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TESTING COMMITTEE

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Sulphide, sulphite and thiosulphate in white and green liquors

1 Principle

In a measured volume of liquor the sum of sulphide, sulphite and thiosulphate is determined by iodometric titration. In another volume the sulphide is precipitated by addition of zinc carbonate, and the sulphite and thiosulphate are then titrated. In an aliquot of the solution treated with zinc carbonate, the sulphite is masked by adding formaldehyde, and thiosulphate alone is titrated.

2 Reagents

All reagents should be of analytical grade.

2.1 *Iodine solution*, 0,1 N, standardized. Normality known to an accuracy of ± 0,0005 N.

2.2 *Sodium thiosulphate solution*, 0,1 N, standardized. Normality known to an accuracy of ± 0,0005 N.

2.3 *Acetic acid*, 2:5. Dilute 200 ml of CH_3COOH (ρ = 1,055–1,058) with 500 ml of distilled water.

2.4 *Starch solution*, 0,2 %, 2 g per litre.

2.5 *Phenolphthalein indicator*, 0,1 %. Dissolve 0,1 g in 100 ml of ethanol.

2.6 *Glycerol*, $C_3H_5(OH)_3$.

2.7 *Zinc sulphate solution*, 290 g of $ZnSO_4 \cdot 7H_2O$ per litre.

2.8 *Sodium carbonate solution*, 106 g of Na_2CO_3 per litre.

2.9 *Formaldehyde*, HCHO.

3 Preparation of sample

If the liquor is turbid or contains solid material, filter it through a sintered glass filter.

4 Procedure

4.A Determination of $Na_2S + Na_2SO_3 + Na_2S_2O_3$

Pipette 25,0 ml of liquor into a 500 ml volumetric flask, dilute with distilled water to the mark and mix thoroughly.

Preliminary test 1: Pipette 10,0 ml of diluted liquor into a conical flask, add 3 drops of phenolphthalein solution and titrate slowly with the acetic acid. Note the consumption.

Preliminary test 2: Acidify 10,0 ml of the diluted liquor with about 2 ml of acetic acid and titrate with 0,1 N iodine solution using starch solution as the indicator. Note the amount of iodine solution consumed in the titration.

Measure from a burette into a conical flask 5 times the amount of 0,1 N iodine solution consumed in Preliminary test 2, measured to the nearest millilitre plus an excess of 7,0 ml. Add 5

times the amount of acetic acid consumed in Preliminary test 1 plus an excess of about 4 ml. Pipette 50,0 ml of the diluted liquor into the acidified iodine solution and titrate with 0,1 N sodium thiosulphate solution using starch solution as the indicator. Note the consumption of sodium thiosulphate solution, *a* ml, and the volume of iodine solution added, *b* ml.

4.B Determination of Na_2SO_3 + $Na_2S_2O_3$

Prepare a zinc carbonate suspension by mixing equal volumes (200 ml) of the zinc sulphate and sodium carbonate solution. Pipette 100,0 ml of liquor into a 1000 ml volumetric flask and add 50 ml of glycerol. Precipitate the sulphide with about 300 ml of the freshly prepared zinc carbonate suspension, added in portions. Shake the flask after each addition. When the precipitate has settled, transfer one drop of the clear solution to a lead acetate paper. If the paper blackens, indicating the presence of residual sulphide, add more of the zinc carbonate suspension to the liquor. When all the sulphide is precipitated, dilute with distilled water to the mark and shake the flask. Filter the solution through a dry, pleated filter paper or a sintered glass filter.

Preliminary test 3: Determine the consumption of acetic acid by 10 ml of the filtrate as described under Preliminary test 1.

Pipette 100,0 ml of the filtrate into a conical flask and acidify with 10 times the amount of acetic acid consumed in Preliminary test 3 plus an excess of 4 to 5 ml. Titrate immediately with 0,1 N iodine solution with starch solution as the indicator. Denote the consumption as *c* ml.

4.C Determination of $Na_2S_2O_3$

Pipette 100,0 ml from the filtrate obtained under 4.B into a conical flask and add 5 ml of formaldehyde. Mix and acidify with 10 times the amount of acetic acid consumed in Preliminary test 3 plus an excess of 4 to 5 ml. Titrate after 1 min with 0,1 N iodine solution using starch solution as the indicator. Denote the consumption as *d* ml.

5 Calculation and report

Calculate as follows:

$$X = 3{,}9 \cdot (4b \cdot n_1 - 4a \cdot n_2 - c \cdot n_1)$$

$$Y = 6{,}3 \cdot (c - d) \cdot n_1$$

$$Z = 15{,}8 \cdot d \cdot n_1$$

where

- a is the 0,1 N sodium thiosulphate consumed in titration A, in ml;
- b is the 0,1 N iodine solution added in titration A, in ml;
- c is the 0,1 N iodine solution consumed in titration B, in ml;
- d is the 0,1 N iodine solution consumed in titration C, in ml;
- n_1 is the normality of the iodine solution;
- n_2 is the normality of the sodium thiosulphate solution;
- X is the content of sodium sulphide, in grams of Na_2S per litre;
- Y is the content of sodium sulphite, in grams of Na_2SO_3 per litre;
- Z is the content of sodium thiosulphate, in grams of $Na_2S_2O_3$ per litre.

Report the result to the first decimal place (Note).

Note – Calculation of sulphidity. The sulphidity can be calculated from the equation:

$$\frac{100\ Na_2S}{NaOH+Na_2S} = \frac{100\ Na_2S}{\text{Active alkali}}$$

The active alkali figure is obtained as described in SCAN-N 2.

6 Literature

1 *Hægland, B. and Løschbrandt, F.*: Norsk Skogindustri 9 (1955): 5, 172-176;
2 TAPPI T 624 – m 44.

This method has been published in:
Norsk skogsindustri 17 (1963): 10, 410-413. (English and Norwegian)
Paperi ja Puu – Papper och Trä 45 (1963): 10, 555-560 (English, Finnish and Swedish).
Svensk Papperstidning 66 (1963): 20, 846-847. (English).
Svensk Papperstidning 66 (1963): 21, 897-898. (Swedish.)

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