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Standard Test Method for Synthetic Anionic Ingredient by Cationic Titration[1]

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 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 Water[2]

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.

[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.

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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.

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* (Na_2SO_4), anhydrous.

6.12 *Sulfuric Acid, Standard* (0.1 *N*)—Prepare a 0.1 *N* solution of sulfuric acid (H_2SO_4).

6.13 *Sulfuric Acid, Standard* (0.5 *N*)—Prepare a 0.5 *N* solution of H_2SO_4.

6.14 *Sulfuric Acid, Standard (1 N)*—Prepare a 1 *N* solution of H_2SO_4.

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* H_2SO_4. 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 H_2SO_4 with standardized 1 *N* NaOH solution.

8.2.8 Determine a blank value by titrating 25 mL of the 0.5 *N* H_2SO_4 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.

W = primary standard used, g.

8.2.10 For best precision and accuracy, temperature and buret corrections should be made when titrating the hydrolysate of the sodium lauryl sulfate with 1 *N* NaOH solution.

8.3 *Alcohols:*

8.3.1 The primary standard, sodium lauryl sulfate, is sold as having not more than 1 weight % (Note 1) of a sum of decyl and tetradecyl alcohol sulfates. The following test should be run in duplicate.

NOTE 1—The term "weight" is temporarily used in this standard because of established trade usage. The word is used to mean both "force" and "mass," and care must be taken to determine which is meant in each case (SI unit for force = newton and for mass = kilogram).

8.3.2 Mix approximately 5 g of sodium lauryl sulfate with 25 mL of 1 *N* H_2SO_4 in a 250-mL round-bottom flask.

8.3.3 Reflux under a water condenser for at least 2 h. Heat moderately at first until the solution clarifies and foaming ceases.

8.3.4 Cool the contents of the flask and transfer with water to a separatory funnel.

8.3.5 Extract this solution with 50 mL of petroleum ether (boiling range 30 to 50°C).

8.3.6 Extract four more times with 25-mL portions of petroleum ether.

8.3.7 Combine the petroleum ether fractions in a 250-mL beaker.

8.3.8 Allow the aqueous phase to settle out; then decant the petroleum ether phase through anhydrous Na_2SO_4 to remove water. Collect the effluent in another 250-mL beaker.

8.3.9 Evaporate the petroleum ether on a steam bath.

8.3.10 Determine the carbon number distribution of the alcohols present by gas liquid chromatography.[5]

8.4 *Free Acid Or Alkali:*

8.4.1 This test, when run on a newly received lot of the primary standard, gives an estimate of the acidity or alkalinity of the material. Subsequently, it can be used as a check on hydrolysis of the sodium lauryl sulfate during storage.

8.4.2 Weigh to two decimal places 1 g of the sodium lauryl sulfate.

8.4.3 Dissolve the sample in about 150 mL of ethanol that has been neutralized to phenolphthalein.

8.4.4 Add a few drops of phenolphthalein indicator solution and titrate with either 0.1 *N* H_2SO_4 or 0.1 *N* NaOH solution.

8.4.5 Record the millilitres of reagent solution necessary to return the solution to neutrality as well as the normality of the titrant.

[5] A method similar to that of Link, Hickman, and Morrissette, *Journal of the American Oil Chemists Society,* Vol 36, 1959, p. 20, is suggested.

9. Preparation of the Mixed Indicator Solution

9.1 *Disulphine Blue.*[6]

9.2 *Dimidium Bromide.*[7]

9.3 *Mixed Indicator Stock Solution*—Weigh 0.5 ± 0.005 g of dimidium bromide into a 50 mL-beaker. Weigh 0.25 ± 0.005 g of disulphine blue into a second 50-mL beaker. Add 25 to 30 mL of 1+10 (v/v) hot ethanol-water solution to each beaker. Stir each until the dye is dissolved; then add both solutions to a 250-mL volumetric flask. Rinse each beaker with the 1+10 ethanol-water solution and add the rinsings to the volumetric flask. Dilute the stock solution to the mark with deionized water. After 6 months, this solution should be discarded.

9.4 *Acid Indicator Solution*—Add 200 mL of water and 20 mL of the mixed indicator stock solution to a 500-mL volumetric flask having a stopper. Add 20 mL of 2.5 *M* H_2SO_4. Mix well and dilute to the mark with water. Store in a dark place.

10. Preparation of 0.004 M Hyamine 1622 Solution[8]

10.1 Weigh between 1.75 and 1.85 g of Hyamine 1622 and dissolve in water. Transfer to a glass-stoppered 1-L volumetric flask. Add 0.4 mL of 50 % NaOH solution (to keep buret clean) and dilute to the mark with water.

10.2 The molecular weight of Hyamine 1622, after removal of one molecule of water by drying, is 448 which corresponds to a weight of 1.792 g required for the preparation of 1 L of a 0.004 *M* solution. If desired, to provide an approximate check on the sodium lauryl sulfate standardization, the Hyamine 1622 may be dried in an oven at 105°C and the dried product accurately weighed for the preparation of the 0.004 *M* solution.

10.3 For the solution quantities larger than 1 L, multiply the amount of Hyamine and NaOH by the number of litres desired.

11. Standardization of Hyamine 1622 Solution

11.1 Pipet 20 mL of 0.004 *N* sodium lauryl sulfate solution into a stoppered 100-mL graduated mixing cylinder.

[6] This product is available as "Patent Blue VF Extra Concentrate" from General Aniline and Film Corp. It is also available as British Drug House's" Erioglaucine (Alphazuring 6 or Disulphine Blue V)" which can be obtained in the United States from Gallard-Schlesinger Chemical Manufacturing Corp. It is not recommended that Disulphine Blue from any other source be substituted for the above without a thorough evaluation of the product because investigation has shown that some of these products are sensitive to the presence of hydrotropes nor is it recommended that the Dimidium Bromide-Disulphine Blue indicator stock solution put out by British Drug House be used.

[7] This product is available as British Drug House's "Dimidium Bromide" which is available in the United States from Gallard-Schlesinger Chemical Manufacturing Corp.

[8] Hyamine 1622 can be obtained from Fluka Chemical Corp., Ronkonkoma, NY 11779, at about 98 % purity, and from Sigma Chemical Co., St. Louis, MO 63178 as benzethonium chloride at greater than 99 % purity with written certification available.

11.2 Add 10 mL of water, 15 mL of chloroform, and 10 mL of acid indicator solution. Precaution, see 7.1.

11.3 Add slightly less than an equivalent amount of the 0.004 *M* Hyamine 1622 solution (that is, about 20 mL); stopper and shake the vessel vigorously for 30 s. Then allow the vessel to stand until the emulsion breaks and two phases appear. The lower layer initially will be colored pink. Continue the titration, shaking vigorously after each addition of titrant for at least 15 s. As the end point is approached, emulsions formed during shaking tend to break easily. Continue the titration with dropwise addition of titrant and shaking between additions, until the end point is reached. Take the end point as the point at which the pink color is completely discharged from the chloroform layer, which later is then a faint grayish blue. With excess Hyamine the chloroform layer is blue. Note the volume of titrant added.

11.4 Calculate the normality of the Hyamine solution as follows:

$$\text{Normality} = (N \times 20)/V \quad (3)$$

where:

N = normality of the sodium lauryl sulfate solution, and
V = Hyamine solution, mL.

12. General Procedure for Anionic-Active Material

12.1 Weigh accurately a quantity of sample to contain approximately 4 meqs of anionic-active material.

12.2 Table 1 may be used as a guide for sample weight, dilution, and aliquot.

12.3 Dissolve the sample in deionized water. Add a few drops of phenolphthalein solution and neutralize to a faint pink color with 1 *N* NaOH solution or 1 *N* H_2SO_4 as required. In the case of liquid detergent samples, it will be found advantageous to first disperse the sample in approximately 5 mL of 3A or 30 alcohol before the addition of water. This will avoid any jelling effect.

12.4 Transfer quantitatively to a volumetric flask and dilute to volume with distilled water. When the solution is up in the neck of the flask, any foam on the surface can be eliminated by the addition of 1 to 2 mL of alcohol prior to the final dilution to the mark.

12.5 Remove a 20-mL aliquot to a 100-mL stoppered measuring cylinder, add 10 mL of water, 15 mL of chloroform, and 10 mL of the acid indicator solution.

12.6 Add slightly less than an equivalent amount of the 0.004 *M* Hyamine 1622 solution; stopper and shake the vessel vigorously for 30 s. Then allow the vessel to stand until the emulsion breaks and two phases appear. The lower layer initially will be colored pink. Continue the titration, shaking vigorously after each addition of titrant for at least 15 s. As the end point is approached, emulsions formed during shaking tend to break easily. Continue the titration with dropwise addition of titrant and shaking between additions, until the end point is reached. Take the end point as the point where the pink color is completely discharged from the chloroform layer, which later is then a faint grayish blue. With excess Hyamine the chloroform layer is blue. Note the volume of titrant added. Calculate the percent active anionic ingredient as follows:

$$\text{Active ingredient, weight \%} = (V \times N \times EW \times D \times 100)/(W_3 \times A \times 1000) \quad (4)$$

where:

V = Hyamine 1622 solution, mL,
N = normality of the Hyamine solution,
EW = gram-equivalent weight of anionic-active,
D = dilution of sample, mL,
A = aliquot of sample dilution, mL, and
W_3 = sample mass, g.

12.7 It should be noted at this point that the conditions used for viewing the end point on samples should be exactly the same viewing conditions as used for standardization of the Hyamine 1622 solution.

TABLE 1 Guide for Sample Weight, Dilution, and Aliquot[A]

Active ingredient in sample, %	Sample weight, g	Dilution	Aliquot
0.1	29	...	...
1	2.9	...	...
5	0.58	...	...
10	14.4	1000	20
15	9.6	1000	20
20	7.2	1000	20
30	4.8	1000	20
40	3.6	1000	20
50	2.9	1000	20
60	2.4	1000	20
70	2.1	1000	20
80	1.8	1000	20
90	1.6	1000	20
100	1.4	1000	20

[A] Values are based on an assumed molecular weight of 350 for the anionic material.

13. Report

13.1 Report the percentage of anionic active ingredient to the nearest 0.01 %. Duplicate runs which agree within 0.37 % absolute are acceptable for averaging (95 % confidence level).

14. Precision and Bias

14.1 The following criteria should be used for judging the acceptability of results:

14.1.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days, has been estimated to be 0.14 % absolute at 40 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.40 % absolute.

14.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.26 % absolute at 7 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.87 % absolute.

15. Keywords

15.1 anionic surfactants; cationic titrations; two-phase titrations