



TAPPI/ANSI T 406 om-13

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TENTATIVE STANDARD – 1960
SUGGESTED METHOD – 1972
OFFICIAL TEST METHOD – 1982
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Reducible sulfur in paper and paperboard

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).

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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 H_2S , 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.

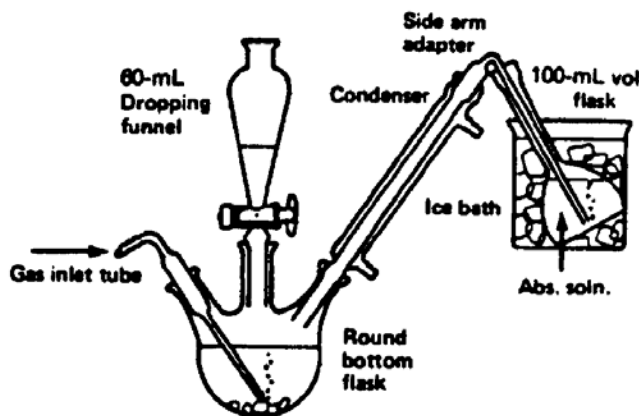


Fig. 1. Reaction apparatus (quantitative determination).

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.

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.

- 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.
- 6.4 *Ferric chloride solution*: dissolve 100 g of ferric chloride hexahydrate (FeCl₃ • 6H₂O) 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, Na₂S • 9H₂O (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 AgNO₃ 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 AgNO₃ as the x axis and emf on the y axis to obtain the usual S-shaped titration curve. Determine the exact amount of AgNO₃ 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 µg 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