Designation: D3566 − 03 (Reapproved 2014)

Standard Practice for
Rubber—Determination of Bromine in the Presence of Chlorine by Oxygen Combustion[1]

This standard is issued under the fixed designation D3566; 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 practice covers the determination of bromine and chlorine in rubber.

1.2 This procedure is applicable to raw or cured NR, SBR, BR, IR, IIR, CIIR, BIIR, and EPDM rubbers and blends of these.

1.3 Iodine interferes, but substances such as Zn^{2+}, S, CN^{-}, and $(CO_3)^{2-}$ do not.

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

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.* Specific safety precautions are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E443 Test Method for Sulfur in Organic Compounds by Oxygen Flask Combustion (Withdrawn 1996)[3]

3. Summary of Practice

3.1 Samples of rubber, wrapped in filter paper, are burned in an oxygen combustion flask containing an aqueous solution of hydrogen peroxide and sodium bisulfite. The carbon and hydrogen of the organic matter are oxidized. The combusted solution is titrated directly for bromine and chlorine.

4. Significance and Use

4.1 This practice outlines a method for the determination of bromine and chlorine, alone or together.

4.2 CIIR and BIIR rubbers contain small amounts of chlorine and bromine and CR rubbers contain large amounts of chlorine. For quality control and research and development, it is sometimes necessary to determine the amount of these halogens in rubber. This practice can be used for these purposes.

5. Apparatus

5.1 *Oxygen Combustion Flask* (*Schöniger Flask*)—A chemical-resistant,[4] thick-walled oxygen combustion flask,[5] 1000 cm^3, with ^{S}J 35/25 ball-joint stopper, platinum sample carrier, and pinch clamp.

5.2 *Infrared Safety Igniter,*[5,6] with cabinet and infrared light (an electrical igniter is also satisfactory).

5.3 *Magnetic Stirring Bar,* covered with a chemical-resistant coating,[5,7] approximately 25 mm (1 in.) long, without a spinning ring around the center.

5.4 *Magnetic Stirrer.*

5.5 *Filter Paper,* 30 by 30 mm, with a 35-mm extension, black[5,8] for infrared or white[5,9] for electrical ignition.

5.6 *pH Meter,*[10]equipped with a billet-type silver electrode[11] and a calomel electrode, in which the potassium chloride

---

[1] This practice is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

Current edition approved July 1, 2014. Published November 2014. Originally approved in 1977. Last previous edition approved in 2009 as D3566 – 03 (2009). DOI: 10.1520/D3566-03R14.

[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Borosilicate glass has been found satisfactory.

[5] The sole source of supply of the apparatus known to the committee at this time is A. H. Thomas Co., Philadelphia, PA, Catalog No. 6514-F20. 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.

[6] The sole source of supply of the apparatus known to the committee at this time is A. H. Thomas Co., Philadelphia, PA, Catalog No. 6516-G10.

[7] Polytetrafluoroethylene has been found satisfactory.

[8] The sole source of supply of the apparatus known to the committee at this time is A. H. Thomas Co., Philadelphia, PA, Catalog No. 6514-F65.

[9] The sole source of supply of the apparatus known to the committee at this time is A. H. Thomas Co., Philadelphia, PA, Catalog No. 6513-C75.

[10] A. Beckman pH meter Model SS-2 has been found satisfactory.

[11] Coleman Catalog No. 3-571 has been found satisfactory. Any equivalent silver electrode may be used. The electrode should not be coated by the user, especially for Test Method B. It may, however, be polished with a mild abrasive such as powdered kitchen cleanser, so that it is bright and shiny.

solution has been replaced by a saturated potassium nitrate solution, or equivalent automatic titrator.

6. Reagents

6.1 *Silver Nitrate Solution* (*0.001 M*) must be freshly prepared. Pipet 10.0 cm^3 of standard[12] 0.1 *M* silver nitrate solution into a 1-dm^3 volumetric flask. Dilute to volume. Protect from light. Determine its molarity by titrating an accurately weighed sample of the reagent grade KCl or NaCl. Calculate the molarity as follows:

$$\text{Molarity} = [A \times 1000]/(B \times C) \quad (1)$$

where:

A = grams of chloride weighed,
B = molecular mass of chloride used, and
C = titration volume, cm^3.

6.2 *Sodium Bisulfite,* 35 % in water,

6.3 *Hydrogen Peroxide,* 3 % solution,

6.4 *Nitric Acid* (*6 M*).

6.5 *Aluminum Nitrate,*

6.6 *Isopropyl Alcohol,*

6.7 *Methyl Orange Indicator* (1 % solution in methyl alcohol), and

6.8 *Oxygen in Compressed Gas Cylinder.*

7. Safety Precautions

7.1 The following safety precautions must be observed in the combustion of rubber samples:

7.1.1 The flask shall not contain residues of organic solvents or vapor, which could cause an explosion. Any such solvents used for cleaning the flask should be rinsed out repeatedly with water.

7.1.2 The pressure generated by the rapid combustion could cause the flask to explode. Therefore, combustion shall take place in a safety chamber with the door locked or behind a safety shield or hood shield (preferably in a safety chamber that is behind a shield); the hands and face shall be withdrawn behind a screen before the flame reaches the sample itself. Goggles or a face shield should be worn while observing the combustion procedure.

7.1.3 The flask should be left in the safety chamber until the last spark is extinguished. At this point it is removed; but since a slight vacuum is formed, goggles or a face shield should still be worn.

8. Sampling

8.1 The representative test portion selected for analysis must be milled or cut into very fine pieces before weighing.

8.2 Due to the small sample size, the rubber and filter paper should be protected from contamination, and all operations prior to combustion should be carried out while wearing plastic gloves.

9. Procedure

9.1 Place 10 cm^3 of water, five drops hydrogen peroxide, and 2 cm^3 of sodium bisulfite solution into the combustion flask.

9.2 Fold the filter paper into a U-shaped sample boat.

9.3 Weigh a sample of 80 to 100 mg (which should not exceed approximately 0.25 milliequivalents of bromine) to the nearest 0.1 mg. Place the sample into the folded filter paper boat.

9.4 Place the folded paper firmly in the platinum sample carrier hung on the hook of the stopper, with the pointed end of the paper projecting outward.

9.5 Insert a tube from the oxygen cylinder close to the bottom of the flask and admit oxygen rapidly for 5 min.

9.6 Carefully remove the oxygen tube and stopper the flask.

9.7 With the stopper upright, clamp the stopper tightly with the pinch clamp.

9.8 Place the flask in the infrared igniter chamber with the pointed end of the paper in line with the infrared beam and approximately perpendicular to it. Close the door and turn on the infrared light (or electric igniter) until the paper ignites.

9.9 After combustion is complete, moisten the stopper externally with a few drops of water to avoid loss of halogen. Let sit 1 min. Shake the flask. Allow to rest for 30 min.

9.10 Remove the pinch clamp, tilt the stopper to release the vacuum, and open the flask.

9.11 Where the bromine and chlorine content, or both, is low, repeat the procedure of 9.1 to 9.10, burning another sample of about the same size over the same liquid.

9.12 Open the flask; wash sides, stopper, and carrier with water.

9.13 Add 3.5 cm^3 of HNO_3 solution. Close flask and shake to dissolve ash in basket.

9.14 Pour solution into 400 cm^3 beaker containing a magnetic stirrer.

9.15 Wash the flask with isopropyl alcohol, adding washings to beaker. The final composition should be close to 80 % alcohol, 20 % water.

9.16 Add 4 g aluminum nitrate and two drops methyl orange. Solution should turn red. If not, add HNO_3 until red color appears.

9.17 Titrate the solution with 0.001 *M* $AgNO_3$ (6.1), using the pH meter arrangement described (5.6) or an equivalent automatic titrator. Add titrant in increments of 0.01 cm^3.

9.18 The first inflection point on the curve of millivolts versus cubic centimetres of titrant, represents bromide; the second inflection point represents chloride. The end point is the point of maximum change in emf for an increment of titrant.

9.19 For a better end point, a known amount of bromide and chloride may be added to the sample solution before titration. Deduct this amount from the total titration.

---

[12] The 0.1 *M* silver nitrate solution should be prepared in accordance with Practice E200 or may be purchased.

9.20 Carry a blank throughout the entire procedure, using the same quantity of reagents, but omitting the sample.

10. Calculation

10.1 Calculate the bromine content as follows:

$$\text{Bromine, \%} = (B - A) \times M \times 7.99/W \quad (2)$$

where:

B = volume of $AgNO_3$ solution required for titration to the first inflection point, cm^3,
A = volume of $AgNO_3$ solution required for titration of the blank,
M = molarity of the $AgNO_3$ solution, and
W = mass of rubber samples burned in the flask, g.

10.2 Calculate the chlorine content as follows:

$$\text{Chlorine, \%} = (C - B) \times M \times 3.55/W \quad (3)$$

where:

C = volume of $AgNO_3$ solution required for titration to the second inflection point, cm^3,
B = volume of $AgNO_3$ solution required for titration to the first inflection point, cm^3,
M = molarity of the $AgNO_3$ solution, and
W = mass of rubber samples burned in the flask, g.

11. Report

11.1 Report the following information:

11.1.1 Sample identification, and

11.1.2 Test result, which is the average of two determinations.

12. Precision and Bias

12.1 This practice has not been tested in a round-robin test program.

13. Keywords

13.1 bromine; chlorine; oxygen combustion

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/