



Designation: D 4251 – 89 (Reapproved 1995)^{ε1}

Standard Test Method for Active Matter in Anionic Surfactants by Potentiometric Titration¹

This standard is issued under the fixed designation D 4251; 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.

^{ε1} NOTE—Keywords were added editorially in February 1995.

1. Scope

1.1 This test method describes a potentiometric titration procedure for determining the anionic active matter in detergents. It is intended for the analysis of anionic surfactants such as detergent range alkylbenzenesulfonates, α -olefin sulfonates, alcohol sulfates, and alcohol ethoxulfates. It has not been tested for surfactant formulations.

1.2 *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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 ASTM Standards:

- D 459 Terminology Relating to Soaps and Other Detergents²
- D 1193 Specification for Reagent Water³
- D 1681 Test Method for Synthetic Anionic Active Ingredient in Detergents by Cationic Titration Procedure²
- D 3049 Test Method for Synthetic Anionic Ingredient by Cationic Titration²
- E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *active matter*—the organic surface-active material present in the detergent and defined in Terminology D 459 as active ingredient of a synthetic detergent.

4. Summary of Test Method

4.1 A detergent sample containing active matter is titrated

¹ This test method is under the jurisdiction of ASTM Committee D-12 on Soaps and Other Detergents and is the direct responsibility of Subcommittee D12.12 on Analysis of Soaps and Synthetic Detergents.

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² *Annual Book of ASTM Standards*, Vol 15.04.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

TABLE 1 Active Matter Content of Various Anionic Surfactants by the Potentiometric Titration and Two-Phase Titration Methods

Anionic Surfactant	Active Matter Content, % weight			
	Potentiometric Titration			Two-Phase Titration
	Orion NO ₃ ⁻ (#1)	Orion NO ₃ ⁻ (#2)	"Old" HNU NO ₃ ⁻	
Sulframin AOS (alpha-olefin sulfonate)	41.03	41.49	40.91	39.21 ^A
	42.50	40.74	41.05	39.26
	42.64	41.34	41.05	
Sulframin 1298 (alkylaryl sulfonate)	94.15	96.26	94.91	95.12 ^B
	95.31	95.67	95.50	95.12
	94.73	96.26	94.91	
NEODOL® 25-3S (alcohol ethoxysulfate sodium salt)	58.12	57.94	57.75	58.19 ^B
	58.81	57.74	57.95	58.24
	58.12	57.94	57.95	

^A Methylene blue method.

^B Mixed indicator method.

potentiometrically in an aqueous medium with a standard solution of Hyamine 1622 using a nitrate ion-selective electrode. The titration reaction involves the formation of a complex between the cationic quaternary ammonium titrant (Hyamine 1622) and the anionic surfactant which precipitates. The nitrate electrode probably responds to the concentration of unreacted anionic surfactant.

5. Significance and Use

5.1 Anionic surfactants are the most widely used of the synthetic detergents. ASTM methods in current use for their determination involve two-phase aqueous/chloroform titrations with the organic dyes methylene blue (Test Method D 1681) or disulphine blue/dimidium bromide (Test Method D 3049) as indicators. One advantage of the potentiometric method is that it eliminates the use of chloroform whose use is restricted for environmental and toxicological reasons.

5.2 This test method is intended for use as described in 1.1.

6. Apparatus

6.1 *Potentiometric Titration Assembly*, consisting of an automatic titrator (Metrohm E536 or equivalent) fitted with a nitrate ion-selective electrode (Orion Model 93-07 Nitrate ISE, or equivalent) and a Ag/AgCl reference electrode (Metrohm EA 440 or equivalent) together with a buret assembly having a 5-mL buret (Metrohm E575) and 150-mL beaker. A TFE-fluorocarbon star-head stirring bar can be used to provide mixing and eliminate foaming during titration. Use of the

Orion electrode with a Metrohm E536 requires an adapter (Metrohm EA-1046/2).

NOTE 1—The conditioning of the electrode is essential for obtaining a good break in the titration curve. Conditioning new electrodes in 0.01 M NaNO₃ aqueous solution for 60 min (or more) prior to use is recommended. Condition previously used electrodes by using again for the titration of aqueous sodium lauryl sulfate with Hyamine.

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) is suggested.

7. Reagents

7.1 *Hyamine 1622*,⁵ diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride.

7.2 *Sodium Lauryl Sulfate*,⁶ primary standard (Note 3).

NOTE 3—Sodium lauryl sulfate must be analyzed for purity according to the Reagent section of Test Method D 3049, before using as a primary standard.

7.3 *Water*, type III reagent water conforming to Specification D 1193.

8. Preparation of Standard Reagents

8.1 *Sodium Lauryl Sulfate Solution*, $4 \times 10^{-2}N$ —Weigh accurately 11.5 ± 0.5 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:

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

where:

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

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

8.2 *Hyamine 1622 Solution*, $4 \times 10^{-2}N$ —Dissolve 18 ± 0.5 g of Hyamine 1622 in deionized water. Transfer to a 1-L volumetric flask. Add 0.4 mL of 50 % NaOH and dilute to volume with water. Standardize following the same procedure described for the sample titration using 5 mL of the sodium lauryl sulfate solution. Calculate the normality of the Hyamine solution as follows:

$$\text{Normality of Hyamine 1622} = \frac{(A)(B)}{(C)} \quad (2)$$

where:

A = sodium lauryl sulfate solution used, mL,
 B = normality of sodium lauryl sulfate, and
 C = Hyamine solution consumed during titration, mL.

9. Procedure

9.1 Add to a 150-mL beaker a known weight of detergent sample together with enough water to make 50 mL of solution

(Note 4). The solution should cover the sensing tips of the electrodes. Titrate initially by adding Hyamine solution at approximately 0.5 mL/min while stirring constantly. 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 4—To determine the amount of sample needed for an approximate 3.75-mL titration (0.15 meq) use the following equation:

$$W = \frac{(0.015)M}{(D)} \quad (3)$$

where:

W = weight of sample to be taken for analysis, g,
 M = average equivalent weight of the anionic active matter present, and
 D = approximate concentration of anionic active matter expected, weight %.

9.1.1 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 0.15 meq of active matter.

9.1.2 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 Kimwipe.

NOTE 5—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.

9.2 Graphically select the inflection point of the curve on the recorder chart. Typical titration curves of several anionic surfactants are shown in Fig. 1.

10. Calculation

10.1 Calculate the anionic active matter content of the sample as follows:

$$\text{Anionic Active Matter, \% w} = \frac{(V)(N)(M)}{(10)(W)} \quad (4)$$

where:

V = Hyamine 1622 solution consumed in titration, mL,
 N = normality of Hyamine,
 W = weight of sample g, and
 M = average equivalent weight of the anionic active matter present.

10.2 Calculate the milliequivalents of active matter per 100 g sample as follows:

$$\text{meq Active Matter/100 g} = \frac{(V)(N)(100)}{(W)} \quad (5)$$

where V , N , and W are as listed previously.

11. Precision

11.1 The following criteria should be used to judge the acceptability of the results (Note 6):^{7,8}

⁵ Available from Gallard Schlesinger Chemical Manufacturing Corp., 584 Mineola Ave., Carle Place, NY 11514.

⁶ Available from British Drug House, LTD, or in the U.S. from Gallard Schlesinger Chemical Mfg. Corp., 584 Mineola Ave., Carle Place, NY 11514.

⁷ Data supporting the precision statements are on file at ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428, Research Report No. D12-1003.

⁸ The statistical analysis was performed in accordance with Practice E 180 for developing precision estimates.