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Standard Test Methods of Sampling and Chemical Analysis of Alkaline Detergents¹

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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:

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Total Alkalinity as Sodium Oxide (Na_2O)	6 – 8	Tetrasodium Pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$)
Sodium Hydroxide (NaOH)	9 – 11	Matter Insoluble in Water 75 – 79
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Sodium Bicarbonate (NaHCO_3)	23 – 25	Sampling 90
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Sodium Metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$)	54	
Sodium Sesquisilicate ($3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$)	55	1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
Matter Insoluble in Water	56 and 57	
Loss on Ignition of Sodium Sesquisilicate ($3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$)	58 and 59	1.4 <i>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.</i> Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.
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Trisodium Phosphate Calculated as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, Na_3PO_4 , and as P_2O_5	65 – 68	
Total Alkalinity as Sodium Oxide (Na_2O)	69 – 71	

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. Referenced Documents

2.1 ASTM Standards:²

D459 Terminology Relating to Soaps and Other Detergents

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 (Na₂O)

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 (CO₂)-free water, wash into a 500-mL volumetric flask, and dilute to volume with CO₂-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 (Na₂O) 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 (Na₂O) as follows:

$$\text{Total alkalinity as Na}_2\text{O, \%} = (A \times 5 \times 3.1)/W \quad (1)$$

where:

A = millilitres of acid required for titration of the Na₂O 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 (BaCl₂·2H₂O) 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 BaCl₂ 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:

$$\text{Na}_2\text{CO}_3, \% = [(A - B) \times 5 \times 5.3]/W \quad (3)$$

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 twoway 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.

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.

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:

$$\text{Na}_2\text{CO}_3, \% = [(C \times 2.409)/W] \times 100 \quad (4)$$

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.

SODA ASH
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
 (Na₂CO₃)**
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 1 min to remove most of the CO₂. 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 (Na₂CO₃) 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 (NaHCO₃)
23. Reagents

23.1 *Silver Nitrate Solution* (100 g/L)—Dissolve 100 g of silver nitrate (AgNO₃) 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 AgNO₃ solution on a spot plate gives a dark color instantly.

25. Calculation

25.1 Calculate the percentage of sodium bicarbonate (NaHCO₃) as follows:

$$\text{NaHCO}_3, \% = \text{mL of 1.0 N NaOH solution} \quad (7)$$

Calculate the percentage of sodium carbonate (Na₂CO₃) as follows:

$$\text{Na}_2\text{CO}_3, \% = A - (\text{NaHCO}_3, \% \times 0.6309) \quad (8)$$

where:

A = total alkalinity as Na₂CO₃, 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 (NaHCO₃) BY
 POTENTIOMETRIC TITRATION**
26. Reagents

26.1 *Barium Chloride, Neutral Solution* (122 g/L)—Dissolve 122 g of barium chloride (BaCl₂·2H₂O) 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 BaCl₂ 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 CO₂ 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 (Na₂CO₃) 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 BaCO₃. 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 BaCO₃ 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 (NaHCO₃) as follows:

$$\text{NaHCO}_3, \% [(A - B)N \times 8.4]/W \quad (9)$$

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.

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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 (Na₂O)

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 (H₂SO₄).

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* H₂SO₄ 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 CO₂. 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 (Na₂O) as follows:

$$\text{Total alkalinity as Na}_2\text{O, percent} = A - (B/10) \quad (12)$$

where:

A = millilitres of H₂SO₄ required for titration of the sample, and
B = millilitres of NaOH solution required for titration of the excess H₂SO₄.

SODIUM BICARBONATE (NaHCO₃) AND SODIUM CARBONATE (Na₂CO₃)

$$\text{NaHCO}_3, \% = \text{mL of 1.0 N NaOH solution} \quad (13)$$

37. Reagents

37.1 *Silver Nitrate Solution* (100 g/L)—Dissolve 100 g of silver nitrate (AgNO₃) 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 AgNO₃ solution on a spot plate gives a dark color instantly.

39. Calculation

39.1 Calculate the percentage of sodium bicarbonate (NaHCO₃) as follows:

39.2 Calculate the percentage of sodium carbonate (Na₂CO₃) as follows:

$$\text{Na}_2\text{CO}_3, \% = [X - (Y \times 0.3690)]1.7097 \quad (14)$$

where:

X = percentage of sodium oxide (Na₂O) (Section 35), and

Y = percentage of NaHCO₃.

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 (NaHCO₃), SODIUM CARBONATE (Na₂CO₃), 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:



The loss in weight of the sample is determined, and the content of NaHCO₃ and free water are calculated from these values. The Na₂CO₃ content is estimated by difference, the result representing the sum of the Na₂CO₃ 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 Anhydron), 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 (H₂SO₄, 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 $+300^{\circ}\text{C}$, 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

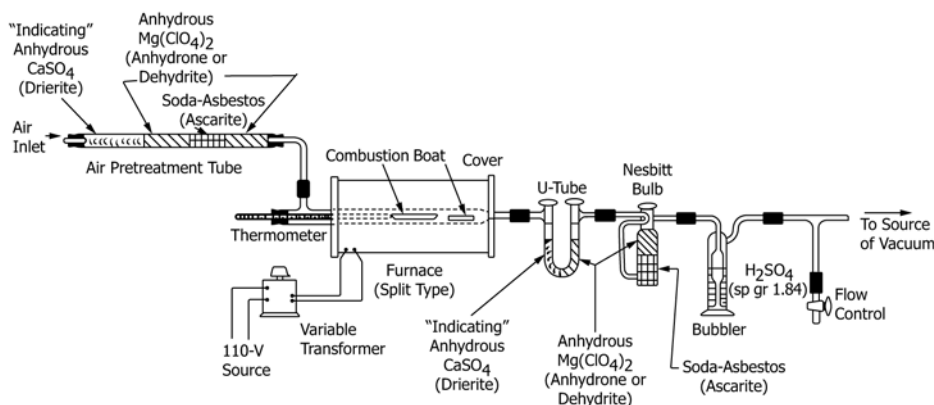


FIG. 1 Apparatus Assembly for Determination of Carbon Dioxide

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 $2\frac{1}{2}$ and 3 h.

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.

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 (Na₂O)

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 (Na₂O) as follows:

$$\text{Total alkalinity as Na}_2\text{O, \%} = (V \times N \times 3.1) / W \quad (17)$$

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 (SiO₂)

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 (H₂SO₄, 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 min, 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 H₂SO₄ (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 H₂SO₄. Heat the crucible, gently at first, over an open flame to drive off H₂SO₄, and finally at a bright red heat. Cool in a desiccator, and weigh. The loss in weight represents SiO₂.

53. Calculation

53.1 Calculate the percentage of silica (SiO₂) as follows:

$$\text{SiO}_2, \% = [(A - B) / W] \times 100 \quad (18)$$

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 ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$)

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:

$$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}, \% = \text{total SiO}_2, \% \times 3.53 \quad (19)$$

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

$$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}, \% = \text{total alkalinity as Na}_2\text{O}, \% \times 3.42 \quad (20)$$

SODIUM SESQUISILICATE ($3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$)

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:

$$3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}, \% = \text{total SiO}_2, \% \times 4.20 \quad (21)$$

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

$$3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}, \% = \text{total Na}_2\text{O}, \% \times 2.71 \quad (22)$$

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 ($3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$)

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, ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) 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 ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), 2.4 g of the monohydrate ($\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$), 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 ($\text{Mg}_2\text{P}_2\text{O}_7$).

64. Calculation

64.1 Calculate the percentage of trisodium phosphate as follows:

$$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \% = (\text{grams of Mg}_2\text{P}_2\text{O}_7 \times 3415.61) / W \quad (25)$$

$$\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}, \% = (\text{grams of Mg}_2\text{P}_2\text{O}_7 \times 1634.97) / W$$

$$\text{Na}_3\text{PO}_4, \% = (\text{grams of Mg}_2\text{P}_2\text{O}_7 \times 1473.09) / W$$

$$\text{P}_2\text{O}_5, \% = (\text{grams of Mg}_2\text{P}_2\text{O}_7 \times 637.72) / W$$

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

TRISODIUM PHOSPHATE CALCULATED AS $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, 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 ($\text{Na}_4\text{P}_2\text{O}_7$) may also be