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Standard Test Methods for Compounding Materials—Flame Atomic Absorption Technique—Determination of Metals¹

This standard is issued under the fixed designation D 4075; 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 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. Current edition approved March 27, 1987; June 10, 2002. Published May 1987; July 2002. Originally published as D 4075 – 81. Last previous edition D 4075 – 87 (1997).

1. Scope

- 1.1 These test methods cover the determination of metals in rubber compounding materials by flame atomic absorption.
- 1.2 The test methods include the following materials:

Zinc oxide	Sections 11 to 20
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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.* For a specific precautionary statement, see Note 1.

2. Referenced Documents

2.1 ASTM Standards:

- D 4004 Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis²
- D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries²
- E 300 Practice for Sampling Industrial Chemicals³

2.2 Other Documents:

- 2.2.1 Literature pertinent to the particular atomic absorption spectrophotometric equipment used for the analysis especially the manufacturer's recommendations for optimum performance. Standard texts on atomic absorption by flame technique are also helpful.

3. Summary of Test Methods

3.1 The compounding material is suitably sampled, prepared according to the appropriate sections of these test methods, and examined by flame absorption spectrophotometry for metals.

3.2 Sample preparation, procedures, calculations, and precision statements will be found in each section dealing with a particular compounding material.

3.3 The analysis of metals in compounding materials depends on the skill of the operator in the use of the flame atomic absorption equipment. It is, therefore, assumed that the operator is familiar with all aspects of this analytical technique. No details are given here for the proper operation of the equipment or interpretation of results obtained.

3.4 These test methods do not cover the determination of metals in raw rubbers or finished products. See Test Methods D 4004 for these methods.

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 *Balances*, capable of weighing accurately to ±0.1 mg or ± 0.1 g, depending on sample mass required.
- 5.2 *Hot Plate*.
- 5.3 *Common Borosilicate Glassware*, especially 10, 100, 200 and 500-cm³ volumetric flasks.

² Annual Book of ASTM Standards, Vol 09.01.

³ Annual Book of ASTM Standards, Vol 15.05.

5.4 *Pipets*, of 1, 2, 5, and 10-cm³ capacity. One cubic centimetre pipets graduated in tenths and hundredths are especially useful.

5.5 *Microlitre Syringes*, 1 and 10 mm³(μ L) are recommended.

5.6 *Plastic Bottles*, suitable for storage of standard solutions.

5.7 *Atomic Absorption Spectrophotometer* operating in the flame mode. The instrument must be operated according to the manufacturer's directions for optimum performance for flame operation.

6. Reagents

NOTE 1—**Caution:** Observe all recognized health and safety precautions while carrying out this procedure. All reagents shall be of analytical grade, and distilled, deionized, or distilled deionized water shall be used for sample preparation and required dilutions.

6.1 Standard solution for metals to be determined in each compounding material may be prepared from pure metals, metallic compounds, or purchased from a chemical supply house as standard solutions. The usual concentrations of solutions is 1000 μ g of the metal per cubic centimetre of solution. Suitable dilutions with water will bring these concentrated solutions into the linear working range of the instrument. It is recommended that standards below 1 μ g/cm³ be prepared fresh, while those above 1 μ g/cm³ may be stored.

7. Sampling

7.1 Sampling shall be carried out in the best possible way to ensure that the sample is representative of the lot (see Practice E 300).

7.2 The analyst shall select a test portion from the sample in such a way that it is as representative of the sample as possible. This sampling shall be at the discretion of the analyst.

8. Calculation

8.1 Calculation may be by graph, by equation, or by calibration techniques appropriate to the atomic absorption spectrophotometer being used.

8.2 Instrument calibration methods (possible with more modern equipment) shall be carried out as suggested by the manufacturer.

9. Report

9.1 Report the metal content as a percent, if more than or equal to 0.1 % or as milligrams per kilogram, if less than 0.1 %.

NOTE 2—Micrograms per gram, parts per million, and milligrams per kilogram are equivalent. Micrograms per gram and milligrams per kilogram are preferred in SI.

10. Precision and Bias

10.1 The precision statements found under each individual compounding material were prepared in accordance with Practice D 4483. Refer to this practice for terminology and other testing statistical concept explanations.

10.2 A test result is the average of two individual determinations that fall within the LSD (Least Significant Difference) limit for repeatability as stated in each precision section.

ZINC OXIDE

11. Scope

11.1 This test method covers the analysis of zinc oxide for copper, cadmium, lead, and manganese.

11.2 Any zinc oxide, suitable for rubber compounding, may be analyzed by this procedure.

11.3 This test method is not suitable for zinc oxide with lead content above about 1.0 % because of dissolution problems.

12. Summary of Test Method

12.1 A "slurry" of zinc oxide and water is heated with HCl, to which a small amount of HNO₃ is added. The metal sought is determined by flame atomic absorption.

13. Significance and Use

13.1 The principal reason for analysis of zinc oxide for copper, cadmium, manganese and lead is for quality assurance, but this test method may be used for other purposes, such as research, process control, etc.

14. Apparatus

14.1 See Section 5.

15. Reagents

15.1 See Section 6, and in addition:

15.2 *Hydrochloric Acid* (HCl) (density 1.19 Mg/m³). (HCl), concentrated,

15.3 *Nitric Acid* (HNO_3) (density 1.42 Mg/m^3), concentrated.

16. Sampling

16.1 See Section 7.

17. Procedure

17.1 Accurately weigh a 0.2 to 10.0-g sample. Weigh to 0.1 mg for small samples and 2 ± 0.1 g for large samples into a 150- cm^3 beaker. Add enough water to make a thick “slurry.” Add enough concentrated HCl to effect complete dissolution of the test portion. For small test portions, 10 cm^3 will suffice, for larger test portions, up to 30 cm^3 may be needed.

NOTE 3—Failure to observe this sequence will result in a hard cake of zinc oxide, which will be difficult to dissolve in the water–acid mixture.

17.2 Heat the solution on a hot plate to the boiling point, then add 1 to 2 cm^3 of concentrated HNO_3 . Continue heating for no more than 5 min. Remove the beaker from the hot plate, allow it to cool and quantitatively transfer the solution to a 200- cm^3 volumetric flask making it up to volume with water.

NOTE 4—Variations in the amount of test portion to weigh and final volume of solution is left to the discretion of the analyst and must be determined by prior knowledge of the approximate amount of copper, cadmium, and lead in the type of zinc oxide being analyzed.

17.3 Carry a blank throughout the entire procedure, using the same quantities of reagents but without a test portion. Subtract any positive blank value, in an appropriate manner, before calculating the metal content of the zinc oxide.

17.4 Complete the analysis, using standard flame atomic absorption techniques appropriate to the instrument used and following the manufacturer’s directions for optimum instrument performance.

NOTE 5—Zinc oxide solution for measurement must fall within the linear range of the instrument. Any solution that does not meet this criterion must be diluted suitably to fall within this range.

18. Calculation

18.1 See Section 8.

19. Report

19.1 See Section 9.

20. Precision and Bias ⁴

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

20.2 A Type 1 (interlaboratory) precision was evaluated. Both repeatability and reproducibility are short term, a period of a few days separates replicate test results. A test result is the average value, as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

20.3 Table 1 gives the details on the interlaboratory testing; materials (types of zinc oxide), number of laboratories, number of testing days.

TABLE 1 Details on Interlaboratory Precision Test Programs

Analysis	Number of Laboratories	Types of ZnO	(Tested) Number of Days
Copper in ZnO	8	1	3
Cadmium in ZnO	8	2	3
Manganese in ZnO	8	1	3
Lead in ZnO	8	2	3

20.4 The results of the precision calculations for repeatability and reproducibility are given in Table 2.

20.5 The precision of this test method for any analysis may be expressed in the format of the following statements which use what is called an “appropriate value” of r , R , (r), or (R), that is, that value to be used in decisions about test results (obtained with this test method). The appropriate value is that value of r or R associated with a mean level in Table 2 closest to the mean level under consideration at any given time, for any given material in routine testing operations.

⁴ Supporting data are available from ASTM Headquarters. Request RR: D11-1019.

TABLE 2 Type 1—Precision for Copper, Cadmium, Manganese, and Lead in Zinc Oxide

NOTE 1—

 S_r = within laboratory standard deviation.

 r = repeatability (in measurement units).

 (r) = repeatability (in percent).

 S_R = between laboratory standard deviation.

 R = reproducibility (in measurement units).

 (R) = reproducibility (in percent).

(ZnO) Material	Analysis For	(mg/kg) Mean Value	Within Laboratories			Between Laboratories		
			S_r	r	(r)	S_R	R	(R)
1	copper	6.5	0.456	1.29	19.9	0.930	2.63	40.5
1	cadmium	1.9	1.07	3.03	159.0	1.41	3.99	210.0
2	cadmium	236.0	5.32	15.1	6.40	27.4	77.5	32.9
1	manganese	41.0	1.19	3.37	8.22	5.38	15.2	37.1
1	lead	12.0	0.70	1.98	16.5	1.81	5.12	42.7
2	lead	932.0	9.42	26.7	2.86	63.0	178.0	19.1

20.6 *Repeatability*—The repeatability, r , of this test method has been established as the appropriate value tabulated in Table 2. 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.

20.7 *Reproducibility*—The reproducibility, R , of this test method has been established as the appropriate value for any parameter tabulated in Table 2. 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.

20.8 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.

20.9 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias, therefore, cannot be determined.

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