



Designation: D3049 – 89 (Reapproved 2016)

Standard Test Method for Synthetic Anionic Ingredient by Cationic Titration¹

This standard is issued under the fixed designation D3049; 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 This test method covers the determination of the amount of synthetic anionic ingredient in a surfactant by direct titration with a standardized cationic reagent. The test method is a simple and convenient means for the quantitative estimation of the anionic material. The end point is detected by the transfer of a colored complex from an organic solvent phase to an aqueous phase. The colored complex is formed by the addition of a solution of dye to a solution of the anionic surfactant. This complex is soluble in the organic-solvent phase and insoluble in the aqueous phase. When this solution is titrated with a standardized solution of a cationic reagent, the dye is displaced from the colored complex and, being water-soluble, migrates to the aqueous phase. Therefore, a cationic titrating solution that has been standardized against a characterized anionic agent can be used to analyze for other anionics of known molecular mass.

1.2 This test method is applicable to alkylaryl sulfonates, alkyl sulfonates, alkyl sulfates and hydroxy-sulfates, alkylphenol- and fatty alcohol ethoxy-sulfates and dialkylsulfosuccinates. It applies to active materials containing one hydrophilic group per molecule.

1.3 The analytical procedures appear in the following order:

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

¹ This test method is under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and is the direct responsibility of Subcommittee D12.12 on Analysis and Specifications of Soaps, Synthetics, Detergents and their Components.

Current edition approved July 1, 2016. Published August 2016. Originally approved in 1972 as D3049– 72 T. Last previous edition approved in 2009 as D3049–89(2009). DOI: 10.1520/D3049-89R16.

responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. A precautionary statement appears in Section 7. Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 *ASTM Standards:*

D1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 An aqueous solution of an anionic-type detergent, to which is added a small amount of mixed indicator (dimidium bromide and disulphine blue), is shaken with aqueous Hyamine solution and chloroform. The pink complex which is formed by the reaction between the anionic detergent and the cationic dye, dimidium bromide, is extracted into the chloroform. Increments of additional Hyamine solution are added with a thorough mixing after each addition. At first the reaction takes place between the Hyamine and the excess anionic-type detergent, during which there is no noticeable change in the color (pink) of the chloroform phase. As the equivalence point between the anionic and cationic materials is approached, the dimidium bromide portion of the anionic detergent active-dimidium bromide complex (pink) is gradually released and transferred to the aqueous layer. As excess Hyamine is added it reacts with the anionic dye, disulphine blue, to form a chloroform-soluble blue complex. During the transition at the end point the chloroform layer, therefore, changes from pink to gray, to blue. The gray color is taken as the end point.

4. Significance and Use

4.1 This test method offers a means of determining anionic detergents commonly found in laundry, dishwashing, and other cleaning materials. Accurate determination of the anionic active substance is highly important in assessing the cost and effectiveness of such cleaning substances.

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.

4.2 This test method is not affected by low molecular weight sulfonates, such as those of toluene and xylene commonly found in detergent formulations, when these substances are present up to 15 weight % of active material.

5. Interferences

5.1 Normal inorganic components of detergent formulations, such as chloride, sulfate, borate, phosphates, perborate, and silicates do not interfere. Soaps, urea, and ethylenediaminetetraacetic acid salts do not interfere. Bleaching agents other than perborate should be destroyed prior to performing this analysis. Low molecular weight sulfonates, such as those of toluene and xylene, do not interfere when present up to 15 % (w) of active material. Since the titration is performed under acidic conditions (about pH 2.0), care should be exercised when using this procedure on products containing significant amounts of alkaline materials, such as carbonates and silicates, to ensure that the final solution is being titrated in the proper pH range.

6. Reagents

6.1 *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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**.

6.3 *Chloroform*.

6.4 *Ethanol*.

6.5 *Petroleum Ether*; boiling range 30 to 50°C.

6.6 *Phenolphthalein Indicator Solution (1 %)*—Dissolve 1 g of phenolphthalein in 95 % ethanol and dilute to 100 mL.

6.7 *Sodium Hydroxide, Standard Solution (0.1 N)*—Prepare a 0.1 N solution of sodium hydroxide (NaOH).

6.8 *Sodium Hydroxide, Standard Solution (1 N)*—Prepare a 1 N solution of NaOH.

6.9 *Sodium Hydroxide, Standard Solution (50 %)*—Prepare a 50 % solution of NaOH.

6.10 *Sodium Lauryl Sulfate, Standard Solution, (0.004 M)*.

6.10.1 Weigh accurately between 1.14 and 1.16 g of sodium lauryl sulfate and dissolve in 200 mL of water.

6.10.2 Transfer to a stoppered graduated 1-L flask and dilute to volume with water.

6.10.3 Calculate the molarity of the solution as follows:

$$\text{Molarity} = (W_2 \times P)/(288.4 \times 100) \quad (1)$$

where:

W_2 = sodium lauryl sulfate, g, and
 P = purity of the sodium lauryl sulfate, %.

6.11 *Sodium Sulfate* (Na₂SO₄), anhydrous.

6.12 *Sulfuric Acid, Standard (0.1 N)*—Prepare a 0.1 N solution of sulfuric acid (H₂SO₄).

6.13 *Sulfuric Acid, Standard (0.5 N)*—Prepare a 0.5 N solution of H₂SO₄.

6.14 *Sulfuric Acid, Standard (1 N)*—Prepare a 1 N solution of H₂SO₄.

7. Safety Precaution

7.1 This test method includes the use of small amounts of chloroform. Appropriate safety practices, such as those included in the Material Safety Data Sheets for chloroform, should be employed. Good ventilation is especially important.

8. Primary Standard

8.1 The primary standard used in this procedure is sodium lauryl sulfate.⁴ Three tests are made on this primary standard as follows:

8.2 *Purity*:

8.2.1 This test should be run in duplicate.

8.2.2 Weigh, to the nearest 0.1 mg, 10 ± 0.2 g of the primary standard into a 250-mL round-bottom flask.

8.2.3 Add exactly 25 mL of 0.5 N H₂SO₄. It is not necessary to standardize this acid.

8.2.4 Reflux under a water condenser for 2 h. Heat moderately in the beginning until the solution clarifies and the foaming ceases; then increase the heat input until a vigorous reflux is attained.

8.2.5 Remove the heat source, cool the flask, and then wash down the condenser with approximately 30 mL of ethanol followed by 50 mL of water. Add the washings to the reaction flask.

8.2.6 Disconnect the condenser and wash the point and the neck with water. Add these washings to the reaction flask.

8.2.7 Add a few drops of 1 % phenolphthalein indicator solution and titrate the H₂SO₄ with standardized 1 N NaOH solution.

8.2.8 Determine a blank value by titrating 25 mL of the 0.5 N H₂SO₄ with the standardized 1 N NaOH solution. This should be done in duplicate and the average used.

8.2.9 Calculate the percent purity of the primary standard as follows:

$$\text{Purity, \%} = [28.84 \times (A - B) \times N]/W \quad (2)$$

where:

A = NaOH solution used in sample titration, mL,
 B = NaOH solution used in blank titration, mL,
 N = normality of the NaOH solution, and

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.

⁴ Manufactured by British Drug House, Ltd. as Product No. 30176. It is sold as being more than 99 % pure. It is available in the United States from Gallard-Schlesinger Chemical Manufacturing Corp., Carle Place, Long Island, NY 11514.