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Standard Test Method for Rubber Chemicals—Determination of Acidity in Sulfur[1]

This standard is issued under the fixed designation D 4569; 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] This test method is under the jurisdiction of ASTM Committee D-11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.
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1. Scope

1.1 This test method covers the determination of the acid material, which disassociates in distilled water, that is present in sulfur. The acidity is determined by an electrometric or visual titration.

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

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 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

3. Significance and Use

3.1 This test method provides a means of determining the acidity of sulfur and may be used for quality control, research and development, or for any other reason for which such a determination is required. A low acidity value indicates to the user that the sulfur used should not adversely affect the vulcanization system.

4. Apparatus

4.1 *pH Meter*, equipped with a glass measuring electrode and calomel reference electrode, operated according to the manufacturer's directions for optimum performance.

4.2 ~~*Ten-cm*^{3} *Burette*, graduated to~~10 cm^3 *Burette*, with 0.05 cm^3 graduations.

4.3 *Laboratory Glassware*, suitable for carrying out the procedure as written.

5. Reagents

5.1 *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.~~3~~[3] 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.

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

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

5.2 *Bromothymol Blue*—Dissolve 0.1 g of 3′,3″-dibromothymolsulfonphthalein in 100 cm^3 of 20 % methanol or use commercical preparations.

5.3 *Sodium Hydroxide*, 0.01 *N*.

6. Procedure

6.1 Weigh 10.0 g of sulfur into a 500-cm^2 beaker, and wet the sample with 25 cm^3 of alcohol.

6.2 Add 200 cm^3 of distilled water, and stir the wetted sulfur thoroughly.

6.3 Place the pH meter electrode in the solution and titrate with 0.01 *N* NaOH to a pH of 7.0. Stir the mixture constantly while titrating. When nearing the end of the titration, wait until the pH reading has reached equilibrium before adding additional NaOH solution to prevent overshooting the end point.

6.4 If a pH meter is unavailable, add 10 drops of bromothymol blue indicator and titrate as above.

6.5 **Important:** Titrate a blank (no sulfur) using the same amounts of alcohol and water to a pH 7.0 end point. Subtract the amount used for the blank from the amount used to titrate a sulfur sample in order to determine the acidity of the sulfur sample.

7. Calculation

7.1 Calculate the percent acidity, *A*, (as H_2SO_4) in accordance with the following equation:

$$A = 4.9 \times V \times N/W \quad (1)$$

where:

V = volume of NaOH for sample-volume NaOH for blank, cm^3,
N = normality of NaOH solution, and
W = sample mass, g.

8. Report

8.1 Report the following information:

8.1.1 Percent acidity as H_2SO_4.

8.1.2 If the pH of the sulfur solution is greater than 7.0 and no titrant is needed, report the result as basic.

9. Precision and Bias [4]

9.1 This precision and bias section has been prepared in accordance with Practice D 4483. Refer to Practice D 4483 for terminology and other statistical details.

9.2 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 any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

9.3 A Type 1 (interlaboratory) precision was evaluated in 1986. 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.

9.4 Three different materials were used in the interlaboratory program. These were tested in seven laboratories on two different days.

9.5 The results of the precision calculations for repeatability and reproducibility are given in Table 1, in ascending order of material average or level, for each of the materials evaluated.

[4] Supporting data are available from ASTM Headquarters. Request RR: D11-1046.

TABLE 1 Type 1 Precision Results—Acidity, % × 100

Material	Average	Within Laboratory[A]		Between Laboratory[A]	
		S_r	r	S_R	R
Oil Treated, 90 % Insoluble Sulfur—A	0.21	0.2315	0.6551	0.2419	0.6847
Oil Treated, 90 % Insoluble Sulfur—B	0.36	0.3505	0.9920	0.3505	0.9920
General Purpose Ground Sulfur	3.73	0.3266	0.9243	0.0137	2.3027
Pooled Values[B]	1.43	0.3062	0.8665	0.5793	1.6394

[A] S_r = repeatability standard deviation.
r = repeatability = 2.83 × the square root of the repeatability variance.
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 × the square root of the reproducibility variance.
[B] No values omitted.

NOTE 1—The percent acidity values have been multiplied by 100 to avoid leading zeros in Table 1. The values of *S*, *r*, *S*, and *R* are influenced by this multiplication factor, that is, *S* (percent ash × 100)/100 = *S* (actual or true percent basis).

9.6 The precision of this test method may be expressed in the format of the following statements which use 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 closest to the mean level under consideration at any given time, for any given material in routine testing operations.

9.7 *Repeatability*—The repeatability, *r*, of this test method has been established as the *appropriate 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 nonidentical sample populations.

9.8 *Reproducibility*—The reproducibility, *R*, of this test method has been established as the *appropriate 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* (for any given level) must be considered to have come from different or nonidentical sample populations.

NOTE 2—The values of *r* and *R* are relatively large, whereas the average or mean test level is small (close to zero). This is typical for this type of precision measurement process. This should be kept in mind whenever use is made of *r* and *R*.

9.9 The relative repeatability (*r*) and reproducibility (*R*) have been omitted from Table 1 since the level of values tested was extremely low and approached the limits of sensitivity of the test method. Under these circumstances, the relative values become trivial.

9.10 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values have not been evaluated for this test method. Bias, therefore, cannot be determined.

10. Keywords

10.1 acidity; oil-treated sulfur; sulfur