WI 170802.03

T 256

DRAFT NO. 4 SARG

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SUBJECT CATEGORY Chemical Properties

RELATED METHODS See "Additional Information"

CAUTION:
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 test method, the user should 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.

Water-soluble chlorides in pulp and paper
(Ten-year review of T 256 cm-07)
(Reconfirmation of T 256 cm-07 as a Classical Method; no changes from previous draft)

1. Scope

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

1.2 The method is suitable for chloride content from 0.01% up to 1% but can be modified to extend this range to a limited extent. It is not intended for electrical grade pulp or papers with chloride content less than 50 ppm.

2. Summary

A pulp or paper specimen is disintegrated in water and boiled. The suspension is filtered and the filtrate is then concentrated. An aliquot is titrated with mercuric nitrate using an acidified s-diphenylcarbazone and xylene cyanol FF mixture as indicator of the mercury-chloride equivalence point.

3. Significance

The method is useful to determine chloride content and buildup due to brackish fresh water and/or other sources of chloride contamination in pulp or paper.

4. Apparatus

4.1 *Laboratory blender*, approximately 1000 mL (1 qt) capacity, similar to high-speed kitchen 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:* 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 *Magnetic stirrer*, with a 2.5-cm (1-in.) Teflon coated bar.

4.9 *Pipet*, 1 mL.

4.10 *Buret*, 10 mL or larger.

4.11 *Graduated cylinder*, 100 mL.

5. Reagents

5.1 *Mecuric nitrate,* 0.0141*N* $Hg(NO_3)_2$. Dissolve 2.3 g $Hg(NO_3)_2$ or 2.5 g $Hg(NO_3)_2 \cdot H_2O$ in 100 mL distilled water containing 0.25 mL concentrated HNO_3 and dilute to just under 1000 mL. Standardize using 5.00 mL of standard NaCl solution and 10 mg $NaHCO_3$ diluted to 100 mL with distilled water. Adjust mercuric nitrate solution to exactly 0.0141*N*. Store in a dark bottle away from the light; 1.00 mL is equivalent to 0.500 mg Cl.

5.2 *Sodium chloride standard*, 0.0141*N* NaCl. Dry NaCl at 140°C. Dissolve exactly 0.8241 g dried NaCl in chloride-free distilled water and dilute to exactly 1000 mL.

5.3 *Indicator-acidifier reagent:* Dissolve, in the order named, 0.25 g s-diphenylcarbazone[1], 4.0 mL concentrated HNO_3, and 0.03 xylene cyanol FF[1] in 100 mL of 95% ethyl alcohol or isopropyl alcohol. This prepared reagent has a shelf life of approximately three months, if stored in a dark bottle in a refrigerator. Deterioration causes a slow endpoint and high results. The nitric acid concentration is an important factor and will neutralize up to 150 mg/1000 mL alkalinity as $CaCO_3$. pH adjustments must be made in strongly alkaline or acidic waters.

5.4 *Sodium bicarbonate*, $NaHCO_3$.

[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.

5.5 *Nitric acid*, approximately 0.1*N* for pH adjustment. Dilute 6.4 mL concentrated HNO_3 to 1000 mL with distilled water.

5.6 *Sodium hydroxide*, approximately 0.1*N*, for pH adjustment dissolve 4.0 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, Fiberboard, 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 sample with perspiration 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 210 "Weighing, Sampling, and Testing Pulp for Moisture" or TAPPI T 412 "Moisture in Paper and Paperboard."

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 chloride-free distilled water using a laboratory blender. Transfer the slurry with a minimum distilled water rinse to a tared 1000-mL beaker. The slurry is at approximately 1% consistency. Care must be taken throughout the procedure to prevent exposure to additional chlorides in the atmosphere or through dirty equipment.

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.

8.1.4 Filter slurry using Büchner funnel and coarse paper into a 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.

8.1.6 Concentrate filtrate to approximately 250 mL on hotplate.

8.1.7 Weigh beaker and contents to nearest 0.5 g.

8.2 *Chloride determination of concentrated extract*

8.2.1 Measure 100 mL of the concentrated extract into a 250-mL beaker and stir with a magnetic stirrer.

8.2.2 Pipet 1.0 mL of indicator-acidifier reagent into the extract. The color of the solution should be green-

blue at this point. A light green indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8. When highly alkaline or acid extracts are analyzed, a preliminary pH adjustment to about pH 8 will be necessary before the indicator-acidifier reagent is added. A calomel electrode pH meter should not be used because of KCl contamination of the extract.

8.2.3 Titrate with 0.0141*N* $Hg(NO_3)_2$ to a definite purple endpoint. The solution will turn from green-blue to a blue a few drops before the endpoint.

8.2.4 Run a blank in place of the extract using 100 mL distilled water with 10 mg of $NaHCO_3$.

9. Calculation

9.1 Calculate the dilution factors as follows:

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

where

A = oven-dried weight of specimen (7.2)
B = slurry weight after boiling, weight from 8.1.3 minus tare
C = filtrate, weight from 8.1.5 minus tare
D = filtrate after concentration, weight from 8.1.7 minus tare

9.2 Calculate concentration of chloride in concentrated filtrate as follows:

$$\text{Cl, ppm} = 5.0\ [(\text{mL } Hg(NO_3)_2 - 0.1]$$

When 100 -mL specimen is used, $Hg(NO_3)_2$ is exactly 0.0141*N* and the blank is 0.1 mL.

9.3 If the above conditions are not met, then:

$$\text{Cl, ppm} = \frac{[\text{mL titrant to sample endpoint - mL titrant to blank endpoint)}\ (N_{\text{titrant}})\ (35.45)\ (1000)}{\text{mL of specimen}}$$

9.4 Calculate chloride in pulp or paper as follows:

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

10. Report

Report the average percent chloride content to two significant figures.

11. Precision

11.1 A single water sample containing 241 ppm chloride was tested by nine laboratories. The standard deviation was 1.1 ppm within a laboratory and 3.5 ppm between laboratories. This corresponds to about 0.009% (or 90 ppm) repeatability and 0.030% (or 300 ppm) reproducibility based on paper, as those terms are defined in TAPPI T 1206 “Precision Statement for Test Methods.” Note that the extraction procedure results in approximately 30 mL of water per g of pulp or paper.

11.1.1 These precision data were copied from precision as reported in the APHA AWWA APCF method (see 13.4).

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

12. Interferences with test

12.1 Iodide and bromide are titrated with mercuric nitrate in the same manner as chloride.

12.2 Sulfite, chromate, and ferric ions interfere when present in excess of 10 ppm in the liquid.

13. Keywords

Pulp, Paper, Chlorides, Water solubles

14. Additional information

14.1 Effective date of issue: to be assigned.

14.2 This method is a complete revision of the chloride portion of TAPPI T 229 m-45 “Water-Soluble

Sulfates and Chlorides in Pulp" and TAPPI T 468 m-60 "Water-Soluble Sulfates and Chlorides in Paper and Paperboard."

14.2.1 Higher results may be obtained using this method when analyzing wet strength or hard sized papers that when using T 468, since the T 468 extraction is inadequate for these papers.

14.2.2 The range of this test may be extended in several ways, primarily in specimen size and concentration. If the test is so modified, then state with the results.

14.3 The sulfate portions of T 229 and T 468 have been revised and combined as a separate method, TAPPI T 255 "Water-Soluble Sulfates in Pulp and Paper."

14.4 Related method: APHA AWWA APCF Method B "Mercuric Nitrate Method for Determination of Chloride," contained in "Standard Methods for the Examination of Water and Wastewater," 13th edn., New York, APHA, 1971, p. 97. This method is based on U.S. Patent 2,784,064 "Indicator for Chloride Titrations" granted to F. E. Clarke on March 5, 1957.

14.5 The use of a potentiometric method, ion chromatography, or other appropriate method for determination of chloride is suggested for electrical papers or any pulp or paper containing less than 50 ppm chloride.

14.6 This method, formerly TAPPI T 256 pm-76, has been reaffirmed in 1997 as classical by the responsible committee.

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