

T 604 cm-09

TENTATIVE STANDARD – 1931
OFFICIAL STANDARD – 1933
SUGGESTED METHOD – 1970
PROVISIONAL METHOD – 1979
CLASSICAL METHOD – 1985
WITHDRAWN – 1996
REVISED AND REINSTATED – 2000
REAFFIRMED – 2004
RECLASSIFIED AS CLASSICAL METHOD – 2009
©2009 TAPPI

The information and data contained in this document were prepared by a technical committee of the Association. The committee and the Association assume no liability or responsibility in connection with the use of such information or data, including but not limited to any liability under patent, copyright, or trade secret laws. The user is responsible for determining that this document is the most recent edition published.

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.

Sulfur dioxide in sulfite cooking liquor

1. Scope

1.1 This method is for the volumetric analysis of sulfite liquors used in the manufacture of sulfite pulp. The method is basically that developed by G. V. Palmrose (1) and is based on titration with potassium iodate for the total SO_2 and titration with sodium hydroxide for the free SO_2 . Liquor containing lignin derivatives requires corrective procedures which are given.

1.2 Sulfur dioxide in cooking liquor can be present as one or two of the following three forms: (1) dissolved sulfur dioxide and sulfurous acid; (2) ammonium, calcium, magnesium, or sodium bisulfite; or (3) ammonium or sodium sulfite (monosulfite). Four bases, ammonium, calcium, magnesium, and sodium have been commercially utilized; limited solubility problems with calcium and magnesium monosulfites restrict these liquors to combinations of (1) and (2), whereas sodium and ammonium monosulfites are soluble in the upper ranges of pH and allow combinations of (2) and (3) to be utilized.

2. Significance

This test is used for the preparation of cooking liquor of the desired concentration, for determining the proper digester charge, and for checking the progress of the cook.

3. Definitions

3.1 *Total sulfur dioxide*, the grams of SO_2 per 100 mL of solution determined by titration with 0.125N potassium iodate and expressed as a percentage of total SO_2 .

3.2 *Free sulfur dioxide*, the portion of the SO_2 which is not combined with the base, plus half of the SO_2 combined as bisulfites.

3.3 *Combined sulfur dioxide*, the difference between the total SO_2 and the free SO_2 .

NOTE 1: Refer also to TIP 0607-25 "Definitions of Terms Used in the Sulfite Pulping Processes."

Approved by the Standard Specific Interest Group for this Test Method

Documents
TAPPI
Document Sharing Hub

4. Apparatus

- 4.1 Balance, accurate to 0.01 g.
- 4.2 Graduated cylinders, 100 mL.
- 4.3 Burets, three 50-mL.
- 4.4 Pipets, 2, 5, and 25 mL.
- 4.5 Erlenmeyer flasks, 250 mL; 1 glass-stoppered.

5. Reagents

5.1 Potassium iodate, 0.125N KIO_3 (4.460 g of KIO_3 per 1000 mL of solution) standardized as follows: Place about 100 mL of cool distilled water in a 250-mL glass-stoppered Erlenmeyer flask and saturate with SO_2 gas by bubbling gas into water for about 5 min. (This solution should be freshly made up for each standardization and the flask kept stoppered between titrations.) Pour about 3 mL of this solution into a 250-mL Erlenmeyer flask containing 50 mL of distilled water and 1 mL starch-KI solution. Titrate with the KIO_3 solution until one drop gives a blue coloration. Record the titration. Discharge the blue color with not more than one drop of 0.1N sodium thiosulfate solution, add three drops of methyl red indicator solution, and titrate with the 0.125N NaOH until one drop gives a yellow coloration. Adjust the strength of the KIO_3 solution until the two titrations are equal. The normality of the KIO_3 will then be the same as that of the NaOH.

5.2 Sodium thiosulfate, approximately 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ (see TAPPI T 610 "Preparation of Indicators and Analytical Reagents and Standardization of Volumetric Solutions").

5.3 Starch-iodide solution: Dissolve 5 g of starch in 1000 mL of distilled water containing about 5 g of KI.

5.4 Thyodene, could be used to replace starch. It dissolves quickly.

5.5 Sodium hydroxide, 0.125N NaOH, accurately standardized (see T 610).

5.6 Methyl red indicator.

5.7 Sulfuric acid, 0.125N H_2SO_4 accurately standardized (see T 610); also approximately 1N.

5.8 Mercuric chloride, saturated solution of HgCl_2 .

5.9 Bromphenol blue indicator (bromphenolsulfonphthalein): Dissolve 0.1 g of the sodium salt of bromphenolsulfonphthalein in 250 mL of distilled water. Adjust to pH 4.0 with acid or alkali.

5.10 Bromcresol green indicator (optional).

5.11 Methyl purple indicator (optional).

5.12 Sulfur dioxide, small cylinder of compressed SO_2 .

6. Safety precautions

Sulfur dioxide is a toxic gas that can cause suffocation and death. Gas masks and other safety devices, as prescribed by the industrial and governmental agencies, should be available at all times when dealing with SO_2 and its various compounds. Certain chemicals that are used in this procedure for testing SO_2 may be toxic and should not be inhaled or ingested. For more specific information, consult TAPPI T 602 "Analysis of Sulfuric Acid" and TAPPI T 613 "Analysis of Caustic Soda" for precautionary measures with sulfuric acid and caustic soda respectively, and the MSDS for handling mercuric chloride.

7. Sampling

Obtain a sample of the cooking liquor from a suitable location and keep in a tightly stoppered bottle until specimens are withdrawn in order to avoid any loss of SO_2 . Samples taken from a hot pipeline or vessel require cooling by passage through a cooling coil before exposure to atmospheric pressure.

8. Test specimens

From the sample obtain 2-mL specimens for analysis in duplicate.