Copper number of pulp, paper, and paperboard
(Reaffirmation of Classical Method T 430 cm-09)

1. Scope and significance

1.1 This method describes a procedure for determining the copper number of bleached and purified pulp, paper, and paperboard, except those containing calcium sulfite, zinc sulfide, melamine resin, or other copper-reducing nonfibrous materials. Papers containing such additives can be tested only if the amount and reducing power of the added material is known.

1.2 It has been well established that hydrolyzed or oxidized cellulose is capable of reducing certain metallic ions to lower valence states, and reactions of this type have served to detect damage to cellulose and to estimate the quantity of reducing groups.
1.3 The copper number may be regarded as an index of those impurities in paper, such as oxycellulose, hydrocellulose, lignin, and sugars, which possess reducing properties. It is useful for determining changes accompanying deterioration and may therefore be considered as a factor having an indirect bearing on the permanence of paper. It should not be applied to papers containing mechanical pulp or unbleached chemical pulp.

2. Definition

Copper number is defined as the number of grams of metallic copper (as Cu₂O) resulting from the reduction of CuSO₄ by 100 g of the pulp or paper fibers.

3. Apparatus

3.1 Grinder¹, which will disintegrate the pulp and paper fibers without appreciably heating, contaminating, or deteriorating them. A Koerner-type grinder or its equivalent has been found satisfactory. After disintegrating, the sample should have an absorbent cotton-like appearance.

NOTE 1: If a Koerner grinder is not available, a small Hammermill or other laboratory equipment may be used to fluff the test portion, provided the cellulose is not degraded as measured by a decrease in CED viscosity [see TAPPI T 230 “Viscosity of Pulp (Capillary Viscometer Method)”).

3.2 Bath, a steam or oil bath maintained at 100° ± 1°C.
3.3 Büchner funnel, 75 mm, with suction flask, 1000 mL.
3.4 Glassware, graduated cylinders, 10, 25, 100, 250, and 500 mL; volumetric flask, 100 mL; Erlenmeyer flask, 125 mL, with loosely fitting glass bulb or stopper; glass rod with flattened end; beaker, 100 mL; buret, 50 mL; and wide-mouth jar with screw cover.
3.5 Mixer, high speed, to slurry the pulp with water.
3.6 Miscellaneous, 100-mm ashless filter paper.

4. Reagents

4.1 Copper sulfate solution. Dissolve 100 g CuSO₄ • 5H₂O in water and dilute to 1000 mL.

¹Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list, available as part of the CD or printed set of Standards, or on the TAPPI website general Standards page.
4.2 *Carbonate-bicarbonate solution.* Dissolve 350 g Na$_2$CO$_3$ • 10H$_2$O (or 129 g of anhydrous Na$_2$CO$_3$) and 50 g NaHCO$_3$ in water and dilute to 1000 mL.

4.3 *Phosphomolybdic acid* (molybdophosphoric acid) *solution.* Dissolve 100 g of sodium molybdate, Na$_2$MoO$_4$ • 2H$_2$O, and 75 mL of phosphoric acid (85%) in a mixture of 275 mL concentrated H$_2$SO$_4$ and 1750 mL of water.

NOTE 2: Always add acid to water, not water to acid.

4.4 *Sodium carbonate,* an approximately 5 % Na$_2$CO$_3$ solution.

4.5 *Potassium permanganate,* 0.05N KMnO$_4$ (see TAPPI T 610 “Preparation of Indicators and Analytical Reagents, and Standardization of Volumetric Solutions” for preparation and standardization).

5. **Sampling and test specimens (pulp)**

5.1 Obtain a sample of the pulp in accordance with a previously determined sampling procedure. Select a representative test portion of at least 10 g dry basis.

5.2 Add the portion to distilled water and slurry it until thoroughly separated, then filter on a paper in the Büchner funnel with suction, and finally air-dry.

NOTE 3: Take care to minimize loss of fines. This loss will substantially lower the copper number.

5.3 After air-drying, “fluff” the portion by passing it through the grinder, then place into a wide-mouth jar and seal.

5.4 Allow the fluffed pulp to equalize in moisture content, then weigh out two test specimens each of about 1.5 g (to the nearest 0.01 g) and transfer each to a 125-mL Erlenmeyer flask. In addition, make moisture and ash determinations in accordance with TAPPI T 210 “Sampling and Testing Wood Pulp Shipments for Moisture” and TAPPI T 211 “Ash in Wood and Pulp,” respectively.

6. **Sampling and test specimens (paper and paperboard)**

6.1 From each test unit obtained in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product” take approximately equal portions (5-10 g), representative of each test unit, and combine into a single composite sample.
6.2 If nonfibrous material may be present, make qualitative tests for them before weighing portions of the sample for test. Examples are: sizing materials such as rosin, starch, glue, and casein; saturants such as waxes; mineral fillers, especially calcium sulfite and zinc sulfide. Do not attempt to apply this procedure if copper-reducing substances are found. (See Section 6.5 for determination of copper reducing substances.)

6.3 If the paper is coated using a casein binder, the coating may be removed in accordance with UM 542 “Amount of Coating on Mineral-Coated Paper.” Air-dry the decoated paper before proceeding. UM 542 is not applicable to latex bound coatings.

6.4 Disintegrate the sample in the grinder.

6.5 Allow the ground composite sample to come to moisture equilibrium with the atmosphere of the balance for at least 1 h. Weigh at least two 1.5-g specimens of the ground paper to the nearest 0.01 g and transfer each to a 125-mL Erlenmeyer flask. At the same time weigh specimens and make determinations for moisture (see TAPPI T 412 “Moisture in Paper and Paperboard”), ash (see TAPPI T 413 “Ash in Paper and Paperboard”), and nonfibrous noncopper reducing materials [see TAPPI T 408 "Rosin in Paper and Paperboard"; TAPPI T 419 "Starch in Paper"; TAPPI T 504 "Glue in Paper (Qualitative and Quantitative Determination)"]; UM 490 "Casein and Soya Protein in Paper (Qualitative)"; TAPPI T 405 “Petroleum Wax in Impregnated Papers”; TAPPI T 421 “Qualitative (Including Optical Microscopic) Analysis of Mineral Filler and Mineral Coating of Paper”].

7. Procedure

7.1 Immediately before use, add 5.0 mL of CuSO\textsubscript{4} solution (4.1) to 95 mL of the carbonate-bicarbonate solution (4.2). Heat the mixture to a boil in 2 min, and pour it into the flask over the test specimen. 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 just above the liquid line in the steam or oil bath. Since fibers tend to float to the surface, shake the flask from time to time to redistribute them.

NOTE 4: The amount of solution (4.1) given above is sufficient for a copper number not greater than 6. This figure is seldom exceeded except with pulps and papers containing highly lignified fibers, such as groundwood, to which this method does not apply, or for pulps and papers which have deteriorated considerably. If the copper number exceeds 6, increase the volume of copper sulfate solution (4.1) to 10 mL and subsequently, the volume of molybdophosphoric acid solution (4.3) to 50 mL or more (to maintain the \(\frac{1}{5}\) ratio).

7.2 At the end of 3 h, remove the flask from the bath. Filter on an ashless filter paper in the Büchner funnel, with suction. Wash by flooding with 100 mL of the 5% Na\textsubscript{2}CO\textsubscript{3} solution (4.4) at about 20°C and then by flooding with 250 mL of hot water at about 95°C. Discard the filtrates. Transfer the fibers and filter paper to a 100-mL beaker, add 25 mL of the molybdosphoric acid solution (4.3) and macerate well with a flattened glass rod. Transfer to a clean Büchner funnel fitted with an ashless filter paper and wash thoroughly with cold water, collecting the filtrate, until all the blue color is removed.
NOTE 5: This final wash should be completed within 30 min because it becomes increasingly difficult to wash the blue molybdenum oxide color from the fibers as time proceeds, resulting in abnormally low copper number values.

7.3 Dilute the filtrate with water to approximately 700 mL and titrate it with 0.05N KMnO₄ (4.5) to a faint pink which persists for 30 s.

7.4 Make a blank determination following the same procedure using the same amounts of reagents and water.

8. Calculation

Calculate the copper number on the basis of 100 g of moisture-free sample by the following formula:

\[
\text{Copper number} = \frac{[6.36 \cdot (V-B) \cdot N]}{W}
\]

where:

\[V = \text{KMnO}_4 \text{ solution to titrate the filtrate from the specimen, mL}\]

\[B = \text{KMnO}_4 \text{ solution to titrate the blank filtrate, mL}\]

\[N = \text{normality of KMnO}_4 \text{ solution}\]

\[W = \text{moisture-free weight in grams of the test specimen, after subtracting the weight of ash and other noncopper reducing nonfibrous components whenever they are present in significant amounts}\]

9. Report

Report the copper number as the average test result of the two determinations, to one decimal place.

10. Precision

10.1 Repeatability (within laboratory) = 10%;

10.2 Reproducibility (between laboratories) = not known;

10.3 The estimate of repeatability is based upon a total of 36 determinations made in one laboratory on three different pulps.
11. **Keywords**

Pulp, Paper, Paperboard, Copper number, Bleached pulps

12. **Additional information**

12.1 Effective date of issue: To be assigned.

12.2 This method is essentially the Braidy (1) modification of the original Schwalbe (2) method, with modifications for its adaptation to paper proposed by Scribner and Brode (3) and by Burton and Rasch (4).

12.3 The Enka method as described by Morgan and Henry (5) was evaluated in the laboratory and found not to be more precise for pulps and give a different level of values from this method.

12.4 It has been found (6) that melamine-formaldehyde resin in paper produces a decrease (0.2 - 0.4) in the copper number of paper. Some unpublished research work indicates that urea-formaldehyde resin gives an increase of 0.2 - 0.4 in the copper number of paper.

12.5 The work of Shaw et al. (7) 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.

12.6 Related methods: ASTM D919; Scandinavian SCAN C-22 (semi-micromodification); Canadian PAPTAC G.22 (substantively similar); German VZPCI 8.

12.7 This method, formerly T 430 om-94, has been reclassified as a Classical Method. Such procedures are no longer in common use or have been superseded by advanced technology; they are technically sound, have a history of use, and contain a body of literature references that make their preservation valuable.

**References**


*Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department.*