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WI _____ 120802.02 _____

T _____ 406 _____

DRAFT NO. _____ 3 _____

DATE _____ April 30, 2013 _____

WORKING GROUP
CHAIRMAN _____ James C. Abbott _____

SUBJECT
CATEGORY _____ Chemical Properties _____

RELATED
METHODS _____ See "Additional Information" _____

CAUTION:

This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Reducible sulfur in paper and paperboard (Revision of T 406 om-08) (no changes from Draft 2)

1. Scope

1.1 This method describes two procedures for the determination of reducible sulfur in paper and paperboard within the context of the given definitions.

1.1.1 The quantitative procedure found in Section 9 gives a measure of the reducible sulfur with the precision shown in Section 12.

1.1.2 The semi-quantitative test described in section 13 indicates the general level of reducible sulfur with limited accuracy.

2. Significance

2.1 The procedures are not necessarily a measure of how much a given test material will tarnish polished metals. When tested by these procedures, paper which 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 TAPPI T 444 “Silver Tarnishing by Paper and Paperboard”).

NOTE 1: If the pH of the paper is low, e.g., 4-4.5 (cold extraction), as little as 0.0002% of reducible sulfur may cause tarnishing of imitation gold bronze prints; whereas, if the pH were higher, e.g., on brush-coated art paper, a much higher quantity of sulfur might be tolerated.

2.2 The procedures 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* (i.e., a fairly mild reduction system) (1).

2.2.1 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.

3. Summary

3.1 The semi-quantitative method (see section 13.3) 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.

3.2 The quantitative method uses the identical reduction system to generate H₂S, 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 a similar manner.

4. Definitions

4.1 Reducible sulfur is that sulfur content of a specimen which is released as hydrogen sulfide gas under the conditions of the test.

4.1.1 The conditions of the test are fairly mild reducing conditions intended to predict tarnishing tendency. They are designed to simulate normal atmospheric or environmental conditions (e.g., high humidity or wetting, acidic

conditions, high temperature, high concentrations of reducing gases in the atmosphere, etc.) which may be encountered in the use of paper or paperboard as a packaging material.

5. Apparatus

5.1 *Reaction apparatus*¹ (Fig. 1), consisting of a 500-mL roundbottomed 3-necked flask as illustrated, equipped with a gas inlet tube adapter with perforated bulb, a 60-mL pear-shaped funnel, a 200-mm condenser, a side-arm adapter, and a heating mantle with variable power supply.

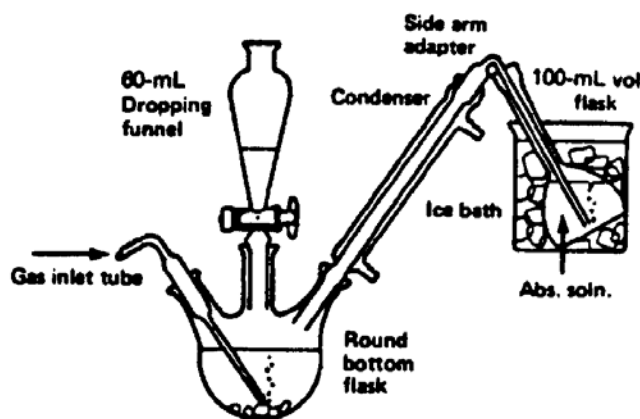


Fig. 1. Reaction apparatus (quantitative determination).

- 5.2 *Absorption apparatus*¹ (Fig. 1), consisting of a 100-mL amber or low-actinic flask in a suitable ice bath.
- 5.3 *Colorimeter or spectrophotometer*, to read at 660-670 nm equipped with 20-50-mm cuvettes.
- 5.4 *Pipets*, 1-, 2-, 5-, 10-mL serological or bacteriological (blow-out).
- 5.5 *Other equipment*, 100- and 1000-mL volumetric flasks; medicine droppers; 10- and 100-mL graduated cylinders; forceps; 10.0-mL volumetric pipets.
- 5.6 *Disintegrator*, a blender or other such rotating-blade device with a small volume container, if possible.
- 5.7 *Constant temperature bath*, at 20-25°C (optional).

6. Reagents and materials

- 6.1 *Aluminum foil*¹, 1145 Alloy, plain (or aluminum weighing pans), not over 0.25 mm thick, sulfur-free.
- 6.2 *Phosphoric acid*, concentrated, 85% H₃PO₄, sulfur-free.

¹ Names 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.

6.3 *Cadmium hydroxide absorption suspension:* dissolve 4.3 g of cadmium sulfate, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ 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.

6.4 *Ferric chloride solution:* dissolve 100 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in water and dilute to 100 mL.

6.5 *Amine solutions*

6.5.1 *Stock amine solution:* dissolve 25 g of *p*-aminodimethylaniline sulfate (i.e., *N,N*-dimethyl-*p*-phenylenediamine sulfate) in 75 mL of cold 1:1 sulfuric acid and dilute to 100 mL with the 1:1 acid.

NOTE 2: Use as high a purity reagent as possible for best reagent blank results.

6.5.2 *Dilute amine solution:* pipet 2.5 mL of the stock solution into a 100-mL volumetric flask and dilute to the mark with 1:1 sulfuric acid.

6.6 *Sodium sulfide standard solutions* (use water deaerated with nitrogen).

6.6.1 *Stock solution:* dissolve 0.4 g sodium sulfide nonahydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (use large crystals which appear dry) in the deaerated water and dilute to 250 mL. After the solution has been diluted to volume, add 5-10 mL of cyclohexane to protect the solution from air oxidation. *This solution should be stable for 1 month.*

6.6.1.1 The stock solution shall be at least 90% of its intended strength as made (6.6.1) when used to prepare the calibration standards (9.3). The exact concentration of NaS in the stock solution may be determined by potentiometric titration with silver nitrate solution using a sulfide-specific electrode using the following procedure which was previously found in TAPPI T 625, which has been withdrawn

6.6.1.2 To an 800-mL beaker, add 100 mL of 20% NaOH solution, 35 mL of 1:99 ammonia, and a 100 mL aliquot of 200 ppm stock sulfide solution. Adjust the beaker contents to 500 mL with water. Titrate immediately with standardized AgNO_3 using magnetic stirring to cause just the beginning of a vortex.

6.6.1.3 Follow the course of the titration potentiometrically, using a silver-silver sulfide indicator electrode and the high pH glass reference electrode. Add the titrant in fixed increments of volume and record the indicated steady emf after each addition. As the end point approaches, there will be an increase in $\Delta E/\Delta V$, that is, there will be an increase in the change of observed emf per increment of titrant. In the immediate vicinity of the end point, a large and sudden change in the observed emf will occur, to the extent of 100 mV or more. When this happens, add two more increments of the titrant and stop the titration.

6.6.1.4 Plot the data on linear coordinates with mL of AgNO_3 as the *x* axis and emf on the *y* axis to obtain the usual S-shaped titration curve. Determine the exact amount of AgNO_3 used at the end point by projecting the inflection point in the curve to the abscissa. Calculate:

$$\text{g/L Na}_2\text{S} = (\text{titre in mL}) (N \text{ AgNO}_3) (0.039)(1000) \text{ aliquot in mL}$$

6.6.2 *Working solution* (prepare daily): pipet 10.0 mL of stock solution into a 1000 mL volumetric flask and dilute to the mark with the deaerated water. One milliliter of this solution contains 2 μ g of sulfur (i.e., solution is 2 ppm in sulfur).

NOTE 3: This solution or the stock solution may be standardized by potentiometric titration with silver nitrate solution using a sulfide-specific electrode (see TAPPI T 625 wd-99 “Analysis of Soda and Sulfate Black Liquor” now withdrawn); the sulfide standard should be at least 90% pure.

6.7 *Nitrogen gas*, sulfur free.

7. Sampling

7.1 Obtain a sample in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product.”

7.2 A minimum of 8 g of sample is required to provide triplicate test specimens, including 2 g for moisture determination.

7.3 Do not touch the test area of sample or test specimens with the fingers; handle with clean forceps only.

8. Test specimens

8.1 From each test unit of the sample, cut three test specimens, each approximately 2 g and weigh to the nearest milligram. Upon agreement between the users of the method, where the interest is only the presence or absence of reducible sulfur and this method is preferred over the semi-quantitative method in Section 13, a single test may be made and reported upon each sample using the quantitative procedure, section 9 of this test method.

8.2 Determine moisture content according to TAPPI T 550 “Determination of Equilibrium Moisture in Paper and Paperboard for Chemical Analysis.”

9. Quantitative procedure

9.1 Disintegrate the test specimen 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 1 aluminum foil weighing dish) which has been cut into 13 mm squares and complete the assembly of the reaction apparatus.

9.2 *Precipitation of cadmium sulfide*

9.2.1 Measure 10 mL of the concentrated (85%) phosphoric acid 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 (i.e., submerged as deeply as possible).

9.2.2 Add the 10 mL of concentrated phosphoric acid 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.

9.2.3 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 test specimen should not be stored in this manner for more than an hour.

9.3 *Preparation of calibration standards* (prepare each time the analysis is performed).

9.3.1 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 (at 20° to 25°C).

9.3.2 Pipet 1, 2, 5, and 10 mL, respectively, of the sodium sulfide standard working solution into four of the volumetric flasks.

9.3.2.1 The “blow-out” (clause 5.4) 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 the flask. “Blow out” pipettes have been used for 9.3.2 in earlier editions of this standard test method to minimize introduction of oxygen into the sodium sulfide stock solution and the diluted calibration standards. A digital pipet may be used for preparation of the calibration standards, provided the solutions are protected from air oxidation during the transfer step.

9.3.3 Swirl gently but adequately. The flask containing no sulfide solutions is the reagent blank. The standards contain 2, 4, 10, and 20 µg sulfur per 100 mL.

9.4 *Color development and read-out*

9.4.1 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 H₂S 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 20-25°C by means of the constant temperature bath or by any other comparable means available.

9.4.2 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 vs. micrograms of sulfur present and draw the best straight line passing through zero. The slope should be about 0.005-0.010 absorbance units per microgram of sulfur per 10 mm of path length. Read the amount of reducible sulfur, in micrograms, in each specimen directly from the chart based on its net absorbance.

NOTE 4: If the reagent blank absorbance is greater than 20% of that of the lowest standard, technique and reagent purity should be examined.

10. Calculations

$$10.1 \quad S = (s_c \times 0.0001)/W$$

where

S = reducible sulfur, %
 S_c = reducible sulfur from chart
 W = weight of specimen, g

11. Report

11.1 Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper to two significant figures.

11.1.1 Report the individual values for each specimen tested (see Section 8.1) which agree to within $\pm 50\%$ relative average deviation as well as reporting the average for the three determinations. Where fewer than three individual values are tested by agreement of those using the data (see 8.1), report the individual value(s) obtained.

12. Precision

12.1 The following estimates of precision are based on limited experience: a within-laboratory study of 3 sets of a linerboard sample, and a round-robin among 3 laboratories on 5 different linerboard samples. The work of Chazin (*1*) is the latest precision study done and is believed to be adequate.

12.1.1 Repeatability (within a laboratory) = 0.91 ppm reducible sulfur (11%)

12.1.2 Comparability (between materials) = not known

12.1.3 Reproducibility (between laboratories) = 24%; in accordance with definitions of these terms in

TAPPI T 1200 "Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility."

13. Semi-quantitative measurement

13.1 Apparatus

13.1.1 *Reaction apparatus*, essentially the same as the quantitative method, 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 2 disks of filter paper between them. The outermost paper disk is impregnated with lead acetate.

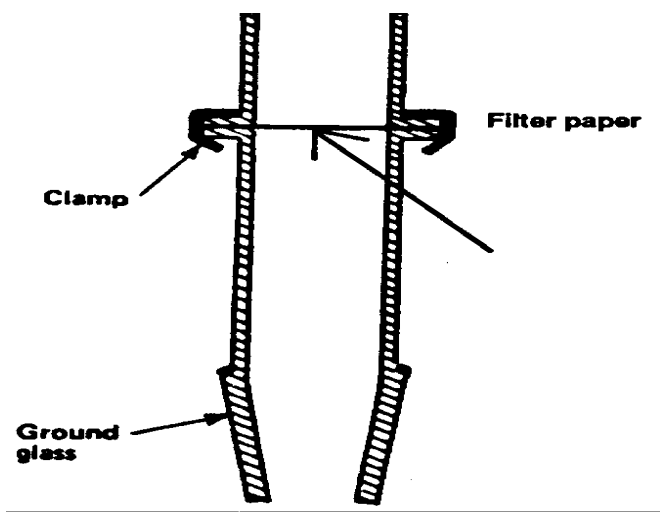


Fig. 2: Reaction apparatus (semi-quantitative determination).

13.1.2 *Other equipment*: as in 5.5, and in addition a buret or pipet graduated in 0.1 mL divisions.

13.1.3 The equipment in 5.2, 5.3, 5.4, and 5.6 is not necessary in this procedure.

13.2 Reagents and materials

13.2.1 *Aluminum foil* as in 6.1.

13.2.2 *Phosphoric acid*, as in 6.2.

13.2.3 *Sodium sulfate standard solution*, as in 6.6.

13.2.4 *Nitrogen gas*, as in 6.7.

13.2.5 *Lead acetate solution*, 20 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ per 100 mL water.

13.2.6 *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 air-tight container under nitrogen. Unimpregnated filter paper of the same diameter should be prepared ready for use.

13.3 Procedure

13.3.1 Follow the procedure in 9.1.

13.3.2 *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 concentrated 85% phosphoric acid 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 phosphoric acid from the dropping funnel to the reaction flask. After the acid has all drained, 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.

13.3.3 *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 as in 13.3.2 above. 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 sulfide on the filter paper. The blank should contain no more than a barely perceptible stain. If the blank is half as intense as the 4 μg standard, discard the experiment and start over by preparing new reagents and washing the glassware thoroughly.

13.3.4 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.

13.3.5 Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper to one significant figure from the calculation in 9.1, except that the micrograms of sulfur are estimated from the relative intensity of the spots compared with the standard disks. Report the individual values for each specimen and the average for the three determinations.

13.4 Calibration standards

13.4.1 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 this method (1, 3, 4). Other evidence, however, conflicts with these results and postulates. Sodium sulfide 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.

13.4.2 With the replacement of thiosulfate as calibration standard, the spot staining technique may show higher results (perhaps twice the previous) 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.

13.5 Related method: ASTM D 984.

13. Keywords

Paper, Paperboard, Sulfur, Reducible sulfur, Polysulfides, Polythionates, Quantitative analysis, Sulfide, Sulfite, Thiosulfates

14. Additional information

14.1 Effective date of issue: to be assigned.

14.2 The 1982 revision was quite extensive and involved the incorporation of colorimetric measurement (1, 2). The original spot staining technique has been replaced but is included for possible use as a semi-quantitative alternative where a colorimeter is not available. It has been modified to include a dynamic sweeping system with nitrogen.

14.3 There were minor editorial revisions of the document in 2013, the major one being the printing of the standardization procedure for the stock sodium sulfide standard as 6.6.1.1. Previous editions of this TAPPI Standard had referenced TAPPI T 625 for this information, but T 625 has been withdrawn, so the standardization procedure for the sulfide is added to this standard. Also, when agreed by the users of the method, single test values on samples may be reported using the procedure in Section 9, Quantitative Procedure, when only semi-quantitative results are needed or desired.

Literature cited

1. Chazin, J. D. "Colorimetric Determination of Reducible Sulfur in Paper and Paperboard," *Tappi* **53** (8): 1514 (1970).
2. Sobolev, I., Bhargava, R., Gosuntov, N., and Russell, R., *Tappi* **39** (9): 628 (1956).
3. Gould, E. S., "Inorganic Reactions & Structure," New York, Holt, Rhinehart and Winston, 1955, p. 293.
4. Browning, B. L., "The Analysis of Paper," Marcel Dekker, 1969, p. 166.

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

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WI _____ 120802.02 _____

T _____ 406 _____

DRAFT NO. _____ 2 _____

DATE _____ December 17, 2012 _____

WORKING GROUP

CHAIRMAN _____ James C. Abbott _____

SUBJECT

CATEGORY _____ Chemical Properties _____

RELATED

METHODS _____ See "Additional Information" _____

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Reducible sulfur in paper and paperboard (Revision of T 406 om-08) (underscores and strikeouts indicate changes from Draft 1)

1. Scope

1.1 This method describes two procedures for the determination of reducible sulfur in paper and paperboard within the context of the given definitions.

1.1.1 The quantitative procedure found in Section 9 gives a measure of the reducible sulfur with the precision shown in Section 12.

1.1.2 The semi-quantitative test described in section 13 indicates the general level of reducible sulfur with limited accuracy.

2. Significance

2.1 The procedures are not necessarily a measure of how much a given test material will tarnish polished metals. When tested by these procedures, paper which 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 TAPPI T 444 “Silver Tarnishing by Paper and Paperboard”).

NOTE 1: If the pH of the paper is low, e.g., 4-4.5 (cold extraction), as little as 0.0002% of reducible sulfur may cause tarnishing of imitation gold bronze prints; whereas, if the pH were higher, e.g., on brush-coated art paper, a much higher quantity of sulfur might be tolerated.

2.2 The procedures 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* (i.e., a fairly mild reduction system) (1).

2.2.1 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.

3. Summary

3.1 The semi-quantitative method (see section 13.3) 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.

3.2 The quantitative method uses the identical reduction system to generate H₂S, 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 a similar manner.

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4.1 Reducible sulfur is that sulfur content of a specimen which is released as hydrogen sulfide gas under the conditions of the test.

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conditions, high temperature, high concentrations of reducing gases in the atmosphere, etc.) which may be encountered in the use of paper or paperboard as a packaging material.

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5.1 *Reaction apparatus*¹ (Fig. 1), consisting of a 500-mL roundbottomed 3-necked flask as illustrated, equipped with a gas inlet tube adapter with perforated bulb, a 60-mL pear-shaped funnel, a 200-mm condenser, a side-arm adapter, and a heating mantle with variable power supply.

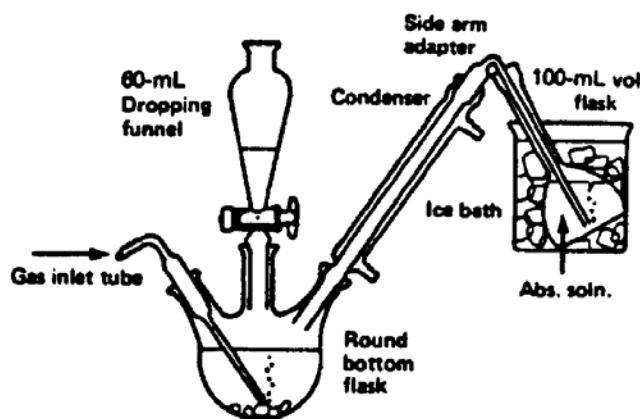


Fig. 1. Reaction apparatus (quantitative determination).

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

5.3 *Colorimeter or spectrophotometer*, to read at 660-670 nm equipped with 20-50-mm cuvettes.

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

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

5.7 *Constant temperature bath*, at 20-25°C (optional).

6. Reagents and materials

6.1 *Aluminum foil*¹, 1145 Alloy, plain (or aluminum weighing pans), not over 0.25 mm thick, sulfur-free.

6.2 *Phosphoric acid*, concentrated, 85% H₃PO₄, sulfur-free.

¹ Names 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.

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6.4 *Ferric chloride solution:* dissolve 100 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in water and dilute to 100 mL.

6.5 *Amine solutions*

6.5.1 *Stock amine solution:* dissolve 25 g of *p*-aminodimethylaniline sulfate (i.e., *N,N*-dimethyl-*p*-phenylenediamine sulfate) in 75 mL of cold 1:1 sulfuric acid and dilute to 100 mL with the 1:1 acid.

NOTE 2: Use as high a purity reagent as possible for best reagent blank results.

6.5.2 *Dilute amine solution:* pipet 2.5 mL of the stock solution into a 100-mL volumetric flask and dilute to the mark with 1:1 sulfuric acid.

6.6 *Sodium sulfide standard solutions* (use water deaerated with nitrogen).

6.6.1 *Stock solution:* dissolve 0.4 g sodium sulfide nonahydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (use large crystals which appear dry) in the deaerated water and dilute to 250 mL. After the solution has been diluted to volume, add 5-10 mL of cyclohexane to protect the solution from air oxidation. *This solution should be stable for 1 month.*

6.6.1.1 The stock solution shall be at least 90% of its intended strength as made (6.6.1) when used to prepare the calibration standards (9.3). The exact concentration of NaS in the stock solution may be determined by potentiometric titration with silver nitrate solution using a sulfide-specific electrode using the following procedure which was previously found in TAPPI T 625, which has been withdrawn

6.6.1.2 To an 800-mL beaker, add 100 mL of 20% NaOH solution, 35 mL of 1:99 ammonia, and a 100 mL aliquot of 200 ppm stock sulfide solution. Adjust the beaker contents to 500 mL with water. Titrate immediately with standardized AgNO_3 using magnetic stirring to cause just the beginning of a vortex.

6.6.1.3 Follow the course of the titration potentiometrically, using a silver-silver sulfide indicator electrode and the high pH glass reference electrode. Add the titrant in fixed increments of volume and record the indicated steady emf after each addition. As the end point approaches, there will be an increase in $\Delta E/\Delta V$, that is, there will be an increase in the change of observed emf per increment of titrant. In the immediate vicinity of the end point, a large and sudden change in the observed emf will occur, to the extent of 100 mV or more. When this happens, add two more increments of the titrant and stop the titration.

6.6.1.4 Plot the data on linear coordinates with mL of AgNO_3 as the *x* axis and emf on the *y* axis to obtain the usual S-shaped titration curve. Determine the exact amount of AgNO_3 used at the end point by projecting the inflection point in the curve to the abscissa. Calculate:

$$\text{g/L Na}_2\text{S} = (\text{titre in mL}) (N \text{ AgNO}_3) (0.039)(1000) \text{ aliquot in mL}$$

6.6.2 *Working solution* (prepare daily): pipet 10.0 mL of stock solution into a 1000 mL volumetric flask and dilute to the mark with the deaerated water. One milliliter of this solution contains 2 μ g of sulfur (i.e., solution is 2 ppm in sulfur).

NOTE 3: This solution or the stock solution may be standardized by potentiometric titration with silver nitrate solution using a sulfide-specific electrode (see TAPPI T 625 wd-99 “Analysis of Soda and Sulfate Black Liquor” now withdrawn); the sulfide standard should be at least 90% pure.

6.7 *Nitrogen gas*, sulfur free.

7. Sampling

7.1 Obtain a sample in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product.”

7.2 A minimum of 8 g of sample is required to provide triplicate test specimens, including 2 g for moisture determination.

7.3 Do not touch the test area of sample or test specimens with the fingers; handle with clean forceps only.

8. Test specimens

8.1 From each test unit of the sample, cut three test specimens, each approximately 2 g and weigh to the nearest milligram. Upon agreement between the users of the method, where the interest is only the presence or absence of reducible sulfur and this method is preferred over the semi-quantitative method in Section 13, a single test may be made and reported upon each sample using the quantitative procedure, section 9 of this test method.

8.2 Determine moisture content according to TAPPI T 550 “Determination of Equilibrium Moisture in Paper and Paperboard for Chemical Analysis.”

9. Quantitative procedure

9.1 Disintegrate the test specimen 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 1 aluminum foil weighing dish) which has been cut into 13 mm squares and complete the assembly of the reaction apparatus.

9.2 *Precipitation of cadmium sulfide*

9.2.1 Measure 10 mL of the concentrated (85%) phosphoric acid 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 (i.e., submerged as deeply as possible).

9.2.2 Add the 10 mL of concentrated phosphoric acid 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.

9.2.3 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 test specimen should not be stored in this manner for more than an hour.

9.3 *Preparation of calibration standards* (prepare each time the analysis is performed).

9.3.1 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 (at 20° to 25°C).

9.3.2 Pipet 1, 2, 5, and 10 mL, respectively, of the sodium sulfide standard working solution into four of the volumetric flasks.

NOTE 4: ~~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 the flask.~~

9.3.2.1 The “blow-out” (clause 5.4) 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 the flask. “Blow out” pipettes have been used for 9.3.2 in earlier editions of this standard test method to minimize introduction of oxygen into the sodium sulfide stock solution and the diluted calibration standards. A digital pipet may be used for preparation of the calibration standards, provided the solutions are protected from air oxidation during the transfer step.

9.3.3 Swirl gently but adequately. The flask containing no sulfide solutions is the reagent blank. The standards contain 2, 4, 10, and 20 µg sulfur per 100 mL.

9.4 *Color development and read-out*

9.4.1 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 H₂S 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 20-25°C by means of the constant temperature bath or by any other comparable means available.

9.4.2 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 vs. micrograms of sulfur present and draw the best straight line passing through zero. The slope should be about 0.005-0.010 absorbance units per microgram of sulfur per 10 mm of path length. Read the amount of reducible sulfur, in micrograms, in each specimen directly from the chart based on its net absorbance.

NOTE 4: If the reagent blank absorbance is greater than 20% of that of the lowest standard, technique and reagent purity should be examined.

10. Calculations

$$10.1 \quad S = (s_c \times 0.0001)/W$$

where

S = reducible sulfur, %
 S_c = reducible sulfur from chart
 W = weight of specimen, g

11. Report

11.1 Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper to two significant figures.

11.1.1 Report the individual values for each specimen tested (see Section 8.1) which agree to within ± 50% relative average deviation as well as reporting the average for the three determinations. Where fewer than three individual values are tested by agreement of those using the data (see 8.1), report the individual value(s) obtained.

12. Precision

12.1 The following estimates of precision are based on limited experience: a within-laboratory study of 3 sets of a linerboard sample, and a round-robin among 3 laboratories on 5 different linerboard samples. The work of Chazin (1) is the latest precision study done and is believed to be adequate.

12.1.1 Repeatability (within a laboratory) = 0.91 ppm reducible sulfur (11%)

12.1.2 Comparability (between materials) = not known

12.1.3 Reproducibility (between laboratories) = 24%; in accordance with definitions of these terms in TAPPI T 1200 "Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility."

13. Semi-quantitative measurement

13.1 Apparatus

13.1.1 *Reaction apparatus*, essentially the same as the quantitative method, 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 2 disks of filter paper between them. The outermost paper disk is impregnated with lead acetate.

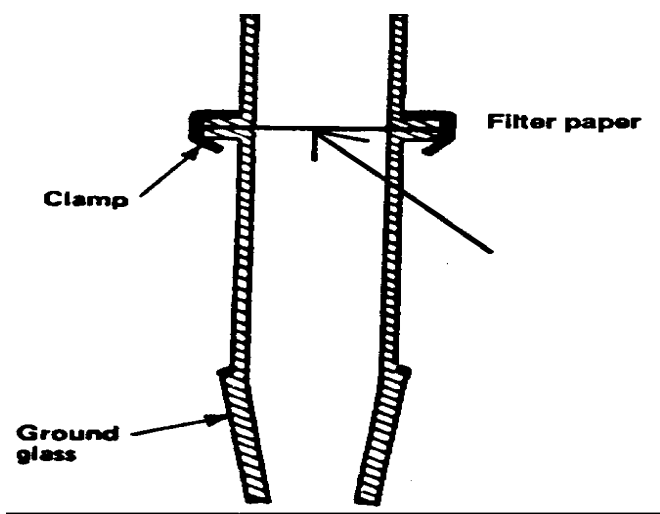


Fig. 2: Reaction apparatus (semi-quantitative determination).

13.1.2 *Other equipment*: as in 5.5, and in addition a buret or pipet graduated in 0.1 mL divisions.

13.1.3 The equipment in 5.2, 5.3, 5.4, and 5.6 is not necessary in this procedure.

13.2 Reagents and materials

13.2.1 *Aluminum foil* as in 6.1.

13.2.2 *Phosphoric acid*, as in 6.2.

13.2.3 *Sodium sulfate standard solution*, as in 6.6.

13.2.4 *Nitrogen gas*, as in 6.7.

13.2.5 *Lead acetate solution*, 20 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ per 100 mL water.

13.2.6 *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 air-tight container under nitrogen. Unimpregnated filter paper of the same diameter should be prepared ready for use.

13.3 *Procedure*

13.3.1 Follow the procedure in 9.1.

13.3.2 *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 concentrated 85% phosphoric acid 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 phosphoric acid from the dropping funnel to the reaction flask. After the acid has all drained, 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.

13.3.3 *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 as in 13.3.2 above. 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 sulfide on the filter paper. The blank should contain no more than a barely perceptible stain. If the blank is half as intense as the 4 μg standard, discard the experiment and start over by preparing new reagents and washing the glassware thoroughly.

13.3.4 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.

13.3.5 Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper to one significant figure from the calculation in 9.1, except that the micrograms of sulfur are estimated from the relative intensity of the spots compared with the standard disks. Report the individual values for each specimen and the average for the three determinations.

13.4 *Calibration standards*

13.4.1 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 this method (1, 3, 4). Other evidence, however, conflicts with these results and postulates. Sodium sulfide 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.

13.4.2 With the replacement of thiosulfate as calibration standard, the spot staining technique may show higher results (perhaps twice the previous) 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.

13.5 Related method: ASTM D 984.

13. Keywords

Paper, Paperboard, Sulfur, Reducible sulfur, Polysulfides, Polythionates, Quantitative analysis, Sulfide, Sulfite, Thiosulfates

14. Additional information

14.1 Effective date of issue: to be assigned.

14.2 The 1982 revision was quite extensive and involved the incorporation of colorimetric measurement (1, 2). The original spot staining technique has been replaced but is included for possible use as a semi-quantitative alternative where a colorimeter is not available. It has been modified to include a dynamic sweeping system with nitrogen.

14.3 There were minor editorial revisions of the document in 2013, the major one being the printing of the standardization procedure for the stock sodium sulfide standard as 6.6.1.1. Previous editions of this TAPPI Standard had referenced TAPPI T 625 for this information, but T 625 has been withdrawn, so the standardization procedure for the sulfide is added to this standard. Also, when agreed by the users of the method, single test values on samples may be reported using the procedure in Section 9, Quantitative Procedure, when only semi-quantitative results are needed or desired.

Literature cited

1. Chazin, J. D. "Colorimetric Determination of Reducible Sulfur in Paper and Paperboard," *Tappi* **53** (8): 1514 (1970).
2. Sobolev, I., Bhargava, R., Gosuntov, N., and Russell, R., *Tappi* **39** (9): 628 (1956).
3. Gould, E. S., "Inorganic Reactions & Structure," New York, Holt, Rhinehart and Winston, 1955, p. 293.
4. Browning, B. L., "The Analysis of Paper," Marcel Dekker, 1969, p. 166.

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

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WI _____ 120802.02 _____

T _____ 406 _____

DRAFT NO. _____ 1 _____

DATE _____ September 21, 2012 _____

WORKING GROUP
CHAIRMAN _____ to be determined _____

SUBJECT
CATEGORY _____ Chemical Properties _____

RELATED
METHODS _____ See "Additional Information" _____

CAUTION:

This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Reducible sulfur in paper and paperboard (Five-year review of T 406 om-08)

1. Scope

1.1 This method describes two procedures for the determination of reducible sulfur in paper and paperboard within the context of the given definitions.

1.1.1 The quantitative procedure found in Section 9 gives a measure of the reducible sulfur with the precision shown in Section 12.

1.1.2 The semi-quantitative test described in section 13 indicates the general level of reducible sulfur with limited accuracy.

2. Significance

2.1 The procedures are not necessarily a measure of how much a given test material will tarnish polished metals. When tested by these procedures, paper which 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 TAPPI T 444 “Silver Tarnishing by Paper and Paperboard”).

NOTE 1: If the pH of the paper is low, e.g., 4-4.5 (cold extraction), as little as 0.0002% of reducible sulfur may cause tarnishing of imitation gold bronze prints; whereas, if the pH were higher, e.g., on brush-coated art paper, a much higher quantity of sulfur might be tolerated.

2.2 The procedures 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* (i.e., a fairly mild reduction system) (1).

2.2.1 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.

3. Summary

3.1 The semi-quantitative method (see section 13.3) 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.

3.2 The quantitative method uses the identical reduction system to generate H₂S, 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 a similar manner.

4. Definitions

4.1 Reducible sulfur is that sulfur content of a specimen which is released as hydrogen sulfide gas under the conditions of the test.

4.1.1 The conditions of the test are fairly mild reducing conditions intended to predict tarnishing tendency. They are designed to simulate normal atmospheric or environmental conditions (e.g., high humidity or wetting, acidic conditions, high temperature, high concentrations of reducing gases in the atmosphere, etc.) which may be encountered in the use of paper or paperboard as a packaging material.

5. Apparatus

5.1 *Reaction apparatus*¹ (Fig. 1), consisting of a 500-mL roundbottomed 3-necked flask as illustrated, equipped with a gas inlet tube adapter with perforated bulb, a 60-mL pear-shaped funnel, a 200-mm condenser, a side-arm adapter, and a heating mantle with variable power supply.

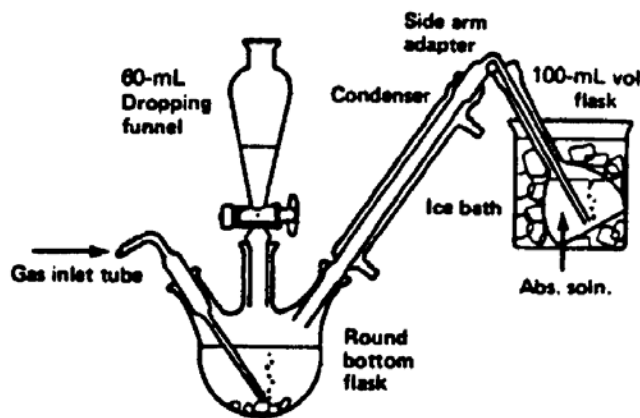


Fig. 1. Reaction apparatus (quantitative determination).

- 5.2 *Absorption apparatus*¹ (Fig. 1), consisting of a 100-mL amber or low-actinic flask in a suitable ice bath.
- 5.3 *Colorimeter or spectrophotometer*, to read at 660-670 nm equipped with 20-50-mm cuvettes.
- 5.4 *Pipets*, 1-, 2-, 5-, 10-mL serological or bacteriological (blow-out).
- 5.5 *Other equipment*, 100- and 1000-mL volumetric flasks; medicine droppers; 10- and 100-mL graduated cylinders; forceps; 10.0-mL volumetric pipets.
- 5.6 *Disintegrator*, a blender or other such rotating-blade device with a small volume container, if possible.
- 5.7 *Constant temperature bath*, at 20-25°C (optional).

6. Reagents and materials

- 6.1 *Aluminum foil*¹, 1145 Alloy, plain (or aluminum weighing pans), not over 0.25 mm thick, sulfur-free.
- 6.2 *Phosphoric acid*, concentrated, 85% H₃PO₄, sulfur-free.
- 6.3 *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.

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.

6.4 *Ferric chloride solution:* dissolve 100 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in water and dilute to 100 mL.

6.5 *Amine solutions*

6.5.1 *Stock amine solution:* dissolve 25 g of *p*-aminodimethylaniline sulfate (i.e., *N,N*-dimethyl-*p*-phenylenediamine sulfate) in 75 mL of cold 1:1 sulfuric acid and dilute to 100 mL with the 1:1 acid.

NOTE 2: Use as high a purity reagent as possible for best reagent blank results.

6.5.2 *Dilute amine solution:* pipet 2.5 mL of the stock solution into a 100-mL volumetric flask and dilute to the mark with 1:1 sulfuric acid.

6.6 *Sodium sulfide standard solutions* (use water deaerated with nitrogen).

6.6.1 *Stock solution:* dissolve 0.4 g sodium sulfide nonahydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (use large crystals which appear dry) in the deaerated water and dilute to 250 mL. After the solution has been diluted to volume, add 5-10 mL of cyclohexane to protect the solution from air oxidation. *This solution should be stable for 1 month.*

6.6.2 *Working solution* (prepare daily): pipet 10.0 mL of stock solution into a 1000 mL volumetric flask and dilute to the mark with the deaerated water. One milliliter of this solution contains $2\mu\text{g}$ of sulfur (i.e., solution is 2 ppm in sulfur).

NOTE 3: This solution or the stock solution may be standardized by potentiometric titration with silver nitrate solution using a sulfide-specific electrode (see TAPPI T 625 wd-99 “Analysis of Soda and Sulfate Black Liquor” now withdrawn); the sulfide standard should be at least 90% pure.

6.7 *Nitrogen gas*, sulfur free.

7. Sampling

7.1 Obtain a sample in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product.”

7.2 A minimum of 8 g of sample is required to provide triplicate test specimens, including 2 g for moisture determination.

7.3 Do not touch the test area of sample or test specimens with the fingers; handle with clean forceps only.

8. Test specimens

8.1 From each test unit of the sample, cut three test specimens, each approximately 2 g and weigh to the nearest milligram.

8.2 Determine moisture content according to TAPPI T 550 “Determination of Equilibrium Moisture in Paper and Paperboard for Chemical Analysis.”

9. Quantitative procedure

9.1 Disintegrate the test specimen 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 1 aluminum foil weighing dish) which has been cut into 13 mm squares and complete the assembly of the reaction apparatus.

9.2 *Precipitation of cadmium sulfide*

9.2.1 Measure 10 mL of the concentrated (85%) phosphoric acid 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 (i.e., submerged as deeply as possible).

9.2.2 Add the 10 mL of concentrated phosphoric acid 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.

9.2.3 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 test specimen should not be stored in this manner for more than an hour.

9.3 *Preparation of calibration standards* (prepare each time the analysis is performed).

9.3.1 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 (at 20° to 25°C).

9.3.2 Pipet 1, 2, 5, and 10 mL, respectively, of the sodium sulfide standard working solution into four of the volumetric flasks.

NOTE 4: 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 the flask.

9.3.3 Swirl gently but adequately. The flask containing no sulfide solutions is the reagent blank. The standards contain 2, 4, 10, and 20 µg sulfur per 100 mL.

9.4 *Color development and read-out*

9.4.1 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 H₂S 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 20-25°C by means of the constant temperature bath or by any other comparable means available.

9.4.2 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 vs. micrograms of sulfur present and draw the best straight line passing through zero. The slope should be about 0.005-0.010 absorbance units per microgram of sulfur per 10 mm of path length. Read the amount of reducible sulfur, in micrograms, in each specimen directly from the chart based on its net absorbance.

NOTE 5: If the reagent blank absorbance is greater than 20% of that of the lowest standard, technique and reagent purity should be examined.

10. Calculations

$$10.1 \quad S = (s_c \times 0.0001)/W$$

where

S = reducible sulfur, %

s_c = reducible sulfur from chart

W = weight of specimen, g

11. Report

11.1 Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper to two significant figures.

11.1.1 Report the individual values for each specimen which agree to within $\pm 50\%$ relative average deviation as well as reporting the average for the three determinations.

12. Precision

12.1 The following estimates of precision are based on limited experience: a within-laboratory study of 3 sets of a linerboard sample, and a round-robin among 3 laboratories on 5 different linerboard samples (I):

12.1.1 Repeatability (within a laboratory) = 0.91 ppm reducible sulfur (11%)

12.1.2 Comparability (between materials) = not known

12.1.3 Reproducibility (between laboratories) = 24%; in accordance with definitions of these terms in TAPPI T 1200 “Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility.”

13. Semi-quantitative measurement

13.1 Apparatus

13.1.1 *Reaction apparatus*, essentially the same as the quantitative method, 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 2 disks of filter paper between them. The outermost paper disk is impregnated with lead acetate.

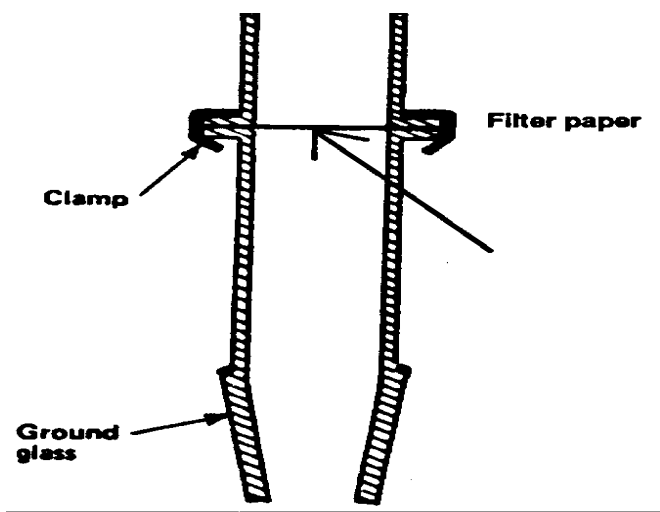


Fig. 2: Reaction apparatus (semi-quantitative determination).

13.1.2 *Other equipment*: as in 5.5, and in addition a buret or pipet graduated in 0.1 mL divisions.

13.1.3 The equipment in 5.2, 5.3, 5.4, and 5.6 is not necessary in this procedure.

13.2 *Reagents and materials*

13.2.1 *Aluminum foil* as in 6.1.

13.2.2 *Phosphoric acid*, as in 6.2.

13.2.3 *Sodium sulfate standard solution*, as in 6.6.

13.2.4 *Nitrogen gas*, as in 6.7.

13.2.5 *Lead acetate solution*, 20 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ per 100 mL water.

13.2.6 *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 air-tight container under nitrogen. Unimpregnated filter paper of the same diameter should be prepared ready for use.

13.3 *Procedure*

13.3.1 Follow the procedure in 9.1.

13.3.2 *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 concentrated 85% phosphoric acid 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 phosphoric acid from the dropping funnel to the reaction flask. After the acid has all drained, 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.

13.3.3 *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 as in 13.3.2 above. 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 sulfide on the filter paper. The blank should contain no more than a barely perceptible stain. If the blank is half as intense as the 4 μg standard, discard the experiment and start over by preparing new reagents and washing the glassware thoroughly.

13.3.4 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.

13.3.5 Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper to one significant figure from the calculation in 9.1, except that the micrograms of sulfur are estimated from the relative intensity of the spots compared with the standard disks. Report the individual values for each specimen and the average for the three determinations.

13.4 *Calibration standards*

13.4.1 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 this method (1, 3, 4). Other evidence, however, conflicts with these results and postulates. Sodium sulfide 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.

13.4.2 With the replacement of thiosulfate as calibration standard, the spot staining technique may show higher results (perhaps twice the previous) 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.

13.5 Related method: ASTM D 984.

13. Keywords

Paper, Paperboard, Sulfur, Reducible sulfur, Polysulfides, Polythionates, Quantitative analysis, Sulfide, Sulfite, Thiosulfates

14. Additional information

14.1 Effective date of issue: to be assigned.

14.2 The 1982 revision was quite extensive and involved the incorporation of colorimetric measurement (1, 2). The original spot staining technique has been replaced but is included for possible use as a semi-quantitative alternative where a colorimeter is not available. It has been modified to include a dynamic sweeping system with nitrogen.

Literature cited

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3. Gould, E. S., "Inorganic Reactions & Structure," New York, Holt, Rhinehart and Winston, 1955, p. 293.
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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department. ■