Standard Test Methods for Chemical Analysis of Alpha Olefin Sulfonates[1]

This standard is issued under the fixed designation D 3673; 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 These test methods cover the chemical analysis of alpha olefin sulfonates. The analytical procedures appear in the following order:

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:*

D 1172 Test Method for pH of Aqueous Solutions of Soaps and Detergents[2]

D 1193 Specification for Reagent Water[3]

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)[4]

D 3049 Test Method for Synthetic Anionic Ingredient by Cationic Titration[2]

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.[5] 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 D 1193.

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 ⅜ 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 condenser shall be about ¼ 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

[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] *Annual Book of ASTM Standards*, Vol 15.04.

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

[4] *Annual Book of ASTM Standards*, Vol 06.04.

[5] *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.

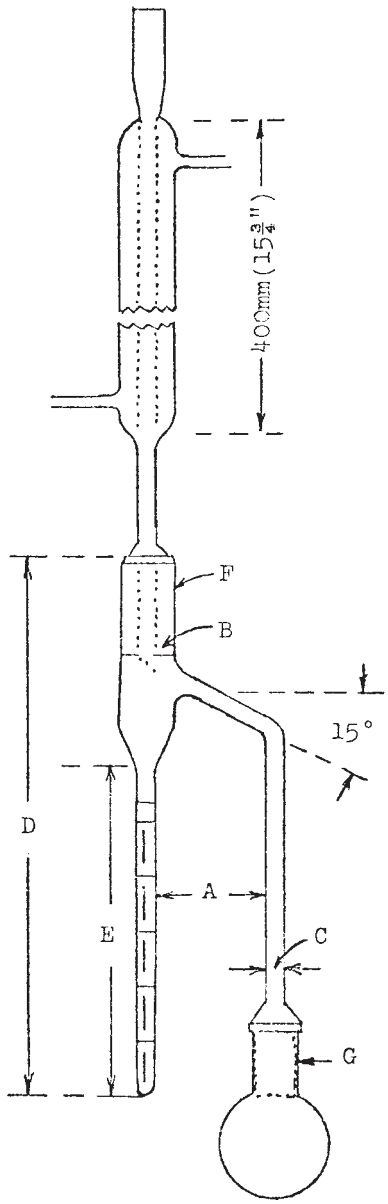

FIG. 1 Assembly of Distillation Apparatus

condenser, but any other condenser fulfilling the detailed requirements of this paragraph may be used.

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 glass[6] 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 Nichrome[7] 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:

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

[6] Borosilicate glass has been found satisfactory for this purpose.
[7] "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 Bias [8]

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 $Ba(ClO_4)_2$ in water and dilute the solution to 1 L.

10.3 *2-Benzyl-2-thiopseudourea Hydrochloride Solution* —(7 %)[9]—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 (Na_2SO_4) 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:

$$\text{Normality, } N_1 = 0.05632 \times W \tag{2}$$

where W = grams of Na_2SO_4.

10.8 *Sulfonazo III Indicator Solution*[10]—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 Na_2SO_4 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 Na_2SO_4 solution with $Ba(ClO_4)_2$ 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 $Ba(ClO_4)_2$ solution is required to produce a good initial lavender color).

11.3 From each titration, calculate the normality of the $Ba(ClO_4)_2$ solution as follows. Average the values obtained.

$$\text{Normality, } N_2 = \frac{5 \times N_1}{V} \tag{3}$$

where:
N_1 = normality of the Na_2SO_4 solution, and
V = millilitres of $Ba(ClO_4)_2$ solution required for 5-mL aliquot of Na_2SO_4 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* $Ba(ClO_4)_2$ 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.

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

[9] Eastman Organic Chemical No. 2124 has been found satisfactory for this purpose.

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

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 Na_2SO_4 as follows:

$$Na_2SO_4\text{, wt \%} = \frac{355\, N_2 \times V}{A \times W} \quad (4)$$

where:
N_2 = normality of $Ba(ClO_4)_2$ solution,
V = volume of $Ba(ClO_4)_2$ solution, mL,
A = volume of aliquot, mL, and
W = weight of sample, g.

14. Precision and Bias [8]

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

16.6 *Sodium Sulfate* (Na_2SO_4), 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 Na_2SO_4 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 Na_2SO_4. Filter the dried layer through a rough, ashless medium-porosity filter (containing an additional 5 g of anhydrous Na_2SO_4) 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 [8]

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.*[11]

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 (HNO_3, sp gr 1.42) containing 0.3 % sodium nitrite ($NaNO_2$) with 1 volume of water.

21.5 *Nitric Acid* (1 + 4)—Mix 1 volume of HNO_3(sp gr 1.42) with 4 volumes of water.

21.6 *Silver Nitrate, Standard Solution* (0.2*N*)—Prepare and standardize a 0.2 *N* silver nitrate ($AgNO_3$) solution as follows: Weigh 17 g of $AgNO_3$ 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 $AgNO_3$ solution as described in Section 22.

21.6.1 Calculate the normality of the $AgNO_3$ solution as follows:

$$N_3 = (A \times 100)/(B \times 58.45) \tag{6}$$

where:

N_3 = normality of the $AgNO_3$ solution,
A = grams of NaCl used, and
B = millilitres of $AgNO_3$ 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 HNO_3(1 + 4). Warm slightly and stir to effect maximum solution. Add 50 mL of acetone.

22.4 Clean the silver electrode in the HNO_3 (1 + 1) containing $NaNO_2$. 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 $AgNO_3$ solution and measure the emf. If appreciable chloride is present, the emf should be in the range of 100 mV.

22.4.2 Add $AgNO_3$ solution slowly in 2 to 3-mL portions until the emf reaches 200 mV. Stir well.

22.4.3 Add $AgNO_3$ 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	$\Delta E'$
21.2	210		
	}	10	
21.3	220	}	10
	}	20	
21.4	240	}	17[A]
	}	37	
21.5	277	}	12
	}	25	
21.6	302		

[A] Maximum rate of change.

$$\text{End point} = 21.4 + ([17/(17 + 12)] \times 0.1) = 21.46 \text{ mL} \tag{7}$$

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:

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

where:

A = weight % of NaCl,
S = millilitres of $AgNO_3$ solution required for titration of the sample,
B = millilitres of $AgNO_3$ solution required for titration of the blank,
N = normality of the $AgNO_3$ solution, and
C = grams of sample used.

24. Precision and Bias [8]

24.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates) obtained by the

[11] The Beckman Model G pH meter has been found satisfactory for this purpose.

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* (0.1*N*)—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* (0.1*N*)—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 ($NaHCO_3$) as follows:

$$NaHCO_3\text{, wt \%} = \left[\frac{(A + B)C - DE}{F}\right] 8.40 \tag{9}$$

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, Na_2CO_3, or $NaHCO_3$ as follows:

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

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

$$Na_2CO_3\text{, wt \%} = \left[\frac{BC - DE}{F}\right] 10.59 \tag{11}$$

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

$$Na_2CO_3\text{, wt \%} = \left(\frac{AB}{F}\right) 10.59 \tag{12}$$

$$NaHCO_3\text{, wt \%} = \left[\frac{(C - A)B - DE}{F}\right] 8.40 \tag{13}$$

where:

- A = millilitres of HCl needed to titrate to the phenolphthalein end point (27.2),
- B = normality of the HCl,
- C = millilitres of excess HCl added (27.2.1),
- D = millilitres of NaOH solution needed to titrate to the phenolphthalein end point (27.2.3),
- E = normality of the NaOH solution, and
- F = grams of sample used.

29. Precision and Bias [8]

29.1 *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 0.003 % absolute at 11 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.01 % absolute.

29.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.01 % absolute at 10 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.03 % absolute.

29.3 *Checking Limits for Duplicates*—Report the free alkali of the sample to the nearest 0.01 %. Duplicate runs that agree within 0.03 % are acceptable for averaging (95 % confidence level).

pH

30. Procedure

30.1 Determine the pH in accordance with Test Method D 1172, except measure 10 min after adjusting the solution of the sample to volume. Prepare the solution by transferring 10 ± 0.001 g of the sample to a 1-L volumetric flask and diluting in accordance with Test Method D 1172.

31. Precision and Bias [8]

31.1 *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 0.04 % 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.

31.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.28 % absolute at 9 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.9 % absolute.

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

DETERMINATION OF COLOR

32. Scope

32.1 This method covers the measurement of color in alpha olefin sulfonates using the platinum-cobalt scale and the Klett-Summerson colorimeter.

32.2 The instrument is calibrated each day with dilutions of Platinum-Cobalt Color Standard (No. 500 APHA). The Pt-Co value for the sample is determined from the calibration curve for the Klett instrument.

33. Significance and Use

33.1 This method is suitable as a quality control test for the measurement of color in alpha olefin sulfonates.

34. Apparatus

34.1 *Klett-Summerson Photoelectric Colorimeter*, industrial model 900-3 Klett.

34.2 *Klett Filter*, No. 42 blue.

34.3 *Solution Cells*, matched pairs, 40 mm in depth.

35. Reagents

35.1 Platinum Cobalt color standard No. 500 APHA,[12] in accordance with Test Method D 1209.

36. Procedure

36.1 Dilute the following accurately bureted volumes of Pt-Co standard No. 500 (**Caution:** Solution is acidic) to the mark in a 100-mL volumetric flask with distilled water:

mL	Pt-Co no.
20.00	100
30.00	150
40.00	200

36.2 Prepare a 5 % active solution of alpha olefin sulfonate in H_2O. Dilute 5 g of active material to 100 mL in a volumetric flask. A few drops of ethanol may be used to eliminate any foam near the mark. After dilution to 100 mL, mix the solution well. Filter, if necessary, to obtain a clear solution for color readings.

36.3 Before turning the colorimeter lamp on, insert Klett filter no. 42, in place between the lamp housing and the instrument.[13]

36.4 Adjust the pointer (lamp off) so that it coincides exactly with the line on the blank pointer scale. Make this adjustment with the small knob just above the pointer and only while the colorimeter lamp is off.

36.5 Fill a glass solution cell with water and place in the instrument. Close the cell compartment with the metal cover and turn the scale until the reading is zero.

36.6 Switch on the colorimeter lamp and allow a few minutes to permit the instrument to reach equilibrium. Adjust the pointer so that it again coincides with the line on the pointer scale using the zero adjustment knob located to the left of the cell compartment (zero setting).

36.7 Remove the cell and replace the blank solution with the Pt-Co standard no. 100 prepared in 35.1. Turn the scale knob until the pointer is brought back exactly to the zero setting and read the Klett number directly from the scale. It is not necessary to adjust the zero setting for successive color readings using the same filter.

36.8 Repeat as described in 36.7 for the Pt-Co numbers 150 and 200.

36.9 On linear graph paper, plot the Klett readings (ordinate) versus the Platinum-Cobalt standard no. (abscissa). Draw the best possible straight line through the points.

36.10 Perform the calibration given in 36.7-36.9 each day that color is to be determined.

36.11 Using the same procedure as in 36.7, measure the Klett color of the 5 % active AOS solution prepared in 36.2. From the Klett reading obtained, find and report the Platinum-Cobalt number for AOS using the calibration curve prepared in 36.9.

37. Precision and Bias [8]

37.1 The following criteria should be used for judging the acceptability of the result:

37.1.1 *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 1.62

[12] Fisher Scientific ΔSo-P-130 or equivalent.

[13] For complete details on operation of the Klett-Summerson Photoelectric Colorimeter, refer to the manual supplied with the instrument.

Platinum-Cobalt units absolute at df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 5.41 Platinum-Cobalt units absolute.

37.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 5.79 Platinum-Cobalt units absolute at 7 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 19.3 Platinum-Cobalt units absolute.

37.1.3 *Checking Limits for Duplicates*—Report the Platinum-Cobalt color of the sample to the nearest whole number. Duplicate runs that agree with 6.65 Platinum-Cobalt units are acceptable for averages (95 % confidence level).

DETERMINATION OF ACTIVE CONTENT BY METHYLENE BLUE TITRATION

38. Apparatus

38.1 *Lighted Viewbox*—The interior of this box is painted white and is equipped with a 75-watt, clear blue, electric light bulb, or a daylight fluorescent-type tube, and a white porcelain plate. The latter serves as a background for more accurately determining the partition of color in the solution that is being titrated. The box is mounted so that the analyst and the light source are located in such a manner as to provide indirect illumination.[14]

38.2 *Glass Stoppered Graduate*, 100 mL, O.D. 30 mm.

38.3 *Semi-Micro Buret*, 25 mL.

38.4 *Pipets*, 10, 15, and 25 mL.

38.5 *Volumetric Flasks*, 250, 1000, and 2000 mL.

39. Reagents

39.1 *Chloroform*.

39.2 *Ethanol*, formula 3A, 95 %.

39.3 *Petroleum Ether*, boiling range 30 to 50°C.

39.4 *Phenolphthalein Indicator Solution* (1 %)—Dissolve 1 g of phenolphthalein in water and dilute to 100 mL.

39.5 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare a 0.1 *N* solution of sodium hydroxide (NaOH).

39.6 *Sodium Hydroxide, Standard Solution* (1 *N*)—Prepare a 1 *N* solution of NaOH.

39.7 *Sodium Hydroxide, Standard Solution* (50 %)—Prepare a 50 % solution of NaOH.

39.8 *Sodium Lauryl Sulfate, Standard Solution*, (0.008 M).

39.8.1 Weigh accurately between 2.28 and 2.32 g of sodium lauryl sulfate and dissolve in 200 mL of water.

39.8.2 Transfer to a stoppered graduated 1 L flask and dilute to volume with water.

39.8.3 Calculate the molarity of the solution as follows:

$$\text{Molarity} = (W_2 \times P)/(288.4 \times 100) \tag{14}$$

where:

W_2 = grams of sodium lauryl sulfate, and
P = purity of the sodium lauryl sulfate, %.

39.9 *Sodium Sulfate* (Na_2SO_4), anhydrous.

39.10 *Sulfuric Acid, Standard* (0.1 *N*)—Prepare a 0.1 *N* solution of sulfuric acid (H_2SO_4).

39.11 *Sulfuric Acid, Standard* (0.5 *N*)—Prepare a 0.5 *N* solution of H_2SO_4.

39.12 *Sulfuric Acid, Standard* (1 *N*)—Prepare a 1 *N* solution of H_2SO_4.

40. Safety Precaution

40.1 This method includes the use of small amounts of chloroform. Appropriate safety practices, such as those included in the Material Safety Data Sheets for chloroform, should be employed. Good ventilation is especially important.

41. Primary Standard

41.1 The primary standard used in this procedure is sodium lauryl sulfate.[15] Tests for purity, alcohols and free acid or alkali of the primary standard should be run in accordance with Test Method D 3049.

42. Preparation of the Methylene Blue Solution

42.1 Dissolve 0.06 g of methylene blue chloride in 500 mL of distilled water. Transfer this solution to a 2 L volumetric flask, add 24 g (13.0 mL) of sulfuric acid, 100 g of sodium sulfate and dilute to the mark with distilled water.

43. Preparation of 0.004M Hyamine 1622 Solution[16]

43.1 Prepare the hyamine solution in accordance with Test Method D 3049.

44. Standardization of Hyamine 1622 Solution

44.1 Pipet 10 mL of 0.008 M sodium lauryl sulfate solution into a stoppered 100-mL graduated mixing cylinder.

44.2 Add 5 mL of 3A alcohol, 25 mL of methylene blue indicator and 15 mL of chloroform. Caution, see 40.1.

44.3 Add slightly less than an equivalent amount of the 0.004 M Hyamine 1622 solution (that is, about 20 mL; stopper and shake the vessel vigorously for 30 s. Allow the vessel to stand until the emulsion breaks and two phases appear. The lower layer initially will be colored dark blue and the upper layer light blue. From this point, the Hyamine solution is added in 0.10 mL increments and the vessel is shaken vigorously for 30 s after each addition until the top layer is of nearly the same intensity blue as the bottom. Continue the titration with dropwise addition of titrant and shaking between additions until the end point is reached. Note the volume of titrant added.

44.4 Calculate the normality of the Hyamine solution as follows:

$$\text{Normality} = (N \times 10)/V \tag{15}$$

where:

N = normality of the sodium lauryl sulfate solution, and
V = millilitres of Hyamine.

[14] A Fisher Illuminator No. 11-991-5 may be used, standing on its side.

[15] Manufactured by British Drug House, Ltd. as Product No. 30176. It is sold as being more than 99 % pure. It is available in the United States from Gallard-Schlesigner Chemical Manufacturing Corp., Carle Place, Long Island, NY 11514.

[16] Hyamine 1622 can be obtained from Rohm and Haas, Philadelphia, PA 19105.

45. General Procedure for Anionic Active Material

45.1 Weigh accurately a quantity of sample to contain approximately 8 meqs of anionic-active material (See Note 1).

NOTE 5—To determine the amount of sample needed for an approximate 20 mL titration use the following equation:

$$W_3 = \frac{20 \times N \times EW \times D \times 100}{\% \times A \times 1000} \quad (16)$$

where:
W_3 = sample mass (g),
20 = mL of Hyamine 1622 solution sought,
N = normality of the Hyamine solution,
EW = gram-equivalent weight of anionic active,
D = dilution of sample (mL),
$\%$ = % active ingredient expected, and
A = aliquot of sample dilution (mL).

45.2 Dissolve the sample in distilled water. Add a few drops of phenolphthalein solution and neutralize to a faint pink color with 1 N NaOH solution or 1 N H_2SO_4 as required.

45.3 Transfer quantitatively to a volumetric flask and dilute to volume with distilled water. When the solution is up in the neck of the flask, any foam on the surface can be eliminated by the addition of 1 to 2 drops of alcohol prior to the final dilution to the mark.

45.4 Remove a 10 mL aliquot to a 100 mL stoppered measuring cylinder, add 15 mL of chloroform, 25 mL of methylene blue indicator solution, and 5 mL of 3A alcohol.

45.5 Add slightly less than an equivalent amount of 0.004M Hyamine 1622 solution; stopper and shake the vessel vigorously for 30 s. Then allow the vessel to stand until the emulsion breaks and two phases appear. The lower layer initially will be colored dark blue and the upper layer light blue. From this point, the Hyamine solution is added in 0.10 mL increments and the vessel is shaken vigorously for 30 s after each addition until the top layer is of nearly the same intensity blue as the bottom. Continue the titration with dropwise addition of titrant and shaking between additions until the end point is reached. Take the end point as the point where the two layers are of the same intensity of blue. Note the volume of titrant added.

$$\%\ \text{active ingredient} = \frac{V \times N \times EW \times D \times 100}{W_3 \times A \times 1000} \quad (17)$$

where:
V = mL of Hyamine 1622 solution,
N = normality of the Hyamine solution,
EW = gram-equivalent weight of anionic active,
D = dilution of sample (mL),
A = aliquot of sample dilution (mL), and
W_3 = sample mass (g).

45.6 It should be noted at this point that the conditions used for viewing the end point on samples should be exactly the same viewing conditions as used for standardization of the Hyamine 1622 solution.

46. Report

46.1 Report the percentage of AOS active ingredient to the nearest 0.10 %. Duplicate runs that agree within 0.40 % absolute are acceptable for averaging (95 % confidence level).

47. Precision and Bias

47.1 The following criteria should be used for judging the acceptability of results:

47.1.1 *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 0.15 % absolute at 12 DF. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.4 % absolute.

47.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.30 % absolute at 11 DF. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.9 % absolute.

48. Keywords

48.1 alpha olefin sulfonates; chemical analysis