Designation: D4711 – 89 (Reapproved 2017)

Standard Test Method for Sulfonic and Sulfuric Acids in Alkylbenzene Sulfonic Acids[1]

This standard is issued under the fixed designation D4711; 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 is applicable to the determination of sulfonic and sulfuric acids in branched and linear alkylbenzene sulfonic acids used as intermediates in synthetic detergents.

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]

D459 Terminology Relating to Soaps and Other Detergents

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

3. Summary of Test Method

3.1 A methanolic solution of the sample is titrated with cyclohexylamine in methanol to yield a potentiometric curve. (See Fig. 1.) The first inflection represents the neutralization of strong acids, such as sulfonics and alkylsulfurics, and the first hydrogen of sulfuric acid. The second inflection represents the neutralization of the second hydrogen of sulfuric acid. The amount of sulfonic acid is calculated based on the titrant volume of the first inflection minus that between the two inflections. The amount of sulfuric acid meanwhile is calculated from the titrant volume between the two inflections, which is equivalent to the amount of base required for neutralization of the bisulfate anion.

4. Significance and Use

4.1 Alkylbenzene sulfonic acids are important intermediates in the synthetic detergent industry and are defined under "alkyl benzene sulfonate" in Terminology D459. This test method is suitable for the rapid monitoring of the sulfonic and sulfuric acid levels, both of which have a vital bearing on final product performance and appearance.

5. Interferences

5.1 Strong acids, like nitric and hydrochloric, interfere, as do weak acids, such as carboxylic acids. Small amounts of water originally present in the sample do not interfere in the determination. However, if as much as 5 % of water is present in the total solution (solvent plus sample), the end point becomes less sharp.

6. Apparatus

6.1 *Potentiometric Titrator,*[4] and combination calomel reference electrode.

6.2 *Buret Assembly,* having a 20 mL buret.[4]

6.3 *Beaker,* 180 mL tall form.

6.4 *Volumetric Flask,* Class A, 500 mL.

6.5 *Magnetic Stirrer,* and stirring bar.

7. Reagents and Materials

7.1 *Methanol,* anhydrous,

7.2 *Cyclohexylamine* (0.10 *N*)—Dissolve 10 g of reagent cyclohexylamine in 1000 mL of anhydrous methanol. Standardize against sulfamic acid as described in Section 8.

7.3 *Sulfamic Acid,* acidimetric standard.[5]

[1] This test 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.

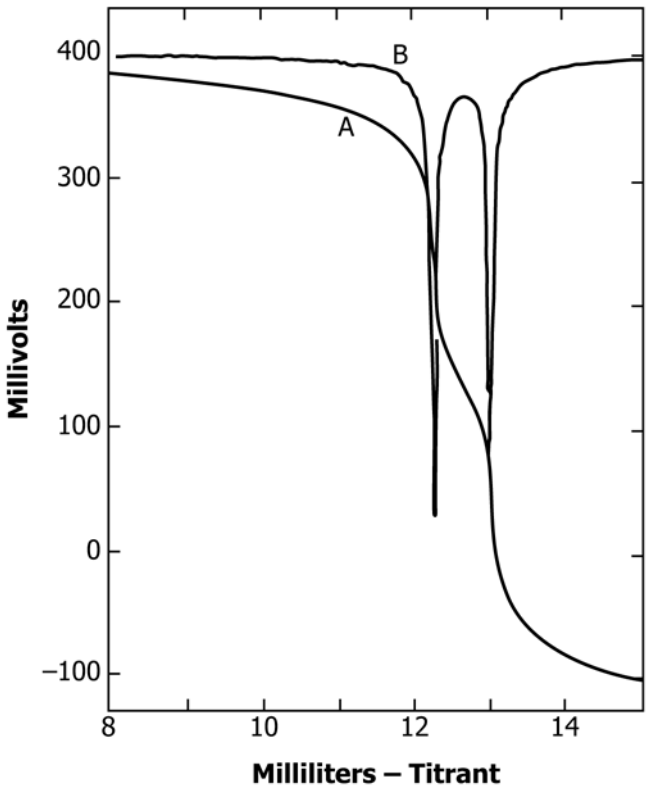
Current edition approved Jan. 1, 2017. Published February 2017. Originally approved in 1987. Last previous edition approved in 2009 as D4711-89(2009). DOI: 10.1520/D4711-89R17.

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

[4] Metrohm A436, or its equivalent, has been found suitable for this purpose. Available from Brinkman Instruments.

[5] J. T. Baker No. 4898, or its equivalent, has been found suitable for this purpose. Available from Sargent-Welch Scientific Co., 7300 Linder Ave., PO Box 1026, Skokie, IL 60077.



Solvent. Methanol
Titrant. 0.1 *N* Cyclohexylamine
A. Differentiating titration curve
B. First derivative curve of the curve A

FIG. 1 Titration of a detergent intermediate containing alkyl sulfonic acid and sulfuric acids.

8. Standardization of 0.10 *N* Cyclohexylamine

8.1 All standardizations should be run in triplicate. This means separate weighings for solution preparations in 8.2.

8.2 Using an analytical balance, accurately weigh 0.10 to 0.12 g of sulfamic acid to the nearest 0.1 mg into a 180 mL tall form beaker. Dissolve in 100 mL of anhydrous methanol. Mix well.

8.3 Titrate with 0.10*N* cyclohexylamine using the combination electrode on the automatic titrator until the complete development of a single break. Record the mL at the inflection point.

8.4 Calculate the normality of the cyclohexylamine solution as follows:

$$\text{Normality of Cyclohexylamine} = (G)(1000)/(M)(97.09) \quad (1)$$

where:

G = grams of sulfamic acid, and
M = mL of cyclohexylamine to inflection point.

9. Procedure

9.1 Using an analytical balance, accurately weigh 1.2 to 1.5 meq to the nearest 0.1 mg of sample directly into a 180 mL tall form beaker. Sample size may be calculated from the following:

$$\text{Grams sample} = 1.35 \text{ meq/meq/g acidity expected} \quad (2)$$

NOTE 1—Most detergent range alkylbenzene sulfonic acids have a total acidity of about 3.35 meq/g meaning that the sample weight should be about 0.35 to 0.45 g. This yields a total titer of about 12 to 15 mL of 0.10 *N* cyclohexylamine and a difference of about 0.45 to 0.68 mL between the two breaks for a sample containing about 1.25 % sulfuric acid.

9.2 Add a magnetic stirring bar, 100 mL of anhydrous methanol, and stir with a magnetic stirrer until dissolved.

9.3 Titrate potentiometrically on the automatic titrator using the combination electrode until a curve yielding two breaks is obtained. (See Fig. 1.)

9.4 Record the volume of titrant to the first break as V_1, and that to the second break V_2.

10. Calculation

10.1 Calculate the weight percent sulfuric acid (H_2SO_4) and weight percent sulfonic acid (RSO_3 H) as follows:

$$\%\ H_2SO_4 = (V_2 - V_1)(N)(98.08)(100)/(W)(1000) \quad (3)$$

$$\%RSO_3H = (2V_1 - V_2)(N)(MW)(100)/(W)(1000) \quad (4)$$

where:

V_1, V_2 = millilitres of titrant at the first and the second end points respectively.
N = normality of titrant,
W = sample weight, g, and
MW = average equivalent weight of sulfonic acid.

11. Precision and Bias[6,7]

11.1 *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 0.03 % absolute at 14 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.08 % absolute.

11.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.05 % absolute at 13 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.16 % absolute.

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

SULFONIC ACID PERCENT

11.4 *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 14 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.48 % absolute.

11.5 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be

[6] Supporting Data on file at ASTM Headquarters. Request RR:D12-1009.
[7] Practice E180 was used to determine precision and bias.

0.36 % absolute at 13 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 1.1 % absolute.

11.6 *Checking Limits for Duplicates*—Report the active content of the sample to the nearest 0.01 %. Duplicate runs that agree within 0.45 % are acceptable for averaging (95 % confidence level).

11.7 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, no statement on bias is being made.

NOTE 2—The precision data were derived from results of cooperative tests by sixteen laboratories on a linear alkylbenzene sulfonic acid having an average equivalent weight of 318.

12. Keywords

12.1 alkylbenzene sulfonic acid; sulfonic acid; sulfuric acid; titration