



# Standard Test Method for Copper Number of Paper and Paperboard<sup>1</sup>

This standard is issued under the fixed designation D 919; 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 approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method (1, 2, 3, and 4)<sup>2</sup> covers the determination of the copper number of bleached and purified paper and paperboard, except those containing calcium sulfite, zinc sulfide, melamine resin, urea-formaldehyde resin, starch, rosin size, or other copper-reducing nonfibrous materials. Paper containing such additives can be tested only if the amount and reducing power of the added material is known.

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 585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Products<sup>3</sup>
- D 586 Test Method for Ash in Pulp, Paper, and Paper Products<sup>3</sup>
- D 644 Test Method for Moisture Content of Paper and Paperboard by Oven Drying<sup>3</sup>
- D 687 Method for Quantitative Determination of Coating on Mineral Coated Paper<sup>4</sup>
- D 1968 Terminology Relating to Paper and Paper Products<sup>3</sup>

## 3. Terminology

3.1 *Definition:* Definitions shall be in accordance with Terminology D 1968 and the *Dictionary of Paper*.<sup>5</sup>

## 4. Significance and Use

4.1 The copper number can be regarded as an index of those impurities in cellulose such as oxycellulose, hydrocellulose, lignin, and sugars which possess reducing properties. It is

valuable for detecting changes accompanying deterioration and may, therefore, be considered as a test for indicating the permanence of paper. In parchment and grease-proof papers, copper number is considered to give an indication of the degree of parchmmentizing.

## 5. Apparatus

5.1 *Grinder*—A grinder that will completely disintegrate the paper without heating or contaminating it. The grinder shall be a Koerner type or its equivalent. After disintegrating, the sample should have an absorbent cotton-like appearance.

5.2 *Bath*—A steam or oil bath that can be maintained at  $100 \pm 1^\circ\text{C}$ .

## 6. Reagents

6.1 *Carbonate-Bicarbonate Solution*—Dissolve 350 g of sodium carbonate dechydrate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) (or 129 g of anhydrous  $\text{Na}_2\text{CO}_3$ ) and 50 g of sodium bicarbonate ( $\text{NaHCO}_3$ ) in water and dilute to 1 L.

6.2 *Copper Sulfate Solution*—Dissolve 100 g of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in water and dilute to 1 L.

6.3 *Molybdophosphoric Acid*—Dissolve 100 g of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) and 75 mL of phosphoric acid ( $\text{H}_3\text{PO}_4$ , 83 %) in a mixture of 275 mL of sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84) and 1.75 L of water.

6.4 *Potassium Permanganate Standard Solution (0.05 N)*—Dissolve 1.5815 g of potassium permanganate ( $\text{KMnO}_4$ ) in water and dilute to 1 L in a volumetric flask. Standardize against sodium oxalate as the primary standard.

6.5 *Sodium Carbonate Solution (50 g/L)*—Dissolve 50 g of  $\text{Na}_2\text{CO}_3$  in water and dilute to 1 L.

6.6 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (sp gr 1.84).

## 7. Sampling

7.1 Sample the material in accordance with Practice D 585.

## 8. Test Specimens

8.1 Cut two or more thoroughly representative test specimens from each test unit of the sample. Disintegrate each specimen in the grinder. For mineral coated samples, remove the coating as described in Method D 687, and air-dry the decoated paper before disintegrating. In the absence of knowledge regarding the respective nonfibrous materials present,

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<sup>2</sup> The boldface numbers in parentheses refer to a list of references at the end of this test method.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.09.

<sup>4</sup> Discontinued, see 1971 *Annual Book of ASTM Standards*, Part 15.

<sup>5</sup> Available from the Technical Association of the Pulp and Paper Industry, P.O. Box 105113, Atlanta, GA 30348.



qualitative tests for sizing (rosin, starch, glue, and casein), saturants (waxes, organic saturants, etc.), mineral fillers (especially calcium sulfite and zinc sulfide), and any other suspected nonfibrous materials shall be made before weighing out portions of the specimen for test.

## 9. Procedure

9.1 Allow the ground specimens to come to moisture equilibrium with the atmosphere of the balance and weigh a portion of 1.5 g to the nearest 0.01 g. Weigh, at the same time, specimens for moisture and ash determinations, and for determination of such other sizing, filling, or other nonfibrous materials as may be found necessary for correction of the copper number, using the applicable methods as shown in Section 2.

9.2 Immediately before use, add 5.0 mL of copper sulfate solution (Note 1) to 95 mL of carbonate-bicarbonate solution. Bring the mixture to a boil in 2 min, and pour it over 1.5 g of the ground sample in a 125-mL Erlenmeyer flask. Stir well with a glass rod in order to distribute the fibers and to remove air bubbles. Fit the flask with a loosely fitting glass bulb or stopper and submerge it completely in a steam bath at atmospheric pressure. Occasionally fibers tend to float to the surface; therefore, the flask should be shaken from time to time to redistribute them. Remove the flask from the steam bath at the end of 3 h. Using suction, filter on an ashless filter paper in a 75-mm Büchner funnel. Wash by flooding with 100 mL of  $\text{Na}_2\text{CO}_3$  solution at about 20°C and then by flooding with 250 mL of hot water at about 95°C discarding the filtrates.

NOTE 1—Five millilitres of copper sulfate solution are sufficient for a copper number not greater than approximately 6, and this figure is seldom exceeded except in papers containing highly lignified fibers, such as groundwood, or in papers that have deteriorated considerably. When a copper number greater than 6 is obtained, the result does not correctly indicate how much the value exceeds 6. If the actual value is desired, re-run the test, increasing the amount of copper sulfate solution to 10 mL and the amount of molybdophosphoric solution to 50 mL or as much more as may be necessary, retaining the correct ratio between the solutions.

9.3 Transfer the fibers and filter paper to a small beaker, add 25 mL of the molybdophosphoric acid solution, and macerate well with a flattened glass rod. Transfer to a Büchner funnel and wash thoroughly with cold water until the blue molybdenum color is removed from the fibers.

9.4 Dilute the filtrate with water to approximately 700 mL and titrate with 0.05 N  $\text{KMnO}_4$  solution to a faint pink.

## 10. Calculation

10.1 Calculate the copper number on the basis of 100 g of moisture-free fiber as follows:

$$\text{Copper number} = [6.36 (V - B) N] / (W) \quad (1)$$

where:

$V$  = volume of  $\text{KMnO}_4$  solution to titrate the filtrate from the specimen,  $\text{cm}^3$ ,

$B$  = volume of  $\text{KMnO}_4$  solution to titrate the blank filtrate,  $\text{cm}^3$ ,

$N$  = normality of  $\text{KMnO}_4$  solution, and

$W$  = moisture-free weight of the test specimen, after subtracting the weight of ash and other non-copper reducing nonfibrous components whenever they are present in significant amounts, g.

## 11. Report

11.1 Report the following information:

11.1.1 The copper number, as the average of the two or more values determined on each test specimen, rounded to the nearest 0.1 units.

## 12. Precision and Bias

12.1 *Precision*

12.1.1 *Repeatability*—The difference between two test results, each of which is the average of two determinations, should be less than 10 %. This estimate of precision is based upon a total of 36 determinations.

12.1.2 *Comparability* —(*Between-Laboratories*)—Not known.

12.1.3 *Reproducibility* (*Between-Materials*)—Not known.

12.2 *Bias*

12.2.1 The procedure for Measuring Copper Number in this test method has no bias because the value of copper number is defined only in terms of this test method.

12.2.2 Further, there is no acceptable reference standard material suitable for determining bias of this test procedure.

12.2.3 The user is advised of the following information, however.

12.2.3.1 It has been found (5) that melamine-formaldehyde resin in paper produces a decrease (0.2 to 0.4) in the copper number of paper. Some unpublished research work indicates that urea-formaldehyde resin gives an increase of 0.2 to 0.4 in the copper number of paper.

12.2.3.2 The work of Shaw et al (6) indicates that glue and starch sizings increase the copper number of paper by about 0.05 copper number unit; also, rosin size, used with alum, was found to increase the copper number in the order of 0.2 copper number unit.

## 13. Keywords

13.1 copper number; paper; permanence



REFERENCES

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