Designation: D5070 – 90 (Reapproved 2014)

Standard Test Method for Synthetic Quaternary Ammonium Salts in Fabric Softeners by Potentiometric Titrations[1]

This standard is issued under the fixed designation D5070; 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 describes a potentiometric titration procedure for the determination of quaternary ammonium salts in fabric softeners. This test method is intended for the analysis of known quaternary ammonium salts such as the dialkyl dimethyl quaternary ammonium compound type and the diamidoamine based quaternary ammonium compound type.

1.2 The quaternary ammonium salts conform to the structures shown in Fig. 1 and Fig. 2.

1.3 The analytical procedure appears in the following order:

1.4 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.* See 6.4, 6.6, 6.7 and Section 8 for specific warning statements.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D3049 Test Method for Synthetic Anionic Ingredient by Cationic Titration

3. Summary of Test Method

3.1 Quaternary ammonium compounds present in fabric softeners, as the active materials, are titrated potentiometrically in an aqueous medium with a standard solution of sodium lauryl sulfate using a nitrate ion-selective electrode. In this potentiometric titration, the reaction involves the formation of a complex between the quaternary ammonium compound and the anionic surfactant which then precipitates. At the end point, the nitrate ion electrode appears to respond to an excess of titrant with a potential change large enough to give a well defined inflection in the titration curve. Alternatively the quaternary ammonium compound can be first complexed with an excess of standard sodium lauryl sulfate; the excess sodium lauryl sulfate is titrated potentiometrically with standard Hyamine 1622.[3]

4. Significance and Use

4.1 This test method is used to determine the quaternary ammonium salts commonly found in fabric softeners. Quaternary ammonium compounds being the active ingredients in fabric softeners requires accurate determination to assess the cost and performance of such compounds.

5. Apparatus

5.1 *Autotitration System*—buret with 10 or 20 mL capacity;[4] magnetic stirrer;[5] evaluating ruler.[6]

5.2 *Electrodes*—(*1*) nitrate specific ion electrode;[7] (*2*) surfactant electrode;[8] (*3*) Ag/AgCl reference electrode.[9]

---

[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 Jan. 1, 2014. Published February 2014. Originally approved in 1990. Last previous edition approved in 2005 as D5070-90(2005). DOI: 10.1520/D5070-90R14.

[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.

[3] The sole source of supply of Hyamine 1622 known to the committee at this time is Gallard Schlesinger Manufacturing Corp., 584 Mineola Ave., Carle Place, NY 11514. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

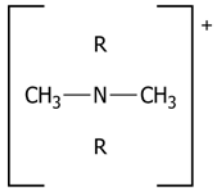
[4] Metrohm-Brinkman E-536, or equivalent, has been found satisfactory. Available from Brinkman Instruments Inc., Cantiague Rd., Westbury, NY 11590.

[5] Potentiograph/E-535 and Dosimat/E-459, or equivalent, have been found satisfactory. Available from Brinkman Instruments Inc., Cantiague Rd., Westbury, NY 11590.

[6] Evaluating Ruler EA-893, or equivalent, has been found satisfactory. Available from Brinkman Instruments Inc., Cantiague Rd., Westbury, NY 11590.

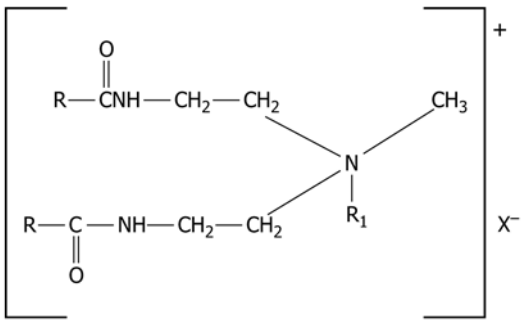
[7] Orion Model 93.07, or equivalent, has been found satisfactory. Available from Orion Research Inc., 529 Main St., Boston, MA 02129.

[8] Orion Model 93.42, or equivalent, has been found satisfactory. Available from Orion Research Inc., 529 Main St., Boston, MA 02129.



X^- = chloride or methyl sulfate
R = fatty alkyl groups saturated or unsaturated, normal or branched C_8 – C_{22}

FIG. 1 Dialkyl Dimethyl Quaternaries



X^- = usually methyl sulfate
R = fatty alkyl groups, saturated or unsaturated, normal or branched C_{12} – C_{18}
R_1 = 2-hydroxyethyl,
2-hydroxypropyl

FIG. 2 Diamidoamine Based Quaternaries

5.3 *Adaptors*—(*1*) coaxial adaptor, required for indicator electrode,[10] (*2*) banana plug adaptor, required for reference electrode.

NOTE 1—To ensure electrical continuity (after assembly) shake down electrode in the manner of a clinical thermometer. Also, the conditioning of the electrode is essential for obtaining a good break in the titration curve. Conditioning new electrodes in 0.01 M KNO_3, aqueous solution for 60 min (or more) prior to use is recommended.

NOTE 2—Other electrodes (for example, a calomel electrode) are suitable as the reference electrode provided they give a stable reference potential during the titration. Reference electrodes having a ceramic or an asbestos junction tend to clog with use. Therefore, a ground-glass sleeve electrode (such as the Metrohm EA 440 or equivalent)[11] is suggested.

6. Reagents

6.1 *Hyamine 1622,*[3]diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride monohydrate.

6.2 *Sodium Lauryl Sulfate,*[12]primary standard (Note 3).

NOTE 3—Sodium lauryl sulfate must be analyzed for purity according to the Reagent section of Test Method D3049, before its use as a primary standard.

6.3 *Water,* type III reagent water conforming to Specification D1193.

6.4 *Isopropanol,* reagent grade. (**Warning**—Highly flammable.)

6.5 *Sodium Borate Decahydrate*—($Na_2B_4O_7$ $10H_2O$), reagent grade.

6.6 *Boric Acid* (H_3 BO_3), reagent grade. (**Warning**—Causes irritation.)

6.7 *Sulfuric Acid* (H_2 SO_4), reagent grade. (**Warning**—Causes severe burns on contact with skin. See Section 8.)

6.8 *Five percent (V/V) Sulfuric Acid Solution*—Using a graduated cylinder, transfer 80 mL of deionized water to a 100-mL volumetric flask. Slowly, carefully, and with stirring, add 5 mL of concentrated sulfuric acid. Cool to room temperature and dilute to the mark with water.

6.9 *Borate Buffer Solution pH 6.00*—In a 500 mL beaker, dissolve 5.0 g ± 0.02 g of sodium borate decahydrate and 7.0 g ± 0.02 g of boric acid in approximately 300 mL water, with stirring; adjust pH to 6.00 with 5 % sulfuric acid solution. Transfer to a 500-mL volumetric flask, mix, and dilute to volume with water.

7. Preparation of Standard Reagents

7.1 *Sodium Lauryl Sulfate Solution*, 4×10^{-3} N—Weigh accurately 1.15 ± 0.01 g of sodium lauryl sulfate to 0.1 mg; dissolve in water and dilute to a final volume of 1 L. Calculate the normality of the solution with the following equation:

$$\text{Normality of sodium lauryl sulfate} = \frac{W \times P}{(288.38)\,(100)} \qquad (1)$$

where:

P = purity of the sodium lauryl sulfate, weight %
W = weight of sodium lauryl sulfate, g

7.2 Keep the solution no longer than 1 month before making a fresh solution.

7.3 *Hyamine 1622 Solution*, 4×10^{-3} N—Dissolve 1.85 ± 0.5 g of Hyamine 1622 in deionized water. Transfer to a 1 L volumetric flask, and dilute to volume with water.

8. Hazards

8.1 All reagents and chemicals should be handled with care. Before using any chemical, read and follow all safety precautions and instructions on the manufacturer's label or MSDS (Material Safety Data Sheet).

9. Standardization of Hyamine 1622 Solution

9.1 This determination must be done in triplicate. Pipet 5.00 mL of the standard lauryl sulfate into a 150 mL beaker. Add approximately 100 mL of deionized water and while stirring add by pipet 2 mL of the borate buffer.

9.2 The electrode should be cleaned between each titration. A satisfactory procedure is to first rinse it with water, then with alcohol (ethyl alcohol) (Note 5) and again with water followed by wiping the surface with a soft tissue.

NOTE 4—The electrode can be quickly washed with ethyl alcohol when followed immediately by a water rinse. Prolonged contact of the electrode with alcohol or other organic solvent can cause failure of the electrode membrane.

[9] Metrohm Model EA-440, or equivalent, has been found satisfactory. Available from Brinkman Instruments Inc., Cantiague Rd., Westbury, NY 11590.

[10] The Metrohm coaxial adaptor, or equivalent, has been found satisfactory for this purpose. Available from Brinkman Instruments Inc., Cantiague Rd., Westbury, NY 11590.

[11] Available from Brinkman Instruments Inc., Cantiague Rd., Westbury, NY 11590.

[12] Available from British Drug House, LTD, or in the U.S. from Gallard Schlesinger Manufacturing Corp., 584 Mineola Ave., Carle Place, NY 11514.

9.3 Titrate potentiometrically with Hyamine 1622 and record the titration volume at the endpoint. The endpoint is marked by the point of inflection on the "S" shaped curve and it is determined by the use of the evaluating ruler.

$$\text{Normality of Hyamine 1622} = \frac{N \times 5.0}{V} \quad (2)$$

where:

N = normality of sodium lauryl sulfate standard solution
5.0 = sodium lauryl sulfate aliquot taken for titration, mL
V = Hyamine 1622 solution consumed during, titration, mL

10. Procedure for Determination of Dialkyl Dimethyl Quaternary

10.1 Weigh accurately a quantity of sample to the nearest 0.1 mg of quaternary ammonium compound active material into a 250 ml beaker.

10.2 Table 1 may be used as a guide for sample weight, dilution, and aliquot. Dilution of sample must be done in isopropanol using volumetric flask and pipetes as indicated in Table 1.

10.3 Add 5 mL of isopropanol. Swirl the beaker until the sample is completely dissolved. Add approximately 150 mL of deionized water and stir. While stirring, add, by pipet, 4 mL of the borate buffer solution.

10.4 Pipet 10 mL of standard solution lauryl sulfate solution while stirring. Transfer the solution to the autotitrator. Titrate potentiometrically with standard Hyamine 1622 solution. As the inflection point is approached, reduce the addition rate, and continue titrating well past the inflection in the titration curve. (Automatic titrators can be preset to automatically slow down the addition rate as the inflection point is approached.) Record the titration volume at the endpoint. The endpoint is marked by the point of inflection on the "S" shaped curve and it is determined by the use of the evaluating ruler. Typical titration curve of the dialkyl dimethyl ammonium salt is shown in Fig. 3.

10.5 Calculate the percent dialkyl dimethyl quaternary ingredient as follows:

TABLE 1 Guide for Sample Weight, Dilution, and Aliquot to be Used

Active Ingredients[A] Sample, %	Sample Weight, g	Dilution, mL (in Isopropanol)	Aliquot, mL
2.5	0.56		
5	0.28		
10	0.15		
20	4.10	200	2
30	2.8	200	2
40	2.1	200	2
50	1.8	200	1
60	2.8	200	1
70	2.4	200	1
80	2.1	200	1
90	1.8	200	1

[A] Values are based on an assumed molecular weight of 649 for the dialkyl dimethyl quaternary.

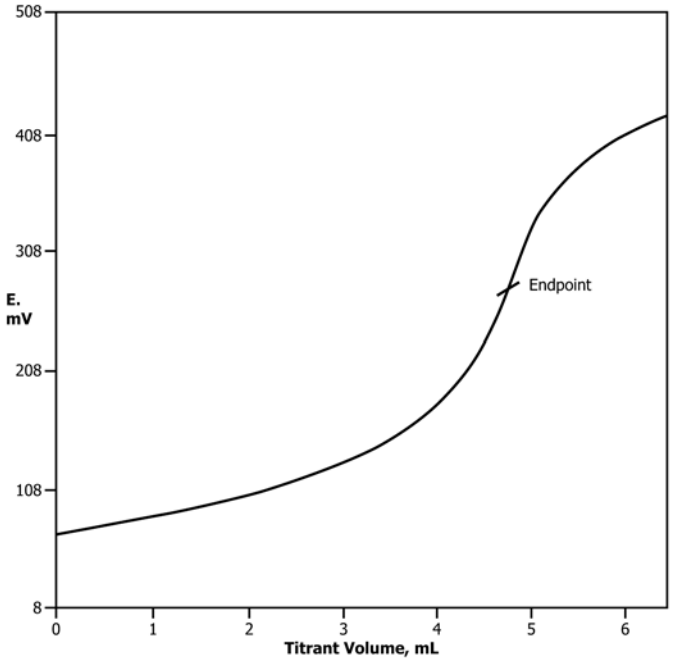


FIG. 3 Sample: Dihydrogenated-Tallow Dimethyl Ammonium Sulfate, Titrant: 0.00405N Hyamine (back titration of sodium lauryl sulfate)[A]

[A] Using nitrate ion-selective electrode

$$\text{Dialkyl dimethyl quaternary, weight \%} = \frac{[(A \times N_1) - (B \times N_2)] \times M \times D \times 100}{S \times 1000 \times A} \quad (3)$$

where:

A = standard sodium lauryl sulfate, mL
N_1 = normality of standard sodium lauryl sulfate
B = standard Hyamine 1622 consumed during titration, mL
N_2 = normality of standard Hyamine 1622 solution
M = average equivalent weight of the dialkyl dimethyl quaternary
D = dilution of sample, mL
S = weight of sample in grams
A = aliquot of sample dilution, mL

11. Procedure for Determination of Diamidoamine Based Quaternary

11.1 Weigh accurately a quantity of sample to contain approximately 0.16 meq of quaternary ammonium compound active material into a 250 mL beaker (Note 5). Add 5 mL of isopropanol. Swirl the beaker until sample is completely dissolved. Add approximately 150 mL of water and stir. While stirring, pipet in 2 mL of the borate buffer solution. Titrate potentiometrically with standard sodium lauryl sulfate solution. As the inflection point is approached, reduce the addition rate, and continue titrating well past the inflection in the titration curve. (Automatic titrators can be preset to automatically slow down the addition rate as the inflection point is approached.)

NOTE 5—To determine the amount of sample needed for an approximately 13.7 mL titration (0.05 meq) use the following equation:

$$W = \frac{0.005 \times M}{D} \quad (4)$$

where:

W = weight of sample to be taken for analysis, g
M = average equivalent weight of the quaternary ammonium salt present
D = approximate concentration of the quaternary ammonium salt expected, weight %

11.2 To obtain accurate weights of sample, it is convenient to make up an aqueous solution (for example 250 mL) and take an aliquot corresponding to a known meq of active matter.

11.3 Record the titration volume at the end point. The endpoint is marked by the point of inflection on "S" shaped curve and it is determined by the use of an evaluating ruler. Typical titration curve of diamidoamine based quaternary is shown in Fig. 4.

12. Calculation

12.1 Calculate the percent diamidoamine based quaternary of the sample as follows:

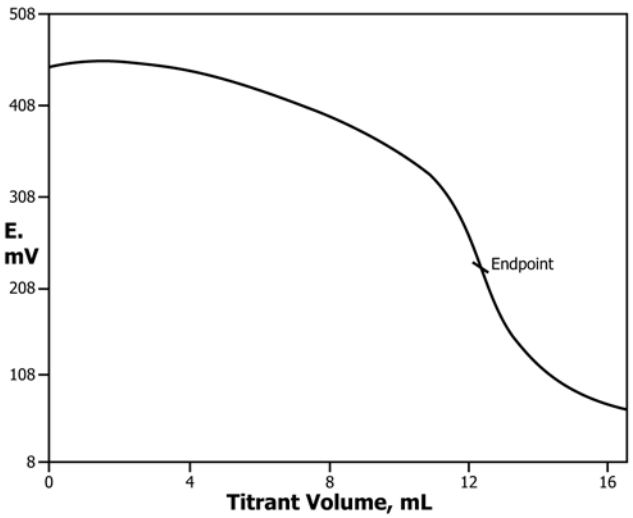


FIG. 4 Sample: Methyl Bis(tallowamidoethyl 2-hydroxyl propyl ammonium methyl sulfate) Titrant: 0.00409N Sodium Lauryl Sulfate [A]

[A] Using nitrate ion-selective electrode

$$\text{Diamidoamine quaternary, weight \%} = \frac{A \times N \times M \times D \times 100}{S \times 1000 \times A} \quad (5)$$

where:

A = tandard sodium lauryl sulfate solution, mL consumed during titrations
N = normality of standard sodium lauryl sulfate solution
M = average equivalent weight of the diamidoamine quaternary
D = dilution of samples, mL
S = weight of sample, g
A = aliquot of sample dilution, mL

13. Precision

13.1 The following criteria should be used to judge the acceptability of the results (Note 6).

13.2 *Repeatability (single analyst)*—The coefficient of variation of results (each the average of triplicate determinations), obtained by the same analyst on different days, was estimated to be 1.24 % relative at 20 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 3.66 % relative.

13.3 *Reproducibility (multilaboratory)*—The coefficient of variation of results (each the average of duplicate determinations) obtained by analysts in different laboratories, has been estimated to be 2.38 % relative at 9 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 7.62 % relative.

13.4 Report the percentage of the component relative to the nearest 0.1 %. Triplicate runs which agree within 4.4 % of the amount present are acceptable for averaging (95 % confidence level).

NOTE 6—The precision data were derived from results of the cooperative tests by eight laboratories on the following quaternary ammonium compounds. (Equivalent weights in parentheses, are based on commercial quaternary ammonium compounds): Dihydrogenated-tallow dimethyl ammonium methyl sulfate (649), Methyl bis (tallowamidoethyl) 2-hydroxypropyl ammonium methyl sulfate (927). Round-robin data is available from ASTM Headquarters. Request RR: D-12-1011.