



Standard Test Method for Metals in Cellulose by Atomic Absorption Spectrophotometry¹

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1. Scope

1.1 This test method covers the determination of the iron, copper, manganese, and calcium content of cellulose pulp from wood or cotton.

1.2 *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:

D 1193 Specification for Reagent Water²

D 1348 Test Methods for Moisture in Cellulose³

D 3516 Test Methods for Ashing Cellulose³

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods⁴

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

3. Summary of Test Method

3.1 The sample is ashed in accordance with Test Methods D 3516.

3.2 This test method is dependent on the fact that metallic elements in the ground state will absorb light of the same wavelength they emit when excited. When radiation from a given excited element is passed through a flame containing ground-state atoms of that element, the intensity of the transmitted radiation will decrease in proportion to the amount of the ground-state element in the flame. A hollow cathode lamp whose cathode is made of the element to be determined provides the radiation. The metal atoms to be measured are

placed in the beam of radiation by aspirating the specimen into an oxidant-fuel flame. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photo-sensitive device measures the attenuated transmitted radiation.

4. Significance and Use

4.1 Manganese in pulp acts as a catalyst in oxidizing cellulose.

4.2 Iron in pulp can cause yellowness in rayon fibers and influence cellulose acetate plastics color. Iron also causes problems in photographic and blueprint papers.

4.3 Copper in pulp can act as a retardant in oxidizing cellulose and can affect viscose ripening. Copper interferes with the dye level of rayon fibers and influences cellulose acetate plastics color.

4.4 Calcium in pulps can cause problems in processing into acetate, rayon, cellophane, etc. Calcium can create undesirable deposits in viscose spinning and film casting operation. Calcium can influence viscosity control during cellulose acetate manufacture.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, consisting of an atomizer and burner, suitable pressure-regulating devices capable of maintaining constant oxidant and fuel pressure for the duration of the test, a hollow cathode lamp for each metal to be tested, an optical system capable of isolating the desired line of radiation, an adjustable slit, a photomultiplier tube or other photosensitive device, and a read-out mechanism for indicating the amount of absorbed radiation.

5.2 *Oxidant*—Air, which has been cleaned and dried through a suitable filter to remove oil, water, and other foreign substances, is the usual oxidant.

5.3 *Fuel*—Acetylene, commercially available, is the usual fuel. Acetone, always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder that has a gage pressure of only 3.5 kPa (50 psi) remaining.

5.4 *Volumetric Flasks*, 25, 100, and 1000-mL.

NOTE 1—In listing the apparatus for this method, the items required for

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.03.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.



the ashing step are not listed. For these items refer to Test Methods D 3516.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

6.2 *Purity of Water*—Unless otherwise indicated, references to water should be understood to mean reagent water conforming to the requirements in Specification D 1193, Type I.

6.3 *Hydrochloric Acid (1 + 1)*—Add 50 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 50 mL of water.

6.4 *Hydrochloric Acid (1 + 99)*—Dilute 10 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1000 mL with water.

6.5 *Nitric Acid (1 + 1)*—Add 50 mL of concentrated nitric acid (HNO₃, sp gr 1.42) to 50 mL of water.

6.6 *Sulfuric Acid (1 + 1)*—Add 50 mL of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) to 50 mL of water.

6.7 *Standard Solutions*—Dilute the solutions that follow with HCl (1 + 99) to prepare the standards to be used for calibration. Store all solutions in polyethylene bottles.

6.7.1 *Iron (1 mL = 1.0 mg Fe)*—Dissolve 1.000 g of pure iron in 100 mL of H₂SO₄ (1 + 1) with the aid of heat. Cool and dilute to 1 L.

6.7.2 *Copper (1 mL = 1.0 mg Cu)*—Dissolve 1.000 g of electrolytic copper contained in a 250-mL beaker in 30 mL of nitric acid (1 + 1). Slowly add 4 mL of H₂SO₄ (1 + 1) and heat until SO₃ fumes evolve. Cool and dilute to 1 L.

6.7.3 *Manganese (1 mL = 1.0 mg Mn)*—Dissolve 3.076 g of manganous sulfate monohydrate (MnSO₄·H₂O) in a mixture of 10 mL of HCl and 100 mL of water. Dilute to 1 L.

6.7.4 *Calcium (1 mL = 1.0 mg Ca)*—Weigh 2.497 g of calcium carbonate (CaCO₃) and transfer it to a 500-mL Erlenmeyer flask. Add 10 mL of water. Pour 10 mL of HCl slowly down the side of the flask. Add an additional 200 mL of water and heat until solution is complete. Cool and dilute to 1 L.

NOTE 2—Acceptable standard solutions are available commercially from any laboratory supply house.

6.8 *Lanthanum Solution (50 g/L)*—Wet 58.65 g of lanthanum oxide (La₂O₃) with water. Add slowly 250 mL of HCl to the mixture. When dissolved dilute to 1 L with water.

7. Preparation of the Sample

7.1 Select a representative sample in the amount of 30 g, 5 g for the determination of moisture and 25 g for the determination of the metals.

8. Procedure

8.1 Weigh about 25 g of pulp to the nearest 0.01 g. At the same time weigh out a separate sample for oven-dry cellulose determination. Ash the sample by Method D in Test Methods D 3516. Determine moisture content in accordance with Test Methods D 1348.

NOTE 3—Method D in Test Methods D 3516 has been listed as the

preferred one because it minimizes opportunity for sample loss during ashing, especially for the iron determination. However for calcium, or manganese greater than 1 mg/kg, low results may occur from sulfate interferences and Method A in Test Methods D 3516 may be preferred.

8.2 Calibration and Standardization of Atomic Absorption Spectrophotometer:

8.2.1 The method of operation varies with different models of atomic absorption spectrophotometers. Therefore, no attempt is made here to describe in detail the steps for placing an instrument into operation.

8.2.2 Prepare working standard solutions daily from those described in 6.7. Make the final calcium dilutions to contain 1 % lanthanum.

8.2.3 Atomize the standards and calibrate the spectrophotometer for the element of interest.

8.3 Analyze the sample solutions prepared from 24.13 and 24.14 of Method D in Test Methods D 3516 in accordance with 8.2. Iron, copper, and manganese normally can be run without further dilutions. Dilutions for calcium should be made 1 % in lanthanum.

NOTE 4—If Method A in Test Methods D 3516 was used, digest the ash from 7.4 with 5 mL HCl (1 + 1) on a steam bath, cool and dilute in a 25-mL volumetric flask to volume with water. Further dilutions for calcium should be made 1 % in lanthanum.

8.3.1 A reagent blank should be used to zero the atomic absorption spectrophotometer before taking sample readings.

9. Calculations

9.1 Calculate the concentration of the metallic ion, in milligrams per litre, using the calibration determined in 8.2.3.

$$M = \frac{C \times V}{W} \quad (1)$$

where:

M = metal content, mg/kg,

C = amount of material determined in sample solution, mg/L,

V = final dilution volume of sample, mL, and

W = weight of oven-dry cellulose, g.

10. Precision and Bias

10.1 *Precision*—An interlaboratory study of this procedure was conducted in accordance with Practice E 691. Four laboratories conducted tests on a single cellulose pulp using both dry ashing and wet ashing procedures. A fifth laboratory used only wet ashing. At the 95 % confidence level, results should agree within the limits shown in new Table 1 and Table 2. Since all sources of error in this procedure are not likely proportional to the test level, these precision statements may not apply at levels far removed from those in the tables.

TABLE 1 Dry Ashing

Metal	Typical Value, mg/kg	95 % Confidence, mg/kg
Iron	4.0	±2.4
Copper	0.22	±0.35
Manganese	2.0	±1.0
Calcium	201	±59

**TABLE 2 Wet Ashing**

Metal	Typical Value, mg/kg	95 % Confidence, mg/kg
Iron	5.9	±4.1
Copper	0.91	±1.43
Manganese	1.9	±1.0
Calcium	193	±32

10.2 *Bias*—In the absence of a suitable reference material, no accuracy determination is possible. It should be noted, however, that dry ashing methods are subject to loss of some metals during ignition, yielding lower results than wet ashing procedures. This may have been the case for the iron and copper results in the interlaboratory test.

11. Keywords

11.1 analysis; atomic absorption; cellulose; metals

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