



Designation: D5460 – 02 (Reapproved 2017)

# Standard Test Method for Rubber Compounding Materials—Water in Rubber Additives<sup>1</sup>

This standard is issued under the fixed designation D5460; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers a procedure for the determination of water in 2-mercaptobenzothiazole sulfenamide accelerators by a Karl Fischer coulometric titration.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.*

1.4 *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. Terminology

### 2.1 Definitions:

2.1.1 *inert filler*—any nonwater soluble additive used as a support, binder, processing aid, dedustant, etc., which may be used in the process of manufacture of a rubber additive.

2.1.2 *lot*—a production quantity representative of a standard production unit.

2.1.3 *test portion*—the actual material used in the analysis; it must be representative of the lot (see 2.1.2).

## 3. Summary of Test Method

3.1 The sulfenamide is heated in an oven to remove water. This water is directed into the titration vessel of a Karl Fischer coulometric titrator with a stream of dry air or nitrogen. The water collected in the titration vessel is quantified coulometri-

cally. Commercial instrumentation exists to carry out this two-step procedure automatically.

## 4. Significance and Use

4.1 This test method is designed to determine the water content of various rubber accelerators. Since 2-mercaptobenzothiazole sulfenamide is hydrolytically unstable, the residual water content is an important characteristic.

## 5. Interferences

5.1 The Karl Fischer titration is inherently unresponsive to the analysis of ketones, aldehydes, and amines. The reagent systems of Section 7 can be used when free amines are present if benzoic acid is added to the titration vessel before analysis. The acid serves to adjust the apparent pH difficulties when free amines are present. Add 5 g of benzoic acid to the titration vessel before starting a series of analyses. This is renewed whenever a drift value exceeds 30 % of the microgram count or when a known amount of water does not produce the correct micrograms count.

5.2 Some rubber chemicals contain amines as part of their structure and may release these amines during the heating process.

## 6. Apparatus

6.1 *Karl Fischer Coulometric Apparatus*, equipped with a heating oven to remove water from the test portion placed in it. The water is directed into the titration vessel by means of a stream of dry air or nitrogen. The evolved water is quantified coulometrically. The instrument must satisfy conditions found in 6.2 and Section 9.

NOTE 1—The apparatus must be used by those versed in its operation. It is not the intent or purpose of this test method to instruct the operator. This information is best obtained from manuals supplied by the manufacturers.

6.2 *Sample Containers*, capable of containing 1 to 4 g of a test portion.

6.3 *Balance*, capable of weighing a test portion mass to  $\pm 0.1$  mg.

6.4 *Syringes and Needles*, to satisfy the requirements of 8.2.

<sup>1</sup> 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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## 7. Reagents

7.1 There are a wide variety of reagents on the market for coulometric analysis. Use the reagent system(s) recommended by the manufacturer of the equipment to be used. The systems may be of the one component type (same vessel and generator solutions) or the two component type (same solution for vessel and generator). Both systems were used in the results reported in the Appendix.

7.2 *Benzoic Acid*, reagent grade.

7.3 *De-Ionized Water and Commercial Water Standards*.

7.4 *Nitrogen, Dry Air or Inert Gas*.

7.5 *Pyridine-Free or Pyridine-Containing Solutions* may be used. Pyridine-free solutions were used for the results reported in the Appendix.

## 8. Calibration

8.1 Karl Fischer coulometric analyzers need no calibration. Operation is based on Faraday's Law which states that one coulomb of electricity is needed to electrolyze one mole of a material.

8.2 Periodic confirmation of this is obtained by injecting a known amount of water into the titration vessel. This must produce the theoretical  $\mu\text{g}$  count within reasonable tolerances. As an example: Injection of  $2.0 \text{ mm}^3$  of water should produce a  $\mu\text{g}$  count of  $2000 \mu\text{g} \pm 50$  to  $100 \mu\text{g}$ .

8.3 Water standards, which are commercially available, can also be used for 8.2. Follow the manufacturers' instructions for using these standards.

## 9. Procedure

9.1 Accurately weigh a well-mixed representative test portion to the nearest 0.1 mg and place it in the oven container. Sample mass will vary with water content. It is recommended that at least  $300 \mu\text{g}$  of water be detected. Follow manufacturers' recommendations for appropriate sample mass and instrument settings and adjust sample mass accordingly.

9.2 Appropriate titrator and oven settings follow. See the Appendix for the actual settings used for this test method.

Coulometer and Vessel:	
Vessel solution	pyridine-containing or pyridine-free
Generator solution	pyridine-containing or pyridine-free
Drift correction	on
Delay	none
Vessel additive	5 g benzoic acid
Oven Conditions:	
Temperature	operator choice
Carried gas	nitrogen, dry air, or inert gas
Carrier gas flow	operator choice
Purge time	none
Delay time	operator choice

9.3 Add benzoic acid to the titration vessel before beginning an analysis. Renew the acid whenever necessary, in accordance with 7.1.

9.4 Place the weighed test portion in the oven and start the analysis. This will proceed automatically and produce a microgram count of calculation on the display at the completion of the process.

9.5 *Calculation:*

$$\% \text{ Water} = (A - B)/C \times 100 \quad (1)$$

where:

- A = mass of water recovered from the test portion (mg),
- B = mass of water from a blank if needed (mg), and
- C = mass of test portion (mg).

## 10. Report

10.1 Report the percent water obtained from individual analysis to two decimal places as described in this test method.

## 11. Precision and Bias

11.1 Precision and bias will be prepared when enough data is accumulated from co-operative studies.

## 12. Keywords

12.1 Karl Fischer coulometric titrator; rubber additive; 2-mercaptobenzothiazole sulfenamide; water

## APPENDIX

(Nonmandatory Information)

### X1. LABORATORY STUDY OF 2-MERCAPTOBENZOTHIAZOLE SULFENAMIDE

X1.1 For this co-operative study, one sample of 2-mercaptobenzothiazole sulfenamide was divided and sent to two laboratories. Analysis was completed with two different instruments with similar but slightly different instrument settings. Instrument settings may be found in Table X1.1.

**TABLE X1.1 Instruments Used**

Instrument	Mitsubishi	Photovolt
Oven temperature, °C	125	110
Vessel reagent	pyridine free	pyridine free
Type solution	single system <sup>A</sup>	double system <sup>A</sup>
Sample holder	aluminum foil lined glass boats	glass boats
Dry nitrogen flow, cm <sup>3</sup> /min	100	250–300

<sup>A</sup>Single System—Same solution for vessel and generator.

Double System—Different solutions for vessel and generator.

**TABLE X1.2 Percentage of Water Recovered**

	% Water Recovery Using This Procedure	
	Mitsubishi	Photovolt
Original Sample		
Day 1	0.06	0.06
Day 1	0.06	0.05
+ 0.25 % Water		
Day 1	0.25	0.24
Day 2	0.25	0.24
+ 0.75 % Water		
Day 1	0.74	0.77
Day 2	0.76	0.75

X1.2 Since the addition of water to the sulfenamide, at a central source and then sending this “wet” sample to the analysts was not feasible, (unwanted degradation occurred), the participants were asked to analyze the sulfenamide initially for water content, then add to this dried sample, a required quantity of water by means of a 5 or 10 microliter syringe, to give a total water content of 0.25 % and 0.75 %. Results may be found in **Table X1.2**.

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