



Standard Test Methods for Chemical Analysis of Soaps Containing Synthetic Detergents¹

This standard is issued under the fixed designation D 820; 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.

1. Scope

1.1 These test methods cover procedures for the chemical analysis of soaps containing synthetic detergents.

1.2 The analytical procedures appear in the following order:

	Sections
Moisture and Other Matter Volatile at 105°C (Oven Method)	5 and 6
Free Alkali or Free Acid	7 and 8
Anhydrous, Salt-Free, Soda Soap	9-12
Alcohol-Soluble Matter	13 and 14
Matter Insoluble in Water	15
Total Alkalinity of Matter Insoluble in Alcohol (Alkaline Salts)	16 and 17
Sodium Silicate	18-20
Phosphates	21-28
Phosphate (Colorimetric Method Using Molybdenum Blue)	29-34
Unsaponified and Unsaponifiable Matter	35-39
Free Fatty Matter	40
Chlorides in Alcohol-Soluble Matter	41-43
Rosin (McNicol Method)	44-47
Synthetic Detergent (by Difference)	48
Neutral, Inorganic Salts	49

1.3 *This standard does not purport to address all of the safety problems, 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.*

2. Referenced Documents

2.1 ASTM Standards:

- D 216 Method for Distillation of Natural Gasoline²
- D 459 Terminology Relating to Soaps and Other Detergents³
- D 875 Method for Calculation of Olefins and Aromatics in Petroleum Distillates from Bromine Number and Acid Absorption⁴
- D 1193 Specification for Reagent Water⁵
- D 1768 Test Method for Sodium Alkylbenzene Sulfonate in Synthetic Detergents by Ultraviolet Absorption³

¹ These test methods are under the jurisdiction of ASTM Committee D-12 on Soaps and Other Detergents and are the direct responsibility of Subcommittee D12.12 on Analysis of Soaps and Synthetic Detergents.

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² Discontinued, see 1987 Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vol 15.04.

⁴ Discontinued, see 1984 Annual Book of ASTM Standards, Vol 05.01.

⁵ Annual Book of ASTM Standards, Vol 11.01.

D 2357 Qualitative Classification of Surfactants by Infrared Absorption³

D 2358 Test Method for Separation of Active Ingredient from Surfactant and Syndet Compositions³

D 3049 Test Method for Synthetic Anionic Ingredient by Cationic Titration³

3. Terminology

3.1 Definitions:

3.2 The term *synthetic detergent* in these test methods is defined in accordance with Terminology D 459, as follows:

3.3 *synthetic detergent*—a detergent produced by chemical synthesis and comprising an organic composition other than soap.

3.4 For definitions of other terms used in these test methods, refer to Terminology D 459.

4. Purity of Reagents and Materials

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.⁶ 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 D 1193.

MOISTURE AND OTHER MATTER VOLATILE AT 105°C (OVEN METHOD)

5. Apparatus

5.1 *Dish*—A porcelain or glass dish about 6 to 8 cm in diameter and about 2 to 4 cm in depth will be required.

6. Procedure

6.1 Weigh 5 ± 0.01 g of the sample in the dish, and dry to

⁶ *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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

constant weight in an air oven at a temperature of $105 \pm 2^\circ\text{C}$. Constant weight is attained when heating for successive 1-h periods shows a loss (or gain) of not more than 0.1 %.

NOTE 1—Because of its established use in the trade, the term *weight* is employed in these methods in place of the technically correct term *mass*.

FREE ALKALI OR FREE ACID

7. Reagents

7.1 *Ethyl Alcohol, Neutral (95 %)*—Freshly boiled, reagent grade, ethyl alcohol, 95 % or higher, neutral to phenolphthalein, and containing only volatile denaturants, 95 mL,⁷ plus 5 mL of water.

7.2 *Phenolphthalein Indicator Solution (10 g/litre)*—Dissolve 1 g of phenolphthalein in 50 mL of neutral ethyl alcohol (95 %) and mix with 50 mL of water (see 7.1).

8. Procedure

8.1 Weigh 5 to 10 ± 0.01 g of the sample into a 300-mL Erlenmeyer flask. Add 200 mL of neutral ethyl alcohol (95 %). Equip the flask with an air-cooled reflux condenser, and digest the sample on a steam bath until the soap is dissolved (see Note 2). Remove the condenser, add 0.5 mL of the phenolphthalein indicator solution, and titrate immediately with standard acid or alkali. Calculate as NaOH, if alkaline, or as oleic acid, if acid.

NOTE 2—In the analysis of soaps known to contain little or no alkaline salts, it is unnecessary to filter the hot alcoholic soap solution. However, the filtration should be carried out in all cases where alkaline salts such as silicates, phosphates, borates, and similar salts are present, since these are known to affect the free alkali determination. Free alkali figures in soap or surfactant mixtures containing borax are unreliable, due to solubility of borax in hot alcohol.

ANHYDROUS, SALT-FREE, SODA SOAP

9. Apparatus

9.1 *Extraction Cylinder*, 250-mL, graduated, glass-stoppered, about 39 mm (1½ in.) in diameter and about 35.5 cm (14 in.) in length.

9.2 *Stokes Flask*, 100-mL, round-bottom (with the bottom blown out), sealed onto a 150-mL Erlenmeyer flask. A diagram of the Stokes flask is shown in Fig. 1.

9.3 *Siphon*, consisting of a two-hole rubber stopper fitted with small-diameter glass tubing as shown in Fig. 2.

10. Reagents

10.1 *Ethyl Alcohol, Neutral (95 %)*—Freshly boiled, reagent grade, ethyl alcohol, 95 % or higher, neutral to phenolphthalein, and containing only volatile denaturants, 95 mL,⁷ plus 5 mL of water.

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

10.3 *Petroleum Ether*—The solvent used shall be of the pentane type, containing a minimum amount of isopentane, isohexane, and hexane, and boiling in the range 35 to 60°C.⁸

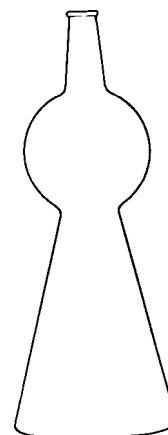


FIG. 1 Stokes Flask

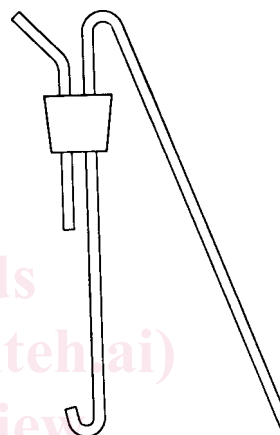


FIG. 2 Siphon

Distillation test: ^A	
Initial boiling point	35 to 38°C
Dry flask end point	52 to 60°C
Distilling under 54°C, min	95 %
Distilling under 40°C, max	60 %
Specific gravity at 15.5/15.5°C (60/60°F)	0.630 to 0.660
Color	water-white
Doctor test	sweet
Evaporation residue, 100 mL, max	0.0011 g
Copper-strip corrosion test ^B	noncorrosive
Unsaturated compounds ^C	trace only permitted
Residue in distilling flask	neutral to methyl orange
Blotter-strip odor test ^D	odorless within 12 min
Aromatic compounds ^E	no nitrobenzene odor
Saponification value	less than 1.0 mg KOH/100 mL

^A The distillation test shall be made in accordance with Method D 216.⁵ As a check on the evaporation residue, 250 mL of the petroleum ether and 0.25 g of stearin or other hard fat (previously brought to constant weight by heating) when dried as in the actual determination (10.4) shall not show an increase in weight exceeding 0.003 g.

^B The copper-strip corrosion test shall be made by inserting a small polished copper strip into the petroleum ether in the distilling flask. There should be no appreciable darkening of the copper.

^C Unsaturated compounds shall be determined by the method for determining olefins described in Method D 875.

^D Odor test: Immerse 1 in. of a strip of white unglazed blotting paper, approximately 1 by 4 by 0.166 in. in size, in the petroleum ether for 30 s, remove the strip, and allow to dry at room temperature in still air for 12 min.

^E Aromatic compounds: Add 5 drops of petroleum ether to 40 drops of sulfuric acid (H₂SO₄, sp gr 1.84) and 10 drops of nitric acid (HNO₃, sp gr 1.42) in a test tube, warm for 10 min, allow to cool for 30 min, transfer to a shallow dish, and dilute with water.

⁷ Fischer Scientific A962, or its equivalent, is suitable for this purpose.

⁸ J. T. Baker Analyzed Reagent 9268, or its equivalent, is suitable for this purpose.

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10.4 *Phenolphthalein Indicator Solution* (10 g/litre)—Dissolve 1 g of phenolphthalein in 50 mL of neutral ethyl alcohol (95 %) and then mix with 50 mL of water (see 10.1).

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

10.6 *Sodium Sulfate* (Na₂SO₄), anhydrous.

10.7 *Sulfuric Acid, Standard* (0.5 N)—Prepare and standardize a 0.5 N sulfuric acid (H₂SO₄) solution.

10.8 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H₂SO₄).

10.9 *Sulfur Acid* (1+1)—Gradually pour 10 g of concentrated sulfuric acid (H₂SO₄) (sp gr 1.84) onto 10 g of cracked ice made from distilled water, gently swirling the mixing vessel; or gradually pour the acid down the sides of the mixing vessel into an equal weight of water, swirling gently, while submersing the vessel in an ice bath.

11. Procedure

11.1 Weigh 2 ± 0.001 g of the sample into a tared 250-mL beaker. Add 25 mL of water and 25 mL of neutral ethyl alcohol (95 %), and warm on the steam bath until solution is complete. Cool, add 5 drops of methyl orange indicator solution, and titrate with 0.5 N H₂SO₄ to a pink color. Add 5 mL of H₂SO₄ (1+1) in excess.

11.2 Transfer the contents of the beaker to a 250-mL extraction cylinder or a Stokes flask, equipped with a siphon. Wash the beaker alternately with equal parts of hot water and hot ethyl alcohol (95 %), adding the washings to the extraction cylinder or Stokes flask. Keep the total volume for extraction under 160 mL in the extraction cylinder, or within the constricted portion of the Stokes flask. Wash the beaker with a small amount of petroleum ether to remove any traces of fatty acids and fatty matter and add to the extraction cylinder or Stokes flask. Cool the cylinder or flask under tap water to a temperature not to exceed 25°C. Add 50 mL of petroleum ether and allow to stand for 1 h without shaking. Remove the greater part of the fatty acids by drawing off the petroleum ether layer as closely as possible, by means of a glass siphon, into a 500-mL separatory funnel. Repeat the extractions five more times with petroleum ether, using 50-mL portions, and shaking the cylinder thoroughly each time.

NOTE 3—If an emulsion appears at this point, it may be broken by the addition of 10 g of anhydrous Na₂SO₄.

11.3 Combine the petroleum ether extracts and wash with small portions of distilled water until the water washings are no longer acid to methyl orange indicator solution. Dry the combined, washed, petroleum ether extracts with anhydrous Na₂SO₄, and filter through paper into the original tared 250-mL beaker. Wash the separatory funnel with two small portions of petroleum ether, filtering and adding the washings to the beaker.

11.4 Evaporate the petroleum ether extract on the steam bath until about 1 mL remains. Then swirl manually until the last trace of solvent evaporates and the odor of petroleum ether is no longer perceptible. Cool in a desiccator and weigh as total fatty matter, which is defined as fatty and rosin acids plus unsaponified and unsaponifiable fatty matter.

11.5 Dissolve the total fatty matter in 50 mL of neutral ethyl alcohol (95 % v) with warming. Add phenolphthalein indicator and titrate with 0.1 NaOH solution to a pink end point.

12. Calculations

12.1 Calculate the percentage of anhydrous, salt-free, soda soap as follows:

$$A = G - F \quad (1)$$

$$G = [(VN \times 0.022) + E]/W \times 100$$

where:

A = weight percent of anhydrous, salt-free, soda soap,

G = weight percent of soda soap plus unsaponified and unsaponifiable fatty matter,

F = weight percent of unsaponified and unsaponifiable fatty matter (Section 39),

V = millilitres of NaOH solution used in titration (11.5),

N = normality of NaOH solution,

E = grams of extract (11.4), and

W = grams of sample (11.1), and

0.022 = net gain in milliequivalent weight from the conversion of the fatty acid to the sodium salt by replacement of a proton with a sodium ion.

ALCOHOL-SOLUBLE MATTER

13. Reagents

13.1 *Ethyl Alcohol, Neutral* (95 %)—Freshly boiled, reagent grade, ethyl alcohol, 95 % or higher, neutral to phenolphthalein, and containing only volatile denaturants, 95 mL⁷ plus 5 mL of water.

13.2 *Ethyl Alcohol, Neutral* (absolute)—Freshly boiled absolute ethyl alcohol, neutral to phenolphthalein.⁷

14. Procedure

14.1 Weigh 2 ± 0.001 g of the sample into a 250-mL beaker. Add 100 mL of neutral ethyl alcohol (95 %), cover the beaker, and heat on the steam bath with frequent stirring and maceration of the sample until completely disintegrated. Let settle and filter the supernatant liquid through a tared Gooch crucible with a glass wool pad, with suction into a tared 300-mL Erlenmeyer flask, retaining as much of the residue as possible in the beaker. Repeat this extraction three times with 25-mL portions of hot neutral ethyl alcohol (95 %), each time retaining as much of the residue as possible in the beaker. Finally, evaporate any remaining alcohol and dissolve the residue in the smallest possible quantity of hot water (5 mL if sufficient). Reprecipitate the alcohol-insoluble matter by slowly adding, while stirring vigorously, 50 mL of neutral ethyl alcohol (absolute).

NOTE 4—Solution and reprecipitation of alcohol-insoluble matter is necessary for complete separation from alcohol-soluble matter.

14.2 Heat the solution to boiling on the steam bath, filter, and transfer the precipitate quantitatively to the Gooch crucible, washing several times with neutral ethyl alcohol (95 %). Evaporate the combined filtrate and washings in the Erlenmeyer flask on the steam bath, and then dry to constant weight at $105 \pm 2^\circ\text{C}$. Calculate total alcohol-soluble matter.

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14.3 Reserve the flask and contents for the determination of free fatty matter (Section 37). Reserve the Gooch crucible and contents, without drying, for the determination of matter insoluble in water (Section 15) and total alkalinity of matter insoluble in alcohol (alkaline salts) (Section 17).

MATTER INSOLUBLE IN WATER

15. Procedure

15.1 Wash the alcohol-insoluble matter retained in the Gooch crucible (Section 14) thoroughly with hot water until the washings are no longer alkaline to phenolphthalein. Reserve the filtrate for determination of total alkalinity of matter insoluble in alcohol (Section 17). Dry the crucible and residue to constant weight at $105 \pm 2^\circ\text{C}$ and calculate the percentage of matter insoluble in water.

TOTAL ALKALINITY OF MATTER INSOLUBLE IN ALCOHOL (ALKALINE SALTS)

16. Reagents

16.1 *Hydrochloric Acid*—Prepare and standardize a 1 N hydrochloric acid solution.

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

17. Procedure

17.1 Titrate the water solution obtained in the determination of matter insoluble in water (Section 15) with the standard 1 N hydrochloric acid solution of 16.1, using methyl orange as indicator.

17.2 Calculate the alkalinity as sodium carbonate (Na_2CO_3) as follows:

$$\text{Na}_2\text{CO}_3, \% \text{ weight} = 106 \text{ VN}/20 \text{ W} \quad (2)$$

where:

V = millilitres of standard acid used,

N = normality of standard acid, and

W = weight of sample (14.1), g

SODIUM SILICATE

18. Reagents

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

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

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

19. Procedure

19.1 When the material contains no mineral matter that is insoluble in water, ignite a portion of the sample containing not to exceed 0.2 g of silica (SiO_2) in a platinum dish (Note 5) at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish, and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with HCl, and finally add the equivalent of from 5 to 10 mL of HCl in excess. The dish or

casserole containing the solution should be covered with a watch glass while adding acid, so as to avoid loss by spray.

NOTE 5—When phosphates are present, a platinum dish should not be used.

19.2 When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol (Section 17) containing not more than 0.2 g of SiO_2 and add 5 to 10 mL of HCl.

19.3 Evaporate the acidified solution obtained in accordance with 19.1 or 19.2 (washing off and removing the cover glass if used) to dryness on a steam bath or hot plate at a temperature not exceeding 120°C . Cool, moisten with HCl and let stand 5 to 10 min, breaking up all lumps with a stirring rod. Add about 25 mL of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

19.4 Evaporate the filtrate to dryness and proceed as described in 19.3, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, then over a blast lamp. Cool in a desiccator, weigh, and repeat until constant weight is obtained.

19.5 If extreme accuracy is desired, moisten the weighed contents of the crucible with water, add 10 mL of HF and 4 drops of concentrated H_2SO_4 , and evaporate to dryness over a low flame. Ignite at the temperature of the blast lamp for about 2 min, cool in a desiccator, and weigh.

20. Calculation

20.1 Calculate the sodium silicate having the ratio 1 Na_2O :3.25 SiO_2 as follows:

$$\text{Sodium silicate, \% w} = (A - B) \times 1.308 \quad (3)$$

where:

A = grams of ignited residue before treatment with HF (19.4), and

B = grams of ignited residue after treatment with HF (19.5).

PHOSPHATES

21. Application

21.1 This test method is applicable to any species of alkali metal phosphates free of interfering ions. This test method can be used for the analysis of soap and synthetic detergent builders if the sample is properly prepared (see Section 26). This test method does not apply when the level of phosphate present is equivalent to or less than 2 % P_2O_5 .

22. Summary of Test Method

22.1 All of the phosphate present is converted, by acid hydrolysis, to the ortho form and titrated between pH 4.3 and 8.8 with NaOH solution.

23. Interferences

23.1 Heavy metals such as iron, aluminum, calcium, magnesium, etc., that will precipitate, either as insoluble phosphates or hydroxides, before the upper end point is reached,