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Standard Test Methods for Chemical Analysis of Alpha Olefin Sulfonates¹

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1. Scope

1.1 These test methods cover the chemical analysis of alpha olefin sulfonates. The analytical procedures appear in the following order:

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

1.3 *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.* For specific precaution statement see 36.1. Material safety data sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1172 Guide for pH of Aqueous Solutions of Soaps and Detergents

D1193 Specification for Reagent Water

D1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)

D3049 Test Method for Synthetic Anionic Ingredient by Cationic Titration

¹ These test methods are under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and are 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.

3. Purity of Reagents

3.1 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean Type III reagent water conforming to Specification D1193.

MOISTURE BY THE DISTILLATION METHOD

4. Apparatus

4.1 The apparatus required shall consist of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask. A suitable assembly of the apparatus is illustrated in Fig. 1.

4.1.1 *Flask*, 1-L capacity, either the short-neck, round-bottom type, or the Erlenmeyer type.

4.1.2 *Heat Source*—Either an oil bath (for example, stearic acid or paraffin wax) or an electric heater provided with a sliding rheostat or other means of heat control.

4.1.3 *Condenser*—A water-cooled glass reflux condenser (Fig. 1), having a jacket approximately 15¾ in. (400 mm) in length, with an inner tube ¾ to ½ in. (9.5 to 12.7 mm) in outside diameter, and not less than ¼ in. (6.35 mm) in inside diameter. The end of the condenser to be inserted in the trap may be ground off at an angle of 30° from the vertical axis of the condenser. When inserted into the trap, the tip of the

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.

7. Calculation

7.1 Calculate the percentage of moisture as follows:

$$\text{Moisture, \%} = [(V \times 0.998)/W] \times 100 \quad (1)$$

where:

V = volume of water, mL at 20°C, and

W = weight of sample, g.

8. Precision and Bias⁶

8.1 *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 0.16 % absolute at 9 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.5 % absolute.

8.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.47 % absolute at 8 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 1.5 % absolute.

8.3 *Checking Limits for Duplicates*—Report the moisture content of the sample to the nearest 0.01 %. Duplicate runs that agree within 1.3 % are acceptable for averaging (95 % confidence level).

SODIUM SULFATE

9. Apparatus

9.1 *Beakers*, 50 and 100-mL capacity.

9.2 *Buret*, 10-mL capacity, with 0.05-mL divisions.

9.3 *Volumetric Flasks*, 50, 250, and 1000-mL capacity.

9.4 *Magnetic Stirrer*, with TFE-fluorocarbon-coated stirring bars.

9.5 *Transfer Pipet*, 5-mL capacity.

9.6 *Viewing Lamp*—Small tungsten lamp or flashlight.

10. Reagents and Materials

10.1 *Acetone*.

10.2 *Barium Perchlorate Solution (0.02N)*—Dissolve 3.4 g of anhydrous Ba(ClO₄)₂ in water and dilute the solution to 1 L.

10.3 *2-Benzyl-2-thiopseudourea Hydrochloride Solution (7 %)*⁷—Dissolve 7 g in 100 mL of water. Prepare the solution fresh daily.

10.4 *Hydrochloric Acid (1 N)*—Dilute 83 mL of hydrochloric acid (HCl, sp gr 1.19) to 1 L with water.

10.5 *Hydrochloric Acid (0.1 N)*—Dilute 8.3 mL of HCl (sp gr 1.19) to 1 L with water.

10.6 *Phenolphthalein Indicator Solution (10 g/L)*—Dissolve 1 g of phenolphthalein in 100 mL of 95 % ethanol.

10.7 *Sodium Sulfate Solution (0.02 N)*—Dry the anhydrous, reagent-grade salt (Na₂SO₄) for 4 h at 105°C. Weigh about 0.355 g of the dried salt into a 100-mL beaker. Record the weight within ±0.1 mg. Dissolve the salt water. Quantitatively transfer the solution to a 250-mL volumetric flask and dilute it to volume with water. Calculate the normality of the solution as follows:

$$\text{Normality, } N_1 = 0.05632 \times W \quad (2)$$

where W = grams of Na₂SO₄.

10.8 *Sulfonazo III Indicator Solution*⁸—Dissolve 0.1 g of Sulfonazo III in 100 mL of water. Pass the solution through a cation exchange column if it looks blue rather than lavender when edge-lighted by a tungsten lamp.

10.9 *Filter Paper*, smooth, hardened, ashless.

11. Standardization

11.1 Pipet 5.0-mL aliquots of standard Na₂SO₄ solution into each of two 50-mL beakers. Place stirring bars in each beaker. Add 20 mL of acetone, 2 drops of 1 N HCl, and 4 to 5 drops of Sulfonazo III indicator solution to each beaker.

11.2 Titrate each Na₂SO₄ solution with Ba(ClO₄)₂ solution using a 10-mL buret. Stir the solution magnetically. Illuminate the solution horizontally with a small tungsten lamp at the side of the beaker. Titrate slowly to a color change from lavender-pink to blue (about 0.3 mL of Ba(ClO₄)₂ solution is required to produce a good initial lavender color).

11.3 From each titration, calculate the normality of the Ba(ClO₄)₂ solution as follows. Average the values obtained.

$$\text{Normality, } N_2 = \frac{5 \times N_1}{V} \quad (3)$$

where:

N_1 = normality of the Na₂SO₄ solution, and
 V = millilitres of Ba(ClO₄)₂ solution required for 5-mL aliquot of Na₂SO₄ solution.

12. Procedure

12.1 Weigh a 2-g sample into a 100-mL beaker or a 50-mL flask. Record the weight to ±1 mg.

12.2 Place a stirring bar in the container. Add 25 mL of water and stir until the sample is dissolved.

12.3 Add a few drops of phenolphthalein indicator solution. Add 0.1 N HCl until the solution is just acid. Do not over-acidify.

12.4 Place the container in a cold-water bath (below 20°C) on the magnetic stirrer. Add 10 mL of 2-benzyl-2-thiopseudourea hydrochloride at a fast drip through a buret with vigorous stirring. Do not whip the liquid into a foam.

12.5 Stir the solution for 15 min more in the cold bath. Remove the solution from the bath and let it settle for a few minutes at room temperature.

⁶ Supporting data are available from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Request RR:D12-1002 and RR:D12-1007.

⁷ Eastman Organic Chemical No. 2124 has been found satisfactory for this purpose.

⁸ Sulfonazo III [3,6-bis-(*o*-sulfophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid] is available from the Aldrich Chemical Co.

12.6 Filter the solution through filter paper into a 50-mL volumetric flask. Wash the filter cake with water. Use the washes to dilute the solution to volume.

12.7 Pipet a 5-mL aliquot into a 50-mL beaker. Add 20 mL of acetone, 2 drops of 1 N HCl, and 4 to 5 drops of Sulfonazo III indicator solution.

12.8 Titrate the solution slowly with 0.02 N Ba(ClO₄)₂ solution. Use magnetic stirring. Illuminate the solution horizontally with a small tungsten lamp at the side of the beaker. Titrate to a color change from lavender-pink to a blue color that persists for 1 min.

NOTE 3—The titration should be between 1 and 5 mL. If the titration is greater than 5 mL, use a smaller aliquot of the sample and add water to bring the aqueous volume to 5 mL total. If the titration is less than 1 mL, pipet a 10-mL aliquot into a 100-mL beaker and add 40 mL of acetone, 4 drops of 1 N HCl, and 8 to 10 drops of Sulfonazo III indicator solution.

13. Calculation

13.1 Calculate the concentration of Na₂SO₄ as follows:

$$\text{Na}_2\text{SO}_4, \text{ wt \%} = \frac{355 N_2 \times V}{A \times W} \quad (4)$$

where:

N_2 = normality of Ba(ClO₄)₂ solution,
 V = volume of Ba(ClO₄)₂ solution, mL,
 A = volume of aliquot, mL, and
 W = weight of sample, g.

14. Precision and Bias⁶

14.1 *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 0.01 % absolute at 8 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.03 % absolute.

14.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.06 % absolute at 7 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.2 % absolute.

14.3 *Checking Limits for Duplicates*—Report the sodium sulfate of the sample to the nearest 0.01 %. Duplicate runs that agree within 0.1 % are acceptable for averaging (95 % confidence level).

NEUTRAL OIL

15. Apparatus

15.1 *Separatory Funnels*, 250-mL capacity, with TFE-fluorocarbon stopcocks.

15.2 *Erlenmeyer Flasks*, 250-mL capacity.

15.3 *Beakers*, 250-mL capacity.

15.4 *Steam Bath*.

15.5 *Vacuum Desiccator*.

16. Reagents

16.1 *Ethanol*, freshly boiled, 95 % or higher and neutral to phenolphthalein indicator, conforming to either Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue.

16.2 *Petroleum Ether*, with a distillation range between 30 and 60°C or *n*-pentane having a distillation range between 33°C and 41°C.

16.3 *Ethanol-Water (1 + 1)*—Mix 1 volume of ethanol with 1 volume of water.

16.4 *Phenolphthalein Indicator Solution*.

16.5 *Sodium Hydroxide Solution (0.1N)*—Dissolve approximately 4 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

16.6 *Sodium Sulfate* (Na₂SO₄), anhydrous, crystalline.

17. Procedure

17.1 Introduce into a 250-mL Erlenmeyer flask sample equivalent to 6 to 8 g of active matter, weighed to the nearest 0.01 g. Add an equivalent volume of 1 + 1 ethanol-water. If, on the addition of 2 drops of phenolphthalein indicator solution, the sample solution remains colorless, neutralize the sample with 0.1 N NaOH solution to the appearance of the pink color.

17.2 Quantitatively transfer the neutralized solution to a 250-mL separatory funnel, rinsing the flask, first with 10 mL of water, followed by 10 mL of ethanol and then by 100 mL of 1 + 1 ethanol-water. Add each rinsing to the separatory funnel. Finally, rinse the flask with 30 mL of petroleum ether, using this rinsing to extract the alcoholic solution in the separatory funnel.

17.3 To achieve efficient extraction, shake the separatory funnel vigorously for 1 min, venting it as necessary. Allow the phases to separate and withdraw the alcoholic solution to a second 250-mL separatory funnel. Using the second and a third 250-mL separatory funnel and transferring the alcoholic solution between them, extract it five more times with 30-mL portions of petroleum ether. Combine all petroleum ether extracts in the first separatory funnel. Rinse the second and third funnels with 10 mL each of petroleum ether and add this to the combined extracts.

17.4 Wash the combined petroleum ether extracts first with 50 mL of 1 + 1 ethanol-water and then with 50 mL of distilled water. Add a few grams of anhydrous Na₂SO₄ to break any emulsions that form. Drain and discard the aqueous alcoholic layers. Dry the petroleum ether by shaking it in the separatory funnel with 5 g of anhydrous Na₂SO₄. Filter the dried layer through a rough, ashless medium-porosity filter (containing an additional 5 g of anhydrous Na₂SO₄) into a tared 250-mL beaker.

17.5 Concentrate the petroleum ether extract to about 5 mL by cautiously heating it on a steam bath under a slow stream of nitrogen. Remove the residual solvent first under a stream of nitrogen without applying any heat, and finally in a vacuum desiccator at 50 mm Hg (6.7 kPa) and ambient temperature for a 15-min period. Repeat the vacuum removal of solvent until successive weighings differ by no more than 2 mg.

18. Calculation

18.1 Calculate the percentage of neutral matter as follows:

$$\text{Neutral matter, wt \%} = \frac{100 \times A}{B} \quad (5)$$

where:

A = residue weight, g, and
B = sample weight, g.

19. Precision and Bias⁶

19.1 *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 0.01 % absolute at 11 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.03 % absolute.

19.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.04 % absolute at 10 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.1 % absolute.

19.3 *Checking Limits for Duplicates*—Report the neutral oil of the sample to the nearest 0.01 %. Duplicate runs that agree within 0.06 % are acceptable for averaging (95 % confidence level).

CHLORIDES CALCULATED AS SODIUM CHLORIDE (NaCl)

20. Apparatus

20.1 *Stirrer Motor and Small Glass Rod Stirrer.*

20.2 *Potentiometer.*⁹

20.3 *Calomel Reference Electrode, saturated.*

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

21. Reagents and Materials

21.1 *Acetone.*

21.2 *Ethanol, freshly boiled, conforming to Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue.*

21.3 *Methyl Orange Indicator Solution.*

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

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

21.6 *Silver Nitrate, Standard Solution (0.2N)*—Prepare and standardize a 0.2 N silver nitrate (AgNO₃) solution as follows: Weigh 17 g of AgNO₃ to the nearest 0.001 g. Dissolve in water and transfer to a 500-mL volumetric flask. Dilute to the mark. Standardize as follows: Dry about 10 g of sodium chloride

(NaCl) at 110°C to constant weight. Weigh about 2.00 g of the dried NaCl to the nearest 0.001 g. 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 10 mL of the NaCl solution to a beaker and titrate with the AgNO₃ solution as described in Section 22.

21.6.1 Calculate the normality of the AgNO₃ solution as follows:

$$N_3 = (A \times 100)/(B \times 58.45) \quad (6)$$

where:

N₃ = normality of the AgNO₃ solution,

A = grams of NaCl used, and

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

22. Procedure

22.1 Chlorides may be determined on the original sample, the alcohol-insoluble portion, or on the alcohol-soluble matter, and should be reported on these bases, the total chlorides calculated as NaCl being reported for the analysis of the original sample.

22.2 Weigh to ±0.001 g a portion of the sample approximately equal to 30 g divided by the percentage of NaCl expected, but the sample should not exceed 10 g.

22.3 Dissolve the sample in 250 mL of hot water, add 2 drops of methyl orange indicator solution, and acidify to the acid color by adding HNO₃ (1 + 4). Warm slightly and stir to effect maximum solution. Add 50 mL of acetone.

22.4 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 and 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:

22.4.1 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.

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

22.4.3 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.

22.4.4 Calculate the end point by the rate of change method (Note 4). The end point is usually in the range of 260 to 270 mV.

NOTE 4—*Example*—The method for determining the maximum rate of change is as follows:

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

⁹ The Beckman Model G pH meter has been found satisfactory for this purpose.

^A Maximum rate of change.

$$\text{End point} = 21.4 + \left[\frac{17}{(17+12)} \times 0.1 \right] = 21.46 \text{ mL} \quad (7)$$

22.5 Run a blank and subtract the value obtained from the value calculated in 22.4.4.

23. Calculation

23.1 Calculate as NaCl the percentage of chlorides present, as follows:

$$A = [(S - B)N \times 5.85]/C \quad (8)$$

where:

A = weight % of NaCl,

S = millilitres of AgNO₃ solution required for titration of the sample,

B = millilitres of AgNO₃ solution required for titration of the blank,

N = normality of the AgNO₃ solution, and

C = grams of sample used.

24. Precision and Bias⁶

24.1 *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 0.01 % absolute at 8 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.03 % absolute.

24.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.06 % absolute at 7 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.2 % absolute.

24.3 *Checking Limits for Duplicates*—Report the chlorides as NaCl of the sample to the nearest 0.01 %. Duplicate runs that agree within 0.06 % are acceptable for averaging (95 % confidence level).

ALKALINITY

25. Apparatus

25.1 *Buret.*

25.2 *Erlenmeyer Flask, 500-mL capacity.*

26. Reagents

26.1 *Hydrochloric Acid, Standard (0.1N)*—Prepare and standardize 0.1 N hydrochloric acid (HCl). Standard acid weaker than 0.1 N may be used to obtain a more appropriate titer.

26.2 *Phenolphthalein Indicator Solution.*

26.3 *Methyl Orange Indicator Solution.*

26.4 *Sodium Hydroxide, Standard Solution (0.1N)*—Prepare and standardize an 0.1 N sodium hydroxide (NaOH) solution. If an acid solution weaker than 0.1 N is used, use an equivalent NaOH solution.

26.5 *Ethanol*, freshly boiled, 95 % or higher and neutral to phenolphthalein indicator conforming to either Formula No. 3A or No. 30 of the U. S. Bureau of Internal Revenue.

27. Procedure

27.1 Weigh 5 g of the sample (to the nearest 0.1 mg) into a 500-mL Erlenmeyer flask. Add 100 to 150 mL of warm water (about 35°C) to dissolve the sample, 50 mL of ethanol to suppress the foaming, and then add 2 drops of phenolphthalein indicator solution and 2 drops of methyl orange indicator solution.

27.2 If the solution is alkaline to phenolphthalein, titrate to the phenolphthalein end point with the 0.1 N acid solution.

27.2.1 Add a measured excess (approximately five times the titer) of standard acid solution.

27.2.2 Boil the solution or sparge the solution with nitrogen for 15 min to remove carbon dioxide.

27.2.3 Back-titrate the remaining acid to the phenolphthalein end point with standard 0.1 N NaOH solution.

27.3 If the solution is acid to phenolphthalein and alkaline to methyl orange, titrate to the methyl orange end point with the 0.1 N acid.

27.3.1 Add a measured excess (approximately twice the titer) of standard acid.

27.3.2 Boil the solution or sparge the solution with nitrogen for 15 min to remove carbon dioxide.

27.3.3 Back-titrate the remaining acid to the phenolphthalein end point with standard 0.1 N NaOH solution.

28. Calculation

28.1 Calculate the alkalinity to the appropriate basis, as follows:

28.1.1 If the sample was acid to phenolphthalein and alkaline to methyl orange, calculate the alkalinity to sodium bicarbonate (NaHCO₃) as follows:

$$\text{NaHCO}_3, \text{ wt \%} = \left[\frac{(A+B)C - DE}{F} \right] 8.40 \quad (9)$$

where:

A = millilitres of HCl needed to titrate to the methyl orange end point (27.3),

B = millilitres of excess HCl added (27.3.1),

C = normality of the HCl,

D = millilitres of NaOH solution needed to titrate to the phenolphthalein end point (27.3.3),

E = normality of the NaOH solution, and

F = grams of sample used.

28.1.2 If the sample was alkaline to phenolphthalein, calculate the alkalinity to NaOH, Na₂CO₃, or NaHCO₃ as follows:

28.1.2.1 If $(A - C)B + DE$ is greater than zero, then:

$$\text{NaOH, wt \%} = \left[\frac{(A - C)B + DE}{F} \right] 4.0 \quad (10)$$

$$\text{Na}_2\text{CO}_3, \text{ wt \%} = \left[\frac{BC - DE}{F} \right] 10.59 \quad (11)$$

28.1.2.2 If $(A - C)B + DE$ is less than or equal to zero, then: