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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis[1]

This standard is issued under the fixed designation D 4004; 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:

	Sections
Method A	8
Method B	9
Method C	10
Method D	14-22
Method E	23-31

1.3 *This standard does not purport to address all of the safety problems, 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 1076 Specification for Rubber—Concentrated, Ammonia Preserved, Creamed, and Centrifuged Natural Latex[2]
D 1224 Test Methods for Zinc and Cadmium in Paper[3]
D 3559 Test Method for Lead in Water[4]
D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]
E 663 Practice for Flame Atomic Absorption Analysis[5]
E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry[5]

2.2 *ISO Standards:*

ISO 1396 Rubber–Copper Content–Photometric Technique–Determination[6]
ISO 1655 Rubber–Manganese Content–Photometric Technique–Determination[6]

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.

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

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

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

[3] *Annual Book of ASTM Standards*, Vol 15.09.

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

[5] *Annual Book of ASTM Standards*, Vol 03.06.

[6] Available from the American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

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 E 663. 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:

11.1.1 The amount of lead and zinc found in the rubber to two significant figures either in percent or mg/kg (ppm),

11.1.2 The test method used,

11.1.3 Graph of absorbances versus concentrations for the lead and zinc standards,

11.1.4 Absorbances measured on the sample test solutions,

11.1.5 A listing of instrumental conditions such as lamp current, wavelength of the analytical line, type of flame, and type of burner,

11.1.6 Calculation of the lead and zinc concentrations in the original rubber, and

11.1.7 Notes on any unusual observations both with respect to the chemical procedure and the instrumental determination.

12. Limits of Detection

12.1 The limits of detection with acceptable error for a minimum absorbance of 0.050 are listed as a function of sample mass and final dilution volume. See Table 1.

13. Precision and Bias [7]

13.1 These precision statements have been prepared in accordance with Practice D 4483. Please refer to this practice for terminology and other testing and statistical concept explanations.

13.2 Precision data obtained at the 3 % Zn and 1 % Pb level are as follows:

13.2.1 *Zinc Precision*—The Type 1 precision is estimated from an interlaboratory study by six laboratories testing three materials on three days. A test result is the average of duplicate determinations.

13.2.1.1 The Type 1 precision is expressed in absolute terms as percentage points. See Table 2.

13.3 *Lead Precision*—The Type 1 precision is estimated from an interlaboratory study by six laboratories testing three materials on three days. A test result is the average of duplicate determinations.

13.3.1 The Type 1 precision is expressed in absolute terms as percentage points. See Table 3.

13.4 Precision data obtained at the mg/kg (ppm) level are as follows:

13.4.1 *Zinc Precision*:

The Type 1 precision is estimated from an interlaboratory study by five laboratories testing three materials on three days. A test result is the average of duplicate determinations (see Table 4).

13.4.1.1 Concentrations less than 1 mg/kg (ppm) cannot be precisely determined by this test method.

13.4.2 *Lead Precision*:

The Type 1 precision is estimated from an interlaboratory study by five laboratories testing two samples on three days. A test result is an average of duplicate determinations (see Table 5).

13.4.2.1 Concentrations less than 1 mg/kg (ppm) cannot be precisely measured by this test method.

13.5 See also Section 31 for additional discussion of precision.

METHOD D

14. Significance and Use

14.1 See 4.1.

TABLE 1 Limits of Detection[A]

	Method A	Method B	Method C
Sample mass (g)	10	1	1
Total volume (cm^3)	10	10	10
Zinc	0.1	2.5	1.0
Lead	1.0	25.0	1.0

[A] The limits of detection for Method C can only be realized if extremely pure acids are used for the digestion. With the usual reagent grade acids, even when a correction is applied on the basis of a blank digestion, the limit of determination is likely a factor of ten to one hundred higher.

TABLE 2 Type 1 Precision—Zinc (Normal Level)

NOTE 1—
Sr = repeatability standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.*SR* = reproducibility standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

Material	Average Level, %	Within Laboratories			Between Laboratories		
		Sr	*r*	*(r)*	*SR*	*R*	*(R)*
6	2.90	0.0996	0.306	10.6	0.108	0.282	9.76
2	3.00	0.113	0.320	10.7	0.134	0.379	12.6
4	3.01	0.116	0.328	10.9	0.133	0.375	12.5

TABLE 3 Type 1 Precision—Lead (Normal Level)

NOTE 1—
Sr = repeatability standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.*SR* = reproducibility standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

Material	Average Level, %	Within Laboratories			Between Laboratories		
		Sr	*r*	*(r)*	*SR*	*R*	*(R)*
2	0.82	0.0264	0.0747	9.11	0.0754	0.213	26.0
4	0.91	0.0296	0.0838	9.23	0.0785	0.222	24.4
6	0.92	0.0363	0.103	11.2	0.0856	0.242	26.3

TABLE 4 Type 1 Precision—Zinc (Low Level)

NOTE 1—
Sr = repeatability standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.*SR* = reproducibility standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

Material	Average Level, mg/kg	Within Laboratories			Between Laboratories		
		Sr	*r*	*(r)*	*SR*	*R*	*(R)*
A	1.5	0.642	2.108	141.	0.745	1.817	121.
B	8.6	1.357	3.840	44.7	1.422	4.02	46.7
C	25.8	1.855	5.25	20.4	6.01	17.0	65.9

14.2 Copper in certain forms is known to catalyze the oxidative breakdown of natural rubber although the mechanism by which degradation is brought about is not fully understood. It is recognized that other forms of copper can be present in the rubber even in relatively large amounts without degradation taking place, but in these cases there is always the possibility that under the influence of some chemicals, notably the unsaturated acids, the copper could assume a more aggressive role when the rubber is compounded.

14.3 It would be advantageous to be able to analytically distinguish between catalytically active and inactive forms of copper but no generally accepted method has yet been put forward to doing so. There is no alternative therefore, but to determine the total amount of copper in the rubber.

14.4 Little is known concerning the influence of copper on the catalytic oxidation of synthetic rubbers, although it is widely accepted that its effect is less severe than in the case of

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[7] Supporting data are available from ASTM Headquarters. Request RR: D-11-1020.

TABLE 5 Type 1 Precision—Lead (Low Level)

NOTE 1—
Sr = repeatability standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.*SR* = reproducibility standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

Material	Average Level, mg/kg	Within Laboratories			Between Laboratories		
		Sr	*r*	*(r)*	*SR*	*R*	*(R)*
B	5.9	0.596	1.687	28.6	0.763	2.16	36.6
C	19.0	1.021	2.890	15.2	2.583	7.31	38.5

natural rubber. Possibly for this reason, the determination of copper in compounds based on the synthetic rubbers is less frequently carried out.[8]

15. Limitations

15.1 This test method should not be used for copper content of heavily loaded rubbers, which contain silica and clay, unless it has been determined that these fillers do not interfere with the test method as written.

16. Apparatus

16.1 See Section 5.

17. Reagents

17.1 See Section 6.

18. Sampling

18.1 See Section 7.

19. Sample Preparation

19.1 Raw rubber may be milled or cut into small pieces.

19.2 Latex should be prepared in the form of a film according to Specification D 1076, Section 5. It is not necessary to weigh the sample prior to film preparation.

20. Procedure

20.1 Weigh a 0.1 g sample of dry rubber to the nearest 0.1 mg, prepared according to 19.1 or 19.2, if the copper content is above 0.5 %, or a 10 g sample weighed to the nearest 0.01 g if the copper content is lower than this.

20.2 Place the test portion in a platinum or porcelain crucible, or a small borosilicate glass beaker, and place in a muffle furnace held at 550 ± 25°C for 1 h. If, at the end of this time, the test portion is not ashed completely, heat for another h. Alternatively use a 250°C muffle for the initial ashing and transfer to a 550°C muffle to complete the ashing. In either case, *do not open the door of the muffle during the initial ashing phase,* for this will only serve to ignite the volatile fumes.

20.3 When ashing is complete (white or yellowish ash devoid of carbon), remove the crucible or beaker from the muffle furnace, cool to room temperature and add 20 cm^3 of hydrochloric acid (see 6.3). Heat the mixture on a low temperature hot plate to dissolve the ash. Cool and transfer the solution, quantitatively, to a 50 cm^3 volumetric flask.

20.4 Determine the copper content by AAS, following commonly accepted practices for the proper operation of the instrument to achieve good analytical results. Keep the matrix of the test portion solution, the blank and standards of the same acid concentration.

20.5 Carry a blank throughout the entire procedure, with all reagents, but eliminating the test portion.

21. Test Report

21.1 See Section 11. All references to lead and zinc, shall read "copper."

22. Precision and Bias [7]

22.1 These precision statements have been prepared in accordance with Practice D 4483. Please refer to this practice for terminology and other testing and statistical concept explanations.

22.2 The Type 1 precision is estimated from an interlaboratory program where six laboratories were supplied with samples of three materials for copper analysis. Duplicate analyses were made on these materials on each of two days.

22.3 A test result is the average of duplicate determinations.

22.4 The within and among laboratory standard deviation (in milligrams per kilogram) increases as the level of copper increases.

22.5 See also Section 31 for more discussion on precision.

METHOD E

23. Significance and Use

23.1 See 4.1.

23.2 Manganese in certain forms is known to catalyze the oxidative breakdown of natural rubber although the mechanism by which degradation is brought about is not fully understood. It is recognized also that other forms of manganese can be present without degradation taking place, but no generally accepted method is available for distinguishing between the active and inactive forms. At present, therefore, there is no alternative to determining the total amount of manganese in the rubber.

23.3 Little is known concerning the influence of manganese on the catalytic oxidation of synthetic rubbers, although it is widely accepted that its effect is less severe than in the case of natural rubber. Possibly, for this reason, the determination of manganese in synthetic rubbers is less frequently carried out.[9]

24. Limitations

24.1 This test method should not be used for the manganese content of heavily loaded rubbers, which contain silica and clay, unless it has been determined that these fillers do not interfere with the test method as written.

25. Apparatus

25.1 See Section 5.

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[8] Paragraphs 17.2 to 17.4 are taken from ISO 1396.

[9] Paragraphs 23.2 and 23.3 are taken from ISO 1655.

26. Reagents

26.1 See Section 6.

27. Sampling

27.1 See Section 7.

28. Sample Preparation

28.1 See Section 19.

29. Procedure

29.1 Weigh a 0.1-g sample of dry rubber to the nearest 0.1 mg, prepared according to 22.1 or 22.2, if the manganese content is about 0.5 %. Weigh up to a 10 g sample to the nearest 0.01 g if the manganese content is lower than this.

29.2 See 20.2 and 20.3.

29.3 Determine the manganese content by AAS following commonly accepted practices for the proper operation of the instrument to achieve good analytical results. Keep the matrix of the test portion solution, the blank and standards of the same acid concentration.

29.4 Carry a blank throughout the entire procedure, with all reagents, but eliminating the test portion.

30. Test Report

30.1 See Section 11. All references to lead and zinc shall read manganese.

31. Precision and Bias [7]

31.1 These precision statements have been prepared in accordance with Practice D 4483. Please refer to this practice for terminology and other testing and statistical concept explanation.

31.2 The Type 1 precision is estimated from an interlaboratory study where six laboratories were supplied with samples of three materials for manganese analysis. Duplicate analyses were made on these materials on each of two days.

31.3 A test result is the average of duplicate determinations.

31.4 The results of all the precision calculations for all test methods for repeatability and reproducibility are given in Tables 2-7, in ascending order of material average or level, for each of the materials evaluated.

31.5 The precision of any of these test methods may be expressed in the format of the following statements that 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 the precision tables closest to the mean level under consideration (at any given time, for any given material) in routine testing operations.

31.6 *Repeatability*—The repeatability *r*, of these test methods have been established as the *appropriate value* tabulated in the precision tables. 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.

TABLE 6 Type 1 Precision—Copper

NOTE 1—
Sr = repeatability standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.*SR* = reproducibility standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

Material	Average Level, mg/kg	Within Laboratories			Between Laboratories		
		Sr	*r*	(*r*)	*SR*	*R*	(*R*)
1	1.32	0.0577	0.163	12.4	0.349	0.988	74.8
2	2.57	0.0913	0.258	10.1	0.517	1.463	56.9
3	9.29	0.1980	0.560	6.0	0.560	1.585	17.1

TABLE 7 Type 1 Precision—Manganese

NOTE 1—
Sr = repeatability standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.*SR* = reproducibility standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

Material	Average Level, mg/kg	Within Laboratories			Between Laboratories		
		Sr	*r*	(*r*)	*SR*	*R*	(*R*)
1	1.06	0.0289	0.0818	7.72	0.120	0.340	32.0
2	7.70	0.187	0.529	6.87	0.661	1.871	24.3
3	19.80	0.270	0.764	3.86	0.843	2.386	12.1

31.7 *Reproducibility*—The reproducibility *R*, of these test methods have been established as the *appropriate value* tabulated in the precision tables. 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.

31.8 Repeatability and reproducibility expressed as a percentage of the mean level, (*r*) and (*R*), have equivalent application statements as above for *r* and *R*. For the (*r*) and (*R*) statements, the difference in the two single test results is expressed as a percentage of the arithmetic mean of the two test results.

31.9 *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 determined for these test methods. Bias, therefore, cannot be determined.

32. Keywords

32.1 copper; flame atomic absorption; lead; manganese; metal content of rubber; zinc