



Standard Test Methods for Reducible Sulfur in Paper¹

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1. Scope

1.1 These test methods cover the determination of reducible sulfur in paper and paperboard within the context of the given definitions.

1.1.1 *Method B*—The semiquantitative method indicates the general level of reducible sulfur with limited accuracy.

1.1.2 *Method A*—The quantitative method gives a measure of the reducible sulfur with much greater accuracy.^{2,3}

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, and Related Product⁴

D 644 Test Method for Moisture Content of Paper and Paperboard by Oven Drying⁴

D 1968 Terminology Relating to Paper and Paper Products⁴

D 2043 Test Method for Silver Tarnishing by Paper⁴

3. Terminology

3.1 *Definitions*—Definitions shall be in accordance with Terminology D 1968 and the *Dictionary of Paper*.⁵

4. Summary of Test Methods

4.1 *Method B*, semiquantitative method, involves the reduction of various forms of sulfur to hydrogen sulfide and the development of a dark spot of lead sulfide on the filter paper

impregnated with lead acetate. The intensity of the spot is compared with spots developed from standards and is proportional to the concentration. No colorimeter or spectrophotometer is needed for this method.

4.2 *Method A*, the quantitative method, uses the identical reduction system to generate hydrogen sulfide, but the sulfide is precipitated by alkaline cadmium sulfate and then converted to methylene blue by reaction with acidic *p*-aminodimethylaniline in the presence of ferric chloride. The methylene blue is measured spectrophotometrically and the intensity is compared with standards prepared in similar manner.

5. Significance and Use

5.1 The test methods outlined are not necessarily a measure of how much a given test material will tarnish polished metals. When tested by these methods, paper that has less than 0.0008 % reducible sulfur, may be assumed to be nontarnishing as far as sulfur is concerned, but if more than 0.0008 %, this does not necessarily mean that tarnishing will occur, because sulfur compounds which may not cause staining are reduced by the treatment with the subsequent evolution of hydrogen sulfide. If more than 0.0008 % reducible sulfur is found, or if the effect of that or other materials causing stains on silver is desired, the paper should be subjected to an accelerated tarnishing test (see Test Method D 2043).

NOTE 1—If the pH of the paper is low (for example, 4.0 to 4.5 (cold extraction)) as little as 0.0002 % of reducible sulfur may cause tarnishing of imitation gold bronze prints; whereas, if the pH were higher, (for example, on brush-coated art paper) a much higher quantity of sulfur might be tolerated.

5.2 The test methods described do not give the total sulfur content, nor the total reducible sulfur content, nor are they intended to. They are limited to the reducible sulfur content determined *under the conditions of the test* (that is, a fairly mild reduction system).³

5.2.1 Those forms of sulfur believed to be “reducible” under the test conditions are (1) sulfide (released by the acid, not actually reduced), (2) elemental sulfur, (3) thiosulfate, (4) other polythionates or polysulfides, and (5) perhaps sulfite. Sulfate is excluded.

¹ These test methods are under the jurisdiction of ASTM Committee D06 on Paper and Paper Products and are the direct responsibility of Subcommittee D06.92 on Test Methods.

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² Sobolev, I., Bhargava, R., Gosuntov, N., and Russell, R., *Tappi* 39(9): 628(1956).

³ Chazin, J. D., “Colorimetric Determination of Reducible Sulfur in Paper and Paperboard,” *Tappi*, Journal of the Technical Association of the Pulp and Paper Industry, TAPPI, Vol 53, No. 8, 1970, p. 1514.

⁴ *Annual Book of ASTM Standards*, Vol 15.09.

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

6. Sampling

- 6.1 Obtain the sample in accordance with Practice D 585.
- 6.2 A minimum of 6 g of sample is required to provide triplicate test specimens.
- 6.3 Do not touch the test area of sample or test specimens with the fingers; handle with clean forceps only.

7. Test Specimens

- 7.1 From each test unit of the sample, cut and weigh 2 g to the nearest 1 mg for each test unit.
- 7.2 Determine the moisture content in accordance with Test Method D 644.

METHOD A—QUANTITATIVE MEASUREMENT

8. Apparatus

- 8.1 *Reaction Apparatus* (Fig. 1), consisting of a 500-mL

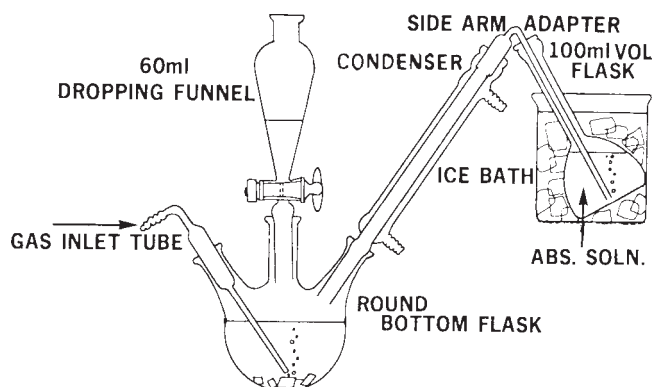


FIG. 1 Reaction Apparatus (Quantitative Determination).

round-bottom three-necked flask as illustrated, equipped with a gas inlet tube adapter with perforated bulb, a 60-mL pear-shaped funnel, a 200-mm West condenser, a side-arm adapter, and a heating mantle with variable power supply.

- 8.2 *Absorption Apparatus* (Fig. 1), consisting of a 100-mL amber or low-actinic flask in a suitable ice bath.

- 8.3 *Colorimeter or Spectrophotometer* to read at 660 to 670 nm equipped with 1-in. cells or 25 to 50-mm cuvettes.

- 8.4 *Pipets*—1, 2, 5, and 10-mL serological or bacteriological (blow-out).

- 8.5 *Other Equipment*—100 and 1000-mL volumetric flasks; medicine droppers; 10 and 100-mL graduated cylinders; forceps; 10.0-mL volumetric pipets.

- 8.6 *Disintegrator*—A blender or other such rotating-blade device with a small volume container, if possible.

- 8.7 *Optional Equipment*—A constant-temperature bath, maintained at 20 to 25°C.

9. Reagents and Materials

9.1 *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 Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

- 9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water.

- 9.3 *Aluminum Foil*, 1145 alloy, plain (or aluminum weighing pans), not over 0.01 in. (0.25 mm) sulfur-free.

- 9.4 *Amine Solutions*:

- 9.4.1 *Stock Amine Solution*—Dissolve 25 g of *p*-aminodimethylaniline sulfate (*N,N*-dimethyl-*p*-phenylenediamine sulfate) in 75 mL of cold sulfuric acid (1 + 1) and dilute to 100 mL with the (1 + 1) acid.

- 9.4.2 *Dilute Amine Solution*—Pipet 2.5 mL of the stock solution into a 100 mL volumetric flask and dilute to the mark with sulfuric acid (H₂SO₄)(1 + 1).

- 9.5 *Cadmium Hydroxide Absorption Suspension*—Dissolve 4.3 g of cadmium sulfate (3CdSO₄·8H₂O) in water; add 0.3 g of sodium hydroxide (NaOH) dissolved in water and 10 g of arabinogalactan; dilute to 1000 mL and stir well. This is a saturated solution of cadmium hydroxide; the suspension is swirled before pouring off an aliquot.

- 9.6 *Ferric Chloride Solution*—Dissolve 100 g of ferric chloride hexahydrate (FeCl₃·6H₂O) in water and dilute to 100 mL.

- 9.7 *Nitrogen Gas*, sulfur-free.

- 9.8 *Phosphoric Acid*—Concentrated phosphoric acid (H₃PO₄) (sp gr 1.69) sulfur-free.

- 9.9 *Sodium Sulfide Standard Solutions* (use water deaerated with nitrogen).

- 9.9.1 *Stock Solution*—Dissolve 1.56 g of sodium sulfide nonahydrate (Na₂S·9H₂O) (use large crystals which appear dry) in the deaerated water and dilute to 1000 mL. Pad the space over the solution with nitrogen, and renew each time the solution is used. *Solution should be stable for 1 month.*

- 9.10 *Working Solution*—Pipet 10.0 mL of stock solution into a 1000-mL volumetric flask and dilute to the mark with the deaerated water. 1 mL of this solution contains 2 μg of sulfur (that is, solution is 2 ppm in sulfur). Prepare solution daily.

NOTE 2—This solution or the stock solution may be standardized by potentiometric titration with silver nitrate solution using a sulfide-specific electrode; the sulfide standard should be at least 90 % pure.

10. Procedure

10.1 Disintegrate the sample in the blender with 75 mL of water and transfer the test specimen from the disintegrator quantitatively to the 500-mL reaction flask using additional aliquots of 5 mL of water to assist in the transfer. Add 2 g of aluminum foil (or one aluminum foil weighing dish) which has been cut into ½-in. (12.7-mm) squares and complete the assembly of the reaction apparatus.

- 10.2 *Precipitation of Cadmium Sulfide*:

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."