Designation: D4936 – 10 (Reapproved 2019)

Standard Test Method for Mercaptobenzothiazole Sulfenamide Assay by Reduction/Titration[1]

This standard is issued under the fixed designation D4936; 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 assay on mercaptobenzothiazole (MBT) sulfenamides. It is based on a titration of the basic amines liberated upon reduction of the sulfenamides with hydrogen sulfide gas (H_2S)[2,3] or 2-mercaptobenzothiazole.

1.2 Any free amine (HNR_2) or weak acid salts of the corresponding amine ($HX{\cdot}HNR_2$) are titrated prior to reduction. This titer is used to calculate percent basic impurity (as free amine) in the sample.

1.3 With the indicated modifications, this test method is applicable to all MBT sulfenamides, that is, *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS), *N,N*-diisopropyl-2-benzothiazyl sulfenamide (DIBS), 2 (morpholinothio) benzothiazole (MBS), *N,N*-dicylohexyl-2-benzothiazyl sulfenamide (DCBS), *N-tert*-butyl-benzothiazole-sulfenamide (TBBS), and 4-morpholinyl-2-benzothiazyl disulfide (MBSS).

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *IpOH/Tol solvent, n*—titration solvent containing five volumes isopropanol and three volumes toluene.

3.1.2 *"lot" sample, n*—a production sample representative of a standard production unit.

3.1.3 *potassium hydrogen phthalate acidimetric standard, n*—Fisher P-243.[5]

3.1.4 *primary titrant, n*—0.25 to 0.30 *N* aqueous hydrochloric acid (HCl).

3.1.5 *reducing solution, n*—IpOH/Tol solvent saturated with hydrogen sulfide gas (H_2S) at 25°C (about 1.1 g H_2S/100 mL solvent).

3.1.6 *test unit, n*—the actual material used in the analysis. It must be representative of the "lot" sample.

3.2 *Abbreviations:*

3.2.1 THAM—tris (hydroxymethyl) aminomethane alkalimetric standard (Fisher T-395).[3]

4. Summary of Test Method

4.1 *Procedure A*—For CBS, TBBS, MBSS, MBS-90, and MBS, a weighed specimen is dissolved in the appropriate solvent, the "free amine" blank is titrated with standard acid, and the sulfenamide is reduced with H_2S. That is,

$$BtSNR_2 + H_2S \rightarrow BtSH + HNR_2 + S \quad (1)$$

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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[2] Goodyear Paper, Industrial and Engineering Chemistry Production Research and Development, Vol 2, 1963, p. 16.

[3] *Elastomerics*, August 1981, pp. 34–44.

[4] 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.

[5] The sole source of supply of the apparatus known to the committee at this time is Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219. 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.

where:

Bt = the 2-benzothiazole radical.
BtSH = 2-mercaptobenzothiazole.
HNR_2 = free amine.

The liberated amine is then titrated with standard acid to an indicator end point.

4.2 *Procedure B*—For sulfenamides of hindered amines (DIBS and DCBS), it is necessary to measure the liberated amine by back titration at 40 to 45°C. Excess hydrochloric acid (HCl) is added, then back titrated with standard sodium hydroxide (NaOH).

4.3 *Procedure C*—This alternative is appropriate for all sulfenamides. A weighed specimen is dissolved in ethanol, the "free amine" blank is titrated with standard acid, and the sulfenamide reduced with MBT. That is,

$$BtSNR_2 + BtSH \rightarrow BtSSBt + HNR_2 \quad (2)$$

where:

BtSSBt = benzothiazole disulfide.

The liberated amine is captured in a known amount of standard acid and the excess acid back titrated with standard sodium hydroxide.

5. Significance and Use

5.1 This test method is designed to assess the purity of 2-mercaptobenzothiazole sulfenamide accelerators. These products are used in combination with sulfur for the vulcanization of rubber.

5.2 The test method is suitable for assessing product specifications in that the property it measures is related to product performance. Since it is the primary property for comparison of product quality at different production facilities, good interlaboratory accuracy and precision is required.

5.3 Based on past experience, two significant sources of error in this test method are: (*1*) incomplete reduction and (*2*) titration end point assessment. Problems in these areas can be avoided by closely following the procedure.

6. Interferences

6.1 Theoretically, any material that is reduced to an acid titratable entity will be measured by this test method. Extensive high-pressure liquid chromatograph (HPLC) analysis of sulfenamides indicates that the most significant interfering impurity is the corresponding sulfinamide, $BtSONR_2$.

6.2 The corresponding sulfonamide, $BtSO_2NR_2$, is present in some samples, but it does not reduce under the analytical conditions.

7. Apparatus

7.1 *Standard Laboratory Glassware and Equipment.*

7.2 *Buret,* 10 cm^3, Class A, graduated in 0.05 cm^3 increments.

7.3 *Buret,* 25 cm^3, Class A, graduated in 0.05 cm^3 increments.

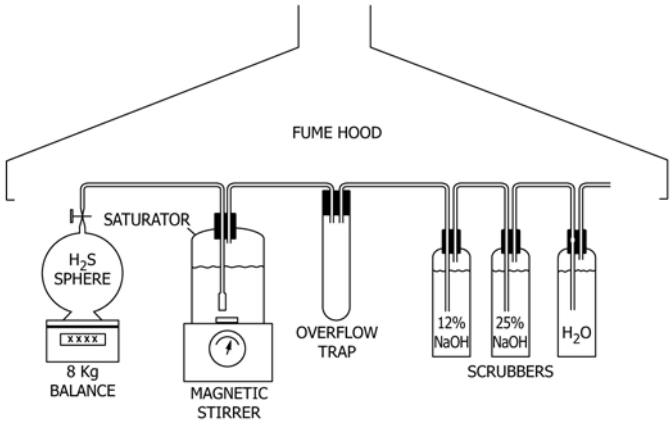

FIG. 1 H_2S Saturation Assembly

7.4 *Buret,* 50 cm^3, Class A, graduated in 0.10 cm^3 increments.

7.5 *Pipet,* 2 cm^3, Class A, graduated in 0.1 cm^3 increments.

7.6 *Pipet,* 25 cm^3, Class A.

7.7 *Hydrogen Sulfide Lecture Sphere* (99.5 % purity),[5] is preferred for convenience, ease, and correctness of saturated solution preparation. Lecture bottles or larger H_2S containers are acceptable, but means should be developed to establish amount used in preparing a saturated solution.

7.8 *H_2S Trap Train,* 1 dm^3 NaOH (12 %) followed by 1 dm^3 NaOH (25 %) followed by a 1 dm^3 water trap (see Fig. 1).

7.9 *Platform Balance,* 8000 g, for weighing the H_2S cylinder to the nearest 1 g.

7.10 *Magnetic Stirrer.*

7.11 *Gas Dispersion Tube,* 12 × 250 mm stem, 40-60 µm pore size; 12C.

7.12 *Gas Valve,* for H_2S cylinder, stainless steel, GCA 110 inlet (fits lecture sphere on lecture bottles).

7.13 *pH Meter* with a sensitivity of 0.1 pH unit with a glass measuring electrode and a calomel reference electrode.

7.14 *Bath,* thermostatically controlled.

7.15 *High Precision Balance,* for weighing specimen to nearest 0.1 mg.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used,

[6] *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.

provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Bromophenol Blue Indicator Solution*—Bromophenol blue (BPB) in isopropanol, 1 % mass⁄volume (Procedure A and B). Bromophenol blue (BPB) in ethanol, 1 % weight/volume (Procedure C).

8.3 *Hydrochloric Acid* (0.25 to 0.30 *N*)—Aqueous hydrochloric acid (HCl) titrant, prepared in an acid carboy (2 dm^3 or more).

8.4 *Hydrochloric Acid* (0.1 *N*)—Aqueous HCl titrant.

8.5 *Hydrochloric Acid* (0.5 *N*)—Aqueous HCl (Procedures B and C).

8.6 *Isopropanol-Toluene Solvent* (IpOH/Tol)—Mix five volumes reagent grade isopropanol with three volumes reagent grade toluene.

8.7 *Phenolphthalein Indicator Solution*—Phenolphthalein in isopropanol, 1 % mass⁄volume.

8.8 *Potassium Hydrogen Phthalate Acidimetric Standard*—Fisher P-243[3] (Procedure B). Store in a desiccator at room temperature.

8.9 *Reducing Solution*—IpOH/Tol solvent saturated with H_2S at room temperature (see 12.1 for saturation procedure).

8.10 *Sodium Hydroxide* (0.25 to 0.3 *N*)—Aqueous sodium hydroxide (NaOH) (Procedure B).

8.11 *Aqueous NaOH* (0.5 *N*)—Procedure C.

8.12 *THAM Alkalimetric Standard*—Fisher T-395.[3] (Store in desiccator at room temperature.)

8.13 *Absolute ethanol.*

8.14 *2-mercaptobenzothiazole (MBT)*, min 99 %—Weigh 4 g MBT to the nearest 0.1 g in a 100 cm^3 volumetric flask, dissolve in absolute ethanol with warming and dilute to volume with absolute ethanol.

8.14.1 Prepare sufficient volume of reagent for the number of tests anticipated at the time.

9. Hazards

9.1 Hydrogen sulfide is a toxic gas and should only be handled in a laboratory hood. (The American Conference of Government Industrial Hygienists gives 14 mg/m^3 as the time weighted average-threshold limit values (TWA-TLVs) and 21 mg/m^3 as the short-term exposure limit (STEL).[7])

9.2 The prescribed traps should be used for "catching" unused H_2S when preparing the reagent. Also, all solutions (after completion of test) should be quenched with 10 % NaOH and discarded in a container maintained in the hood. The glassware should then be rinsed with additional caustic solution before being removed from the hood.

9.3 Toluene and isopropanol, with TLVs of 200 mg/kg (ppm) and 400 mg/kg (ppm), respectively, and high flammability, should be handled with appropriate precaution.

9.4 Good laboratory safety practices should be followed in handling all chemicals and carrying out manipulations.

10. Sampling

10.1 To ensure sample homogeneity, a minimum of 10 g of a "lot" sample should be ground with a mortar and pestle. (This is not necessary for analytical standards.) The test unit (2 g) should be taken from this composite.

11. Calibration and Standardization

11.1 As is the case with any titration method, it is extremely important that the titrants be accurately standardized. The organic base THAM is used as the primary standard since it is soluble in the isopropanol-toluene solvent and has an equivalence point at essentially the same pH as the amines being titrated (see Appendix X1).

11.2 The primary titrant (0.25 to 0.30 *N* HCl) is prepared by diluting concentrated HCl (12 *N*) 44 to 1 with water. To prepare 2 dm^3 , add 45 cm^3 concentrated HCl to a 2-dm^3 container partially filled with deionized water and dilute to volume with additional water. Mix thoroughly before standardization.

11.3 Weigh 1.3 to 1.5 g THAM to the nearest 0.1 mg in a 250 cm^3 Erlenmayer flask, dissolve in 10 cm^3 of water, and add 150 cm^3 IpOH/Tol solution. Add five drops of indicator and titrate with the primary titrant to the green (pH 4). This is the point where the green hue is approaching yellow (see Fig. 2).

11.4 An illustration of the color changes, as a function of pH near the end point, is presented in Appendix X1. This should be carefully reviewed with each individual carrying out the test.

11.5 Also note that the rate of titrant addition should be slowed progressively as the end point is approached. When the blue-green is initially detected (pH 5), the addition increments should be no more than about 0.1 cm^3 (two drops).

11.6 The normality, *N*, of the primary titrant is calculated as follows:

$$N = \frac{T}{(V_{HCl})\,(0.12114)} \tag{3}$$

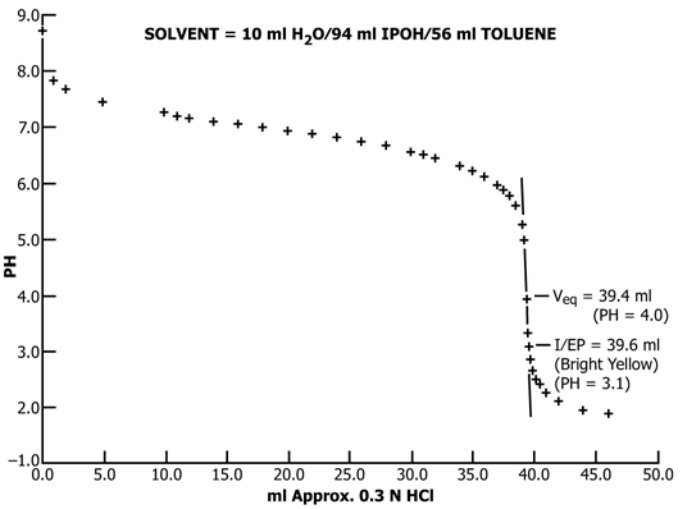

FIG. 2 Titration of 1.3755 g THAM

[7] American Conference of Government Industrial Hygienists, 1980.