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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 *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

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

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 of Soaps and Synthetic Detergents.

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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.

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 15 $\frac{3}{4}$ in. (400 mm) in length, with an inner tube $\frac{3}{8}$ to $\frac{1}{2}$ in. (9.5 to 12.7 mm) in outside diameter, and not less than $\frac{1}{4}$ 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 condenser shall be about $\frac{1}{4}$ in. (7 mm) above the surface of the liquid in the trap after the distillation conditions have been established. Fig. 1 shows a conventional sealed-in type of condenser, but any other condenser fulfilling the detailed requirements of this paragraph may be used.

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.

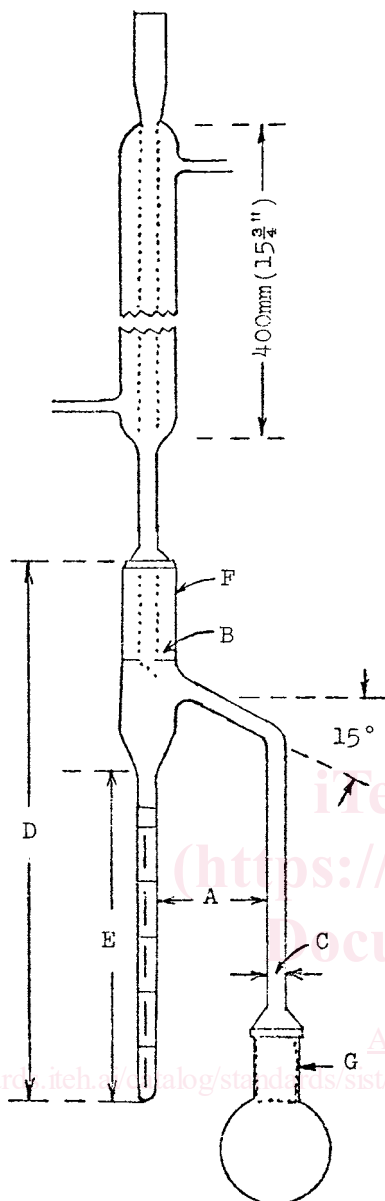


FIG. 1 Assembly of Distillation Apparatus

4.1.4 *Trap*—For greatest accuracy several trap sizes are allowable, depending upon the percentage of moisture expected:

Moisture Expected, %	Size of Trap, mL
0 to 5, incl	5
Over 5 to 17, incl	10
Over 17 to 30, incl	25
Over 30 to 50, incl	25
Over 50 to 70, incl	25
Over 70 to 85, incl	25

Traps made of well-annealed glass, constructed essentially as shown in Fig. 1, and graduated to contain one of the following specified volumes at 20°C shall be used:

4.1.4.1 *Trap*, 5-mL capacity, subdivided into 0.1-mL divisions with each 1-mL line numbered (5 mL at top). The error in any indicated capacity may not be greater than 0.05 mL.

4.1.4.2 *Trap*, 10-mL capacity, subdivided from 0 to 1 mL in 0.1-mL divisions and from 1 to 10 mL in 0.2-mL divisions.

4.1.4.3 *Trap*, 25-mL capacity, subdivided from 0 to 1 mL in 0.1-mL divisions and from 1 to 25 mL in 0.2-mL divisions.

NOTE 1—The condenser and trap should be thoroughly cleaned before use.

5. Solvent

5.1 *Xylene*—Saturate xylene with water by shaking with a small quantity of water and distill. Use the distillate for the determination.

6. Procedure

6.1 Transfer to the 1000-mL flask (equipped with the size of the trap specified in 4.1.4) an amount of sample according to the percentage of moisture expected, as follows:

Moisture Expected, %	Weight of Sample to Be Used, g ^A
0 to 5, incl	50 ± 5
Over 5 to 17, incl	50 ± 5
Over 17 to 30, incl	40 ± 4
Over 30 to 50, incl	30 ± 3
Over 50 to 70, incl	30 ± 3
Over 70 to 85, incl	25 ± 2

^A Weighed to the nearest 0.25 g.

Immediately add about 250 mL of xylene. Place a small, thin sheet of long-fiber, chemical-resistant glass⁴ wool on the surface of the xylene. The glass wool should be thoroughly dried in the oven and held in the desiccator before use.

6.2 Connect the flask and receiver to the condenser and pour sufficient xylene down the condenser tube to cause a slight overflow through the side tube. Wrap the flask and tube leading to the receiver with glass wool, so that refluxing will be under better control.

6.3 Heat the oil bath with a gas burner or other source of heat, or apply heat directly to the flask with an electric heater and distill slowly. The rate at the start should be approximately 100 drops per minute. When the greater part of the water has distilled over, increase the distillation rate to 200 drops per minute until no more water is collected. Rinse during the distillation with 5-mL portions of xylene to wash down any moisture adhering to the walls of the condenser. The water in the receiver may be made to separate from the xylene by using a spiral copper or Nichrome⁵ wire. Move the wire up and down in the condenser occasionally, thus causing the water to settle at the bottom of the receiver. Reflux for at least 2 h, and shut off the heat at the end of this period.

NOTE 2—In especially difficult cases of boil-over, add 10 to 15 mL of oleic acid before beginning the distillation. Wash down the condenser with 10 mL of xylene. Adjust the temperature of the distillate to 20°C and read the volume of water.

7. Calculation

7.1 Calculate the percentage of moisture as follows:

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

⁴ Borosilicate glass has been found satisfactory for this purpose.

⁵ "Nichrome" is a trademark of the Driver-Harris Co.

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* (0.02*N*)—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.

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

⁶ Supporting data are available from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Request D12-1002 and 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-naphthalenedi-sulfonic acid] is available from the Aldrich Chemical Co.

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 Bias ⁶

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 Bias ⁶

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