Designation: D 6174 – ~~97~~01

Standard Test Method for Inorganic Sulfate in Surfactants by Potentiometric Lead Titration[1]

This standard is issued under the fixed designation D 6174; 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 describes a potentiometric titration procedure for determining the inorganic sulfate content of surfactants. It is intended for the analysis of α-olefin sulfonates, alkane sulfonates, alcohol sulfates, alcohol ether sulfates, alkylbenzenesulfonates, and the like.

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

2. Referenced Documents

2.1 *ASTM Standards:*

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[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 of Soaps and Synthetic Detergents.

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D 1193 Specification for Reagent Water[2]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *inorganic sulfate*, *n*—sulfate species present as sulfuric acid, ionic salts of this acid, or mixtures of these.

4. Summary of Test Method

4.1 A surfactant sample containing inorganic sulfate is titrated in ethanolic medium with a standard lead solution. Lead sulfate precipitate is formed during the titration. Ethanol and sodium perchlorate are present to decrease the solubility of lead sulfate, thus sharpening the endpoint. Acetic acid is added to remove possible interference from carbonate. The endpoint is signaled by an increase in lead ion activity, as measured by a lead-selective electrode.

5. Significance and Use

5.1 Anionic surfactants, such as those listed in 1.1, commonly are used in detergent formulations. Their acceptability for use depends on their purity. Sulfate content, as measured by this test method, can be used to estimate the purity of an anionic surfactant under test.

6. Apparatus

6.1 *Potentiometric Titration Assembly*, consisting of an automatic titrator fitted with a lead ion-selective electrode, a double-junction reference electrode, and a 10-mL buret. The reference electrode should be filled with the standard inner and outer filling solutions supplied with it. A TFE-fluorocarbon-coated magnetic stirring bar should be used for mixing during titration, with a separate magnetic stirring motor if the autotitrator is not so equipped.

NOTE 1—Proper care of the lead-selective electrode is essential for obtaining high-quality titration curves. Follow manufacturer's instructions.

7. Reagents

7.1 *Glacial Acetic Acid*.

7.2 *Lead Nitrate*, reagent grade.

7.3 *Sodium Sulfate*, anhydrous, reagent grade.

7.4 *Sodium Perchlorate*, reagent grade.

7.5 *Ethanol*, denatured, formula 3A.

7.6 *Water*, Type III reagent water conforming to Specification D 1193.[3]

8. Preparation of Standard Solutions

8.1 *10 % Acetic Acid*—Dilute glacial acetic acid 1/10 with water.

8.2 *Lead Titrant, 0.05 M*—Dissolve 16.6 g lead nitrate in 300 mL water. Pour into a 1-L bottle and fill with 3A ethanol. Mix well. Standardize according to 9.1.

8.3 *Sulfate Standard, 0.05 M*—Dry 5 g anhydrous sodium sulfate at 110°C for 1 h. Accurately weigh about 3.5 g into a 500-mL volumetric flask, dilute to volume with water, and mix to dissolve. Calculate the exact concentration as follows:

$$\frac{G}{(142.02)(0.500)} = \text{Molarity} \tag{1}$$

where:

G = weight in grams of Na_2SO_4 dissolved in the 500 mL and 142.02 is its gram molecular weight.

8.4 *Ethanolic Sodium Perchlorate, 0.05 M*—Dissolve approximately 7 g sodium perchlorate in 300 mL water. Pour into a 1-L bottle, fill with 3A ethanol, and mix well.

9. Standardization

9.1 The exact concentration of the lead titrant shall be determined experimentally by titration of the sulfate standard of 8.3. Pipet 5.00 mL sulfate standard solution into a 50-mL beaker. Add approximately 20 mL ethanolic sodium perchlorate solution and approximately 1 mL 10 % acetic acid. Prepare the autotitrator for operation, immerse the electrodes in the titration solution, and titrate to the potentiometric endpoint with lead titrant.

9.2 The standardization should be repeated until satisfactory precision has been achieved. Calculate the concentration of the lead titrant as follows:

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

[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.

$$\frac{(V)(S)}{T} = M_{lead} \tag{2}$$

where:
V = mL of sulfate standard solution added,
S = molarity of the sulfate, and
T = average mL of lead titrant.

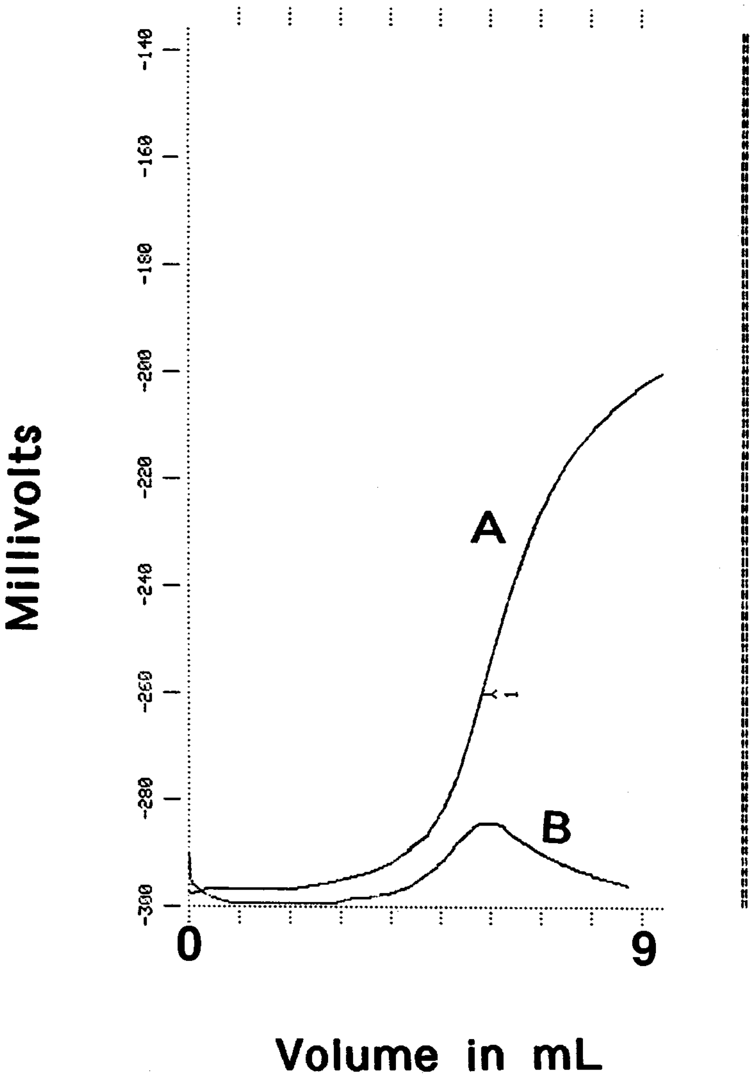
10. Analysis

10.1 The sample should be well mixed to ensure homogeneity. A representative portion shall be taken for analysis.

10.1.1 For inhomogeneous materials, it may be best to dissolve a large sample, for example 50 g, in a known volume and take an aliquot for titration.

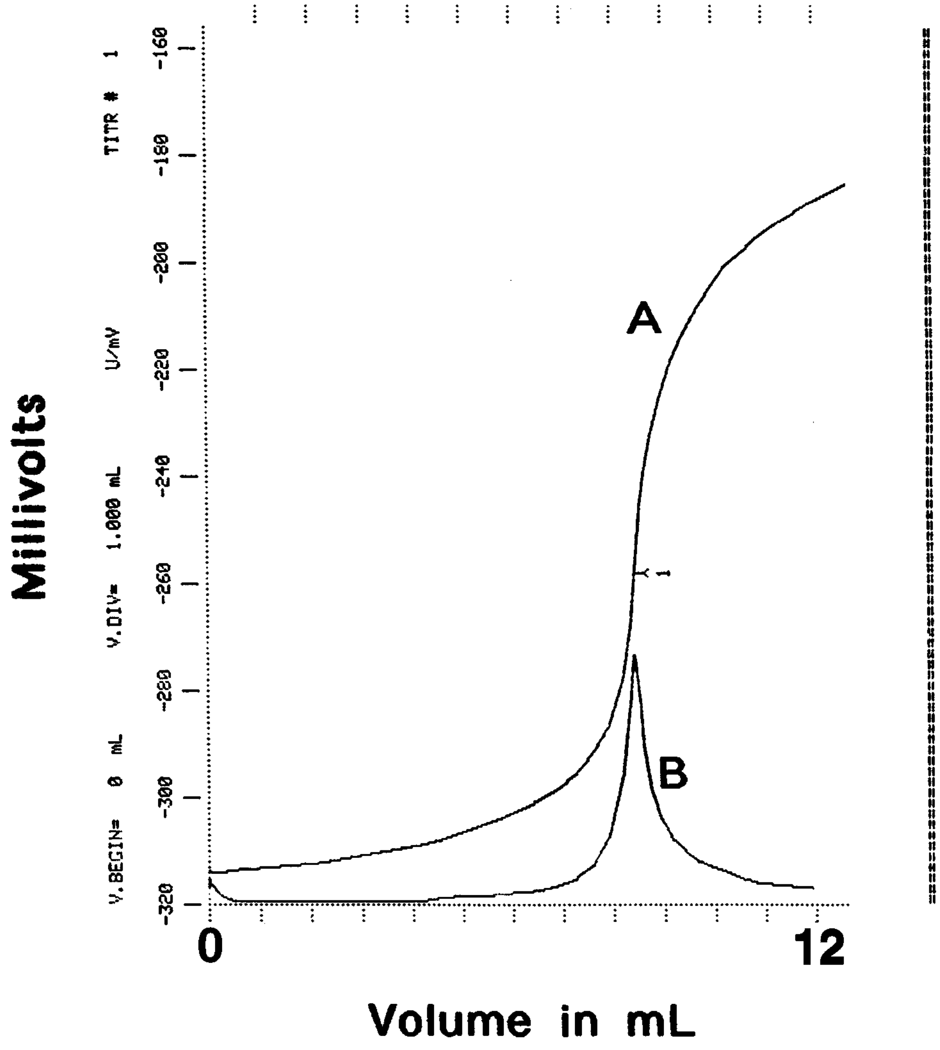
10.2 Transfer a portion of test surfactant, equivalent to 30–50 mg sodium sulfate, to a 50-mL beaker. For example, if a surfactant is expected to contain 1 % sodium sulfate, weigh 3–5 g to analytical precision into the beaker, or an equivalent aliquot from 10.1.1. Add approximately 20 mL ethanolic sodium perchlorate and approximately 1 mL 10 % acetic acid. Prepare the autotitrator for operation, immerse the electrodes in the titration solution, and titrate to the potentiometric endpoint with lead titrant. Typical titration curves are shown in Fig. 1 and Fig. 2. The titration should be repeated until satisfactory precision has been achieved.

NOTE 2—The sample should be acidic to pH paper before titrating. If 1 mL 10 % acetic acid is insufficient to achieve this, more acid should be added.



A = titration curve
B = first derivative curve of Curve A

FIG. 1 Sample: Sodium Alpha Olefin (C-14, 16) Sulfonate



A = titration curve
B = first derivative curve of Curve A

FIG. 2 Sample: Sodium Alkylbenzene (C-12) Sulfonate

11. Calculation

11.1 Calculate the inorganic sulfate content of the surfactant sample as follows:

$$\frac{(V)(M)(F)}{(G)(D)} = wt\ \%\ \mathrm{Na_2SO_4} \tag{3}$$

where:
V = mL lead titrant,
M = molarity of lead titrant,
F = factor, (11.1.1),
G = weight in grams of surfactant sample taken for analysis, and,
D = dilution factor, if any, from 10.1.1.

11.1.1 The calculation factor *F* depends on the way the result is to be expressed. To express as wt % sodium sulfate, $F = 14.202$; for other expressions, use F = (mol wt)/10.

12. Precision

12.1 The precision of this test method was evaluated by interlaboratory analysis of surfactant samples containing five different sulfate levels. The collected data are displayed in Table 1 ($r = 2.8S_r$, $R = 2.8S_R$).

TABLE 1 Repeatability and Reproducibility

	Sulfate Level (wt %)	r (wt %)	R (wt %)
	~~0.14~~	~~0.011~~	~~0.015~~
Sodium Lauryl Sulfate	0.14	0.011	0.015
	~~0.22~~	~~0.018~~	~~0.024~~
Sodium Lauryl Ether (3 mol E0) Sulfate	0.22	0.018	0.024
	~~0.95~~	~~0.061~~	~~0.067~~
Sodium Alkylbenzene (C-12) Sulfonate	0.95	0.061	0.067
	~~1.05~~	~~0.053~~	~~0.072~~
Sodium Alphaolefin (C–14,16) Sulfonate	1.05	0.053	0.072
	~~1.57~~	~~0.020~~	~~0.026~~
Sodium Octane Sulfonate	1.57	0.020	0.026

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