



Designation: D 1681 – 92 (Reapproved 1997)

Standard Test Method for Synthetic Anionic Active Ingredient in Detergents by Cationic Titration Procedure¹

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1. Scope

1.1 Direct titration of an anionic surfactant with a standardized cationic reagent is a simple and convenient method for the quantitative determination of the content of active ingredient. The end point is detected by the transfer of a colored complex from an organic solvent phase to an aqueous phase. The relationship between anionic and cationic agents is not always stoichiometric, and for maximum accuracy the anionic type of interest should first be characterized and then used to standardize the cationic reagent. In most cases, however, the different anionic surfactants likely to be encountered react in the same proportions. That is, a cationic titrating solution standardized against a characterized anionic agent can be used to analyze other anionics of known molecular weights.

1.2 This test method is applicable to alkylaryl sulfonates and fatty alkyl sulfates. Low results are obtained with alkylbenzene sulfonates having the alkyl chain length less than eight carbon atoms. Low results are also obtained for alkyl sulfates with the alkyl chain length of less than twelve carbon atoms. The anionic surfactants characterized in accordance with Sections 16-22 should be the sodium salt and not amine, ammonium, or potassium salts. In case only amine or ammonium salts are available, they should be first converted to the sodium salt before proceeding with this analysis.

1.3 The analytical procedures appear in the following order:

	Sections
Separation of Alcohol-Soluble Matter	7 and 8
Separation of Oil-Free Sulfonate	9 and 10
Determination of Sodium Chloride (NaCl) Content	11-16
Characterization of Anionic Surfactant Standard:	
Part I. Determination of Surfactant, SO ₃ Content, and Solution Molarity	17-19
Part II. Determination of Surfactant, SO ₃ and Active Ingredient Contents Combining Weight, and Solution Molarity	20-23
Standardization of Cationic Reagent	24-28
Quantitative Determination of Anionic Surfactant by Cationic Titration	29-32

1.4 *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 D-12 on Soaps and Other Detergents and is the direct responsibility of Subcommittee D12.12 on the Analysis of Soaps and Synthetic Detergents.

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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 1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 This test method involves isolating alkylaryl sulfonate or fatty alkyl sulfate by extraction with ethyl alcohol to remove inorganic salts, extracting the alcohol-soluble material with petroleum ether to remove unsulfonatable matter, correcting for sodium chloride present, and determining the active ingredient combining weight. The characterized surfactant is used to standardize a cationic reagent which in turn is used to titrate similar anionic surfactants.

4. Significance and Use

4.1 This test method determines 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.

5. Interferences

5.1 With the exception of picrate, perchlorate, thiocyanate, nitrate, dichromate, and chromate, common inorganic anions and low molecular weight organic anions do not interfere with this analysis. However, sulfonates of xylene, cumene, or toluene interfere positively. Since the cationic titration is conducted under acidic conditions, soap does not interfere. Soap must not be present in the anionic surfactant characterized in accordance with Sections 16-22.

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,

² *Annual Book of ASTM Standards*, Vol 11.01.

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 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.³

SEPARATION OF ALCOHOL-SOLUBLE MATTER

7. Solvent

7.1 *Ethyl Alcohol*—Freshly boiled ethyl alcohol conforming to Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue. The alcohol should not be neutralized. Redistilled alcohol must be used if alkali absorption is more than 0.2 mL of 100 mL of 0.1 N NaOH solution.

8. Procedure

8.1 Weigh out a sample, to the nearest 0.01 g, to correspond to surfactants with the following ranges of active ingredient contents and transfer to a 600-mL beaker:

Active Ingredient, wt %	Weight of Sample, g
10 to 25	30
25 to 40	15
40 to 60	10
60 to 80	7
Over 80	5.5

8.2 Add 300 to 350 mL of hot alcohol. Cover with a watch glass and heat on the steam bath for at least 2 h, stirring frequently to disperse solids and break up lumps. Have a prepared Gooch crucible or sintered glass filter inserted in the 1000-mL vacuum flask.

8.3 At the end of 2 h, remove the beaker from the bath and decant the alcohol solution rapidly through the filter, retaining as much as possible of the residue in the beaker. Add 50 mL of hot alcohol to the residue in the beaker. Heat to boiling on a hot plate, breaking up any lumps of the residue. Decant the alcohol through the filter as before. Repeat with another 50-mL portion of hot alcohol.

8.4 Evaporate the residual alcohol from the residue in the beaker on the steam bath, stirring at intervals, especially near the end. Dissolve the residue in the beaker with 10 mL of hot water, heating on the steam bath until solution is effected.

8.5 Dilute the water solution with 200 mL of hot alcohol, bring to a boil on the steam bath, and filter. Transfer the precipitate onto the filter with the aid of hot alcohol and policeman. Wash the beaker and the residue with hot alcohol three or four times. For samples being prepared for Part I of the characterization of anionic surfactant (Sections 17-19), continue as directed in 8.6. For samples being prepared for eventual use in Part II of the characterization of anionic

surfactant (Sections 20-23), continue in accordance with the separation of oil-free sulfonate (Sections 9 and 10).

8.6 Transfer the filtrate to a 1000-mL beaker. Wash the filter flask with alcohol and 10 mL of water followed by an alcohol wash. Evaporate the filtrate to about 400 mL and transfer to a 1000-mL volumetric flask. Dilute with water to mark. Designate as Solution I and reserve for use in Part I of the characterization of the anionic surfactant (Sections 17-19).

SEPARATION OF OIL-FREE SULFONATE

9. Reagents

9.1 *Ethyl Alcohol*—See Section 7.

9.2 *Petroleum Ether*, having a boiling point of 30 to 60°C.

10. Procedure

10.1 Transfer the alcohol solution quantitatively to a 1000-mL beaker (with the 100-mL volume marked on the side) and concentrate to 100 mL on a steam bath or hot water bath. Transfer the concentrate quantitatively to a 500-mL, pear-shaped separatory funnel by rinsing the beaker with 100 mL of water in several portions. Add the remainder of water to the funnel to bring the total volume to 200 mL.

10.2 Extract the aqueous-alcoholic solution with three 50-mL portions of petroleum ether, using additional separatory funnels. Combine the ether extracts and wash with 3 to 50-mL portions of 50% aqueous ethanol. Add the aqueous ethanol washings to the extracted aqueous alcohol solution. Discard the petroleum ether extracts. Transfer the oil-free aqueous alcoholic solution quantitatively to a 1000-mL beaker by rinsing the separatory funnel with small portions of water. Heat the solution in a 400-mL beaker in a water bath at 40 to 50°C in a hood to vent off petroleum ether fumes. When free of ether, transfer the oil-free salt-free solution quantitatively to a 1000-mL volumetric flask. Add 300 mL of alcohol and dilute to volume with water. Designate as Solution II and reserve for use in Part II of the characterization of the anionic surfactant (Sections 20-23).

DETERMINATION OF SODIUM CHLORIDE (NaCl) CONTENT

11. Scope

11.1 Sections 12-16 cover the determination of the sodium chloride content of the surfactant in order that appropriate corrections can be made in the values obtained in the characterization of the anionic active ingredients and the quantitative determination of an unknown anionic active ingredient.

12. Apparatus

12.1 *Stirrer Motor and Small Glass Rod Stirrer*.

12.2 *Potentiometer*.⁴

12.3 *Calomel Reference Electrode*, saturated.

12.4 *Silver Wire Electrode*, 1mm in diameter by 120 mm in length.

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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁴ The Beckman Model G pH meter, or its equivalent, has been found satisfactory for this purpose.

13. Reagents and Materials

13.1 *Acetone*.

13.2 *Ethyl Alcohol*—Freshly boiled ethyl alcohol conforming to Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue.

13.3 *Methyl Orange Indicator*.

13.4 *Nitric Acid* (1+1)—Mix 1 volume of HNO₃ (sp gr 1.42) containing 0.3 % sodium nitrite (NaNO₂) with 1 volume of water.

13.5 *Nitric Acid* (1+4)—Mix 1 volume of nitric acid (HNO₃, sp gr 1.42) with 4 volumes of water.

13.6 *Silver Nitrate, Standard Solution* (0.2 N)—Prepare and standardize a 0.2 N silver nitrate (AgNO₃) solution as follows: Weigh 17 g of AgNO₃ to the nearest 1 mg. Dissolve in water and transfer to a 500-mL volumetric flask. Dilute to the mark. Standardize as follows:

13.6.1 Dry about 10 g of NaCl at 110°C to constant weight. Weigh about 2.00 g of the dried NaCl to the nearest 1 mg. Dissolve in a solvent consisting of 60 % water and 40 % alcohol. Transfer to a 100-mL volumetric flask and dilute to the mark with solvent. Pipet 100 mL of the NaCl solution to a beaker and titrate with the AgNO₃ solution as described in Section 14.

13.6.2 Calculate the normality of the AgNO₃ solution as follows:

$$\text{Normality} = (A \times 100)/(B \times 58.45) \quad (1)$$

where:

A = grams of NaCl used, and

B = millilitres of AgNO₃ solution required for titration of the NaCl.

14. Procedure for Qualitative Determination

14.1 Place 5 mL of Solution I or II in a test tube and acidify with HNO₃ (1+4). Add several drops of AgNO₃ solution. If the solution becomes turbid, it contains NaCl. Presence of soap will also cause turbidity. Soap must not be present with the surfactant to be characterized.

15. Procedure for Quantitative Determination

15.1 Pipet 100-mL portions of Solution I or II into each of two 400-mL beakers. Add 2 drops of methyl orange indicator solution and acidify to the acid color by using HNO₃(1+4). Warm slightly and stir to effect maximum solution. Add 50 mL of acetone.

15.2 Clean the silver electrode in the HNO₃ (1+1) containing NaNO₂. Set up the titration cell with the silver electrode connected to the top terminal, the saturated calomel cell connected to the bottom terminal. Set the pH meter on + mV. Start the stirring and titrate the solution potentiometrically as follows:

15.2.1 Add 0.5 mL of AgNO₃ solution and measure the emf. If appreciable chloride is present, the emf should be in the range of 100 mV.

15.2.2 Add AgNO₃ solution slowly in 2 to 3-mL portions until the emf reaches 200 mV. Stir well.

15.2.3 Add AgNO₃ solution in 0.1-mL portions, allowing sufficient time after each addition for the solution to reach equilibrium (60 to 80 s). Measure the emf (stirrer off) at each 0.1-mL point.

15.2.4 Calculate the end point by the rate of change method (Note 1). The end point is usually in the range from 260 to 270 mV.

NOTE 1—*Example*—The method for determining the maximum rate of change is as follows:

mL	emf	ΔE	ΔE'
21.2	210}	10}	10
21.3	220}	20}	17 ^A
21.4	240}	37}	12
21.5	277}	25	
21.6	302		

^A Maximum rate of change.

$$\text{End point} = 21.3 + \frac{17}{17 + 12} \times 0.1 \quad (2)$$

$$= 21.46 \text{ mL} \quad (2)$$

15.3 Run a blank and subtract the value obtained from the value calculated in 15.2.4.

16. Calculations

16.1 Calculate the grams of NaCl present in 250 mL of Solution I or II as follows:

$$A = (B \times N \times 0.05845 \times 250)/100 \quad (3)$$

where:

A = grams of NaCl present in 250 mL of Solution I or II,
B = millilitres of AgNO₃ solution required for titration of the NaCl, and

N = normality of the AgNO₃ solution.

16.2 Calculate the grams of NaCl equivalent to sodium sulfate (Na₂SO₄) present in 250 mL of Solution I or II as follows:

$$A = (B \times 71.03)/58.45 \quad (4)$$

where:

A = grams of Na₂SO₄ equivalent to the NaCl in 250 mL of Solution I or II, and

B = grams of NaCl present in 250 mL of Solution I or II.

CHARACTERIZATION OF ANIONIC SURFACTANT STANDARD

Part I. Determination of Surfactant, SO₃ Content, and Solution Molarity

17. Reagents

17.1 *Ethyl Alcohol*—See Section 6.

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

18. Procedure

18.1 Pipet 250 mL of Solution I (8.6) into each of two 250-mL beakers. Evaporate to near dryness on a steam bath or under an infrared lamp. Transfer quantitatively the concentrated solution from the beaker into a tared, ignited, platinum