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Technical Association of Pulp and Paper Industry
Standard Method T 406 Su-72
An American National Standard

Standard Test Methods for Reducible Sulfur in Paper[1]

This standard is issued under the fixed designation D 984; 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.

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 Product[4]

D 644 Test Method for Moisture Content of Paper and Paperboard by Oven Drying[4]

D 1968 Terminology Relating to Paper and Paper Products[4]

D 2043 Test Method for Silver Tarnishing by Paper[4]

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.

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[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 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.

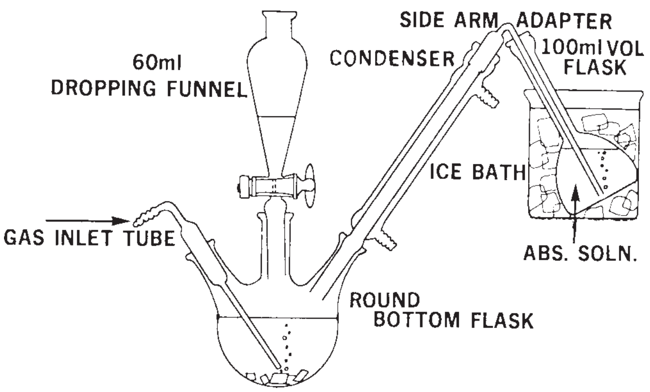

FIG. 1 Reaction Apparatus (Quantitative Determination).

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 (H_2SO_4)(1 + 1).

9.5 *Cadmium Hydroxide Absorption Suspension*—Dissolve 4.3 g of cadmium sulfate ($3CdSO_4\cdot 8H_2O$) 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 ($FeCl_3\cdot 6H_2O$) in water and dilute to 100 mL.

9.7 *Nitrogen Gas*, sulfur-free.

9.8 *Phosphoric Acid*—Concentrated phosphoric acid (H_3PO_4) (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 ($Na_2S\cdot 9H_2O$) (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*:

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[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."

10.2.1 Measure 10 mL of the concentrated H_3PO_4 (sp gr 1.69) into the dropping funnel and 75 mL of the cadmium hydroxide absorption suspension (which is swirled before pouring and should include some solids) into the darkened 100-mL volumetric collecting flask. Start bubbling the nitrogen at the rate of about 5 bubbles per second, taking care to ensure that *there are no leaks*. Use top quality sulfur-free stopcock grease at the joints and if necessary tie the joints with clamps or rubber bands. After the nitrogen has been adjusted submerge the delivery tube into the absorption suspension in the 100-mL volumetric flask and put the ice bath in place, taking care to assure that the tip is to the bottom of the flask (that is, submerged as deeply as possible).

10.2.2 Add the 10 mL of concentrated H_3PO_4 from the dropping funnel. Leave a small amount of acid in the tip, close the stopcock on the funnel, and start heating the mixture to a boil. Take care that the absorption solution does not back up in the delivery tube while the mixture is heating. It may be necessary to adjust the nitrogen flow to prevent this.

10.2.3 Discontinue heating after 45 min, remove the volumetric flask together with the side-arm adapter by dislodging it at the condenser, and stop the nitrogen flow. Keep the adapter together with the flask until the amine reagent is added in the color development step because the cadmium sulfide often hangs up in the tube tip. The sample should not be stored in this manner for more than 1 h.

10.3 *Preparation of Calibration Standards*—Add 75 mL of the cadmium hydroxide absorption suspension to each of five 100-mL darkened volumetric flasks and place in the constant temperature bath (20 to 25°C) if available. Pipet 1, 2, 5, and 10 mL, respectively, of the sodium sulfide standard working solution into four of the volumetric flasks. Prepare each time the analysis is performed. Swirl gently but adequately. The flask containing no sulfide solution is the reagent blank. The standards contain 2, 4, 10, and 20 µg of sulfur per 100 mL.

NOTE 3—The "blow-out" pipets are used to pipet the sodium sulfide working solution aliquots. They are immersed into the absorption solutions and allowed to drain slowly while the tips are below the surface. When drainage is complete, gently blow out the last drops while still immersed and then remove from the flask.

10.4 *Color Development and Read-Out*:

10.4.1 To the test specimen, reagent blank, and calibration standard 100-mL volumetric flasks, add 2 mL of the dilute amine solution. Allow the dense amine solution to flow down the side of the flask to the bottom of the absorption solution. Stopper the flask and swirl gently but adequately a few times without shaking (heat will be regenerated). Immediately add 10 drops of the ferric chloride solution and shake vigorously to react any hydrogen sulfide (H_2S) which may have come out of the solution. Dilute each solution to the mark with water, mix well, and allow to stand for at least 20 min. The color development should be conducted in the dark and if possible at 20 to 25°C by means of the constant-temperature bath or by any other comparable means available.

10.4.2 Read the maximum absorbance at the peak at or near 670 nm, using water as the reference. Subtract the absorbance of the reagent blank (as the correction) from the calibration standards and the test specimen. Plot the corrected absorbance of the calibrated standards versus micrograms of sulfur present and draw the best straight line passing through zero. (The slope should be about 0.005 to 0.010 absorbance units per 1 µg of sulfur per 10 nm of path length.) Read the amount of reducible sulfur, in micrograms, in each specimen directly from the chart based on its net absorbance.

11. Calculation

11.1 Calculate the parts per million of reducible sulfur in the specimen, P, as follows:

$$P = R/W \tag{1}$$

where:

R = reducible sulfur from chart, µg, and

W = weight of specimen, g.

11.2 Calculate the percent reducible sulfur, P', as follows:

$$P' = P \times 0.0001 \tag{2}$$

12. Report

12.1 Report the following information:

12.1.1 Amount of reducible sulfur as a percentage by weight of the moisture-free paper to two significant figures, and

12.1.2 Individual values for each specimen which agree to within ±50 % relative average deviation, as well as reporting the average for the three determinations.

13. Precision and Bias

13.1 *Precision*:

13.1.1 The following estimates of precision are based on limited experience: a within-laboratory study of three sets of a linerboard sample and a round-robin among three laboratories on five different linerboard samples.

13.1.2 *Repeatability (Within Laboratory)*—0.91 ppm reducible sulfur (11%).

13.1.3 *Comparability (Between Materials)*—Not known.

13.1.4 *Reproducibility (Between Laboratories)*—24%.

13.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias has not been determined.

METHOD B—SEMIQUANTITATIVE MEASUREMENT

14. Apparatus

14.1 *Reaction Apparatus*—Essentially the same as the quantitative method (8.1), except that the side arm adapter and the absorption apparatus are replaced by a glass tube with suitable ground-glass joint (Fig. 2). The tube should be 100 mm in length with flanged heads ground flat on both sides and a means of clamping the flanges together with two disks of filter paper between them. The outermost paper disk is impregnated with lead acetate.

14.2 *Other Equipment*—Same as 8.5, and in addition a buret or pipet graduated in 0.1-mL divisions.

15. Reagents and Materials

15.1 *Aluminum Foil*, as in 9.3.

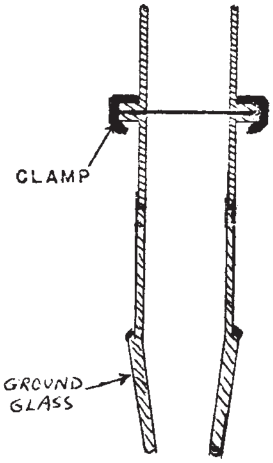

FIG. 2 Reaction Apparatus (Semiquantitative Determination)

15.2 *Lead Acetate Solution*—Add 20 g $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ per 100 mL water.

15.3 *Nitrogen Gas*, as in 9.7.

15.4 *Phosphoric Acid*, as in 9.8.

15.5 *Sodium Sulfide Standard Solution*, as in 9.9.

15.6 *Test Paper*—Fresh, high-quality, rapid filtering grade of paper handled only with forceps and (if available) the same diameter as the flanged tube. This paper is immersed in lead acetate solution, dried and if not of proper size cut to fit between the flanges. Store in an airtight container under nitrogen. Unimpregnated filter paper of the same diameter should be prepared ready for use.

16. Procedure

16.1 Follow the procedure in 10.1.

16.2 *Precipitation of Lead Sulfide Spots*—Clamp the filter paper impregnated with the lead acetate along with the unimpregnated paper (on the inside) between the flanges and moisten with a minimum amount of water. Measure 10 mL of the concentrated H_3PO_4(sp gr 1.69) into the dropping funnel. Start bubbling the nitrogen at the rate of 5 bubbles per second, taking care to assure there are no leaks. Add the 10-mL of concentrated H_3PO_4 (sp gr 1.69) from the dropping funnel slowly. Close the stopcock on the dropping funnel after the acid has all drained and heat the mixture to a boil. Keep the lead acetate paper moist throughout the heating period. After 45 min, remove the apparatus from the heating mantle and remove the flanged head from the condenser, carefully separating the lead acetate paper.

16.3 *Preparation of Calibration Standards*—Prepare with each set of samples a set of spot stained disks. Remove the dropping funnel from the reaction flask and pipet 2.0 mL of the sodium sulfide standard working solution into the flask containing 2 g of the cut-up aluminum foil. Add 80 mL of water and replace the dropping funnel. Proceed in accordance with 16.2. Repeat for each of the following aliquots: 2.0, 4.0, 6.0, 8.0, and 10.0 mL and for a reagent blank containing no added standard solution. The disks prepared in this fashion contain approximately 4, 8, 12, 16, and 20 µg of sulfur as stains or spots of lead acetate on the filter paper. The blank should contain no more than a barely perceptible stain. If it is half as intense as the 4 µg standard, discard the experiment, prepare new reagents, wash the glassware thoroughly, and start over.

16.4 Compare the spots developed for the samples with the spots developed for the calibration standards. Bracket the sample between the most likely standards by placing the spots side by side and viewing under intense light with a white background.

17. Report

17.1 Report the following information:

17.1.1 Amount of reducible sulfur as a percentage by weight of the moisture-free paper to 1 significant figure from the calibration in 11.1, except that the micrograms of sulfur are estimated from the relative intensity of the spots compared with the standard disks, and

17.1.2 Individual values for each specimen, and the average of three determinations.

18. Precision and Bias

18.1 *Precision*—It is not practical to specify the precision of the procedure in this test method because the method gives only semiquantitative results of limited accuracy, as stated in the scope.

18.2 *Bias*:

18.2.1 Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias has not been determined.

18.2.2 A change in the calibration material used in the method in past years may impact reported data. The user should be aware of the following information:

18.2.2.1 The thiosulfate standard previously used has been replaced with sodium sulfide. There is evidence in the literature and experimentally that only 50 % of the sulfur in thiosulfate is recovered by the reduction system specified for in this method. Other evidence, however, conflicts with these results and postulates. Sodium sufide has, therefore, been specified as the calibration standard in both techniques. The question of the reduction of thiosulfate and other polythionates should be investigated and resolved.

18.2.2.2 With the replacement of thiosulfate as calibration standard, the spot-staining technique may show higher results (perhaps twice the previous results) with the sodium sulfide standard for the same paper. This may be evaluated for a particular laboratory which has previously used the method on a particular paper by evolving two sets of calibration standards, one thiosulfate and one sulfide.

19. Keywords

19.1 paper; paperboard; reducible sulfur; tarnish

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