SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

SCAN-N 6:85
Revised 1985

White and green liquors

Sulphate content

0 Introduction

This Scan-test Method replaces SCAN-N 6:64 which was based on a gravimetric procedure involving precipitation of barium sulphate. This revised Method prescribes a titrimetric procedure that is less timeconsuming and is less liable to both systematic and random errors.

1 Scope and field of application

This Scan-test Method specifies a method for the determination of sulphate ions in all kinds of white or green liquors. Large amounts of chloride may interfere with the determination.

2 Principle

A sample of liquor is added to a mixture of water, acetone and formaldehyde and the pH value is adjusted to 3. The formaldehyde acts as a masking agent for interfering sulphur compounds, such as sulphide and sulphite. The solution is titrated with lead perchlorate solution of known concentration. Solid lead sulphate is formed. The end point of the titration is detected potentiometrically by means of a lead-sensitive electrode.

The acetone is added in order to reduce the solubility of lead sulphate. This increases the sensitivity and precision of the procedure.

3 Apparatus

3.1 *Automatic titration equipment*
3.2 *Lead-sensitive electrode*
3.3 *Reference electrode*, for example a double junction electrode.

4 Reagents

All reagents should be of analytical grade. Commercially available solutions may be used.

4.1 *Acetone*, CH_3COCH_3

4.2 *Formaldehyde solution*. Dilute 200 ml of HCHO, ca 35 %, with 300 ml of distilled water.

4.3 *Perchloric acid*, concentrated $HClO_4$, density 1660 kg/m^3.

4.4 *Perchloric acid*, 1 mol/l. Mix 8 ml of concentrated perchloric acid with distilled water and dilute to 100 ml.

4.5 *Sodium hydroxide solution*, NaOH, 2,5 mol/l. Dissolve 10 g of sodium hydroxide in distilled water and dilute to 100 ml.

4.6 *Sodium sulphate solution*, 50 mmol/l, for calibration. Ignite a portion of anhydrous sodium sulphate, Na_2SO_4, at 550 °C, in a crucible of platinum or porcelain. Allow to cool to room temperature in a desiccator. Weigh 7,10 g of the dry salt and transfer it to a 1 litre flask. Dissolve the salt in distilled water and make up the solution to 1 litre. Calculate the exact concentration (d millimoles per litre).

4.7 *Lead perchlorate solutioin*, 50 mmol/l. Dissolve 23 g of $Pb(ClO_4)_2 \cdot 3H_2O$ in distilled water and dilute to 1 litre.

Determine the concentration in the following way: In a 150 ml beaker mix 50 ml of acetone (4.1) and 50 ml of formaldehyde solution (4.2) and add 5,00 ml of the 50 mmol/l sodium sulphate solution (4.6). Adjust the pH value to 3,0 ± 0,5 with 1 mol/1 perchloric acid (4.4). Place the beaker on the magnetic stirrer and place the electrodes in position in the solution. Fill the burette with lead perchlorate solution. Start the titration and record the titration curve.

Determine the end-point of the titration from the inflexion point of the S-shaped curve. Calculate the concentration c of the perchlorate solution in millimoles per litre as

$$c = \frac{5 \cdot d}{a}$$

where

a is the volume (in millilitres) of lead perchlorate solution consumed,

d is the concentration of the sodium sulphate solution (4.6) in millimoles per litre.

5 Procedure

Work in a hood to avoid exposure to formaldehyde fumes.

Add to a 150 ml beaker 50 ml of the formaldehyde solution (4.2), and 50 ml of acetone (4.1). Transfer preferably 5,00 ml of the sample to the beaker. (Never take more than 10 ml of sample). Avoid any solid particles that may have settled at the bottom.

Adjust the pH value of the solution to 3,0 ± 0,5 with the concentrated perchloric acid (4.3). If necessary, make the final adjustment by adding sodium hydroxide solution (4.5).

Place the beaker on the magnetic stirrer and place the electrodes in position in the solution. Titrate with the lead perchlorate solution (4.7) and record the titration curve. Determine the end-point of the titration from the inflexion point of the S-shaped curve. To avoid side-reactions, it is important that there is no unnecessary time delay from the addition of the sample until the end of the titration.

Note – The lead-sensitive electrode will loose its sensitivity rather rapidly unless it is polished regularly. Follow the instructions and use the polishing paper provided by the manufacturer of the electrode. In some cases it may be necessary to polish the electrode after each titration.

6 Calculation

Calculate the sulphate ion content of the liquor according to the expression:

$$X = \frac{96,06 \cdot b \cdot c}{(1000 \cdot v)}$$

where

X is the sulphate ion content in grams per litre

b is the volume of lead perchlorate solution consumed in the titration in millilitres,

c is the concentration of the lead perchlorate solution in millimoles per litre,

v is the sample volume taken for analysis, normally 5,00 ml,

96,06 is the relative molecular mass of sulphate ion in g/mol,

1000 is the factor to convert millimoles to moles.

or by the expression

$$Y = \frac{b \cdot c}{v}$$

where

Y is the sulphate ion content in millimoles per litre,

b is the volume of lead perchlorate solution consumed in the titration in millilitres,

c is the concentration of the lead perchlorate solution in millimoles per litre,

v is the sample volume taken for analysis, normally 5,00 ml.

7 Report

Report the sulphate ion content of the liquor to the nearest 0,1 g/l. The report shall include reference to this Scan-test Method and the following particulars:

a) time and place of testing,
b) identification mark of the sample,
c) the results,
d) any departure from this Method and any other circumstances that may have affected the test results.

8 Precision

Samples of the same liquors (one white liquor and one green liquor) were sent to seven different laboratories for determination of sulphate. For the white liquor the mean result reported was 6,3 g/l and the relative standard deviation was 1,6 %. For the green liquor the mean was 5,3 g/l and the relative standard deviation 1,1 %.

9 Literature

Lokka, E.J: Potentiometric determination of sulphate in white and green liquors using a lead ion-selective electrode and acetone as solvent. Paperi ja Puu - Papper och Trä 60(1978):8, 441-447.

SCAN-test Methods are issued and recommended by KCL, PFI and STFI-Packforsk for the pulp, paper and board industries in Finland, Norway and Sweden.
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