Designation: D4004 – 06 (Reapproved 2012)

Standard Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis[1]

This standard is issued under the fixed designation D4004; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the determination of lead, zinc, copper, and manganese in raw rubber and rubber compounds, vulcanized or unvulcanized. The level at which the metals are present is taken into account by suitable adjustments of sample mass and dilution.

1.2 Certain compounding ingredients, present in the rubber sample will dictate which of the methods should be used. Refer to Section 3. Five methods of determination are as follows:

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Method A	8
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1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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:*[2]

D1076 Specification for Rubber—Concentrated, Ammonia Preserved, Creamed, and Centrifuged Natural Latex

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

E663 Practice for Flame Atomic Absorption Analysis (Withdrawn 1997)[3]

2.2 *ISO Standards:*

ISO 1396 Rubber–Copper Content–Photometric Technique–Determination[4]

ISO 1655 Rubber–Manganese Content–Photometric Technique–Determination[4]

3. Summary of Test Methods

3.1 *Method A*—Determination of lead and zinc in rubber not containing any halogen; in the case of lead, also not containing any silica filler. See Section 8.

3.1.1 In Method A, the rubber is furnace-dried in a platinum crucible at 250°C, followed by furnace ashing for 1 to 2 h at 550°C. The ash is dissolved with the aid of concentrated hydrochloric acid (HCl) and the resulting solution suitably diluted for Atomic Absorption Spectrometric (AAS) determination of the lead and zinc.

3.2 *Method B*—Determination of lead and zinc in rubber containing silica filler, but no halogen. See Section 9.

3.2.1 In Method B the rubber is ashed in platinum as in Method A. The ash is then fused with a lithium or sodium tetraborate or metaborate flux, after which the fused mixture is dissolved with the aid of HCl for subsequent AAS analysis.

3.3 *Method C*—Determination of lead and zinc in rubber containing halogen. See Section 10.

3.3.1 In Method C the rubber is wet-ashed with the aid of concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3), evaporated to dryness, and further ashed in a muffle furnace at 550°C, after which the ash is dissolved as in Method A for subsequent AAS analysis.

3.4 *Method D*—Determination of copper in raw rubber and rubber latex, both synthetic and natural (see 14.2).

3.4.1 In Method D the rubber is ashed at 550°C, the ash is then digested in hydrochloric acid, and copper is determined by AAS analysis.

[1] These test methods are under the jurisdiction of ASTM Committee D11 on Rubber and are the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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[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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

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3.5 *Method E*—Determination of manganese in raw natural rubber and rubber latex, both synthetic and natural (see 23.2).

3.5.1 In Method E the rubber is ashed at 550°C, the ash is digested in hydrochloric acid and the manganese is determined by AAS analysis.

3.5.2 See 3.6.

3.6 Because this standard does not contain procedures for optimizing instrument performance, nor does it instruct the analyst in the basics of flame atomic absorption, it is recommended that the references found in Section 2 be studied for these purposes.

4. Significance and Use

4.1 These test methods are suitable for process control, for product acceptance, and for research and development.

5. Apparatus

5.1 *Laboratory Balance.*

5.2 *Laboratory Muffle Furnace.*

5.3 *Hot Plate.*

5.4 *Platinum Crucibles,* 25 cm^3 content minimum.

5.5 *Common Borosilicate Glassware.*

5.6 *Meker Burner.*

5.7 *Atomic Absorption Spectrophotometer,* operated in accordance with the manufacturer's directions for optimum instrument performance.

6. Reagents

NOTE 1—Observe all recognized health and safety precautions while carrying out this procedure.

6.1 All reagents used shall be of analytical grade and distilled de-ionized water (DDW) shall be used for any dilutions.

6.2 *Hydrochloric Acid* (HCl) (density 1.19 Mg/m^3).

6.3 *Hydrochloric Acid* (6 *M*)—Dilute concentrated HCl with an equal volume of water.

6.4 *Lithium Carbonate* (Li_2CO_3).

6.5 *Lithium Metaborate* ($LiBO_2$).

6.6 *Lithium Tetraborate* ($Li_2B_4O_7$).

6.7 *Nitric Acid* (HNO_3) (density 1.42 Mg/m^3).

6.8 *Sodium Carbonate* (Na_2CO_3).

6.9 *Sodium Tetraborate* ($Na_2B_4O_7 \cdot 10\ H_2O$).

6.10 *Sulfuric Acid* (H_2SO_4) (density 1.83 Mg/m^3).

7. Sampling

7.1 Selection of a test portion shall be at the discretion of the analyst and shall be as representative of the sample as possible.

METHOD A

8. Procedure

8.1 Weigh 0.1 g of dry rubber into a platinum 25-cm^3 or 50-cm^3 crucible if lead and zinc are present at levels higher than 0.5 %. Weigh a larger amount (up to 10 g) when the lead and zinc levels are lower. Record the mass of rubber, *W*, to the nearest 0.1 mg.

8.2 Place the test portion in the muffle furnace at 250°C for 0.5 h. Raise the temperature to 550°C for 1 h. If not completely ashed, continue ashing for another hour or two.

8.3 Cool the crucible to room temperature and add 5 cm^3 of 6 *M* HCl. Heat on a hot plate until the ash is completely dissolved and transfer quantitatively to a 25-cm^3 volumetric flask. Fill to the mark with DDW. For lead levels less than 10 mg/kg (µg/g) dissolve the ash in 2 cm^3 of 6 *M* HCl and transfer to a 10-cm^3 volumetric flask.

8.4 Determine the lead and zinc by AAS following Practice E663. Keep the matrix of the blank, of the standard, and of the sample solutions as identical as possible. Any necessary dilutions of the sample solution are carried out with DDW.

METHOD B

9. Procedure

9.1 Ash in platinum crucibles as described under 8.1 and 8.2 using 1 g of rubber.

9.2 To the ash obtained, add 1 g of a 3-to-1 mixture of sodium carbonate (Na_2CO_3) and sodium tetraborate ($Na_2B_4O_7 \cdot 10\ H_2O$) and mix the compounds using a clean quartz or platinum rod. Fuse the mixture for a few minutes over a Meker burner. Using platinum-tipped tongs, turn the crucible, so that all of the mixture fuses properly.

NOTE 2—Alternative fusing agents are a 3-to-1 mix of lithium carbonate (Li_2CO_3) and lithium tetraborate ($Li_2B_4O_7$), and lithium metaborate ($LiBO_2$) which, in that order, fuse at somewhat higher temperatures.

9.3 Cool to room temperature and dissolve the fused mass with 5 cm^3 of 6 *M* HCl. Magnetic stirring will speed up the dissolution. If necessary, add 5 to 10 cm^3 of DDW to aid solution.

9.4 Transfer the solution quantitatively to a 25-cm^3 volumetric flask. Fill to the mark with DDW.

9.5 Continue as set out in 8.4.

METHOD C

10. Procedure

10.1 Weigh 1 g of rubber in the form of small pieces in a platinum crucible or borosilicate beaker.

10.2 Add 25 cm^3 of concentrated H_2SO_4 and heat on a hot plate until the rubber is disintegrated (approximately 0.5 to 1 h).

10.3 Cool to room temperature and add dropwise 10 cm^3 of concentrated HNO_3.

10.4 Heat on a hot plate until the solution has become clear (approximately 1 to 3 h). Then evaporate to dryness and ash the residue in a muffle furnace at 550°C.

10.5 Continue as set out in 8.3 and 8.4.

11. Test Report

11.1 The report shall include the following:

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