Designation: D4252 – 89 (Reapproved 2009)

Standard Test Methods for Chemical Analysis of Alcohol Ethoxylates and Alkylphenol Ethoxylates[1]

This standard is issued under the fixed designation D4252; 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 various test methods used to evaluate those properties pertinent to the characterization of alcohol ethoxylates and alkylphenol ethoxylates with respect to suitability for desired uses.

1.2 The procedures for sampling and analysis appear in the following order:

	Sections
Sampling	
Liquids	6
Solids	7
Methods of Chemical Analysis	
Water or moisture	8
Refractive index	9 and 10
pH	11
Acidity or basicity	12 and 13
Hydroxyl number	14-20
Cloud point	21
Iodine number	22
Ash	23
Iron	24
Ethylene oxide content	25
Polyethylene glycols	26-32

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage. Specific hazard statements appear in Section 5 and Note 1 and Note 3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D459 Terminology Relating to Soaps and Other Detergents

D482 Test Method for Ash from Petroleum Products

D1068 Test Methods for Iron in Water

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)

D1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids

D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D1959 Test Method for Iodine Value of Drying Oils and Fatty Acids[3]

D2024 Test Method for Cloud Point of Nonionic Surfactants

D2959 Test Method for Ethylene Oxide Content of Polyethoxylated Nonionic Surfactants

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E203 Test Method for Water Using Volumetric Karl Fischer Titration

E394 Test Method for Iron in Trace Quantities Using the 1,10-Phenanthroline Method

3. Significance and Use

3.1 Alcohol ethoxylates and alkylphenol ethoxylates are important surfactants in household and industrial cleaners. They may be used as either nonionic surfactants or sulfated and

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[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] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

used as anionic surfactants. Careful control of the ethoxylate characteristics is desired as variations may result in either desirable or undesirable end-use properties.

4. Purity of Reagents

4.1 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.[4] 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.

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

5. Safety Precautions

5.1 All reagents and chemicals should be handled with care. Before using any chemical, read and follow all safety precautions and instructions on the manufacturer label. Clean up any spill immediately. For information on cleaning up spills refer to the Laboratory Disposal Manual, Manufacturing Chemists Association, Washington, DC.

SAMPLING

6. Liquids

6.1 Thoroughly mix the sample before sampling. If a solid layer or crystals have formed on the bottom of the bottle, melt in an oven or water bath at 55°C and mix well before sampling.

7. Solids

7.1 Melt in an oven or water bath at 55°C and mix well before sampling. If it is necessary to heat at temperatures above 60°C, replace the gas cap with an inert gas, such as oxygen-free nitrogen, helium, or argon before heating.

WATER OR MOISTURE

8. Procedure

8.1 Determine water or moisture in accordance with Test Method E203.

REFRACTIVE INDEX

9. Procedure

9.1 Measure the refractive index at 50°C in accordance with Test Method D1218.

10. Precision

10.1 The following criteria should be used for judging the acceptability of results:[5,6]

10.1.1 *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 0.00021 units absolute at 36 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.00059 units absolute.

10.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.00059 units absolute at 7 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.0020 units absolute.

10.1.3 *Checking Limits for Duplicates*—Report the refractive index of the sample to the nearest 0.0001. Duplicate runs that agree within 0.00025 units are acceptable for averaging (95 % confidence level).

pH

11. Procedure

11.1 Determine the pH in accordance with Test Method D1172, except prepare the solution by transferring 1 ± 0.001 g of the sample to a 100 mL volumetric flask and diluting in accordance with Test Method D1172. Measure the pH 10 min after diluting the sample solution to volume.

ACIDITY OR BASICITY

12. Procedure

12.1 Determine acidity or basicity in accordance with Test Method D1613 using a 3+1 solution of isopropyl alcohol and water as the solvent and a 10-g sample.

13. Precision

13.1 The following criteria should be used for judging the acceptability of results:[6,7]

13.1.1 *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 0.017 meq/100 g at 27 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.049 meq/100 g.

13.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been established to be 0.12 meq/100 g at 5 df. Two such averages should be

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[4] *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.

[5] The precision estimates are based on an interlaboratory study on ALFONIC® 1412-60, MAKON®-10, NEODOL® 25-9, PLURONIC® 25R1, and TERGITOL 15-S-3 by nine laboratories.

[6] Statistical analysis was performed in accordance with Practice E180 for developing precision estimates. Data supporting the precision statements are on file at ASTM International Headquarters. Request RR: D12-1004.

[7] The precision estimates are based on an interlaboratory study on ALFONIC® 1412-60, MAKON®-10, NEODOL® 25-9, PLURONIC® 25R1 and TERGITOL® 15-S-3 by six laboratories.

considered suspect (95 % confidence level) if they differ by more than 0.44 meq/100 g.

13.1.3 *Checking Limits for Duplicates*—Report the acidity or basicity of the sample to the nearest 0.05 meq/100 g. Duplicate runs that agree within 0.051 meq/100 g are acceptable for averaging (95 % confidence level).

HYDROXYL NUMBER

14. Terminology

14.1 Definition:

14.1.1 *hydroxyl number*—the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample.

15. Summary of Test Method

15.1 The hydroxyl groups are esterified by reaction with phthalic anhydride in a pyridine medium at the temperature of reflux of the mixture. After cooling, the excess of phthalic anhydride is hydrolyzed with water and the phthalic acid formed is titrated to the phenolphthalein end point with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and of the sample solution.

16. Apparatus

16.1 *Reflux Assembly*, consisting of a reflux condenser and a 250-mL Erlenmeyer flask, 24/40 standard taper joint with TFE-fluorocarbon sleeves.

16.2 *Buret*, 50 mL, graduated in 0.1-mL intervals. Class A or equivalent.

16.3 *Pipet*, 25-mL capacity, Class A or equivalent.

16.4 *Insulating Pad*, 3½ by 3½ by 1 in., preferably not asbestos.

17. Reagents

17.1 *Pyridine, A. R.*—To be acceptable, each lot should pass the following quality test: Place 7 g of phthalic anhydride and 50 mL of pyridine (**Warning**—see Note 1) in a glass-stoppered flask, shake vigorously until dissolved. Heat at 50 or 60°C for 30 min, allow to stand at room temperature in the dark for 24 h and then measure the Pt-Co color (Test Method D1209). The pyridine is acceptable if the color does not exceed 200.

NOTE 1—**Warning:** Avoid breathing pyridine vapors, as they are toxic. Dispose of pyridine wastes in a well ventilated hood.

17.2 *Sodium Hydroxide*, (1 *N*), carbonate free. Purchase or prepare, standardize, and store according to Practice E200.

17.3 *Phthalic Anhydride Reagent*—Dissolve 98 ± 1 g of phthalic anhydride in 700 mL of pyridine (Note 1), shake to effect solution. Store in a brown bottle. Preferably, the solution should stand overnight before using. Prepare a fresh reagent each week or more frequently if the Pt-Co color (Test Method D1209) exceeds a value of 200.

17.4 *Sodium Hydroxide* (0.1 *N*)—Purchase or prepare, standardize, and store according to Practice E200.

17.5 *Hydrochloric Acid* (0.1 *N*)—Purchase or prepare by diluting 8.3 mL of concentrated hydrochloric acid to 1 L with distilled water. Standardize and store according to Practice E200.

17.6 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of pyridine.

17.7 *Isopropyl Alcohol*, A. R.

18. Procedure

18.1 Weigh into a clean and dry 250-mL Erlenmeyer flask with ground glass joint to the nearest 0.1 mg an amount of sample calculated by means of the following equation but do not use more than 10 g of sample:

$$\text{Amount of Sample, g} = \frac{M}{F \times 100} \quad (1)$$

where:

M = molecular weight of sample and

F = number of hydroxyl groups per molecule.

18.2 Pipet accurately 25 mL of phthalic anhydride reagent into the flask and swirl to effect solution. Add two boiling chips, attach a dry reflux condenser with a ground glass joint fitted with a TFE-fluorocarbon sleeve to the flask, and reflux for 1 h on an electric hotplate.

18.3 Turn off the hotplate and insert an insulated pad between the flask and the hot plate. Allow to cool for 20 min. Wash down the condenser, first with 25 mL of pyridine and then with 25 mL of water.

18.4 Remove the flask from the condenser. Add 4 or 5 drops of phenolphthalein indicator to the flask and titrate with standard 1 *N* sodium hydroxide solution to a faint pink end point (Note 2).

18.5 Make a blank determination following 18.2-18.4.

NOTE 2—It is *essential* that the sample titration requires at least three fourths of the blank titration. The difference between the two titrations should be of the order of 10 mL. If this is not the case the sample size should be adjusted accordingly and the analysis rerun.

18.6 Determine the free acidity or free alkalinity as described in Section 12 or as follows: To 25 mL of a 3 + 1 isopropyl alcohol/water mixture in a 250-mL Erlenmeyer flask add 2 to 3 drops of phenolphthalein indicator solution and titrate with standard 0.1 *N* sodium hydroxide solution to a faint pink. Accurately weigh 10 to 20 g of sample and add to the contents of the flask.

18.7 If the solution is colorless titrate with standard 0.1 *N* sodium hydroxide solution to a faint pink. If the solution is pink titrate with standard 0.1 *N* hydrochloric acid to just colorless.

19. Calculations

19.1 Calculate the hydroxyl number from the following equations:

19.1.1 *For samples containing free acidity*:

$$\text{Hydroxyl Number, mg KOH/g} = \left[\frac{(B - S)N}{W} + \frac{C \times N_1}{W_1}\right] \times 56.1 \quad (2)$$

19.1.2 *For samples containing free alkalinity*:

$$\text{Hydroxyl Number, mg KOH/g} = \left[\frac{(B - S)N}{W} - \frac{C \times N_1}{W_1}\right] \times 56.1 \quad (3)$$

where:

B = volume of 1 N sodium hydroxide solution required for blank titration (18.5), mL,
S = volume of 1 N sodium hydroxide solution required for sample titration (18.4), mL,
N = normality of 1 N sodium hydroxide solution,
W = weight of sample taken (18.1), g,
C = volume of 0.1 N sodium hydroxide/hydrochloric acid required for acidity/alkalinity titration (18.7), mL,
N_1 = normality of 0.1 N sodium hydroxide/hydrochloric acid used for acidity/alkalinity titration (18.7), and
W_1 = weight of sample used for acidity/alkalinity titration (18.6), g.

19.2 Calculate the apparent molecular weight from the following equation:

$$\text{Apparent Molecular Weight} = \frac{56,100}{H} \times F \qquad (4)$$

where:

H = hydroxyl number (mg KOH/g sample).
F = number of hydroxyl groups per molecule.

20. Precision

20.1 The following criteria should be used for judging the acceptability of the results:[6,8]

20.1.1 *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 1.10 % relative at 30 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 3.18 % relative.

20.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 1.80 % relative at 6 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 6.21 % relative.

20.1.3 *Checking Limits for Duplicates*—Report the hydroxyl number of the sample to the nearest unit. Duplicate runs that agree within 2.03 % relative are acceptable for averaging (95 % confidence level).

CLOUD POINT

21. Procedure

21.1 Determine the cloud point in accordance with Test Method D2024.

IODINE NUMBER

22. Procedure

22.1 Measure the Iodine Number (Iodine Value) in accordance with Test Method D1959, except do not filter the sample. Use 10 g of sample and chloroform (**Warning**—See Note 3) instead of carbon tetrachloride as the solvent.

NOTE 3—**Warning:** Chloroform is an embryo toxin as well as a suspected carcinogen in man.[9] Avoid breathing vapors and contact with the skin. Handle only in a well-ventilated hood.

ASH

23. Procedure

23.1 Determine the ash content in accordance with Test Method D482.

IRON

24. Procedure

24.1 Dissolve the residue from the ash determination (23.1) in 10 mL of 10 % aqueous hydrochloric acid and determine the iron content on the resulting solution in accordance with Test Method E394, or in accordance with Test Methods D1068, Method C, Atomic Absorption.

ETHYLENE OXIDE CONTENT

25. Procedure

25.1 Determine the ethylene oxide content in accordance with Test Method D2959.

POLYETHYLENE GLYCOLS

26. Scope

26.1 This method describes a procedure for the determination of polyethylene glycols in ethoxylated detergent range alcohols that have ratios of ethoxy groups to alkyl groups of three or more.

27. Summary of Test Method

27.1 The ethoxylated alcohol sample, aqueous sodium chloride solution and ethyl acetate are mixed in a separatory funnel. The polyethylene glycols enter the aqueous phase which is separated and extracted from the salt solution with chloroform which is removed by evaporation. The weight of the residue is taken as a measure of the polyethylene glycols in the sample.

28. Apparatus

28.1 *Separatory Funnels*, 250-mL capacity, equipped with Teflon stopcock and stopper.

28.2 *Steam Bath*, for evaporation of chloroform.

28.3 *Vacuum Oven*, capable of being heated at 50°C while maintaining a pressure of 200 or 300 mm of mercury.

29. Reagents

29.1 *Acetone*.

29.2 *Chloroform* (**Warning**—see Note 3).

29.3 *Ethyl Acetate*, 95 to 98 %.

29.4 *Sodium Chloride Solution*, 0.29 g/mL. To prepare, dissolve 293 g of crystal sodium chloride in water and dilute to 1 L.

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[8] The precision estimates are based on an interlaboratory study on ALFONIC® 1412-60, MAKON®-10, NEODOL® 25-9, PLURONIC® 25R1 and TERGITOL® 15-S-3 by seven laboratories.

[9] American Conference of Governmental Industrial Hygienists, ISBN: 0-936712-39-2, 6500 Glenway Ave., Cincinnati, OH 45211.

30. Procedure

30.1 In a 250-mL separatory funnel, add 50 mL of ethyl acetate and 50 mL of sodium chloride solution.

30.2 Transfer to the separatory funnel, approximately 10 g of sample weighed to the nearest 0.01 g.

30.3 Shake the stoppered funnel for two min and allow to stand to permit complete separations of the phases. (All subsequent extractions should follow this general procedure.) Drain the lower (aqueous sodium chloride) phase into a second separatory funnel.

30.4 Extract the ethyl acetate phase remaining in the first funnel with an additional 50 mL of the sodium chloride solution. Combine the aqueous extracts and counter extract with 50 mL of ethyl acetate.

30.5 Transfer the resulting aqueous (lower) phase to a clean (third) separatory funnel and discard the ethyl acetate solutions.

30.6 Extract the salt solution with 50 mL of chloroform.

30.7 Drain the chloroform (bottom) phase from the separatory funnel, through a pledget of cotton in a small filter funnel, into a tared 150-mL beaker (weighed to nearest milligram).

30.8 Make a second extraction with 50 mL of chloroform and filter the chloroform phase into the beaker.

30.9 Evaporate the chloroform on a steam bath in a well-ventilated hood.

30.10 Add 10 mL of acetone and look for the presence of insoluble sodium chloride (as suspended crystals). If any sodium chloride is present, filter it out using additional acetone for transferring and washing. Collect the filtrate and washings in a tared 150-mL beaker and evaporate off the acetone.

30.11 Dry the residue in the beaker in a vacuum oven at 50°C and 200 to 300 mm Hg for 1 h. Cool the beaker in a desiccator and weigh.

30.12 Repeat the oven drying and weighing until successive weights agree within 1 mg.

31. Calculation

31.1 Calculate the polyethylene glycol content of the sample by means of the following equation:

$$\text{Polyethylene Glycol, \% w} = 100\, A/W \tag{5}$$

where:

A = weight of the residue, g, and

W = weight of sample, g.

32. Precision

32.1 The criteria in Table 1 should be used for judging the acceptability of the results.[6,10]

33. Keywords

33.1 alcohol ethoxylates; alkylphenol ethoxylates; chemical analysis

TABLE 1 Acceptability of Results

	$\bar{s}$ Absolute Weight %	Degrees of Freedom	95 % Confidence Absolute Weight %
Repeatability	0.015	16	0.045
Reproducibility	0.070	4	0.27
Checking duplicates	0.012	32	0.035

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[10] Precision estimates are based on an interlaboratory study on ALFONIC® 1412-60, MAKON®-10 and NEODOL® 25-9 by nine laboratories.