Designation: D 5044 – 02

Standard Test Method for Rubber Chemicals—Free 2-Mercaptobenzothiazole (MBT) in Benzothiazyl Disulfide (MBTS)[1]

This standard is issued under the fixed designation D 5044; 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 the procedure for estimation of the acidic impurities in benzothiazyl disulfide (MBTS).

1.2 The values stated in SI units are to be regarded as the 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[3]

3. Summary of Test Method

3.1 A sample of MBTS is dissolved in solvent. After addition of an acetate buffer, water, and starch solution, the solution is titrated with iodine.

3.2 MBTS is sparingly soluble in any organic solvent. MBT, major impurity in MBTS, is very soluble. Stirring therefore will dissolve MBT, MBTS could stay undissolved.

4. Significance and Use

4.1 2-Mercaptobenzothiazole (MBT) is usually the major impurity in MBTS. Free MBT may be determined by this test method.

4.2 MBT and MBTS are used for rubber and latex vulcanization acceleration. The amount of MBT in MBTS may be of importance in predicting performance in rubber compounds and for raw material purchase and control.

4.3 This test method may be used as a quality control tool and for research and development work.

5. Apparatus

5.1 *Erlenmeyer Flask*, 300-cm^3.

5.2 *Graduated Cylinders*, 10-cm^3, 50-cm^3, 250-cm^3.

5.3 *Buret*, 10-cm^3.

5.4 *Analytical Balance*, having a sensitivity of ±0.1 mg.

6. Reagents

6.1 *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, where such specifications are available.[4] 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types I, II, or III of Specification D 1193.

6.3 *Isopropanol*, analytical reagent.

6.4 *Toluene*, analytical reagent.

6.5 *Acetic Acid*, 100 % analytical reagent.

6.6 *Sodium Acetate*, analytical reagent.

6.7 *Water*, distilled.

6.8 *Iodine Solution* (0.1 *N*).

6.9 *Starch Indicator Solution*—Slurry 2 g of soluble starch with 10 cm^3 of water and dilute with 90 cm^3 of boiling water.

6.10 *Sodium Acetate Solution*—Dissolve 60 g of sodium acetate in water to make 600 cm^3 of solution.

6.11 *Acetate-Buffer*—Add 100 cm^3 acetic acid (see 6.5) to 600 cm^3 sodium acetate solution (6.9).

6.12 *Solvent*—Mix 5 volumes Isopropanol with 3 volumes toluene.

7. Sampling

7.1 Sampling shall be at the discretion of the analyst to

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

[3] *Annual Book of ASTM Standards*, Vol 09.01.

[4] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

obtain as representative a sample as possible of the lot to be tested.

8. Procedure

8.1 Accurately weigh about 1 g of the test specimen to the nearest 0.1 mg and carefully transfer to a 300-cm^3 Erlenmeyer flask.

8.2 Add 50 cm^3 of solvent to the specimen which may not dissolve completely.

8.3 With stirring, add the reagents in the following sequence: 150 cm^3 distilled water, 10 cm^3 acetate buffer, and 5 cm^3 starch solution.

8.4 Titrate immediately with 0.1 *N* iodine solution until the color change from colorless to light violet is stable for 1 min. (See 3.2)

8.5 Obtain a blank titration by proceeding from steps 8.2 through 8.4.

9. Calculation

9.1 Calculate the percent free MBT as follows:

$$\text{Percent Free MBT} = \frac{(A - B) \times N \times 0.1672}{W} \times 100 \quad (1)$$

where:

A	=	volume of iodine (see 6.7) required for titration of the sample, cm^3,
B	=	volume of iodine (see 6.7) required for titration of the blank, cm^3,
W	=	mass of the test specimen in g,
N	=	normality of the iodine solution, and
0.1672	=	millimole mass of MBT.

10. Report

10.1 Report the following information:

10.1.1 Proper identification of the sample and

10.1.2 Results obtained from two individual determinations and their average, reported to the nearest 0.1 %.

11. Precision and Bias [5]

11.1 This precision and bias section has been prepared in accordance with Practice D 4483. Please refer to this practice for terminology and other statistical calculation details.

11.2 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (rubbers, etc.) used in the particular interlaboratory program as described below. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that the parameters are applicable to the particular group of materials and the specific testing protocols of the test method.

11.3 A Type 1 interlaboratory test program (ITP) was conducted in 1997 on a sample of IRM-MBTS. Six laboratories participated in the ITP conducting duplicate tests on each of 2 successive test days. A test result for free MBT is the value obtained from one analysis operation. The database generated by this ITP was divided into two parts; Part 1 used the first of the duplicates on each day and Part 2 used the second of the duplicates. A complete statistical analysis according to D 4483 was conducted for each part. The results of each part where then combined (averaged) for the final values as given in this section. Thus the precision results pertain to between day single determinations for free MBT.

11.4 The data of the ITP showed that two laboratories could not detect free MBT with good sensitivity reporting only less than 0.2 percent for all analysis runs. The data for these two were deleted from the analysis and thus the reported precision is based on a four laboratory database. This is an insufficient number of laboratories for a reliable assessment of precision but it is given as the best effort as of this time.

11.5 *Repeatability*—The repeatability r, of this test method has been established as the value tabulated in Table 1. 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 non-identical sample populations.

11.6 *Reproducibility*—The reproducibility R, of this test method has been established as the value tabulated in Table 1. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated R must be considered to have come from different or non-identical sample populations.

11.7 *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 cannot therefore be determined.

12. Keywords

12.1 mercaptobenzothiazole; mercaptobenzothiazole–disulfide

TABLE 1 Precision for Free MBT in MBTS[A]

	Mean	Within-Laboratory			Between Laboratory		
Material	Value (a)	Sr	r	(r)	SR	R	(R)
IRM-MBTS	0.179	0.00604	0.017	9.5	0.0365	0.103	57.4

[A] precision results for 4 laboratories, mean value for free percent MBT
Sr = repeatability standard deviation
SR = reproducibility standard deviation
r = repeatability, in measurement units
R = reproducibility, in measurement units
(r) = repeatability (relative) in percent
(R) = reproducibility (relative) in percent

[5] Supporting data for the precision evaluation program of this test method are available from ASTM headquarters. Request RR-D11-1083.