WI 170802.02

T 255

DRAFT NO. 4 SARG

DATE May 18, 2021

WORKING GROUP CHAIRMAN

SUBJECT CATEGORY Chemical properties

RELATED METHODS See "Additional Information"

Water-soluble sulfates in pulp and paper

(Ballot for reconfirmation T 255 cm-07 as a Classical Method)

(No changes from Draft 2; Third ballot required due to low percentage of votes returned on Ballot 2)

1. Scope

1.1 This method is for the volumetric determination of water-extractable sulfate in pulp or paper.

1.2 The method is suitable for sulfate content from 0.01% up to 1%. It can be modified to extend this range.

1.3 This method does not measure total sulfur. It is not designed for the analysis of papers containing fillers composed of sulfides, sulfites, or sulfates. Sulfites and thiosulfates do affect results of the test.

2. Summary

A pulp or paper specimen is disintegrated in water and boiled. The suspension is filtered, and the filtrate is then concentrated. Metallic ions are removed from the concentrate by passage through an ion exchange column. An aliquot of the deionized concentrate is diluted with alcohol, Arsenazo III indicator is added, an excess of barium perchlorate is added, and the excess is back titrated with sulfuric acid.

3. Significance

The sulfate content of rosin sized paper is important as an indicator of alum carried with the wet sheet.

4. Apparatus

4.1 *Laboratory blender,* approximately 1000 mL (1 qt) capacity, similar to high-speed kitchen type blenders.

4.2 *Büchner funnel and flask,* 150 mm.

4.3 *Filter paper,* 150 mm diameter, coarse texture.

4.4 *Balance,* laboratory, 100 g capacity, accurate to 0.001 g.

4.5 *Balance,* 2 kg capacity, accurate to 0.1 g.

4.6 *Beakers,* 100, 150, 250, and 1000 mL capacity; 1000 mL beaker tared to nearest 0.5 g.

4.7 *Hot plate,* preferably with temperature control.

4.8 *Ion exchange column,* an 11 x 300 mm column with Teflon stopcock is recommended, but other sizes are satisfactory (see Appendix for preparation and regeneration). A regular 50 mL buret may be used as a substitute.

4.9 *Magnetic stirrer,* with a 25 mm Teflon-coated bar.

4.10 *Pipet,* 5, 10, and 25 mL capacity.

4.11 *Buret,* 10 mL or larger.

4.12 *Graduated cylinder,* 250 mL.

4.13 *Funnel,* 80 mm diameter.

5. Reagents

5.1 *Barium perchlorate,* 0.0100 *N* $Ba(ClO_4)_2$; dissolve 2.0 g $Ba(ClO_4)_2 \cdot 3H_2O$ in distilled water to make 1000 mL. Accurately standardize with 0.01*N* H_2SO_4 using test procedure.

5.2 *Sulfuric acid,* 0.01*N* H_2SO_4. Prepare 0.100*N* H_2SO_4 by diluting 3.0 mL (5.5 g) of pure, concentrated H_2SO_4 (specific gravity 1.84) to 1000 mL with distilled water. Standardize with sodium carbonate using the procedure for hydrochloric acid in TAPPI T 610 “Preparation of Indicators and Analytical Reagents, and Standardization of Volumetric Solutions.” Dilute exactly 100 mL of 0.100*N* H_2SO_4 to 1000 mL with distilled water.

5.3 *Arsenazo III indicator,* dissolve 0.2 g Arsenazo III in 100 mL of distilled water.

5.4 *Cation exchange resin,* Dowex 50 W-X8 or similar.

5.5 *Isopropyl alcohol,* reagent grade.

5.6 *Glass wool.*

5.7 *Hydrochloric acid,* approximately 1*N*. Dilute 85 mL of concentrated HC1 (sp. gr. 1.20) to 1000 mL with distilled water.

5.8 *Magnesium carbonate.*

5.9 *Hydrogen peroxide,* 30%.

5.10 *Sodium hydroxide,* approximately 0.1*N*. Dissolve 4 g NaOH in distilled water and dilute to 1000 mL.

6. Sampling

6.1 Obtain a clean sample of pulp (in accordance with a predetermined sampling plan) or paper (in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product") from the shipment or batch to be tested and tear into small pieces. Use clean rubber gloves and/or tongs, and be extremely careful not to contaminate the sample while handling.

6.2 If the moisture content is not known, determine it on a duplicate sample by drying to constant weight in accordance with TAPPI T 412 "Moisture in Pulp, Paper and Paperboard" or TAPPI T 550 "Determination of Equilibrium Moisture in Pulp, Paper and Paperboard for Chemical Analysis."

7. Test specimens

7.1 Weigh out duplicate specimens of approximately 10 g (oven dry basis) to the nearest 0.01 g.

7.2 Correct for moisture content (weight *A*).

8. Procedure

8.1 *Water extraction*

8.1.1 Disintegrate pulp or paper specimen in 800 to 900 mL of sulfate-free distilled water using laboratory blender. Transfer the slurry with minimum distilled water rinse to a tared 1000 mL beaker. The slurry is at approximately 1% consistency.

8.1.2 Gently boil slurry on hotplate for 60 min without water addition.

8.1.3 Weigh beaker and contents to nearest 0.5 g (weight *B*).

8.1.4 Filter slurry using Büchner funnel and coarse paper into clean, dry flask without rinsing. Transfer most of the filtrate into a dry tared beaker.

8.1.5 Weigh beaker and contents to nearest 0.5 g (weight *C*).

8.1.6 Concentrate filtrate to approximately 100 mL on hotplate.

8.1.7 Weigh beaker and contents to nearest 0.5 g (weight *D*).

8.2 *Sulfate determination of concentrated extract*

8.2.1 Pass 25 mL of extract from 8.1.6 through the ion exchange column and discard. Pass an additional 60 mL of extract through the column for analysis. This will have the same sulfate content as that entering the column.

8.2.2 Pipet 25.0 mL of column effluent into a 250 mL beaker. A smaller volume should be used if effluent is expected to contain over 150 ppm sulfate.

8.2.3 Add 125 mL isopropyl alcohol. The solution must contain over 70% alcohol for sharp end point.

8.2.4 Add four drops of Arsenazo III indicator solution.

8.2.5 Add 0.01*N* $Ba(ClO_4)_2$ from a buret to the solution while stirring with a magnetic stirrer until the

solution turns blue. Add 1.0 additional mL. Record volume added.

8.2.6 Back titrate with 0.01*N* H_2SO_4 to true rose pink color. The solution will gradually change from blue through purple before the endpoint, but there will be a sharp change with one to two drops from a pinkish purple to true rose pink.

8.2.7 Run a blank in place of solution using 25 mL distilled water, and the same volume of $Ba(ClO_4)_2$ as was used for the sample, to check normality of solutions. Adjust reagents if necessary. One drop of H_2SO_4 (0.05 mL) is usually necessary to obtain a pink color when no barium is present.

9. Calculations

9.1 Calculate the dilution factor as follows:

$$\text{Factor} = \frac{B}{A} \times \frac{D}{C}$$

where:

A = oven dry weight of specimen (7.2).

B = slurry weight after boiling, weight *B* - tare (8.1.3).

C = filtrate weight before concentration, weight *C* - tare (8.1.5).

D = filtrate weight after concentration, weight *D* - tare (8.1.7).

To simplify the dilution factor calculation, terms *B* and *C* may usually be ignored. This introduces only a very small total error.

9.2 Calculate concentration of sulfate in concentrated filtrate as follows:

where:

$$\text{ppm } SO_4 = \frac{(V_B - V_S)\, N \times 48{,}000}{S}$$

V_B = volume of H_2SO_4 for blank, mL

V_s = volume of H_2SO_4 for effluent titration, mL

N = normality of H_2SO_4

S = volume of effluent titrated, mL

The blank should be determined using 25 mL of sulfate-free distilled water and the same quantity of $Ba(ClO_4)_2$ as for the effluent (usually 10.0 mL).

9.3 Calculate sulfate in pulp or paper as follows:

$$\text{Sulfate, \%} = \frac{\text{ppm } SO_4 \text{ in filtrate} \times \text{dilution factor}}{10{,}000}$$

10. Report

Report the average percent content to two significant figures.

11. Precision

11.1 *Repeatability.* Duplicate tests on 87 samples of water in one laboratory indicate a standard deviation during the titration of 0.057 mL, which is equivalent to 1.1 ppm SO_4 in the water. This corresponds to a repeatability of 0.003% (30 ppm) based on paper as defined in TAPPI T 1200 "Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility." Note that the extraction procedure results in approximately 10 mL of water per gram of pulp or paper.

11.2 The precision of the extraction portion of this method has not yet been determined.

11.3 *Reproducibility.* The reproducibility of this method has not been determined.

12. Interferences with test

12.1 Calcium, barium, and most cations seriously interfere with the sulfate determination portion of the test. The cation exchange part of the method is therefore necessary.

12.2 Chlorides have a negligible effect on the titration if they are under 1000 ppm in the column effluent; Nitrates also have a negligible effect under 250 ppm.

12.3 Sulfites and thiosulfates react with one-half to one-third the equivalent amount of barium perchlorate giving erroneous answers. They may be oxidized to sulfate using the procedure under 13.1 and results expressed as total water-soluble sulfur.

12.4 Phosphate interferes by partially reacting with the barium perchlorate. If phosphate is believed to be over 30 ppm in the filtrate, it should be removed using the procedure in 13.2.1.

13. Supplemental treatments

13.1 The following modifications will change the test results, and their use must be stated in the report.

13.1.1 Supplemental oxidation of sulfites and thiosulfates.

13.1.1.1 Add 5 mL of 30% H_2O_2 and 5 mL of 0.1*N* NaOH to filtrate after weighing *C* but before concentration

under procedure 8.1.6.

13.1.1.2 Continue with procedure 8.1.6.

13.1.1.3 This modification does not change calculations but results become "total soluble sulfur as sulfate."

13.1.2 *Supplemental removal of phosphates*

13.1.2.1 Phosphates should be removed if they are believed to be above 30 ppm. If the phosphate content is low and is known, then:

$$\text{ppm } SO_4 = \text{indicated ppm } SO_4 - \frac{(\text{ppm phosphate})}{3}$$

13.1.2.2 If removal is necessary, add 0.5 g $MgCO_3$ to filtrate after concentration to below 150 mL under procedure 8.1.5.

13.1.2.3 Boil an additional 5 min.

13.1.2.4 Cool to below 10°C in an ice bath.

13.1.2.5 Weigh beaker and contents to nearest 0.5 g (weight *D*).

13.1.2.6 Filter into dry beaker or directly into ion exchange column and continue with procedure 8.2.1.

13.1.2.7 This modification does not change calculations.

14. Keywords

Sulfates, Water solubles, Pulp, Paper

15. Additional Information

15.1 Effective date of issue: to be assigned.

15.2 This method is based on a volumetric titration of Hozumi (*1*,*2*), Aldrich (*3*), and others rather than the gravimetric method for determining barium sulfate.

15.2.1 Higher results may be obtained using this method when analyzing wet strength or hard sized papers or papers with very low sulfate content than when using the extraction procedures in withdrawn TAPPI method T 468.

15.2.2 The range of this test may be extended in several ways, primarily by changing specimen size and concentration of filtrates. If the test is so modified it should be stated with the results.

15.2.3 Methanol (*l*), ethanol, and acetone have been found to be suitable replacements for isopropanol in 8.2.3 with approximately the same alcohol/water ratio required. Their substitution should be noted in the report.

15.2.4 Limited data on comparison of this titration method with the gravimetric procedure described in withdrawn TAPPI method T 468 for the determination of small amounts of sulfate indicate agreement provided the solubility of barium sulfate is considered. A comparison follows:

Determination of sulfate in sample of bleached board:

Volumetric method: 345 ppm SO_4

Gravimetric method: 108 ppm SO_4

Solubility of $BaSO_4$ @ 25°C = 2.46 ppm

Five hundred milliliters of filtrate were obtained from 5 g so 2.46 x (500/5) is equivalent to 246 ppm SO_4 in paper remaining in solution of the filtrate by the gravimetric method.

15.3 Related method: total sulfur portion of 24 "Oxygen Flask Combustion Method," The Pharmacopoeia of Japan, Eighth Edition, Part 1, page 883, English Edition 1973.

15.4 Alternative method: sulfates in the water extracts from pulp and paper matrices may also be analyzed by ion chromatography (IC) by TAPPI T 699 "Analysis of Pulping Liquors by Suppressed Ion Chromatography." Ion chromatography does not significantly suffer from the chemical interferences as method T 255 does. Method T 255 would then be used to prepare samples for analysis by IC.

15.5 This method was reclassified as a Classical Method by committee action in 1997. There were no changes to this 2007 version.

Appendix A: Preparation and regeneration of ion exchange column

A.1 Prepare column by placing a small wad of glass wool just above stopcock, adding 10 mL of resin (Dowex 50-W-X8 or similar) and placing another wad of glass wool above the resin. This should leave at least 15 mL of liquid capacity above the resin.

A.2 The resin is usually satisfactory for 20 to 50 determinations between regenerations. Regenerate using the following procedure when indicated by a slight change in color of the top fourth of column or when erratic results indicate possible exhaustion.

A.2.1 Pass through column two successive 15 mL portions of 1*N* HC1.

A.2.2 Pass through column three successive 15 mL portions of distilled water.

References

1. Pharmacopoeia of Japan, 8th Edn., Part I, page 833; English Edition, 1973.
2. Hozumi, K., Umemoto, K., *Michrochem, J.* **12**: 45 (1967).
3. Aldrich, L. C., *Tappi* **57** (7):122 (1974).

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