *Air-Pretreatment Tube,* approximately 30 mm in diameter and 30 cm in length, packed as follows, the various materials, in approximately equal proportions, being separated by glass-wool plugs: "indicating" anhydrous calcium sulfate (Drierite)[4] at the entry end, followed by anhydrous magnesium perchlorate (Dehydrite or Anhydrone), soda-asbestos (Ascarite), and anhydrous magnesium perchlorate again.

43.1.5 *Moisture-Absorption Tube,* consisting of a U-tube with ground-glass stopcocks, the over-all height being approximately 15 cm and the bore 13 cm, packed with "indicating" anhydrous calcium sulfate and anhydrous magnesium perchlorate.

43.1.6 *Carbon Dioxide Absorption Tube*—A standard Nesbitt bulb, approximately 13.5 cm in height, packed with sodaasbestos, with a relatively thin layer of anhydrous magnesium perchlorate at the exit end.

43.1.7 *Sample Boat,* platinum, with a close-fitting cover, approximately 9.5 cm in over-all length, 12 mm wide, and 9 mm high.

43.1.8 *Bubbler Tube,* having an orifice 5 mm in inside diameter, and containing concentrated sulfuric acid (H_2SO_4, sp gr 1.84).

43.1.9 *Connections*—Chemically resistant plastic tubing (Tygon or equivalent) connections of suitable internal diameter, predried in a vacuum desiccator for 24 h followed by heating at 110°C for 30 min prior to use, and with the inner surface coated very lightly with silicone stopcock grease or a thin film of castor oil.

[4] The commercially available grade that shows a distinct color change with use is preferred for this purpose.

43.1.10 *Cooling Chamber,* consisting of an aluminum disk approximately 15 cm in diameter and 3 cm in thickness, and a petri dish with the lip ground to fit the disk, as a cover.

43.1.11 *Thermometer*—An ASTM Partial Immersion Thermometer, having a range from – 5 to + 300°C, and conforming to the requirements for Thermometer 2C as prescribed in Specification E1.

NOTE 6—The rate of sweeping and the heating procedure are such that back-diffusion of the products of decomposition is prevented. At 120°C, approximately 12 mL of gaseous decomposition products per min are released from a 2.5-g sample of sodium bicarbonate. The specified flow rate (50 mL/min) is in excess of four times this amount, providing an air velocity of approximately 10 cm/min. Too rapid heating, or inadequate sweeping, may be evidenced by condensation of moisture at the entry end of the decomposition tube. In this case the determination should be discarded, since absorption of carbon dioxide (CO_2) from the sample in the air-pretreatment tube can occur. To prevent this occurrence, the recommended heating schedule and sweeping rate should be observed. The bubbler tube may be roughly calibrated by the use of a wet-test meter, as an aid in establishing adequate sweeping rates.

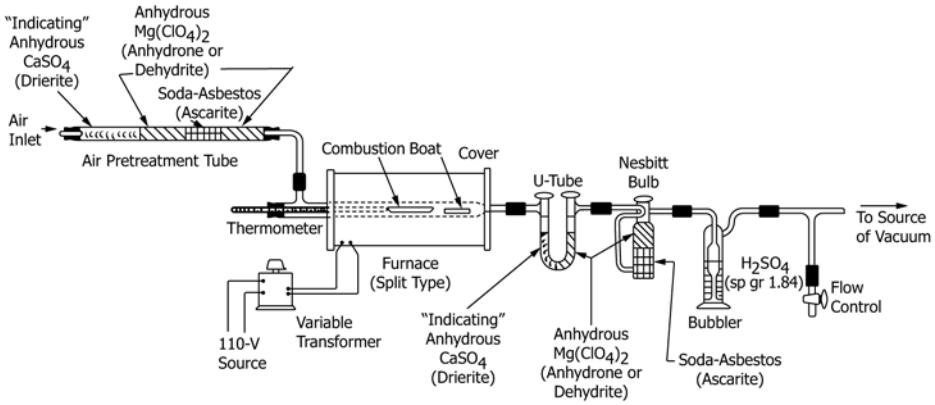


FIG. 1 Apparatus Assembly for Determination of Carbon Dioxide

44. Procedure

44.1 Sweep the assembled apparatus at room temperature, without sample, by drawing air through it for 15 min at a fairly rapid rate. Remove the Nesbitt bulb. Wipe it, and an identical bulb to be used as a counter-weight, with a moist chamois skin or lintless cloth, allow both bulbs to stand in the balance case for 15 min, and then weigh. In order to check the apparatus for leaks, the sweeping and weighing may be repeated. The change in weight in the bulb should be less than 0.1 mg.

44.2 Weigh 2 to 3 g of the sample of sodium bicarbonate to the nearest 0.1 mg into the platinum combustion boat, using the cover. Quickly insert the boat into the decomposition tube at room temperature, removing the cover and allowing it to remain in the tube. Close the tube by inserting the stopper bearing the thermometer. The boat should be located approximately two thirds of the length of the tube from the inlet end, and the thermometer should extend nearly the same distance. Open the stopcocks in the U-tube and in the Nesbitt bulb, and adjust the air flow so that a moderately rapid stream of bubbles passes through the H_2SO_4 bubbler. The minimum rate of flow should be 50 mL of air per min.

44.3 Turn on the electric furnace, and control the temperature by means of the variable transformer in accordance with the following schedule:

44.3.1 Increase the temperature from room temperature to 95°C as rapidly as desired.

44.3.2 After reaching 95°C, adjust the transformer so that the temperature does not exceed 120°C at the end of 1 h.

44.3.3 During the second hour of sweeping, gradually increase the temperature to 275°C.

44.3.4 Discontinue heating, and continue sweeping for at least 30 min.

The total time covered by 44.3.1 – 44.3.4 should be between 2½ and 3 h.

44.4 Close the stopcocks, on the Nesbitt bulb and on the U-tube. Open the furnace, place the cover on the boat, and remove the boat, placing it immediately in the aluminum block cooling chamber. Allow to cool 2 min, and then quickly weigh. Remove the Nesbitt bulb from the assembly, and carefully wipe it free of any silicone grease that may adhere to the tube. Open the stopcock momentarily to the atmosphere to equalize pressure, and wipe both the bulb and the tare with a moist chamois skin or lintless cloth. Allow to stand in the balance case for 15 min, and then weigh to the nearest 0.1 mg.

45. Calculation

45.1 Calculate the percentages of sodium bicarbonate ($NaHCO_3$), free water, and sodium carbonate (Na_2CO_3) as follows:

$$A = (3.818D/E) \times 100 \quad (16)$$

$$B = [(F - 1.409D)/E] \times 100$$

$$C = 100 - (A + B)$$

where:

A = percentage of $NaHCO_3$,
B = percentage of free water,
C = percentage of Na_2CO_3,
D = grams of CO_2 (Section 44),
E = grams of sample used for CO_2 determination, and
F = ignition loss, in grams (original weight of boat and sample minus weight of boat and residue after ignition (see 44.2 and 44.3).

NOTE 7—The Na_2CO_3 values reported represent the sum of the Na_2CO_3

and the other nonvolatile impurities that may be present.

MATTER INSOLUBLE IN WATER

46. Procedure

46.1 Determine the matter insoluble in water in accordance with the procedure described in Section 29.

SODIUM METASILICATE, SODIUM SESQUISILICATE AND SODIUM ORTHOSILICATE

47. Sampling

47.1 Sodium metasilicate, sodium sesquisilicate and sodium orthosilicate shall be sampled by removing portions from various parts of the container. Samples shall not be taken from those portions of the material where caking is noticeable due to the absorption of moisture and carbon dioxide through the container. If the material is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

TOTAL ALKALINITY AS SODIUM OXIDE (Na_2O)

48. Reagents

48.1 *Hydrochloric Acid, Standard* (0.5 *N)*—Prepare and standardize 0.5 *N* hydrochloric acid (HCl).

48.2 *Methyl Orange Indicator Solution* (1 g/L)—Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

49. Procedure

49.1 Weigh 20 g of the sample to the nearest 1 mg in a stoppered weighing bottle. Transfer directly to a 500-mL volumetric flask, dissolve in water, dilute to exactly 500 mL, and mix thoroughly. Transfer a 50-mL aliquot to a 250-mL beaker. Titrate with 0.5 *N* HCl, using methyl orange as the indicator to the first permanent color change. Reserve the titrated solution for the determination of total silica as described in Section 52.

50. Calculation

50.1 Calculate the total alkalinity as sodium oxide (Na_2O) as follows:

$$\text{Total alkalinity as } Na_2O,\ \% = (V \times N \times 3.1)/W \qquad (17)$$

where:

V = millilitres of HCl required for titration of the sample,
N = normality of the HCl, and
W = grams of sample in the aliquot.

TOTAL SILICA AS SILICA (SiO_2)

51. Reagents

51.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

51.2 *Hydrochloric Acid* (1 + 1) —Mix 1 volume of HCl (sp gr 1.19) with 1 volume of water.

51.3 *Hydrofluoric Acid* (sp gr 1.15)—Prepare a solution of hydrofluoric acid (HF) having a specific gravity of 1.15.

51.4 *Sulfuric Acid* (1 + 1) —Add 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) carefully with stirring to 1 volume of water.

52. Procedure

52.1 Transfer the titrated solution as obtained under Section 49 to a porcelain evaporating dish, add 25 mL of HCl (sp gr 1.19), and evaporate to apparent dryness on a steam bath. Triturate the dehydrated residue with the smooth end of a stirring rod, moisten the residue with 10 mL of HCl (1 + 1), and again evaporate to apparent dryness on the steam bath. Dehydrate at 110°C for 1 h, take up the residue with 10 mL of HCl (1 + 1) and 20 mL of water, and digest a short time on the steam bath to effect solution of the soluble salts. Filter the silica on a fine-texture paper by washing the dish with hot water. Scrub the dish with a rubber policeman and again wash thoroughly with hot water. Wash the residue and paper free of acid with hot water and reserve.

52.2 Evaporate the filtrate and washings on the steam bath in the porcelain dish used before, moisten the residue with 10 mL of HCl (1 + 1), and again evaporate to dryness. Dehydrate at 110°C for 1 h, take up the residue with 10 mL of HCl (1 + 1) and 20 mL of water, digest as before to dissolve soluble salts, and filter off any additional silica on a separate filter paper. Scrub the dish and wash the residue and filter paper free from acid as before.

52.3 Transfer both papers and residues to a platinum crucible previously ignited and weighed without cover, and ignite in a muffle furnace until free from carbon, heating slowly at first. Cover the crucible with a platinum cover, heat to the highest temperature of a blast lamp for 15 mm, cool in a desiccator, and weigh without the crucible cover.

52.4 Add 5 mL of water to the contents of the crucible and 2 or 3 drops of H_2SO_4 (1 + 1), then slowly introduce approximately 10 mL of HF. Evaporate to a small volume on the steam bath, add another portion of about 10 mL of HF, and evaporate to fumes of H_2SO_4. Heat the crucible, gently at first, over an open flame to drive off H_2SO_4, and finally at a bright red heat. Cool in a desiccator, and weigh. The loss in weight represents SiO_2.

53. Calculation

53.1 Calculate the percentage of silica (SiO_2) as follows:

$$SiO_2,\ \% = [(A - B)/W] \times 100 \qquad (18)$$

where:

A = grams of ignited residue before treatment with HF 52.3,
B = grams of ignited residue after treatment with HF 52.4, and
W = grams of sample in aliquot.

SODIUM METASILICATE ($Na_2SiO_3 \cdot 5H_2O$)

54. Calculation

54.1 If the ratio of the percentage of silica (SiO_2) divided by the percentage total alkalinity as sodium oxide (Na_2O) is less than 0.969, calculate the percentage of sodium metasilicate as follows:

$$Na_2SiO_3 \cdot 5H_2O, \% = \text{total } SiO_2, \% \times 3.53 \quad (19)$$

54.2 If this ratio is greater than 0.969, calculate the percentage of sodium metasilicate as follows:

$$Na_2SiO_3 \cdot 5H_2O, \% = \text{total alkalinity as } Na_2O, \% \times 3.42 \quad (20)$$

SODIUM SESQUISILICATE ($3Na_2O \cdot 2SiO_2 \cdot 11H_2O$)

55. Calculation

55.1 If the ratio of the percentage of silica (SiO_2) divided by the percentage total alkalinity as sodium oxide (Na_2O) is less than 0.646, calculate the percentage of sodium sesquisilicate as follows:

$$3Na_2O \cdot 2SiO_2 \cdot 11H_2O, \% = \text{total } SiO_2, \% \times 4.20 \quad (21)$$

55.2 If the ratio is greater than 0.646, calculate the percentage of sodium sesquisilicate as follows:

$$3Na_2O \cdot 2SiO_2 \cdot 11H_2O, \% = \text{total } Na_2O, \% \times 2.71 \quad (22)$$

MATTER INSOLUBLE IN WATER

56. Procedure

56.1 Weigh 100 g of the sample to the nearest 0.5 g and transfer to a 1-L beaker. Dissolve by stirring with water at room temperature and dilute to approximately 900 mL. Filter by suction through a prepared, dried, and weighed Gooch crucible, using on the crucible a pad made of asbestos fiber only. Wash the beaker and residue free from alkali with water, and dry the crucible to constant weight in an oven at 110°C. Cool in a desiccator, and weigh.

57. Calculation

57.1 Calculate the percentage of matter insoluble in water from the average gain in weight of two checking duplicate determinations as follows:

$$\text{Matter insoluble in water, \%} = \text{grams of residue} \quad (23)$$

LOSS ON IGNITION OF SODIUM SESQUISILICATE ($3Na_2O \cdot 2SiO_2 \cdot 11H_2O$)

58. Procedure

58.1 Weigh about 2 g of sand in a clean platinum crucible with a tight-fitting lid, and ignite to constant weight. Weigh about 2 g of the sodium sesquisilicate in the crucible, and heat with a low flame until the silicate is melted. Increase the heat gradually as the water is driven off, care being taken to prevent spattering. Ignite to constant weight. Cool in a desiccator, and weigh.

59. Calculation

59.1 Calculate the loss on ignition as follows:

$$\text{Loss on ignition, \%} = (L/W) \times 100 \quad (24)$$

where:

L = grams loss in weight, and
W = grams of sample used.

SODIUM ORTHOSILICATE (Na_4SiO_4)

60. Results

60.1 Express the results of analysis of sodium orthosilicate in terms of sodium oxide (Na_2O), silica (SiO_2), and matter insoluble in water.

TRISODIUM PHOSPHATE

61. Sampling

61.1 Trisodium phosphate, hydrated or anhydrous, shall be sampled by removing portions from various parts of the container. Samples shall not be taken from those portions where caking is noticeable due to the absorption of moisture and carbon dioxide through the container. If the trisodium phosphate is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

TRISODIUM PHOSPHATE (Na_3PO_4) CONTENT AND PHOSPHORUS PENTOXIDE (P_2O_5)

62. Reagents

62.1 *Ammonium Chloride* (NH_4Cl).

62.2 *Ammonium Hydroxide* (1 + 1) —Mix 1 volume of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90) with 1 volume of water.

62.3 *Ammonium Hydroxide* (1 + 20) —Mix 1 volume of NH_4OH (sp gr 0.90) with 20 volumes of water.

62.4 *Hydrochloric Acid* (1 + 1) —Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

62.5 *Hydrochloric Acid* (1 + 20) —Mix 1 volume of HCl (sp gr 1.19) with 20 volumes of water.

62.6 *Magnesia Mixture Reagent*—Dissolve 50 g of magnesium chloride, ($MgCl_2 \cdot 6H_2O$) and 100 g of NH_4Cl in 500 mL

of water. Add NH_4OH in slight excess, allow to stand over night, and filter. Make just acid with HCl, dilute to 1 L, and keep in a glass-stoppered bottle.

62.7 *Methyl Red Indicator Solution.*

63. Procedure

63.1 Weigh 5 g of trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$), 2.4 g of the monohydrate ($Na_3PO_4 \cdot H_2O$), or 2.2 g of the anhydrous sample (Na_3PO_4) in a weighing bottle, transfer directly to a 500-mL volumetric flask, dissolve in water, dilute to exactly 500 mL, and mix thoroughly. If any turbidity exists, filter through a dry paper into a dry beaker, discard the first 100 mL of filtrate, and then transfer a 50-mL aliquot to a 400-mL beaker. Add 5 g of NH_4Cl, 40 mL of water, a drop or two of methyl red indicator solution, and make slightly acid with HCl, cool, and add 25 mL of magnesia mixture. Slowly add NH_4OH (1 + 1), while stirring constantly. When the white crystalline precipitate of magnesium phosphate begins to appear, stop the addition of NH_4OH, stir until no further precipitate appears, and then add NH_4OH (1 + 1) a few drops at a time, while stirring constantly, until the solution is alkaline. Add 15 mL of NH_4OH (1 + 1) in excess and set the solution aside for 4 h in an ice bath or preferably over night at room temperature.

63.2 Filter without attempting to transfer the precipitate, and wash the vessel, residues, and paper a few times with NH_4OH (1 + 20). Dissolve the precipitate in 25 mL of HCl (1 + 1) catching the solution in the original beaker containing the bulk of the precipitate, and wash the filter thoroughly with HCl (1 + 20). Dilute the solution to 100 mL and add 2 mL of the magnesia mixture reagent. Precipitate the magnesium phosphate with NH_4OH (1 + 1), while stirring constantly, as described in 63.1, and finally add 10 mL of NH_4OH (1 + 1) in excess. Allow the solution to stand at least 2 h in an ice bath or preferably over night at room temperature.

63.3 Filter on an ashless filter paper, transfer the precipitate to the filter, and wash with NH_4OH (1 + 20) until free from chlorides. Transfer the precipitate and filter paper to an ignited, tared platinum or porcelain crucible; dry, and heat carefully, preferably in a muffle furnace, until the paper chars without inflaming. Burn off the carbon at the lowest possible temperature and then ignite to constant weight at 950 to 1000°C. Cool in a desiccator, and weigh as magnesium pyrophosphate ($Mg_2P_2O_7$).

64. Calculation

64.1 Calculate the percentage of trisodium phosphate as follows:

$$Na_3PO_4 \cdot 12H_2O, \% = (\text{grams of } Mg_2P_2O_7 \times 3415.61)/W \quad (25)$$

$$Na_3PO_4 \cdot H_2O, \% = (\text{grams of } Mg_2P_2O_7 \times 1634.97)/W$$

$$Na_3PO_4, \% = (\text{grams of } Mg_2P_2O_7 \times 1473.09)/W$$

$$P_2O_5, \% = (\text{grams of } Mg_2P_2O_7 \times 637.72)/W$$

where *W* in all cases is the grams of the original sample used.

TRISODIUM PHOSPHATE CALCULATED AS $Na_3PO_4 \cdot 12H_2O$, $Na_3PO_4 \cdot H_2O$, Na_3PO_4, AND AS P_2O_5 (Alternative Method)

65. Apparatus

65.1 *Filter,* by means of suction through a ¼-in. paper-pulp filter pad, supported on a 1-in. perforated porcelain plate, into a 500-mL suction flask.

65.2 *Filter Aid*—A suspension of purified diatomaceous earth.

66. Reagents

66.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

66.2 *Ammonium Molybdate Solution*—Dissolve 118 g of molybdic acid (85 % MoO_3) in a mixture of 400 mL of water and 80 mL of NH_4OH (sp gr 0.90). Cool, filter if necessary, and pour, while stirring, into a cool mixture of 400 mL of concentrated nitric acid (HNO_3, sp gr 1.42) and 600 mL of water. Add about 0.05 g of disodium hydrogen phosphate (Na_2HPO_4) dissolved in a little water. Mix and let settle over 24 h. Use the clear, supernatant liquor, filtering if necessary. Store in a cool, dark place.

66.3 *Methyl Orange Indicator Solution* (1 g/L)—Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

66.4 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

66.5 *Nitric Acid* (1 + 15) —Mix 1 volume of concentrated nitric acid (HNO_3 , sp gr 1.42) with 15 volumes of water.

66.6 *Nitric Acid, Standard* (0.324 *N*)—Prepare 0.324 *N* HNO_3, using carbon dioxide (CO_2)-free water. Standardize against the 0.324 *N* NaOH solution (66.9).

66.7 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 50 mL of ethyl alcohol and then mix with 50 mL of water.

66.8 *Potassium Nitrate Solution* (10 g KNO_3/L)—Dissolve 10 g of potassium nitrate (KNO_3) in water and dilute to 1 liter.

66.9 *Sodium Hydroxide, Standard Solution* (0.324 *N*)—Prepare a 0.324 *N* solution of sodium hydroxide (NaOH), using carbon dioxide (CO_2)-free water. Standardize against the National Institute of Standards and Technology standard sample No. 39 of benzoic acid. One millilitre of 0.324 *N* NaOH solution equals 0.001 g of P_2O_5 in the titration of ammonium phosphomolybdate.

NOTE 8—For work of average precision, the percentage of total P_2O_5 can be calculated on the basis that 1 mL of the net standard alkali is equivalent to 0.001 g of P_2O_5. Use of this factor has been found to give results correct to within about 1 % of the absolute value. In order to obtain a higher degree of accuracy, it is advisable to standardize the base against a standard sample with an exactly known phosphorus content and having a composition very similar to that of the unknown being analyzed. It has proved very satisfactory in the case of the analysis of commercial phosphate salts to standardize the NaOH with pure potassium dihydrogen phosphate (KH_2PO_4), using an amount of the standard KH_2PO_4 to give a volume of phosphomolybdate precipitate nearly equal to that of the unknown. Recrystallized sodium pyrophosphate ($Na_4P_2O_7$) may also be

used as a standard. It should be noted that the KH_2PO_4 sample should contain about the same amount of sulfate and chloride ion as the unknown.

67. Procedure

67.1 Weigh out 1.45 g of the sample of trisodium phosphate dodecahydrate or an equivalent amount of the monohydrate or anhydrous material in a weighing bottle and transfer to a 500-mL volumetric flask, dissolve in water, and dilute to volume.

67.2 Transfer a 25-mL aliquot of the sample to a 500-mL Erlenmeyer flask containing 100 mL of HNO_3 (1 + 15). Add a drop or two of methyl orange indicator, make just neutral with NH_4OH, and then acidify with HNO_3 (sp gr 1.42) to 5 to 10 % excess by volume of HNO_3. Adjust the temperature between 40 to 50°C, add 60 mL of ammonium molybdate solution, and shake vigorously for 5 to 10 min. Let settle for 10 to 30 min and filter, using suction, through a paper-pulp filter pad that has been coated with a suspension of filter aid, into a 500-mL suction flask. After the contents of the Erlenmeyer flask have been transferred to the filter, rinse the flask with about 25 mL of KNO_3 solution and pour this onto the filter. Repeat this rinsing operation five times. Finally, carefully rinse the filter five times more with KNO_3 solution.

67.3 Transfer the filter pad and its contents to the flask in which the precipitation was made and add about 150 mL of water. Then add 0.324 *N* NaOH solution until the yellow precipitate is dissolved and an excess of 5 to 8 mL of NaOH solution is present. Add 5 to 10 drops of phenolphthalein indicator solution and discharge the pink color with 0.324 *N* HNO_3. Finally, titrate to a perceptible pink color with the NaOH solution.

68. Calculation

68.1 Calculate the percentage of total phosphorus pentoxide (P_2O_5) as follows:

$$\text{Total } P_2O_5, \% = [(A - B)F \times 2000]/W \quad (26)$$

where:

A = millilitres of 0.324 *N* NaOH solution added,
B = millilitres of 0.324 *N* HNO_3 required for titration of the excess NaOH,
F = equivalent value of 0.324 *N* solution in terms of P_2O_5 as calculated (0.001) or that obtained by actual standardizing against KH_2PO_4, and
W = grams of sample used.

68.2 Calculate the equivalent percentages of trisodium phosphate dodecahydrate, monohydrate, and anhydrous form, as follows:

$$Na_3PO_4 \cdot 12H_2O, \% = \text{total } P_2O_5, \% \times 5.356 \quad (27)$$

$$Na_3PO_4 \cdot H_2O, \% = \text{total } P_2O_5, \% \times 2.564$$

$$Na_3PO_4, \% = P_2O_5, \% \times 2.310$$

TOTAL ALKALINITY AS SODIUM OXIDE (Na_2O)

69. Reagents

69.1 *Hydrochloric Acid, Standard* (1.0 *N*)—Prepare and standardize 1.0 *N* hydrochloric acid (HCl).

69.2 *Methyl Orange Indicator Solution* (1 g/L)—See 66.3.

69.3 *Sodium Chloride* (NaCl).

70. Procedure

70.1 Weigh 6 g of the sample and dissolve in 50 mL of water. Dissolve 5 g of NaCl in the solution, add 2 drops of methyl orange solution, cool to 15°C, and titrate with 1.0 *N* HCl to slight but distinct pink color.

71. Calculation

71.1 Calculate the total alkalinity as Na_2O as follows:

$$\text{Total alkalinity as } Na_2O, \% = (A \times N \times 3.1)/W \quad (28)$$

where:

A = millilitres of HCl required for titration of the sample,
N = normality of HCl, and
W = grams of sample used.

MATTER INSOLUBLE IN WATER

72. Procedure

72.1 Weigh 20 g of the sample into a 400-mL beaker and dissolve in 300 mL of water at room temperature. Filter by suction through a prepared, dried, and weighed Gooch crucible using on the crucible a pad made of asbestos fiber only. Wash the beaker and residue free from alkali with water and dry the crucible to constant weight in an oven at 110°C. Cool in a desiccator, and weigh.

73. Calculation

73.1 Calculate the percentage of matter insoluble in water as follows:

$$\text{Matter insoluble in water, \%} = \text{grams of residue} \times 5 \quad (29)$$

TETRASODIUM PYROPHOSPHATE

74. Sampling

74.1 Tetrasodium pyrophosphate ($Na_4P_2O_7$) shall be sampled by removing portions from various parts of the container. Samples shall not be taken from those portions where caking is noticeable due to the absorption of moisture and carbon dioxide through the container. If the tetrasodium pyrophosphate is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

TETRASODIUM PYROPHOSPHATE ($Na_4P_2O_7$)

75. Scope

75.1 This procedure describes an indirect determination of tetrasodium pyrophosphate by titration of sulfuric acid liberated by the action of zinc sulfate on an acid pyrophosphate in accordance with the following reactions:

$$Na_4P_2O_7 + 2HCl = Na_2H_2P_2O_7 + 2NaCl \quad (30)$$

$$Na_2H_2P_2O_7 + 2ZnSO_4 = Zn_2P_2O_7 + Na_2SO_4 + H_2SO_4$$

This titration is a measure of the pyrophosphate content. This test method for pyrophosphate is inaccurate in the presence of polyphosphates.

76. Apparatus

76.1 *Electrometric Titration Apparatus,* consisting of a potentiometer and glass electrode assembly.

77. Reagents

77.1 *Hydrochloric Acid, Standard* (0.2 *N*)—Prepare and standardize 0.2 *N* hydrochloric acid (HCl).

77.2 *Sodium Hydroxide Solution* (0.2 *N*)—Prepare a 0.2 *N* sodium hydroxide (NaOH) solution and standardize against $Na_4P_2O_7$ that has been recrystallized three times from water and dried at 400°C to constant weight.

77.3 *Zinc Sulfate Solution*—Dissolve 125 g of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) in water and dilute to 1 L. Filter, and adjust the pH to 3.8.

78. Procedure

78.1 Weigh accurately approximately 1 g of the sample and dissolve in sufficient water in a 250-mL beaker so that the resulting solution will just cover the electrodes of the glass electrode assembly. Adjust the pH of the solution to exactly 3.8 with 0.2 *N* HCl. Add 50 mL of $ZnSO_4$ solution and allow 5 min for the reaction to become complete as shown by the pH becoming constant. Titrate the liberated acid with 0.2 *N* NaOH solution until a pH of 3.8 is again reached.

79. Calculation

79.1 Calculate the percentage of tetrasodium pyrophosphate ($Na_4P_2O_7$) as follows:

$$Na_4P_2O_7, \% = (A \times F \times 100)/W \quad (31)$$

where:

A = millilitres of NaOH solution required for titration of the sample,
F = grams of $Na_4P_2O_7$ equivalent to 1 mL of 0.2 *N* NaOH solution used for titration as calculated by standardization against $Na_4P_2O_7$, and
W = grams of sample used.

MATTER INSOLUBLE IN WATER

80. Procedure

80.1 Weigh 100 g of the sample to the nearest 0.5 g and transfer to a 1-L beaker. Dissolve by stirring with water at room temperature and dilute to approximately 900 mL. Filter by suction through a prepared, dried, and weighed Gooch crucible, using on the crucible a pad made of asbestos fiber only. Wash the beaker and residue free from alkali with water, and dry the crucible to constant weight in an oven at 110°C. Cool in a desiccator and weigh.

81. Calculation

81.1 Calculate the percentage of matter insoluble in water from the average gain in weight of two checking duplicate determinations as follows:

$$\text{Matter insoluble in water, \%} = \text{grams of residue} \quad (32)$$

LOSS ON IGNITION

82. Procedure

82.1 Weigh 3 g of the sample into a porcelain crucible that has previously been ignited to constant weight. Heat in a muffle furnace at 400°C for 2 h, cool in a desiccator, and weigh.

83. Calculation

83.1 Calculate the loss on ignition as follows:

$$\text{Loss on ignition, \%} = (L/W) \times 100 \quad (33)$$

where:

L = grams loss in weight, and
W = grams of sample used.

BORAX

84. Sampling

84.1 Borax ($Na_2B_4O_7 \cdot 10H_2O$) shall be sampled by removing portions from various parts of the container. Samples shall not be taken from those portions where caking is noticeable. If the borax is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

TOTAL BORATE AND EXCESS ALKALINITY OR ACIDITY

85. Reagents

85.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

85.2 *Hydrochloric Acid* (0.5 *N*)—Prepare and standardize 0.5 *N* hydrochloric acid (HCl).

85.3 *Mannitol,* made neutral to phenolphthalein.

85.4 *Methyl Red Indicator Solution.*

85.5 *Phenolphthalein Indicator Solution* (1 g/L)—Dissolve 0.1 g of phenolphthalein in 50 mL of ethyl alcohol and then mix with 50 mL of water.

85.6 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* sodium hydroxide (NaOH) solution. The solution should be protected from carbon dioxide in the air.

86. Procedure

86.1 Dissolve 20 ± 0.01 g of the sample in 350 mL of hot water. If insoluble matter is present, filter and wash the filter and insoluble matter with hot water until the wash water attains a pH between 6 and 7. Cool to room temperature, transfer to a 500-mL volumetric flask, dilute to volume, and mix well. Titrate a 50-mL aliquot with 0.5 *N* HCl, using 2 drops of methyl red solution as indicator. The end point is a sharp change from light yellow to bright red.

86.2 To a 25-mL aliquot of the solution of the sample prepared in accordance with 86.1, add 25 mL of water. Make slightly acid with HCl (1.19) and reflux for 2 min. Cool the solution and make neutral to methyl red with 0.5 *N* NaOH solution. This point is indicated by a change in color from red to yellow. Add 8 g of mannitol (if glycerin is preferred, add 75 mL of neutral glycerin) and 2 or 3 drops of phenolphthalein indicator solution. Titrate the mixture with 0.5 *N* NaOH solution until the solution color changes from yellow to pink. Add more mannitol or glycerin; if no discharge of pink color is noted, the results are final. If the solution does change to yellow, continue the titration until the pink color appears again, repeating until the end point does not fade on the addition of more mannitol or glycerin.

87. Calculation

87.1 Calculate the percentages of sodium tetraborate ($Na_2B_4O_7$) and of excess alkalinity, calculated as Na_2O, or excess acidity, as follows:

$$Na_2B_4O_7, \% = BN_B \times 5.0319 \quad (34)$$

87.1.1 If AN_A is greater than BN_B,

$$\text{Excess acidity, calculated as } Na_2O, \% = (AN_A - BN_B) \times 1.55 \quad (35)$$

87.1.2 If AN_A is less than BN_B,

$$\text{Excess acidity, calculated as } H_3BO_3, \% = (BN_B - AN_A) \times 6.184 \quad (36)$$

where:

B = millilitres of NaOH solution required for titration of the aliquot (86.2),
N_B = normality of the NaOH solution,
A = millilitres of HCl required for titration of the aliquot (86.1), and
N_A = normality of the HCl.

MATTER INSOLUBLE IN WATER

88. Procedure

88.1 Dissolve 20 ± 0.01 g of the sample in 500 mL of warm water in a 600-mL beaker. Filter through a previously prepared, dried, and weighed Gooch crucible. Wash the residue with warm water until the pH of the washings is between 6 and 7. Dry in an oven at 105°C, cool, and weigh.

89. Calculation

89.1 Calculate the percentage of matter insoluble in water as follows:

$$\text{Matter insoluble in water, \%} = \text{grams of residue} \times 5 \quad (37)$$

SODIUM TRIPHOSPHATE

90. Sampling

90.1 Sodium triphosphate shall be sampled by removing portions from various parts of the container. Samples shall not be taken from those portions where caking is noticeable, due to the absorption of moisture and CO_2 through the container. If the sodium triphosphate is caked, the sample shall be obtained by thoroughly mixing and quartering the entire contents of the package.

TITRATABLE SODIUM OXIDE (Na_2O)

91. Apparatus

91.1 *pH Meter,* equipped with a glass electrode.

92. Reagents

92.1 *Hydrochloric Acid, Standard* (0.1 *N)*—Prepare and standardize 0.1 *N* hydrochloric acid (HCl).

93. Procedure

93.1 Dissolve 5.0 g of the sample in water, transfer to a 500-mL volumetric flask, and dilute to volume. Transfer a 50-mL aliquot to a 250-mL beaker and titrate with 0.1 *N* HCl to an end point of pH 4.5 electrometrically.

94. Calculation

94.1 Calculate the percentage of titratable sodium oxide (Na_2O) as follows:

$$\text{Titratable } Na_2O, \% = (AN \times 3.1)/W \quad (38)$$

where:

A = millilitres of HCl required for titration of the sample,
N = normality of the HCl, and
W = grams of sample used.

TOTAL P_2O_5 (Preferred Method)

95. Reagents

95.1 *Ammonium Chloride* (NH_4Cl).

95.2 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

95.3 *Ammonium Hydroxide* (1 + 1) —Mix 1 volume of NH_4OH (sp gr 0.90) with 1 volume of water.

95.4 *Ammonium Hydroxide* (1 + 20) —Mix 1 volume of NH_4OH (sp gr 0.90) with 20 volumes of water.

95.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

95.6 *Hydrochloric Acid* (1 + 1) —Mix 1 volume of HCl (sp gr 1.19) with 1 volume of water.

95.7 *Hydrochloric Acid* (1 + 20) —Mix 1 volume of HCl (sp gr 1.19) with 20 volumes of water.

95.8 *Magnesia Mixture*—Dissolve 50 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) and 100 g of NH_4Cl in 500 mL of water. Add NH_4OH (sp gr 0.90) in slight excess, allow to stand overnight, and filter. Make just acid with HCl, dilute to 1 L, and keep in a glass-stoppered bottle.

95.9 *Methyl Red Indicator Solution.*

95.10 *Potassium Chloride* (KCl).

96. Procedure

96.1 Weigh 3.2 ± 0.001 g of the sample in a weighing bottle, transfer to a 500-mL volumetric flask, and dissolve in water. Dilute to exactly 500 mL and mix thoroughly. If any turbidity exists, filter through a dry paper into a dry beaker and discard the first 100 mL of filtrate.

96.2 Transfer a 25-mL aliquot to a 400-mL beaker. Add about 10 mL of HCl (sp gr 1.19) and about 75 mL of water. Cover with a watch glass and boil for 30 min. Keep the volume up at about 100 mL.

96.3 Cool the solution, add a drop or two of methyl red indicator solution, and adjust the acidity with NH_4OH until the solution is still slightly on the acid size. Cool and add 25 mL of magnesia mixture. Slowly add NH_4OH (1 + 1), while stirring constantly. When the white crystalline precipitate of magnesium ammonium phosphate $MgNH_4PO_4 \cdot 6H_2O$ begins to appear, stop the addition of NH_4OH, and stir until no further precipitate appears. Then add NH_4OH (1 + 1) a few drops at a time, while stirring constantly, until the solution is alkaline. Add 15 mL of NH_4OH (1 + 1) in excess and set the solution aside for 4 h in an ice bath or preferably overnight at room temperature.

96.4 Filter without attempting to transfer the precipitate and wash the beaker, residues, and paper a few times with NH_4OH (1 + 20). Dissolve the precipitate in 25 mL of HCl (1 + 1), catching the solution in the original beaker containing the bulk of the precipitate. Wash the filter thoroughly with HCl (1 + 20). Dilute the solution to 100 mL and add 2 mL of the magnesia mixture. Precipitate the magnesium ammonium phosphate with NH_4OH (1 + 1) while stirring constantly, as described in 96.1.3. Finally, add 10 mL of NH_4OH (1 + 1) in excess. Allow the solution to stand at least 2 h in an ice bath or preferably overnight at room temperature.

96.5 Filter on an ashless filter paper, transfer the precipitate to the filter, and wash with NH_4OH (1 + 20) until free of chlorides. Transfer the precipitate and filter paper to an ignited, tared platinum or porcelain crucible. Dry, and heat carefully, preferably in a muffle furnace until the paper chars without inflaming. Burn off the carbon at the lowest possible temperature and then ignite to constant weight at 950 to 1000°C. Cool in a desiccator, and weigh as magnesium pyrophosphate ($Mg_2P_2O_7$).

97. Calculation

97.1 Calculate the percentage of P_2O_5 as follows:

$$P_2O_5, \% = W \times 398.57 \quad (39)$$

where:

W = grams of $Mg_2P_2O_7$.

TOTAL P_2O_5 (Alternative Method)

98. Apparatus

98.1 *Filter*—Suitable apparatus for filtration by means of suction through a ¼-in. paper-pulp filter pad, supported on a 1-in. perforated porcelain plate, into a 500-mL suction flask.

98.2 *Filter Aid*—A suspension of purified diatomaceous earth.

99. Reagents

99.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

99.2 *Ammonium Molybdate Solution*—Dissolve 118 g of molybdic acid (85 % MoO_3) in a mixture of 400 mL of water and 80 mL of NH_4OH (sp gr 0.90). Cool, filter if necessary, and pour, while stirring, into a cool mixture of 400 mL of concentrated nitric acid (HNO_3, sp gr 1.42) and 600 mL of water. Add about 0.05 g of disodium hydrogen phosphate (Na_2HPO_4) dissolved in a little water. Mix and let settle over 24 h. Use the clear, supernatant liquor, filtering if necessary. Store in a cool dark place.

99.3 *Ammonium Nitrate (NH_4NO_3).*

99.4 *Methyl Orange Indicator Solution* (1 g/L)—Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

99.5 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

99.6 *Nitric Acid Standard* (0.324 *N*)—Prepare 0.324 *N* HNO_3, using CO_2-free water. Standardize against the 0.324 *N* NaOH solution (99.9).

99.7 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 50 mL of ethyl alcohol and then mix with 50 mL of water.

99.8 *Potassium Nitrate Solution* (10 g/L)—Dissolve 10 g of potassium nitrate (KNO_3) in water and dilute to 1 L.

99.9 *Sodium Hydroxide, Standard Solution* (0.324 *N*)—Prepare a 0.324 *N* solution of sodium hydroxide (NaOH) using CO_2-free water. Standardize against the National Institute of Standards and Technology standard sample No. 39 of benzoic acid. One millilitre of 0.324 *N* NaOH solution equals 0.001 g of P_2O_5 in the titration of ammonium phosphomolybdate (Note 9).

NOTE 9—For work of average precision, the percentage of total P_2O_5 can be calculated on the basis that 1 mL of the net standard alkali is equivalent to 0.001 g P_2O_5. Use of this factor has been found to give results correct to within 1 % of the absolute value. In order to obtain a higher degree of accuracy, it is advisable to standardize the base against a standard sample with an exactly known phosphorus content and having a composition very similar to that of the unknown being analyzed. It has proved very satisfactory in the case of the analysis of commercial phosphate salts to standardize the NaOH with pure potassium dihydrogen phosphate (KH_2PO_4) using an amount of the standard KH_2PO_4 to give a volume of phosphomolybdate precipitate nearly equal to that of the unknown. Recrystallized sodium pyrophosphate ($Na_4P_2O_7$) may also be used as a standard. It should be noted that the KH_2PO_4 sample should contain about the same amount of sulfate and chloride ion as the unknown.

100. Procedure

100.1 Weigh 1.4 g of the sample into a 400-mL beaker and dissolve in about 200 mL of water. Add about 20 mL of HNO_3 (sp gr 1.42), cover with a watch glass, and boil for 30 min. Keep the volume at about 200 mL by the addition of water. Quantitatively transfer to a 500-mL volumetric flask, dilute to volume, and mix well.

100.2 Transfer a 25-mL aliquot to a 500-mL Erlenmeyer flask and dilute to about 100 mL with water. Add a drop or two of methyl orange indicator solution, make just neutral with NH_4OH and then acid with HNO_3 (sp gr 1.42) to a 5 to 10 % excess. Add 5 to 8 g of NH_4NO_3 and dissolve.

100.3 Take up the residue in 100 mL of water and add a drop or two of methyl orange indicator solution. Make just neutral with NH_4OH and then acid with HNO_3 (sp gr 1.42) to a 5 to 10 % excess by volume of HNO_3. Adjust the temperature between 40 and 50°C, add 60 mL of ammonium molybdate solution, and shake vigorously for 5 to 10 min. Let settle for 10 to 30 min and filter, using suction, through a paper-pulp filter pad that has been coated with a suspension of filter aid, into a 500-mL suction flask. After the contents of the Erlenmeyer flask have been transferred to the filter, rinse the flask with about 25 mL of KNO_3 solution and pour this onto the filter. Repeat this rinsing operation five times. Carefully rinse the filter five times more with KNO_3 solution.

100.4 Transfer the filter pad and its contents to the flask in which the precipitation was made and add about 150 mL of water. Then add 0.324 *N* NaOH solution until the yellow precipitate is dissolved and an excess of 5 to 8 mL of NaOH solution is present. Add 5 to 10 drops of phenolphthalein indicator solution and discharge the pink color with 0.324 *N* HNO_3. Finally, titrate to a perceptible pink color with the NaOH solution.

101. Calculation

101.1 Calculate the percentage of total P_2O_5 as follows:

$$\text{Total } P_2O_5, \% = [(A - B) \times F \times 2000]/W \quad (40)$$

where:

A = millilitres of 0.324 *N* NaOH solution added,
B = millilitres of 0.324 *N* HNO_3 required for titration of the excess NaOH,
F = equivalent value of 0.324 *N* solution in terms of P_2O_5 as calculated (0.001) or that obtained by actual standardization against KH_2PO_4, and
W = grams of sample used.

TOTAL P_2O_5 BY pH TITRATION (Alternative Method)

102. Summary of Test Method

102.1 By hydrolysis of the condensed phosphates to the orthophosphate, the total phosphorus can be obtained by titrating the orthophosphoric acid and its salts between the end points near pH 4.5 and 9. Titration between the two end points of orthophosphoric acid forms the basis of this test method. The titration is based on neutralization of the second hydrogen of orthophosphoric acid according to the following equation for the sodium salt:

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O \quad (41)$$

102.2 This test method can be used in the presence of strong acids, strong bases, and their salts if the salts that may be present are soluble at any pH. For routine analysis of soluble salts, this procedure for total P_2O_5 is the most rapid and convenient.

103. Apparatus

103.1 *pH Meter,*[5] equipped with a glass electrode.

104. Reagents

104.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

104.2 *Sodium Hydroxide Solution* (80 g/L)—Dissolve 80 g of carbonate-free sodium hydroxide (NaOH) in water and dilute to 1 L.

104.3 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize an 0.1 *N* solution of sodium hydroxide (NaOH).

105. Procedure

105.1 Weigh out 2.8 g of the sample, dissolve in water, transfer to a 500-mL volumetric flask, and dilute to volume.

105.2 Transfer a 50-mL aliquot to a 250-mL beaker. Add about 10 mL of HCl (sp gr 1.19) and about 50 mL of water. Cover the beaker with a watch glass and boil for 30 min. Keep the volume at about 100 mL by adding water. Cool and adjust pH of the solution to about 3 with NaOH solution (80 g/L).

105.3 Commence the titration with 0.1 *N* NaOH solution, using a glass-electrode pH meter. If a continuous-recording pH meter is not used, then a number of points should be taken in the two pH ranges of 3 to 5.5 and 7.0 to 10.0; pH values outside these ranges are unessential. The end points near pH 4.5 and 9 are precisely measured by bisecting the straight portion of the S-shape curves at the end points, or a plot of pH against milliliters of NaOH solution may be used.

106. Calculation

106.1 Calculate the percentage of total P_2O_5 as follows:

$$\text{Total } P_2O_5, \% = (AN \times 7.098)/W \quad (42)$$

where:

A = millilitres of NaOH solution required for titration of the sample between the specified end points,
N = normality of the NaOH solution, and
W = grams of sample represented by the aliquot used.

107. Precision

107.1 Reproducibility of readings obtained in titration of the sample should be between ±0.05 and ±0.01 mL, depending upon the type of apparatus used.

QUANTITATIVE SEPARATION AND MEASUREMENT OF VARIOUS PHOSPHATES BY REVERSE FLOW ION-EXCHANGE CHROMATOGRAPHY (Preferred Procedure)

108. Scope

108.1 This test method can be used to analyze completely any mixture of low molecular weight phosphates including *ortho*, *pyro*, triphosphate, tetra*meta* and tri*meta*. The higher molecular weight phosphates can only be determined by difference if the procedure is followed as given here. This test method is specifically designed for completely analyzing commercial sodium triphosphate which seldom contains these higher molecular weight phosphates.

109. Summary of Test Method

109.1 A solution of commercial sodium triphosphate is placed in a resin column, and the species fractionated by means of a pressurized, continuous-gradient, reverse-flow elution. A quantitative determination of the eluted phosphate species is made by an improved molybdenum blue colorimetric method. Only one fraction is collected and analyzed for each species. The order of elution is *ortho*, *pyro*, triphosphate, tetra*meta*, and tri*meta*. Long chain phosphates are not displaced.

110. Apparatus

110.1 *Ion-Exchange Apparatus,* as shown in Figs. 2-4, including the following:

110.1.1 *Tube,* chromatographic, 20-mm inside diameter by 400-mm length, chemical-resistant glass with fritted-glass disk at bottom.

110.1.2 *Tubing,* capillary, chemical-resistant glass, 1½-mm inside diameter, 7 mm in outside diameter.

110.1.3 *Tubing,* vinyl (Tygon), ¼ in. in inside diameter, ⅜-in. outside diameter.

110.1.4 *Flask,* flat-bottom ring-neck, chemical-resistant glass, 1000-mL capacity.

110.1.5 *Carboys,* 5-gal chemical-resistant glass, wide-mouth (No. 12 stopper).

110.1.6 *Solenoid Pinch Clamp* (optional), for automatic regeneration. The solenoid must be rated as continuous duty; normally be closed for operation on 115 to 120-V, 60-Hz ac; and used in conjunction with a clock timer.

110.2 *Photometer*—A spectrophotometer or filter photometer suitable for measurements at approximately 650 nm and equipped with appropriate cells to give both a 10-mm and a 50-mm light path.

111. Reagents for Ion-Exchange Separation

111.1 *Hydrochloric Acid* (1.0 M)—Dilute 85.5 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 L with water.

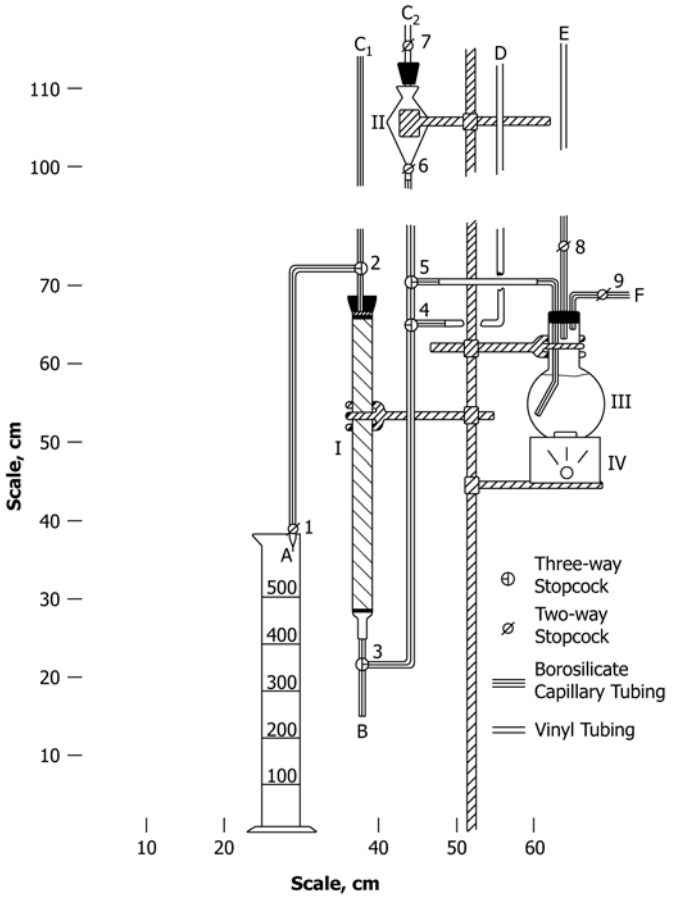
111.2 *Potassium Acetate* (0.8 M)—Dissolve 78.5 g of potassium acetate ($KC_2H_3O_2$) in water and dilute to 1 L. Adjust the pH to 5.0 with glacial acetic acid (Note 10).

NOTE 10—A small pinch of phenyl mercuric chloride or acetate is sometimes effective as a mold inhibitor.

111.3 *Potassium Chloride* (1.0 M)—Dissolve 74.55 g of potassium chloride (KCl) in water and dilute to 1 L after adding buffer solution. Buffer at a pH of 5.0 by adding 100 mL of the $KC_2H_3O_2$ buffer solution (0.8 *M*) to every 16 L (Note 10).

111.4 *Potassium Chloride* (0.10 M)—Dissolve 7.46 g of KCl in water and dilute to 1 L after adding buffer solution. Buffer at a pH of 5.0 by adding 100 mL of the $KC_2H_3O_2$ buffer solution (0.8 *M*) to every 16 L.

[5] The Precision-Dow Recording Titrimeter and the Beckman Autotitrator have been found suitable for this purpose.



I—Chromatographic tube containing packed resin bed approximately 37 cm in height.

II—Sample funnel.

III—One-litre mixer, initially containing 0.1 *M* KCl solution.

IV—Magnetic stirrer.

(*1*) Sample addition: Place sample aliquot in II. Flow is through 6, 5, 4, 3, 2, 1 and out *A*.

(*2*) Sample elution (upflow): Flow is from 1.0 *M* KCl carboy through *E*, 8, III, 5, 4, 3, 2, 1, and out at *A*; magnetic stirrer IV is on at all times.

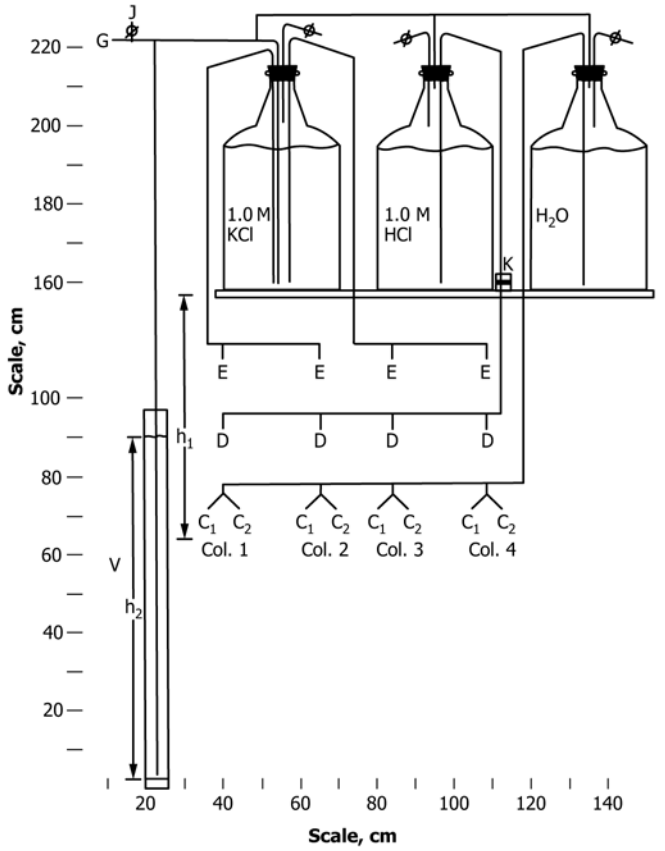
(*3*) Column regeneration (upflow): Flow is from 1.0 *M* HCl carboy and through *D*, 4, then up through 3, 2, 1 and out at *A*.

(*4*) Column wash:

Downflow—Flow is from distilled water carboy through C_1, 2, 3, and out at *B*. Also rinse tube from 2 through 1 and out at *A*, and flush manifold.

Upflow—Flow is through C_2, 7, 6, 5, 4, 3, 2, 1, and out at *A*.

FIG. 2 Column Construction Details



V—Supplementary pressure regulator; an open line from compressed air line *G* is immersed in a column of water V to regulate supplementary application of pressure to columns; supplementary pressure is regulated by adjusting height of water column in V. Flow rate is then regulated by adjusting Valve J. The sum of h_1 and h_2 is proportional to the total pressure applied to the columns and is generally equal to 200 cm for a flow rate of about 6 mL per min.

FIG. 3 Pressurized Feed System

111.5 *Ion-Exchange Resin*—Strongly basic anion-exchange resin, 200 to 400-mesh, chloride form, capacity of 3.2 meq per dry gram (**Warning**—This test method as written is based on the use of Dowex 1X-10 anion exchange resin. Comparable results may not be obtained with other resins.). Prepare the resin for use as follows:

111.5.1 Allow about ½ lb of crude resin per column. Make a 2 + 1 slurry of water and resin and decant off fines. Repeat the procedure until the supernatant liquid remains clear.

111.5.2 Make a 3 + 1 slurry of water and resin, allowing oversize particles and any foreign material to settle. Decant off main slurry of water and resin, saving this portion and discarding residue in bottom of beaker. Repeat until resin is free of oversize particles and foreign material.

111.5.3 Soak the sized resin in 1.0 *M* HCl for a minimum of 48 h. Decant the supernatant acid twice each day, adding fresh acid and reslurrying after each decantation.

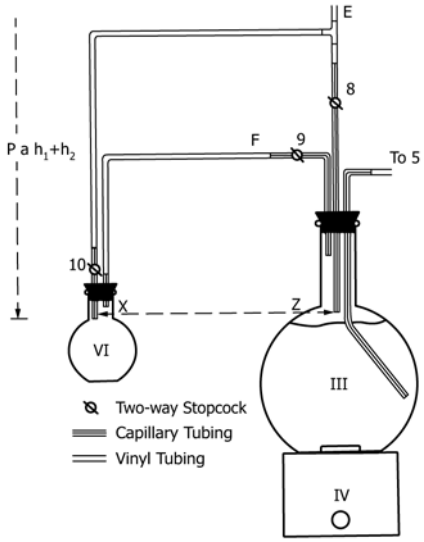
111.5.4 After packing the resin in the chromatographic columns, run HCl under pressure through the resin until the eluate shows no foam upon shaking and is free from odor other than that normal to hydrochloric acid. One litre or more of HCl should be used.

112. Reagents for Colorimetric Phosphorus Pentoxide (P_2O_5) Determination

112.1 *Reducing Solution* (0.15 %) —Prepare the reducing solution as follows:

NOTE 11—The solution must be prepared in the absence of direct ultraviolet light, such as from fluorescent light or daylight.

112.1.1 Purify amino-naphthol-sulfonic acid by dissolving 15 g of crude 1-amino-2-naphthol-4-sulfonic acid in 1 L of water at 90°C containing 150 g of sodium bisulfite ($NaHSO_3$) and 10 g of sodium sulfite (Na_2SO_3). Filter while hot through rapid paper, cool to room temperature, and add 10 mL of concentrated hydrochloric acid (HCl, sp gr 1.19). Filter off crystals, washing first with water and then with methyl alcohol, and air-dry in the dark.



III—Mixer.

IV—Magnetic stirrer.

VI—Pressure equalizer flask.

This mixer pressure equalization is performed before sample elution:

(*1*) Apply full pressure to be used during elution to feed system after closing all valves leading to and from mixer, column, and equalizer.

(*2*) Adjust height of emply equalizer bulb (VI) so that *X* and *Z* are at the same level.

(*3*) Open valves 9 and 10, allowing 1.0 *M* KCl solution to flow into VI.

(*4*) When the flow ceases, the pressure has been equalized. Close valves 9 and 10 and open valve 8. No 1.0 *M* KCl solution should flow through 8 into mixer until sample elution is started by allowing the pressurized 0.1 *M* KCl solution to flow from the mixer into the column.

FIG. 4 Automatic Pressure Equalizer

112.1.2 Dissolve 1.500 g of the recrystallized 1-amino-2-naphthol-4-sulfonic acid in 75 mL of water containing 7 g of Na_2SO_3.

112.1.3 Dissolve 90 g of $NaHSO_3$ in 700 mL of water and mix with solution of amino-naphthol-sulfonic acid described in 112.1.2. Dilute to 1000 mL in a volumetric flask. The solution is stable for about 1 month when protected from ultraviolet light.

112.2 *Ammonium Molybdate* (100 g/L)—Dissolve 100 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in water and dilute to 1 L.

112.3 *Sulfuric Acid* (8 N)—Dilute 222 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 L by adding to water carefully with stirring.

112.4 *Orthophosphate, Standard Solution* (1 mL = 1 mg P_2O_5)—Dissolve 1.9172 g of dry potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1000 mL in a volumetric flask.

113. Preparation of Ion-Exchange Column

113.1 *Preparation of New Column:*

113.1.1 Fill the clean chromatographic column halfway to top with 1.0 *M* HCl, freeing frit and space below frit of air. Fill remainder of column with a 1 + 1 slurry of resin and 1.0 *M* HCl and immediately pack resin in the column by applying a vacuum (water aspirator) at the column bottom valve. Do not let the liquid level in the column fall below the resin level, or let air become entrapped in the resin bed, or vaporize the water in the resin bed by applying too much vacuum. Continue the procedure until the packed resin bed reaches the column shoulder (approximately 37 cm).

113.1.2 Place a mat of glass wool on top of the bed and firmly seat the rubber stopper on top of the wool in order to hold the bed in place. Alternate a pressurized upflow and downflow of 1.0 *M* HCl through the resin bed until no further redistribution and contraction occurs (as indicated by disappearance of any void between the bed and the glass frit). Compensation for a void may be made by the addition of resin or glass wool. Appearance of a large void indicates insufficient vacuum used in packing the resin.

113.2 *Regeneration of Used Column:*

113.2.1 The column should always be regenerated before analyzing a sample. If the column has been idle for more than a few days since a previous full regeneration and has not been stored in 1.0 *M* HCl, simply use a pressurized upflow of 500 mL of 1.0 *M* HCl through the resin before a pressurized washing with water.

113.2.2 In order to accomplish full regeneration (pressurized), after analysis of each sample and before analysis of the next sample, upflow 200 to 300 mL of 1.0 *M* HCl through the column and let soak overnight (minimum of 12 h). Resume regeneration in the morning by upflowing 500 mL of 1.0 *M* HCl through the column (automatic regenerator). Wash the column (downflow) with water until acid free (250 mL), then reverse the flow (upflow) and wash with an additional 100 to 200 mL of water. Proceed immediately with sample addition after the upflow wash.

114. Calibration of Ion-Exchange Column

114.1 This calibration is necessary in order to ascertain exactly when each phosphate species is leaving the column and in what volume it will be contained. Each lot of resin requires calibration only once, and if all columns of a series contain the same lot of resin, only one column of the series needs to be calibrated. A large quantity of resin purchased initially will eliminate frequent recalibrations.

114.2 Using a reference sodium triphosphate sample representative of the material to be analyzed, proceed in accordance with Section 116 with the following exceptions:

114.2.1 Adjust pressurized flow rate to 6 mL/min with a maximum variation of ±0.25 mL/min, and

114.2.2 Collect forty-five to forty-six 25-mL fractions (numbered in sequence).

114.2.3 Analyze fractions as described in Section 31 and plot P_2O_5 concentration against each fraction number. Determine volume of eluate in which each species is contained (Fig. 5).

115. Preparation of Calibration Curve for P_2O_5 Determination

115.1 Make a series of appropriate volumetric dilutions and then prepare a series of aliquots covering a range of 0 to 4 µg of P_2O_5 per mL for the 50-mm absorption cells and 0 to 20 µg of P_2O_5 per mL for the 10-mm absorption cells. Develop the

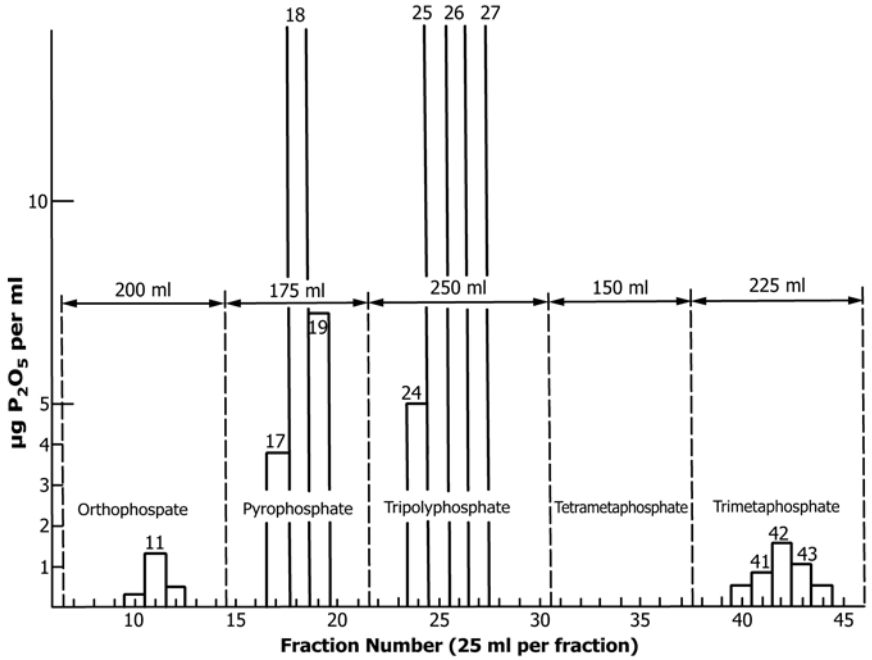


FIG. 5 Elution Curve for Continuous Gradient Upflow Elution—Dowex IX-10 200 to 400-Mesh Resin

color as described in Section 31 and prepare calibration curves. The reagent blanks and the standards for the curve should be 0.1 *M* in KCl.

116. Procedure for Separation of Phosphates

116.1 Regenerate and wash the resin (Figs. 2-4).

116.2 Flush the manifold system and fill the mixer with 0.10 *M* KCl solution. Stopper the flask, start the stirrer, and equalize the pressure (Fig. 4).

116.3 Dissolve 0.5000 g of the sample in water in a 500- mL volumetric flask and dilute to the mark. Pipet a 20-mL aliquot containing approximately 11 to 12 mg of P_2O_5 into the funnel and drain into the column, rinsing the funnel with three 10-mL portions of water. If desired, the sample may be forced in under pressure.

116.4 Start the pressurized elution, adjusting flow (Valve *J*, Fig. 3) to 6.0 ± 0.25 mL/min. Collect the phosphate species in respective graduated cylinders, changing receivers when the proper volume (as determined in column calibration) has been collected. The first 100 to 150 mL collected constitutes the column blank.

116.5 Analyze each fraction as described in Section 117. The column blank *ortho*, tri- and tetra*meta* fractions need not be transferred from the 250-mL glass-stoppered cylinders, but may be hydrolyzed and analyzed in their original containers. The *pyro* and triphosphate fractions should be transferred to larger volumetric flasks (500 and 1000 mL) to ensure accuracy of dilution and to keep the absorbancy on scale. A reagent blank shall be run with each series of determinations in order to determine the net absorbance. If the column blank exceeds the reagent blank by more than 0.005 absorbancy units, the calculation shall be handled by subtracting the column blank absorbance from that of the *ortho* fraction and subtracting the reagent blank from the rest of the fractions. If the column blank is much higher than the reagent blank (0.02 incomplete regeneration, contamination, or channeling is indicated.

116.6 In order to accurately calculate the recovery of P_2O_5 from the column and the percentage of each species present, total P_2O_5 may be determined on each sample by any standard method such as the volumetric phosphomolybdate procedure (see Sections 95 – 107).

117. Procedure for Determining P_2O_5

117.1 Add 3 mL of H_2SO_4 (8 *N*) per 100 mL of final sample volume (final acidity equivalent to 0.24 *N*). If the solution contains other than *ortho*phosphate, hydrolyze for 1.5 h in a boiling water bath and cool to room temperature.

117.2 Add 1 mL of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ per 100 mL of final volume (final concentration equivalent to 0.10 %). Add 2 mL of the reducing solution per 100 mL of final volume (final concentration equivalent to 0.003 %). Dilute to volume, mix, and develop the color at room temperature for 35 min (until constant absorbancy is obtained). Read absorbancy at 650 nm. The 10-mm cells are generally used only for the triphosphate fraction.

118. Calculation

118.1 Calculate the P_2O_5 in any fraction as percentage of the total P_2O_5 recovered, as follows:

$$P_2O_5, \% = (A/B) \times 100 \quad (43)$$

where:

A = micrograms of P_2O_5 in a given fraction, and
B = total micrograms of P_2O_5 recovered in all fractions.

118.2 Calculate the percentage of any given species such as disodium phosphate, tetrasodium pyrophosphate, sodium triphosphate, etc., as follows:

$$\text{Given species, \%} = [(A \times B)/(C \times D)] \times 100 \quad (44)$$

where:

A = micrograms of P_2O_5 in a given fraction,
B = percentage of P_2O_5 in the sample,
C = total micrograms of P_2O_5 recovered in all fractions, and
D = theoretical percentage of P_2O_5 in the given species (Note 12).

NOTE 12—The theoretical percentage of P_2O_5 in any given species is as follows:

	P_2O_5 %
Sodium triphosphate ($Na_5P_3O_{10}$)	57.9
Tetrasodium pyrophosphate ($Na_4P_2O_7$)	53.4
Disodium phosphate (*ortho*) (Na_2HPO_4)	50.0
Trimetaphosphate ($Na_3P_3O_9$)	69.6
Tetrametaphosphate ($Na_4P_4O_{12}$)	69.6

118.3 Calculate the over-all column recovery as follows:

$$\text{Column recovery} = A/(B \times C) \quad (45)$$

where:

A = total micrograms of P_2O_5 recovered in all fractions,
B = percentage of P_2O_5 in the sample and
C = micrograms of sample added to the column.

Recovery should be between 97 and 100.5 % of the P_2O_5 added (Note 13).

NOTE 13—Low recovery may be caused by channeling due to a poorly packed resin bed, mold in the resin or KCl solution, or errors in the P_2O_5 determinations. Resin or KCl containing mold should be discarded. Sterilize the column and the KCl container before refilling.

119. Precision

119.1 This test method has been shown to have the following precision:

	*Ortho*phosphate, %	*Pyro*phosphate, %	Triphosphate, %	Tri*meta*phosphate, %
Standard deviation:				
Among laboratories	0.14	0.30	0.47	0.17
Test error	0.13	0.27	0.37	0.29
Total error of the test method[A]	0.19	0.41	0.60	0.33

[A] Combined error, that is, among laboratories and within laboratory.

QUANTITATIVE SEPARATION AND MEASUREMENT OF VARIOUS PHOSPHATES BY THE PAPER CHROMATOGRAPHIC METHOD (Alternative Procedure)

120. Scope

120.1 In addition to the triphosphate content of a sample, this procedure also gives the percentages of *ortho*phosphates, *pyro*phosphates, and tri*meta*phosphates, and the combined total of all material with molecular weight higher than pentaphosphate. Tetraphosphates and pentaphosphates are distributed partially in the triphosphate and high-molecular-weight bands but are not ordinarily encountered in commercial triphosphate samples.

120.2 If the procedure is used for analyzing commercial samples of triphosphate that generally contain 1 percent or less of *ortho*phosphate, high-molecular-weight phosphate, and tri*meta*phosphate combined, the work involved can be considerably reduced without serious loss in accuracy by omitting the two-directional analysis for tri*meta*phosphate, and disregarding the *ortho*- and higher molecular weight phosphate zones in the one-directional run. The one-directional chromatographic pattern gives a qualitative picture of the over-all make-up of the sample. If unusually large quantities of one of the minor constituents mentioned above are indicated in the one-directional pattern, this suggested shortened procedure should not be followed.

121. Summary of Test Method

121.1 Separation of the phosphate species that might be present in commercial sodium triphosphate is accomplished in ascending paper chromatography, since the rf values are sufficiently different in the special solvents used. Bands of materials are cleanly separated in runs of a few hours' duration. The phosphorus contained in the separated bands is determined colorimetrically, after cutting of the paper, leaching, and hydrolyzing to *ortho*phosphate. The percentage P_2O_5 of the total P_2O_5 in each band is then converted to percentage by weight of sodium phosphate, using the value for total P_2O_5 content of the sample.

122. Apparatus

122.1 *Battery Jars*—Two rectangular battery jars, about 12 by 8 by 6 in. with glass plate covers.

122.2 *Chromatographic Spray Bottle.*

122.3 *Cylindrical Jars* (such as pickle jars), about 6 in. in diameter with a 3½-in. opening, about 11 in. high, and fitted with Petri dish covers. At least four jars will be required.

122.4 *Photometer*—A filter photometer with a light path of 10 to 20 mm, and equipped with a red filter with its maximum at 620 to 650 nm.

122.5 *Filter Paper*—Special filter paper for paper chromatography,[6] in 9 by 6-in. sheets. The necessary markings of these sheets are shown in Fig. 6. Sheet A is for the one-directional run and sheet B is for the two-directional run.

122.6 *Oven,* capable of maintaining a temperature of 50°C and equipped with an exhaust.

122.7 *Pipets*—Two micropipets, 50 microlitres with subdivisions for 10 microlitres, with two micropipet screw controls; about eighteen 5-mL transfer pipets; and a 10-mL automatic pipet.

122.8 *Platinum Wire,* about 0.02 in. in diameter. About 1 ft of the wire will be required.

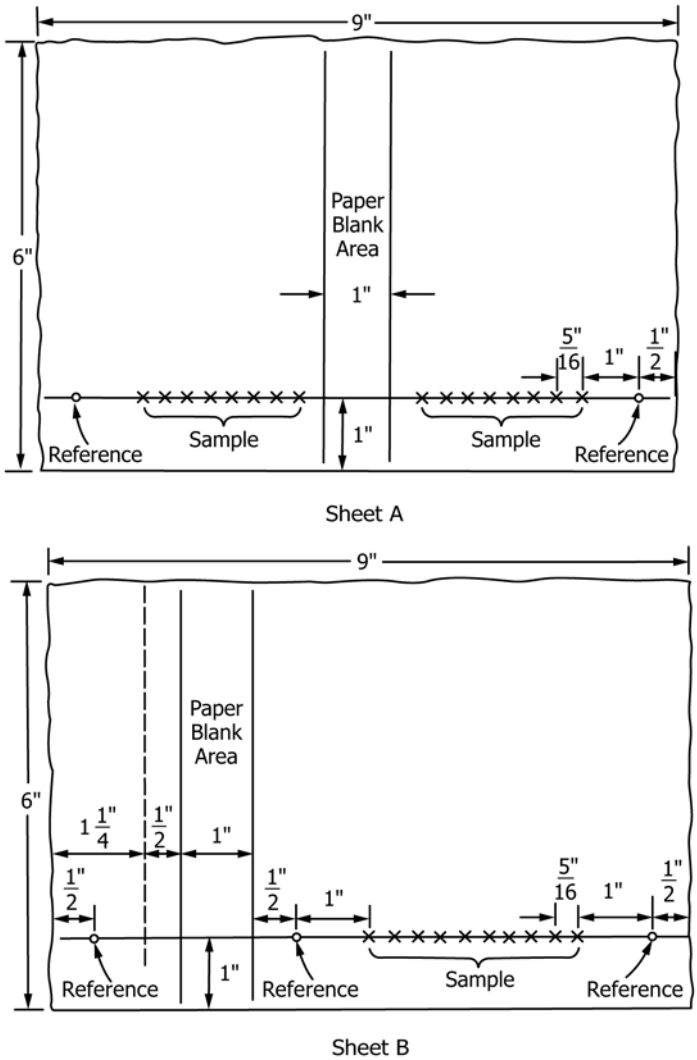
122.9 *Borosilicate Shaking Flasks,* with 25-mL mark. About three dozen of these flasks should be provided.

122.10 *Safety Aspirator.*[7]

122.11 *Ultraviolet Lamp,* long-wave. It is suggested that the base size of the lamp be 18 by 5 in.

[6] Schleicher & Schuell No. 589, orange ribbon, filter paper has been found satisfactory for this purpose.

[7] The Propipette, available from the Will Corp., has been found satisfactory for this purpose.



NOTE 1—Each half of sheet A provides space for one analysis. Sheet B is used for a single analysis.

Metric Equivalents						
in.	½	5/16	1	1¼	6	9
mm	12.7	7.5	25	32	152.4	228.6

FIG. 6 Marked Sheets for Chromatographic Analysis

122.12 *Water Bath,* consisting of a hot plate with several 600-mL glass beakers and Hengar granules.

123. Reagents

123.1 *Reagents for Chromatographic Separation:*

123.1.1 *Acid Solvent*—Mix 735 mL of isopropyl alcohol (having a boiling point between 82 and 83°C) with a solution of 50 g of trichloroacetic acid in 265 mL of water. Add 2.5 mL of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90).

123.1.2 *Basic Solvent*—Mix 387 mL of isopropyl alcohol (boiling point between 82 and 83°C), 200 mL of isobutyl alcohol (boiling point between 106 and 108°C), 408 mL of water, and 5 mL of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90).

123.1.3 *Chromatographic Spray*—Mix 5 mL of $HClO_4$ (60 to 72 %), 1 mL of concentrated HCl, and 1 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and dilute to 100 mL with water.

123.2 *Reagents for Extraction and Hydrolysis:*

123.2.1 *Ammonium Hydroxide* (8 *N*)—Mix equal volumes of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90) and water. Adjust the concentration to 8.0 ± 0.5 *N*.

123.2.2 *Sulfuric Acid* (8 *N*)—Dilute 222 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 L by adding to water carefully with stirring.

123.3 *Reagents for Colorimetric Determination:*

123.3.1 *Ammonium Molybdate Solution*—Dissolve 50 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 450 mL of water.

123.3.2 *Benzene.*

123.3.3 *Isobutyl Alcohol,* boiling point between 106 and 108°C.

123.3.4 *Isobutyl Alcohol-Benzene Mixture*—Mix equal volumes of isobutyl alcohol and benzene.

123.3.5 *Methyl Alcohol.*

123.3.6 *Reducing Agent*—Dilute 0.5 mL of $SnCl_2$ solution (122.3.7) to 100 mL with H_2SO_4 (1 + 35). Prepare fresh daily.

123.3.7 *Stannous Chloride Solution*—Dissolve 10 g of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 25 mL of concentrated hydrochloric acid (HCl, sp gr 1.19); store in a small glassstoppered brown bottle. This solution is not stable longer than four weeks.

123.3.8 *Sulfuric Acid* (1 + 35) —Add 1 volume of concentrated sulfuric acid ($H_2 SO_4$, sp gr 1.84) to 35 volumes of water carefully with stirring.

123.3.9 *Sulfuric Acid, Alcoholic* (1 + 49) —Mix 20 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 980 mL of methyl alcohol.

123.4 *Phosphate Reference Standard Solution*—Dissolve approximately 0.4 g of potassium dihydrogen *ortho*phosphate (KH_2PO_4), 0.7 g of sodium *pyro*phosphate ($Na_4P_2O_7 \cdot 10H_2O$), 0.5 g of tripolyphosphate ($Na_5P_3O_{10} \cdot 6H_2O$), and 0.35 g of tri*meta*phosphate ($(Na_3PO_3)_3$) in 250 mL of water.

124. Preparation of Sample

124.1 Homogenize the sample sufficiently that a small amount of material will be representative of the batch being analyzed. Dissolve 6.0 ± 0.1 g of the homogenized sample in 1 L of water and mix well.

125. Procedure for One-Directional Separation

125.1 Fold the filter paper sheet A (Fig. 6) into a cylinder by clipping together the centers of the 6-in. edges with a 1-in. piece of platinum wire in such a way that the edges do not touch.

125.2 Place the sample solution on the starting line by delivering a 5-µg droplet for each mark, using the micropipet screw control. In the same way, place a 5-µg droplet of reference solution on each of the two reference marks. Allow the spots to dry.

NOTE 14—Under very humid conditions, use a desiccator.

125.3 Expose the sheet to the vapors of the acid solvent in a rectangular battery jar for 40 min, avoiding contact of the sheet with the liquid.

125.4 Place 150 mL of acid solvent in a 1-gal cylindrical jar (Note 15). Transfer the preconditioned sheet without delay from the rectangular battery jar to the 1-gal cylindrical jar. Insert the sheet into the jar, with the starting line down, in such a way that splashing or wave-like movement of the solvent is avoided. Cover the jar immediately and allow the solvent to ascend 5 in. from the bottom of the paper (Note 16).

NOTE 15—The solvent can be used repeatedly if the volume is replenished after several runs with fresh solvent.

NOTE 16—The time required varies from 1 to 2½ h, depending on conditions.

125.5 Remove the paper sheet from the jar by first deforming the cylinder slightly at the top into a cone. Remove the excess solvent from the paper by gently touching the bottom of the upright cylinder to an absorbent paper towel several times. Leave the sheet cylinder standing on the paper towel for about 10 min.

125.6 Transfer to a 50°C drying oven and dry 10 min more.

EVALUATION OF THE CHROMATOGRAM

125.7 Remove the platinum wire and bend the sheet flat. Using the chromatographic spray bottle, apply a fine mist of chromatographic spray solution evenly over the entire sheet, including the blank area. Avoid the formation of wet-appearing areas and droplets on the paper.

125.8 Dry the paper at 50°C in the drying oven for 10 min.

125.9 Place the sheet under the ultraviolet lamp and irradiate until the bands of phosphate species appear as blue zones.

NOTE 17—If the sheet has been covered evenly by the spray and the irradiation, this operation is complete after the reference spots are clearly visible. The appearance of the pattern varies with humidity of the air in the room. In a very dry room, it may be necessary to spray the sheet again after the irradiation in order to make the bands clearly visible. In a very moist room, heavy blue background masks the pattern but can be removed by exposing the sheet to ammonia vapor.

125.10 Promptly mark the zones in pencil for cutting as illustrated by the dotted lines in Fig. 7 (Notes 18 and 19). Cut the bands and a corresponding strip of the paper blank area along the dotted lines shown in Fig. 7 (Note 20).

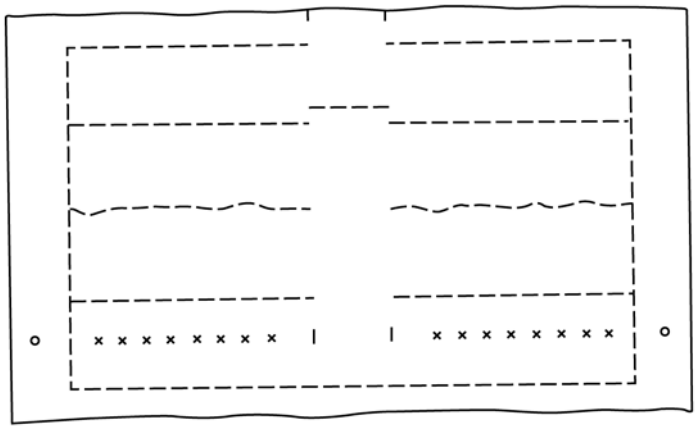


FIG. 7 Chromatographic Patterns Typical for Sodium Triphosphate (Sheet Marked for Cutting)

NOTE 18—The paper areas must be matched within ¼ in.^{2} because the quantity of paper present in the subsequent colorimetric determination affects the results. If extra paper is needed in matching the areas, use paper from the paper blank area and reduce the amount of paper in the blank.

NOTE 19—The line between the *pyro*phosphate and triphosphate bands should be drawn such as to include as much as possible of the space between the bands in the triphosphate band. The line between the triphosphate and high-molecular-weight bands shall be drawn just below the tri*meta*phosphate level, as indicated by the reference spot near the margin.

NOTE 20—In series of commercial samples containing fractional percentages or less of *ortho*phosphate and high-molecular-weight material, the procedure can be considerably shortened without serious loss in accuracy by cutting and extracting only the *pyro* phosphate and triphosphate bands.

125.11 Insert each strip into a 25-mL flask (Note 21). Add 1 mL of 8 *N* NH_4OH and about 7 mL of water to each flask, swirl, and allow to stand for 5 to 10 min. Then add 3 mL of 8 *N* H_2SO_4 to each flask. Handle all the flasks containing the fractions of one analysis as a group to ensure similar treatment.

NOTE 21—Use of narrow-neck volumetric flasks requires either cutting the paper bands into approximately ½ by ⅛-in. pieces or employing special techniques for cleaning the flasks.

125.12 Place the flasks in the water bath and keep at boiling temperature for 20 min. Remove the flasks from the bath and cool to room temperature.

125.13 Add exactly 10 mL of benzene-isobutyl alcohol mixture to each flask, followed by 2 mL of ammonium molybdate solution. Dilute to volume with water and shake vigorously for at least 20 s. After the layers have separated, withdraw exactly 5 mL of the supernatant organic layer from each flask and transfer to other 25-mL volumetric flasks.

125.14 Dilute with about 10 mL of the alcoholic H_2SO_4, swirl, and add 1 mL of reducing agent. Mix well and dilute to volume with the alcoholic H_2SO_4. Homogenize the solution carefully, and after 10 min read the absorbance at about 650 nm (red filter) in microcells against the solution obtained with the blank paper area (Note 22).

NOTE 22—The absorbance value of each fraction is proportional to the quantity of phosphorus in that fraction.

126. Procedure for Two-Directional Separation for Tri *meta*phosphate

126.1 Fold the filter paper sheet B (Fig. 5) into a cylinder as described in 125.1.

126.2 Place 5-µg droplets of sample and reference solutions on the paper and allow the spots to dry in the manner described in 125.2.

126.3 Expose the sheet to the vapors of the basic solvent in a rectangular battery jar for 40 min, avoiding contact of the sheet with the liquid.

126.4 Place 150 mL of the basic solvent (Note 15) in a 1-gal cylindrical jar and start the run the same as indicated in 125.4. Allow the solvent to ascend until the solvent front is within about 1 in. of the upper edge.

126.5 Remove the paper cylinder, blot the lower edge, and allow to dry at room temperature.

126.6 Remove the platinum wire and cut off the strip carrying the reference spots along the dotted line. Spray this strip of paper with the chromatographic spray, dry it, and make the spots visible under the ultraviolet light. Using the reference strip, mark the upper edge of the fastest moving phosphate fraction (tri*meta*phosphate) on the unsprayed main sheet.

126.7 Cut the main sheet ¾ in. above this level, coil into a cylinder again, and insert upside down into a cylindrical jar containing about 150 mL of acid solvent (Note 15). Allow the solvent to ascend until the solvent front is within 1 in. of the upper edge.

126.8 Remove, dry, and develop the pattern on the sheet as described for the one-directional run in 125.5 – 125.9.

126.9 Mark the ring band, following the band contour halfway between the ring phosphate band and the adjacent wide band (Note 23). Cut out the ring phosphate band and a corresponding strip of the paper blank area and also cut the wide band into two or three areas, each equal in size to the paper area carrying the tri*meta*phosphate (Note 12).

NOTE 23—The tri*meta*phosphate is located in the band furthest away from the original starting line. The *ortho*phosphates and chain phosphates are contained in a wide area between the starting line and the ring phosphate band. If the ring phosphate band is poorly visible, use the reference spots as a guide for marking.

126.10 Insert each strip into a 25-mL flask (Note 21). Complete the analysis exactly as described for the one-directional separation in 125.11 – 125.14.

127. Calculation

127.1 Calculate the percentage P_2O_5 of the total P_2O_5 for any given fraction in the one-directional analysis as follows:

$$\text{Percentage } P_2O_5 \text{ of total } P_2O_5, \text{ for any given fraction} = \left(A_x/\sum_1 A_x\right) \times 100 \quad (46)$$

where:

A = absorbance,
A_x = A_o = absorbance of the *ortho*phosphate fraction, or
= A_p = absorbance of the *pyro*phosphate fraction, or
= A_{tm} = absorbance of the triphosphate plus tri*meta*-phosphate fraction, or
= A_h = absorbance of the high-molecular weight fraction, and
$\sum_1 A_x$ = total absorbance of all the fractions cut out and analyzed in the one-directional separation.

127.2 Calculate the percentage P_2O_5 of the total P_2O_5 for the tri*meta*phosphate fraction in the two-dimensional analysis as follows:

$$\text{Percentage } P_2O_5 \text{ of total } P_2O_5 \text{ present as tri}meta\text{phosphate} = \left(A_m/\sum_2 A_y\right) \times 100 \quad (47)$$

where:

A_m = absorbance of tri*meta*phosphate fraction, and
$\sum_2 A_y$ = total absorbance of all the fractions cut out and analyzed in the two-directional separation.

127.3 Calculate the percentage P_2O_5 of the total P_2O_5 present in the triphosphate fraction as follows:

$$\text{Percentage } P_2O_5 \text{ of total } P_2O_5 \text{ as triphosphate} = \left[\left(A_{tm}/\sum_1 A_x\right) - \left(A_m/\sum_2 A_y\right)\right] \times 100 \quad (48)$$

127.4 Calculate the percentages of sodium phosphates contained in the sample as follows:

$$\text{Percentage of a given sodium phosphate in the sample} = \left(P_x/P_c\right) \times \text{total } P_2O_5 \quad (49)$$

where:

P_x = percentage of P_2O_5 of the total P_2O_5 present in the appropriate fraction, and
P_c = percentage by weight of P_2O_5 in the given compound.

NOTE 24—The total P_2O_5 in the sample can be determined by any of several methods. Suitable methods are covered in Sections 95 – 107.

$$\text{Percentage } Na_5P_3O_{10} \text{ in sample} = \frac{\left[\left(A_{tm}/\sum_1 A_x\right) - \left(A_m/\sum_2 A_y\right)\right] \times 100}{57.88} \times \text{total } P_2O_5 \quad (50)$$

$$\text{Percentage } Na_4P_2O_7 \text{ in sample} = \frac{\left(A_p/\sum_1 A_x\right) \times 100}{53.38} \times \text{total } P_2O_5$$

$$\text{Percentage } Na_3PO_4 \text{ in sample} = \frac{\left(A_o/\sum_1 A_x\right) \times 100}{43.29} \times \text{total } P_2O_5$$

$$\text{Percentage } (NaPO_3)_3 \text{ in sample} = \frac{\left(A_m/\sum_2 A_y\right) \times 100}{69.60} \times \text{total } P_2O_5$$

$$\text{Percentage high} - \text{molecular} - \text{weight sodium phosphates in sample (approximate)} = \frac{\left(A_h/\sum_1 A_x\right) \times 100}{69.60} \times \text{total } P_2O_5$$

127.5 To minimize errors from excessively high temperatures and extended runs, apply hydrolysis corrections for temperatures above 20°C during the one-directional chromatographic separation as follows:

127.5.1 Add to the percentage $Na_5P_3O_{10}$ in the sample a correction calculated as follows:

$$f \times t \times \text{percentage } Na_5P_3O_{10} \text{ in sample} \quad (51)$$

127.5.2 Deduct from the percentage $Na_4P_2O_7$ in the sample a correction calculated as follows:

$$f \times t \times \text{percentage } Na_5P_3O_{10} \text{ in sample} \quad (52)$$

where:

f = 0.002 for 22°C, 0.003 for 25°C, and 0.007 for 30°C, and
t = time the acidic solvent was allowed to ascend in the onedirectional separation.

pH OF 1 % SOLUTION

128. Procedure

128.1 Determine the pH at 25°C of a portion of the solution of the sample (Section 94) prepared for determination of titratable sodium oxide (Na_2O) in accordance with Method E70.

TURBIDITY

129. Procedure

129.1 Prepare a 5 % solution of the sample and determine its turbidity by measurement of the percentage of light transmitted through the solution in a standard length cell using any convenient photoelectric colorimeter equipped with a green filter transmitting at 520 nm. The instrument shall be calibrated against standard turbidity samples.

TEMPERATURE RISE

130. Scope

130.1 There are two types of sodium triphosphate, both of which may be found in commercial samples. Form I hydrates more rapidly than Form II. The relative quantities of each may be determined by the temperature rise test. The procedure described in the following Sections 131 – 135 has been calibrated against X-ray diffraction analysis. For reliable results it is essential to follow exactly the standard procedure.

131. Apparatus

131.1 The apparatus shall have the form and dimensions shown in . A narrow tall-form beaker of 180-mL capacity[8] shall be inserted up to the top rim into the neck of a wide-mouth half-gallon sample bottle. The beaker shall be fitted into a circular hole cut into the metal screw cap of the bottle (considerable insulation is accomplished by this arrangement). A stirrer shall be provided, having two rings 1⅜ in. in diameter attached 1 in. apart to a handle made from ⅛-in. stainless steel welding rod. In addition a thermometer (131.2) and a timing device shall be provided.

131.2 *Thermometer*—An ASTM Titer Test Thermometer having a range from – 2 to + 68°C and conforming to the requirements for Thermometer 36°C as prescribed in Specification E1.

132. Reagent

132.1 *Glycerin,* dry, having a specific gravity of 1.249 to 1.250 at 25°C.

133. Procedure

133.1 Bring the apparatus to room temperature. Weigh 50.0 ± 0.1 g of glycerin, at room temperature, into the dry beaker. Weigh out 50 ± 0.1 g of the powdered sample, also at room temperature, and put it on top of the glycerin. Suspend the beaker in the neck of the bottle, insert the dry stirrer, and begin the test by stirring exactly 2 min, with vertical strokes, starting the timer simultaneously. Prevent dust and losses of sample by moving the stirrer only slowly for the first few seconds, until powder and glycerin are well mixed. Then increase the stirring rate quickly to 240 complete cycles/min and maintain this rate for the last 90 s. (A complete cycle always means lifting the bottom ring from the bottom of the beaker just to the surface of the mixture and pushing it back down until it touches the

[8] The beaker available as Catalog No. 1140, Corning Glass Works, has been found satisfactory for this purpose.

bottom again; scraping of the sides is desirable.) Stop stirring. Clamp the dry thermometer in a central position with the tip 10 mm above the bottom of the beaker (lower it until it touches the bottom and lift 10 mm, checking the height by the aid of the thermometer scale). Read and record the temperature of the glycerin sample mixture exactly 4 min + 45 s after starting the test (initial temperature).

133.2 Exactly 5 min after the start of the test, add rapidly 25.0 ± 0.3 mL of water, at room temperature, and resume stirring at the rate of 240 complete cycles/min (2 s should cover these operations). Stir for 30 s, push the stirrer down to the bottom of the beaker, and stop stirring. Observe the temperature without stirring until it has reached a maximum and has decreased again at least 0.1°C. Deduct the initial temperature from the maximum temperature reading and report the difference, in degrees Celsius, as the temperature rises.

134. Calculation

134.1 Calculate the percentage of sodium triphosphate ($Na_5P_3O_{10}$) present in form I, as follows:

$$\text{Sodium triphosphate, form I, \%} = (R - 6) \times 4 \quad (53)$$

where:

R = temperature rise, in degrees Celsius.

SULFATE

135. Apparatus

135.1 *Photoelectric Densitometer.*

135.2 *Filter,* transmitting light in the red.[9]

135.3 *Optical Cell,* 40 by 40 by 60-mm,

135.4 *Measuring Scoop,* 0.2-mL capacity.[10]

136. Reagents

136.1 *Barium Chloride*—Barium chloride ($BaCl_2 \cdot 2H_2O$) crystals, 20 to 30 mesh.

136.2 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

136.3 *Sodium Sulfate, Standard Solution* (1 mL = 0.001 g Na_2SO_4)—Dissolve 1.000 g of anhydrous sodium sulfate (Na_2SO_4) in water and dilute to 1 L in a volumetric flask. Mix well.

136.4 *Sulfate-Free Polyphosphate*—Recrystallize sodium tripolyphosphate ($Na_5P_3O_{10}$) from water enough times to remove all the sulfate.

137. Preparation of Calibration Curve

137.1 Add from a buret, to a series of conical flasks, aliquots of the standard Na_2SO_4 solution corresponding to 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 12 mg of Na_2SO_4. Add to each flask 2.00 g of sulfate-free polyphosphate and 3.0 mL of HCl; dilute to 100 mL.

137.2 Continue as directed for the sample in 138.4. Plot the percentage transmission of each of the standards against the milligrams of Na_2SO_4 present.

138. Procedure

138.1 Dissolve 2.000 g of the sample in about 80 mL of water. Add from a buret 3.0 mL of HCl. Boil at a moderate rate for at least 1 h. Filter if any turbidity remains.

138.2 Transfer to a 250-mL Erlenmeyer flask, cool to room temperature, and dilute to 100 mL with water.

138.3 Add slowly, while swirling, one scoopful (approximately 0.3 g) of $BaCl_2$ crystals and continue swirling until the crystals dissolve. Ten minutes after the crystals are dissolved, read the turbidity of the sample in the densitometer in terms of percentage light transmission.

139. Calculation

139.1 Calculate the percentage of sodium sulfate (Na_2SO_4) as follows:

$$Na_2SO_4, \% = (A \times 0.1)/B \quad (54)$$

where:

A = milligrams of Na_2SO_4 found, and
B = grams of sample used.

IGNITION LOSS

140. Procedure

140.1 Transfer 2.0 g of the sample to a previously ignited and weighed porcelain crucible. Place in a cool muffle and gradually raise the temperature to 600°C, maintaining this temperature for 1 h. Cool in a desiccator and weigh.

141. Calculation

141.1 Calculate the percentage of ignition loss as follows:

$$\text{Ignition loss, \%} = (A \times 100)/W \quad (55)$$

where:

A = grams loss in weight on heating, and
W = grams of sample used.

MATTER INSOLUBLE IN WATER

142. Apparatus

142.1 *Shaking Device,* suitable for agitating the contents of a 500-mL Erlenmeyer flask.

142.2 *Gooch Crucible,* prepared as follows: Prepare a pad of fine asbestos fibers; then coat the pad with diatomaceous earth filter aid. Dry the crucible to constant weight at 110°C just prior to use, or store in a desiccator until needed.

143. Procedure

143.1 Add slowly, while swirling, 10.0 g of the sample to 100 mL of water contained in a narrow-neck 500-mL Erlenmeyer flask. Stopper and shake on a mechanical flask shaker until the phosphate is in solution. Filter on a tared Gooch crucible.

[9] The Wratten Gelatin Filter F-29 (red), or equivalent, is suitable for this purpose.

[10] A suitable scoop is available from W. H. & L. D. Betz Co., Gillingham and Worth Sts., Philadelphia, PA.

143.2 Rinse the contents of the flask into the crucible with two or three small washings of water; then wash the crucible until free of soluble phosphate. Dry at 110°C to constant weight.

144. Calculation

144.1 Calculate the percentage of matter insoluble in water as follows:

$$\text{Matter insoluble in water, \%} = R \times 10. \quad (56)$$

where:

R = grams of dried residue.

PARTICLE SIZE

145. Procedure

145.1 Determine particle size in accordance with Test Method D502.

ORTHOPHOSPHATE

146. Principle of Test Method

146.1 This test method depends upon the conversion of orthophosphate to phosphomolybdic acid, extraction of the acid with benzene-isobutyl alcohol solution, reduction to a blue complex by means of stannous chloride, and measurement of the absorbance of the final solution. The absorbance is measured in a spectrophotometer and referred to a standard curve which is prepared from data obtained in a similar manner, starting with known amounts of orthophosphate.

147. Apparatus

147.1 *Spectrophotometer,* suitable for measurements at 720 to 730 nm,[11] and equipped with matched, glass-stoppered, 10-cm absorption cells. A10-cm cell attachment and cell holder are also required.

147.2 *Test Tubes,* of heat-resistant glass,[12] approximately 25 by 200 mm.

148. Reagents

148.1 *Benzene,* thiophene-free.

148.2 *Ethyl Alcohol* (95 %)—Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue.

148.3 *Isobutyl Alcohol.*[13]

148.4 *Isobutyl Alcohol-Benzene Solution*—Mix equal volumes of isobutyl alcohol and benzene.

NOTE 25—Due to the toxic nature of this reagent a rubber bulb or similar device should be employed for pipeting it.

148.5 *Molybdate Reagent*—To 400 mL of water add slowly, with stirring, 111 mL of H_2SO_4 (sp gr 1.84). Cool to room temperature and dissolve 50 g ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in this solution. Dilute to 1 L in a glass-stoppered volumetric flask.

148.6 *Phosphate, Standard Solution* (1 mL = 0.004 mg P_2O_5)—Dissolve exactly 0.3836 g of potassium dihydrogen phosphate (KH_2PO_4) (dried for 1 h at 105°C) in 250 mL of water. Dilute 25 mL of this solution to 500 mL. Dilute 25 mL of this latter solution to 250 mL. One milliliter of this final solution is equivalent to 0.004 mg of P_2O_5.

148.7 *Stannous Chloride Solution* (400 g/L)—Dissolve 10 g of stannous chloride ($SnCl_2\cdot 2H_2O$) in 25 mL of HCl, (sp gr 1.19) and store in a small, glass-stoppered brown bottle. This solution is stable for only 4 weeks (Note 25).

148.8 *Stannous Chloride Solution* (2 g/L)—Dilute 1 mL of the $SnCl_2$ solution (400 g/L) to about 100 mL with water. Add 11.1 mL of H_2SO_4 (1 + 1) (prepared by mixing equal volumes of H_2SO_4 (sp gr 1.84) and water) and dilute to 200 mL. Prepare this solution fresh daily and discard if any turbidity develops. This solution is stable for only a few hours (Note 25).

148.9 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

148.10 *Sulfuric Acid, Alcoholic*—Dissolve 20 mL of H_2SO_4 (sp gr 1.84) in 980 mL of ethyl alcohol (95 %).

NOTE 26—For extremely precise work, absolute alcohol must be used in preparing this reagent. Experimental data indicate that if 95 %, Formula No. 3A ethyl alcohol is used, the color of the complex fades to about 60 % of its expected value in 19 h. An all-glass, 500-mL wash bottle is recommended for delivering the alcoholic H_2SO_4.

149. Preparation of Calibration Curve (Note 27)

149.1 From a 10-mL buret measure 1.00, 2.00, 4.00, 6.00, and 8.00 mL of the standard phosphate solution (corresponding to 0.004, 0.008, 0.016, 0.024, and 0.032 mg P_2O_5 respectively) into separate test tubes and treat each one as follows: Add from a graduate sufficient water to bring the volume up to 15 mL; then by means of pipets add 25 mL of isobutyl alcohol-benzene solution (Note 25) and 5 mL of molybdate reagent. Stopper the test tube and immediately shake the mixture vigorously for 15 s. Allow the two phases to separate. Pipet 10 mL of the upper layer (Note 25 and Note 28) into a 50-mL volumetric flask and wash the pipet with 5 to 10 mL of the alcoholic H_2SO_4, catching the washings in the volumetric flask (Note 29). Dilute this solution to approximately 45 mL with alcoholic H_2SO_4 , add 1 mL of $SnCl_2$ solution (2 g/L), dilute to the mark with alcoholic H_2SO_4, and mix well. Carry a blank of 15 mL of water through the same procedure.

NOTE 27—Because of the small amounts of phosphate present, it is imperative that all glassware used be chemically clean.

NOTE 28—Only 10 mL of the isobutyl alcohol-benzene layer is used in obtaining data for the standard curve and also for analyzing the sample solution. However, for convenience in calculating the results, it is assumed that the absorbance readings are due to the original weight of material in every case.

NOTE 29—The isobutyl alcohol-benzene solution does not drain completely from the pipet; therefore, the pipet is rinsed with alcoholic H_2SO_4 solution in order to effect quantitative transfer. To prepare the pipet for succeeding determinations, wash it with water, then acetone, and finally air-dry it by attaching to the vacuum line and drawing air through it.

[11] The Beckman Model DU Spectrophotometer, having a Mazda lamp as a light source, has been found suitable for this purpose.

[12] Borosilicate glass has been found satisfactory for this purpose.

[13] Eastman Kodak Co. isobutyl alcohol No. 303 has been found satisfactory for this purpose.

149.2 Measure the absorbance of the phosphate solutions at approximately 725 nm in a 10-cm cell in the spectrophotometer. Adjust the spectrophotometer to read zero absorbance for the blank, and make the absorbance readings within 1 h at approximately 0.02 mm slit width.

149.3 Plot the absorbances of the phosphate solutions against milligrams P_2O_5 and from these data construct a calibration curve.

NOTE 30—The red-sensitive photocell must be used for all measurements. The spectral transmission curve for this complex has an absorbance peak between 720 and 730 nm, and may vary within these limits for different instruments. It is suggested that the calibration curve be run on the sample containing 0.024 mg P_2O_5 and that all subsequent absorbances be measured at the wavelength corresponding to the peak of this curve.

150. Procedure

150.1 Weigh 2 g of the sample to the nearest 0.001 g and transfer to a 250-mL volumetric flask. Dissolve in water, dilute to the mark, and mix. Pipet 25 mL of this solution into a 100-mL volumetric flask, dilute to the mark with water, and mix. Pipet 10 mL of this latter solution into a 100-mL volumetric flask, dilute to the mark with water, and mix.

150.2 Pipet a 15-mL aliquot of the most dilute solution into a test tube and proceed as directed in Section 138 at the similar point, carrying along a blank measuring the absorbance as described.

150.3 Determine the milligrams of P_2O_5 due to orthophosphate in the aliquot by referring the absorbance readings to the calibration curve.

NOTE 31—The developed curve is sensitive to such variables as pH, purity of reagents, volumes, and technique. Accurate results are assumed only by rigid adherence to the outlined details. Dilution of the sample solution is necessary if an absorbance value of 0.8 or higher is obtained. The size of the sample may be decreased until a suitable reading is obtained, but larger amounts are not permissible.

151. Calculation

151.1 Calculate the percentage of orthophosphate as follows:

$$\text{Orthophosphate as } Na_2HPO_4, \% = [(A \times 2 \times 100)/(B \times 1000)] \quad (57)$$

where:

A = milligrams of P_2O_5 corresponding to the absorbance of the aliquot of the sample solution, and

B = grams of sample in aliquot taken for color development.

152. Keywords

152.1 alkaline builder; borax; caustic soda; detergent; ignition loss; insoluble; particle size; phosphate; silicate; soda ash; turbidity