Designation: D4936 – 10 (Reapproved 2015)

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

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,

$$BtSNR_2 + H_2S \rightarrow BtSH + HNR_2 + S \tag{1}$$

where:

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

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[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber 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.

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,

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

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.

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.

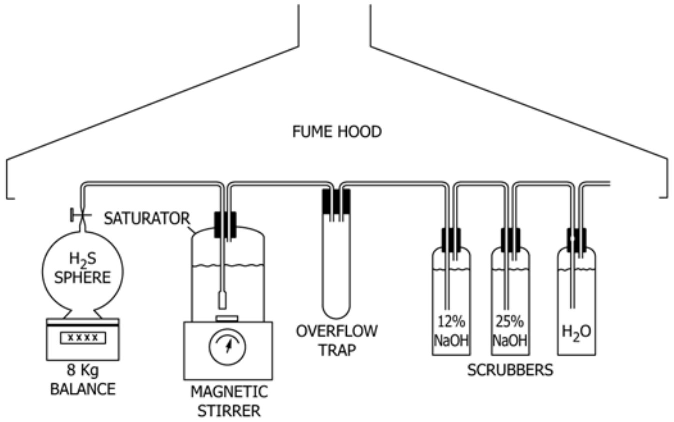

FIG. 1 H_2S Saturation Assembly

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, 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).

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[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.

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 Erlenmeyer 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:

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

where:

T = mass of THAM, g,
V_{HCl} = volume of HCl, cm^3, and
0.12114 = equivalent mass of THAM divided by 1000.

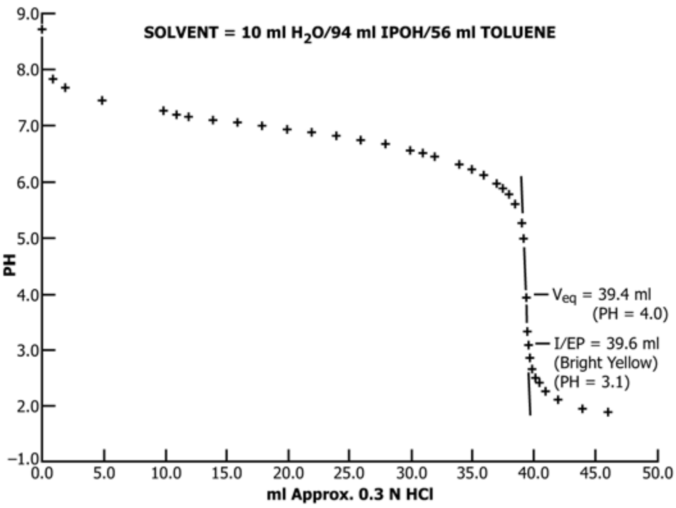

FIG. 2 Titration of 1.3755 g THAM

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

The titrant normality, *N*, should be assigned as the average of at least three replicates that check within 0.0004 *N*. (Run additional standards for those outside this range.)

11.7 The secondary titrant (0.1 *N* HCl) should be standardized in a similar manner but using only 0.1 to 0.2 g THAM. Although care is needed in standardizing this solution, it is much less critical than the primary titrant. (It is also acceptable to prepare the secondary titrant by quantitative dilution of the primary titrant, thus saving standardization time.)

11.8 When using Procedure B, it is necessary to prepare and standardize aqueous NaOH (0.3 *N*) and aqueous HCl (0.5 *N*) solutions.

11.8.1 Dissolve 12 g NaOH pellets in 1 dm^3 of water to prepare 0.3 *N* NaOH. To standardize, weigh, to nearest 1 mg, about 2.3 g of potassium hydrogen phthalate, dissolve in 100 cm^3 water, add three drops phenolphthalein indicator, and titrate with NaOH to phenolphthalein end point.

11.8.2 Prepare 0.5 *N* HCl by diluting concentrated HCl (12 *N*) 25 to 1 with water. Standardize as in 11.3.

11.8.3 When using Procedure C, it is necessary to prepare and standardize aqueous NaOH (0.5 *N*) in addition to the HCl (0.1 *N* and 0.5 *N*) described in 11.7 and 11.8.2 respectively. Dissolve 20 g NaOH pellets in 1 dm^3 water and standardize as in 11.8.1.

12. Procedure

12.1 *Preparation of Reducing Solution*—Just prior to use, prepare enough solution to analyze the number of samples anticipated by the following procedure. Set up the apparatus shown in Fig. 1 in a high draft hood. Sparge 15 g of H_2S per litre of IpOH/Tol solvent at a rate of approximately 0.5 g/min at room temperature. Stir the solution continuously until saturation is achieved. This condition is indicated by an increase in bubble rate and size in the solvent as well as greater "activity" in the first caustic trap. The measured solubility of H_2S in IpOH/Tol is 1.08 g/100 cm^3 at 25°C. If the H_2S is fed by weight (or volume) and this solubility factor is kept in mind, complete saturation will always be achieved. (Incomplete saturation is a major cause of bad results by this test method.)

12.2 Store the reducing solution loosely capped at a temperature 25°C. In the event that it will not be used immediately, cool to 5°C below saturation temperature by storing in a water bath. At the conclusion of the analysis set, discard unused solution by quenching in 10 % caustic. (Although it may be acceptable to resaturate solution and use later, it becomes difficult to be assured that saturation is achieved.)

12.3 *Procedure A*—This procedure is for CBS, TBBS, MBSS, and MBS.

12.3.1 Prepare the sample according to 10.1 and weigh the test unit (2.0 g to nearest 0.1 mg) into a 250 cm^3 Erlenmeyer flask. Add a magnetic stirring bar and cap flask with a loose fitting rubber stopper.

12.3.2 Add 50 cm^3 IpOH/Tol, stopper, and dissolve by "slowly" stirring on a magnetic stirrer or periodic swirling. (Take care not to splash solids onto the sides of the flask.) Allow at least 10 min for this step to ensure that all sulfenamide is dissolved. (MBTS in a degraded or otherwise low quality sample may not dissolve entirely.)

12.3.3 Add five drops of bromophenol blue (BPB) indicator and titrate the excess base with 0.1 *N* HCl to the BPB "first" yellow end point (EP). This generally only requires a few drops (<0.5 cm^3), and it should be done as quickly as possible since sample hydrolysis can occur (fading EP), particularly on poor quality samples. In cases of fading EPs, stop the titration at the first detection of EP color and add the reducing solution immediately.

12.3.4 Record the volume of 0.1 *N* HCl as V_{FA} and use it in calculation in 13.1.1.

12.3.5 Immediately after neutralizing the excess base, add 125 cm^3 of the reducing solution, replace the stopper, and set aside for a minimum of 90 min at 25 to 30°C to complete the sulfenamide reduction. (If the sample is completely in solution, no agitation is needed.)

NOTE 1—A longer reduction period should not adversely affect the results. Completely reduced samples will generally be wine or rust in color.

12.3.6 While stirring rapidly with a magnetic stirrer, titrate the liberated amine with the primary titrant to the green EP (pH 4.0). As described in 11.3, this is the point where the green hue is approaching yellow. The rate of titrant addition should be slowed progressively as the EP 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).

NOTE 2—Two drops of additional indicator added near the end point will intensify the color change.

12.3.7 Record the volume of primary titrant as V_A and use in the calculations in 13.1.2.

12.3.8 With occasional samples, the end point may appear to fade. This can be caused by incomplete reduction or very impure samples. If the fading end point is still observed on repeat analysis, record the initial volume to the desired color and report the observation.

12.3.9 Discard waste solutions in accordance with 9.2.

12.4 *Procedure B*—This modification is for DIBS and DCBS.

12.4.1 Follow Procedure A steps 12.3.1 – 12.3.5 and record V_{FA} for calculation of free amine content.

12.4.2 After adding saturated H_2S and allowing to stand for 1 h, neutralize the generated amine by quantitatively adding (pipet or buret) 20 cm^3 of 0.5 *N* HCl. (The color will change from dark blue to bright yellow.)

12.4.3 Warm the sample to 40 to 45°C on a stirring hotplate and titrate the excess HCl with 0.3 *N* NaOH to the yellow-green end point. (Since this is a back titration, the color will change from yellow to yellow-green to green to blue as one titrates beyond the end point.)

12.5 *Procedure C—Use of MBT as Reducing Agent:*

12.5.1 Prepare the sample according to 10.1 and weigh the test unit (2.0 g to nearest 0.1 mg, 1.6 g in case of TBBS) into a 250 cm^3 beaker, dissolve in 50 cm^3 ethanol; if turbid warm to 55°C and allow to cool. Add three drops of bromophenol blue indicator and titrate the free amine with 0.1 *N* HCl to the blue-green endpoint.

12.5.2 Record the volume of 0.1 N_{HCl} as V_{FA} for use in calculation 13.3.1.

12.5.3 Immediately after neutralizing the free amine, add 50 cm^3 of the alcoholic solution of MBT followed by 25 cm^3 (V_{HCl}) of 0.5 N_{HCl}.

12.5.4 Agitate with a magnet stirrer in a thermostatically controlled bath at 55°C for 5 min.

12.5.5 Titrate with 0.5 *N* NaOH potentiometrically. As the equivalence point approaches add the titrant in small (0.1 cm^3) increments allowing at least 20 seconds for equilibration.

12.5.6 Determine the end point graphically and record the volume of 0.5 N_{NaOH} as V_{NaOH}. Use this value in calculation 13.3.2.

12.5.7 The ethanol may be replaced by the isopropanol/toluene. In this case, instead of the glass electrode, use the bromophenol blue solution as indicator.

13. Calculation

13.1 *Procedure A:*

13.1.1 Determine the percent free amine content, *FA*, as follows:

$$FA = \frac{V_{FA}N_{HCl}\,M_A}{S} \times 100 \tag{4}$$

where:

V_{FA} = volume of 0.1 N_{HCl} from 12.3.4, cm^3,
N_{HCl} = normality of HCl,
S = test unit mass, g, and
M_A = for:
CBS 0.0991
TBBS 0.0731
MBS 0.0871
MBSS 0.0871

13.1.2 Determine the percent assay, *A*, as follows:

$$A = \frac{V_A N_{HCl} M_S}{S} \times 100 \tag{5}$$

where:

V_A = volume of primary titrant, cm$^{3,\text{ and}}$
M_S = for:
CBS 0.2644
TBBS 0.2384
MBS 0.2524
MBSS 0.2844

13.2 *Procedure B:*

13.2.1 Determine the percent free amine content as follows:

$$FA = \frac{V_{FA}N_{HCl}M_A}{S} \times 100 \tag{6}$$

where:

M_A = for:
DIBS 0.1012
DCBS 0.1813

13.2.2 Determine the percent assay, *A*, as follows:

$$A = \frac{(V_{HCl}N_{HCl} - V_{NaOH}N_{NaOH})M_S}{S} \times 100 \tag{7}$$

where:

V_{HCl} = volume of HCl, cm^3,
V_{NaOH} = volume of NaOH, cm^3,
N_{NaOH} = normality of NaOH solution, and
M_S = for:
DIBS 0.2664
DCBS 0.3464

13.3 *Procedure C:*

13.3.1 Determine the percent free amine content, *FA*, as follows:

$$FA = \frac{V_{FA}\,N_{HCl}\,M_A}{S} \times 100 \tag{8}$$

where:

V_{HCl} = volume of 0.1 N_{HCl} from 12.5.2,
N_{HCl} = normality of 0.1 N_{HCl},
S = specimen mass, g
M_A = 0.0991 (CBS)
0.0731 (TBBS)
0.0871 (MBS)
0.1813 (DCBS)
0.1012 (DIBS)

13.3.2 Determine the percent assay, *A*, as follows:

$$A = \frac{(V_{HCl}\,N_{HCl} - V_{NaOH}\,N_{NaOH})\,M_S}{S} \times 100 \tag{9}$$

where:

V_{HCl} = volume of 0.5 N_{HCl} from 12.5.3 (25 cm^3),
N_{HCl} = normality of 0.5 N_{HCl},
V_{NaOH} = volume of 0.5 N_{NaOH} from 12.5.6,
N_{NaOH} = normality of 0.5 N_{NaOH},
S = specimen mass, g
M_S = 0.2644 (CBS)
0.2384 (TBBS)
0.2524 (MBS)
0.3464 (DCBS)
0.2664 (DIBS)

14. Report

14.1 Report the following information:

14.1.1 Identification of the sulfenamide accelerator tested.

14.1.2 Free amine content to the nearest 0.01 %.

14.1.3 Assay to the nearest 0.1 %.

14.1.4 Procedure used (A, B, or C).

14.1.5 Test data from individual titrations plus their average.

14.1.6 Any deviations from the standard.

15. Precision and Bias

15.1 This precision and bias section has been prepared in accordance with Practice D4483. Refer to Practice D4483 for terminology and other statistical calculation details.

15.1.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (rubbers) used in the particular interlaboratory programs as described below. The precision parameters should not be used for acceptance/rejection testing of a group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

15.2 A Type 1 (interlaboratory) precision was evaluated in 1988. Both repeatability and reproducibility are short term. A period of a few days separates replicate test results. A test result is the mean value, as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

15.3 An analysis for free amine and assay (percent active material) was conducted using two test procedures, A and B. For Procedure A, three different materials were used in the interlaboratory program. These were tested in six laboratories on two different days.

15.4 For Procedure B, two materials were tested in five laboratories on two different days. The results of the precision calculations for repeatability and reproducibility are given in Table 1 and Table 2 in ascending order of material average or level, for each of the materials evaluated, for each analysis parameter and for each test procedure.

15.5 The precision of this test method may be expressed in the format of the following statements which use what is called an "appropriate value" of *r, R*, (*r*) or (*R*), that is, that value to be used in decisions about test results (obtained with the test method). The *appropriate value* is that value of *r* or *R* associated with a mean level in Table 1 and Table 2 closest to the mean level under consideration at any given time, for any given material, analysis procedure, and test method in routine testing operations.

15.6 *Repeatability*—The repeatability, *r*, of this test method has been established as the *appropriate value* tabulated in Table 1 and Table 2. Two single test results, obtained under normal test method procedures, that differ by more than this tabulated *r* (for any given level) must be considered as derived from different or nonidentical sample populations.

15.7 *Reproducibility*—The reproducibility, *R*, of this test method has been established as the *appropriate value* tabulated in Table 1 and Table 2. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated *R* (for any given level) must be considered to have come from different or nonidentical sample populations.

15.8 Repeatability and reproducibility expressed as a percent of the mean level, (*r*) and (*R*), have equivalent application statements as above for *r* and *R*. For the (*r*) and (*R*) statements, the difference in the two single test results is expressed as a percent of the arithmetic mean of the two test results.

15.9 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias, therefore, cannot be determined.

15.10 For Procedure C, the precision and bias data was obtained in an interlaboratory test organized in France in 1988. In this program one material was analyzed by eight different laboratories. Three measurements were taken over two days and the measurement protocol repeated after a one week interval. The results from this precision and bias study are given in Table 3.

16. Keywords

16.1 accelerator; assay; mercaptobenzothiazole; *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS); *N*-dicyclohexyl2-benzothiazyl sulfenamide (DCBS); *N*-diisopropyl-2benzothiazyl sulfenamide (DIBS); *N-tert*-butyl-benzothiazole sulfenamide (TBBS); sulfenamide; 2-(morpholinothio) benzothiazole (MBS); 4 morpholinyl-2-benzothiazyl disulfide (MBSS)

TABLE 1 Type 1 Precision Percent Active Material Assay—Procedure A

Material	Average	Within Laboratory[A]			Between Laboratory[A]		
		S_r	*r*	(*r*)	S_R	*R*	(*R*)
4—MBSS	93.23	0.8155	2.3078	2.475	0.8155	2.3078	2.475
5050 CBS/TBBS	97.48	0.4266	1.2073	1.239	0.8610	2.4367	2.500
2—MBS	95.72	0.5158	1.4596	1.525	0.6791	1.9217	2.008
Pooled values[B]	93.61	0.5688	1.6096	1.720	0.7287	2.0622	2.203

[A]

S_r = repeatability standard deviation.
r = repeatability = 2.83 times the square root of the repeatability variance.
(r) = repeatability (as a percent of material average).
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 times the square root of the reproducibility variance.
(R) = reproducibility (as a percent of material average).

[B] No values omitted.

TABLE 2 Type 1 Precision Percent Active Material Assay—Procedure B

Material	Average	Within Laboratory[A]			Between Laboratory[A]		
		S_r	r	(r)	S_R	R	(R)
3—DCBS	87.99	0.4254	1.2040	1.368	0.5065	1.4333	1.629
2—DIBS	97.83	0.0530	0.1501	0.153	1.1788	3.3359	3.407
Pooled values[B]	97.53	0.2435	0.6892	0.707	1.3550	3.8348	3.932

[A]

S_r = repeatability standard deviation.
r = repeatability = 2.83 times the square root of the repeatability variance.
(r) = repeatability (as a percent of material average).
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 times the square root of the reproducibility variance.
(R) = reproducibility (as a percent of material average).

[B] No values omitted.

TABLE 3 Type 1 Precision Percent Active Material Assay—Procedure C

Material	Average	Within Laboratory			Between Laboratory		
		S_r	r	(r)	S_R	R	(R)
CBS	97.63	0.140	0.397	0.41	0.619	1.735	1.80

APPENDIX

(Nonmandatory Information)

X1. TITRATION CURVES

X1.1 A titration curve for THAM is included as Fig. 2.

X1.2 Titration curves for the generated amines in CBS, TBBS, and MBS are shown in Fig. X1.1, Fig. X1.2, and Fig. X1.3, respectively. In each case, the equivalence point (V_{eq}) and the point where the indicator reaches a bright yellow is noted. Thus, it is apparent that the stoichiometric point is in the yellow-green region.

X1.3 For the purpose of this test method, it is suggested that "first yellow" be identified as the end point. This is defined as the point where a definite yellow can be detected, although there still may be a hint of green.

X1.4 The true stoichiometric point can be found by pH titrations. However, it was decided that utilization of the pH end point introduced another source of error that was more difficult to control in a control lab environment (for example, maintenance of precise pH calibration in different laboratories).

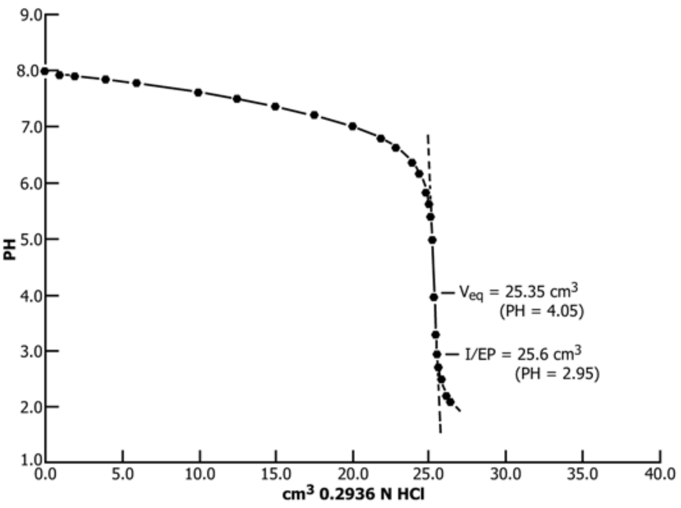

FIG. X1.1 Titration of CBS by Means of H_2S Reduction Method

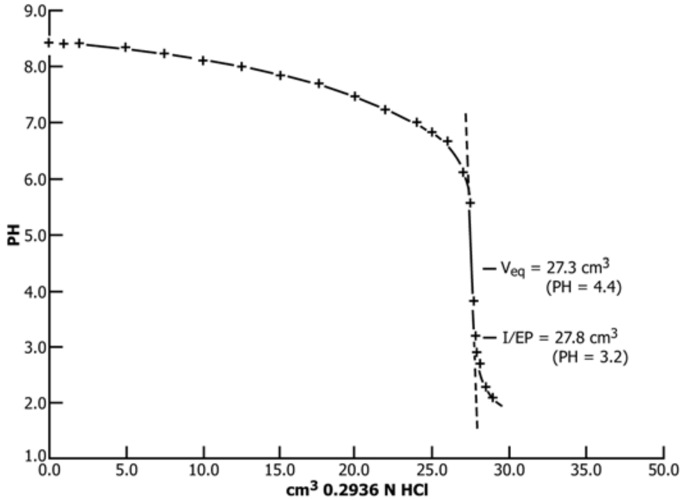

FIG. X1.2 Titration of TBBS by Means of H_2S Reduction Method

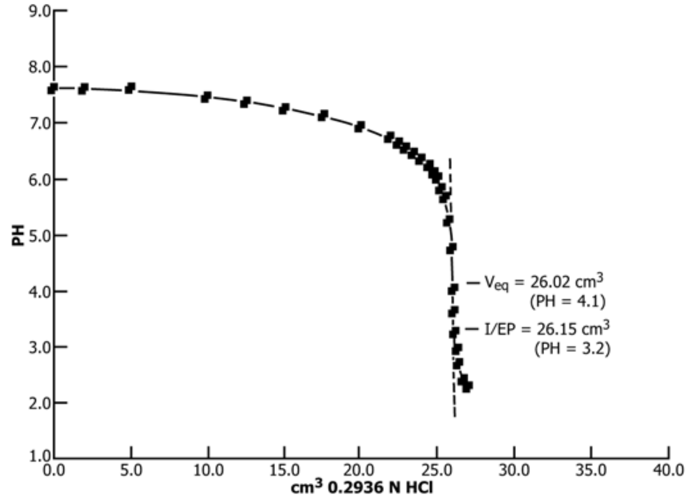

FIG. X1.3 Titration of MBS by Means of H_2S Reduction Method

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