Designation: D2959 − 95 (Reapproved 2017)

Standard Test Method for
Ethylene Oxide Content of Polyethoxylated Nonionic Surfactants[1]

This standard is issued under the fixed designation D2959; 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 This test method covers the determination of ethylene oxide in polyethoxylated nonionic surfactants. It can also be used for compounds containing propylene oxide or any compounds (glycols and glycol and polyglycol ethers and esters) which form unstable 1,2-diiodides on reaction with hydriodic acid.

NOTE 1—Compounds in which the oxyalkylene group is connected to a nitrogen cannot be entirely decomposed. This can be used to determine the percent of an ethoxylated surfactant in a mixture, if the ethylene oxide content of the ethoxylated surfactant is known.

NOTE 2—This method reports results as percent ethylene oxide. If this method is applied to unknown compounds or compositions, the analyst should be aware of the possible presence of material other than ethylene oxide.

NOTE 3—For use on built syndet compositions the organic active ingredient must be isolated in accordance with Test Method D2358.

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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

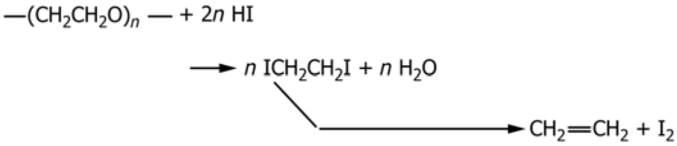
2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D2358 Test Method for Separation of Active Ingredient from Surfactant and Syndet Compositions

3. Summary of Test Method

3.1 By cleaving nonionic surfactants containing polyethylene oxide chains with hydriodic acid, the unstable 1,2-diiodoethane is formed. This vicinal diiodide decomposes to form ethylene and iodine.



$$-(CH_2CH_2O)_n- + 2n\,HI \rightarrow n\,ICH_2CH_2I + n\,H_2O$$

$$ICH_2CH_2I \rightarrow CH_2{=}CH_2 + I_2$$

3.2 The percent ethylene oxide is determined by measuring the amount of free iodine formed, since one mole of iodine is formed for each mole of ethylene oxide in the polyoxyalkylene chain. The free iodine is titrated with a standard sodium thiosulfate solution.

4. Apparatus (Fig. 1)

4.1 *Heat Sources,* two. The source of heat should be an electric heater provided with a sliding rheostat or other means of heat control.

4.2 *Flasks,* two, 100-mL, round bottom. Each flask should be equipped with a standard ground-glass joint to accommodate a vertical condenser, and with a side arm through which carbon dioxide can be passed to blanket the reaction mixture.

4.3 *Condensers,* two, with standard joints to fit the flasks.

4.4 *Gas Bubbler,* filled with dibutyl phthalate.

4.5 *Buret,* 50-mL, with 0.1-mL graduations.

4.6 *Pipet,* 5-mL.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

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[1] This method is under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and is 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.

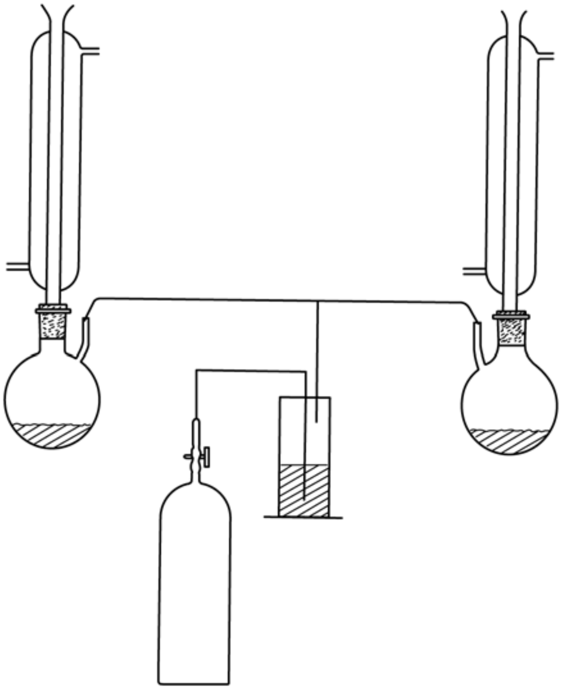

FIG. 1 Apparatus

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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type III reagent water conforming to Sections 1, 2, and 3 of Specification D1193.

5.3 *Carbon Dioxide or Nitrogen,* cylinder gas.

5.4 *Lubricant* for ground-glass joints.

5.5 *Dibutyl Phthalate.*

5.6 *Glass Beads.*

5.7 *Hydriodic Acid (55 to 58 %) (suitable for methoxyl determinations)*—The hydriodic acid (HI) should not contain hypophosphorus acid (H_3PO_2) stabilizer. The free iodine content should be less than 10 mL of 0.1 *N* sodium thiosulfate solution/5 mL of HI.

5.8 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

5.9 *Methanol.*

5.10 *Potassium Dichromate* ($K_2Cr_2O_7$), primary standard.

5.11 *Potassium Iodide Solution* (*200 g/L*)—Dissolve 200 g of potassium iodide (KI) in distilled water and dilute to 1000 mL.

5.12 *Sodium Thiosulfate, Standard Solution* (*0.1 N*)—Dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3$) in water and dilute to 1000 mL. Standardize by accurately weighing 0.16 to 0.22 g of finely ground and dried $K_2Cr_2O_7$ into a 500-mL iodine flask. Dissolve in 25 mL of water, add 5 mL of HCl and 15 mL of KI solution and swirl to mix. Allow to stand for 5 min, then add 100 mL of distilled water. Titrate with standard $Na_2S_2O_3$ solution, shaking continuously until the yellow color has almost disappeared. Add a small amount of Paragon indicator[4] or 1 to 2 mL of starch indicator solution and continue the titration, adding the $Na_2S_2O_3$ solution slowly until the blue color has just disappeared. Calculate the normality of the $Na_2S_2O_3$ solution as follows:

$$N = C/(0.04904 \times D) \tag{1}$$

where:

N = normality of the $Na_2S_2O_3$ solution,
C = grams of $K_2Cr_2O_7$ used, and
D = millilitres of $Na_2S_2O_3$ solution required for titration of the solution.

5.13 *Starch Indicator Solution*—Make a homogeneous paste of 10 g of soluble starch in water. To this add with rapid stirring 1 L of boiling water and then cool. As a preservative, add 1.25 g of salicylic acid per litre. Store the indicator in a refrigerator at 4 to 10°C. Prepare fresh indicator when the titration end point from blue to colorless fails to be sharp.

6. Procedure

6.1 Assemble the apparatus as shown in Fig. 1. Lubricate the ground-glass joints with a very thin film of lubricant. The dual apparatus is designed to permit a sample and a blank to be run simultaneously; however, it should not be necessary to make more than two blank determinations each day.

6.2 Accurately weigh a sample of such size that 4 to 5 meq of iodine will be liberated (about 0.15 g of a nonionic surfactant that contains 60 % ethylene oxide) into a 100-mL round bottom flask. Pipet exactly 5.0 mL of HI into the flask, and add a glass bead. Connect the vertical condenser to the flask using a thin seal of lubricant at the outer edge. Prepare a blank by pipetting 5.0 mL of HI into a second flask containing a glass bead. Connect the condenser as described above, and allow water to circulate through the condensers.

6.3 Attach the tubes from the carbon dioxide manifold to the sidearms on the flasks. Open the valve on the gas cylinder and adjust the flow to a rate of 1 to 5 bubbles per second through the bubbler, blanketing the solutions in the reaction flasks. The flow of carbon dioxide should continue for 10 min before heat is applied to the reaction flasks. After 10 min turn on the heat, and reflux the contents gently for 90 min.

6.4 After the 90-min boiling period, wash the walls of each condenser with 15 mL of 20 % KI solution to dissolve any free iodine in the condensers. Wash the condensers with two 10-mL

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[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.

[4] The sole source of supply of the Paragon indicator for iodine titrations known to the committee at this time is Eastern Chemical Corp., 34 Spring St., Newark, NJ 07104.. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

portions of water and disconnect. Wash the tips of the condensers with water, adding the washings to the flasks. Transfer the contents of the reaction flasks to Erlenmeyer flasks by washing with water.

NOTE 4—Rinse any iodine that adheres to the condensers into the flasks with a small amount of methanol. On rare occasions some samples leave a tarry residue as a button. Add methanol to dissolve the residue, and wash into the Erlenmeyer flask.

6.5 Titrate with standard $Na_2S_2O_3$ solution, shaking continuously until the yellow color has almost disappeared. Add a small amount of Paragon indicator or 1 to 2 mL of starch indicator solution and continue the titration, adding the $Na_2S_2O_3$ solution slowly until the blue color has just disappeared.

7. Calculation

7.1 Calculate the ethylene oxide content as follows:

$$\text{Ethylene oxide, weight \%} = [(A - B) \times N \times 2.203]/W \tag{2}$$

where:

A = millilitres of $Na_2S_2O_3$ solution required to titrate the sample,
B = millilitres of $Na_2S_2O_3$ solution required to titrate the blank,
N = normality of $Na_2S_2O_3$ solution, and
W = grams of sample.

8. Precision and Bias

8.1 The following criteria should be used for judging the acceptability of results (Note 5):

8.1.1 *Repeatability* (*Single Analyst*)—The standard deviation of results obtained by the same analyst was estimated to be 0.47 % absolute at 9 df. Two such values should be considered suspect (95 % confidence level) if they differ by more than 1.5 % absolute.

8.1.2 *Reproducibility (Multilaboratory)*[5]—The standard deviation of results (each the average of duplicate determinations), obtained by analysts in different laboratories, has been estimated to be 1.81 % absolute at 7 df. Two such values should be considered suspect (95 % confidence level) if they differ by more than 6.0 % absolute.

NOTE 5—The precision estimates are based on an interlaboratory study on Igepal CO 630 by nine laboratories. However, this procedure as written calls for the use of 100-mL reaction flasks (instead of 50-mL flasks which were used in the interlaboratory study). Data obtained by Continental Oil Co. indicate an improvement in precision when the larger flask is used.

9. Keywords

9.1 ethylene oxide content; nonionic surfactants

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[5] Data supporting the precision statements are on file at ASTM Headquarters. Request Research Report No. RR:D12-1000.