



White and green cooking liquors

Total sulphur

0 Introduction

This SCAN-test Method replaces SCAN-N 5:63 which was based on an acidometric procedure. This revised Method prescribes a procedure which is more specific for sulphur and less liable to interference than that previously recommended in SCAN-N 5:63.

1 Scope and field of application

This SCAN-test Method specifies a method for the determination of total sulphur in white liquors used as cooking liquors in the manufacture of sulphate pulp, and in green liquors used for the preparation of white liquors.

2 Principle

A sample of the liquor is treated with hydrogen peroxide to oxidize all forms of the element sulphur to sulphate ions. These are determined by potentiometric titration with lead perchlorate solution.

3 Apparatus

3.1 *Automatic titrator* with a recorder or, alternatively for manual titration, a millivoltmeter suitable for potentiometric titration (such as a pH meter) which can be read to the nearest 1 mV and a 20 ml piston burette which can be read to the nearest 0,01 ml.

3.2 *A magnetic stirrer*

3.3 *Lead-sensitive electrode*, Orion Model 94-82 (Manufactured by Orion Research Inc., Cambridge, Massachusetts 02139, USA) or equivalent.

3.4 *Reference electrode*, calomel electrode or equivalent.

4 Reagents

All reagents shall be of analytical grade (pro analysis).

4.1 *Hydrogen peroxide*, H_2O_2 , 300 g/kg.

4.2 *Cobalt nitrate solution*, 5 mmol/l. Dissolve 1,45 g of $Co(NO_3)_2 \cdot 6H_2O$ in distilled water and dilute to 1 litre.

4.3 *Ethanol*, 95 % C_2H_5OH .

4.4 *Perchloric acid*, 1 mol/l. Mix 8 ml of concentrated perchloric acid, $HClO_4$, density 1660 kg/m³ with distilled water and dilute to 100 ml.

4.5 *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 in distilled water and dilute to 1 litre. Calculate the exact concentration (*d* millimoles per litre).

4.6 *Lead perchlorate solution, 50 mmol/l.*
Dissolve 23 g of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in distilled water and dilute to 1 litre.

Determine the concentration in the following way:

Transfer 10,0 ml of the sodium sulphate solution to a 150 ml beaker, add 10 ml of distilled water and 80 ml of ethanol. Adjust the pH to a value near 4 with a few drops of the perchloric acid (4.4) and titrate with the lead perchlorate solution as described in section 5. Calculate the concentration c in millimoles per litre.

$$c = \frac{d \cdot 10}{a}$$

where

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

d is the concentration of the sodium sulphate solution (4.5) in millimoles per litre.

4.7 *Peroxide-sensitive indicator paper*, for example that manufactured by E. Merck, Darmstadt, Germany (registered trade name "Merckoquan10011 Peroxid-Test").

5 Procedure

5.1 Oxidation and dilution

Carry out the procedure in duplicate. With a precision pipette transfer 1,00 ml of the sample solution to a 100 ml beaker. Add 10 ml of distilled water and hydrogen peroxide (4.1) in portions of 0,5 ml until the solution remains clear and colourless. Normally 5 ml of the peroxide will be sufficient for this purpose. Heat the solution until it boils. Check with the aid of a strip of peroxide-sensitive indicator paper (4.7) that there is an excess of peroxide.

Add 0,2 ml of the cobalt nitrate solution (4.2) and boil gently for 1 min to destroy excess peroxide. Allow to cool and transfer the solution to a 50 mL volumetric flask. Dilute to the mark.

5.2 Titration

Transfer 20 ml (v ml) of the oxidized solution to a 150 ml beaker. Add 80 ml of ethanol (4.3) and adjust to a pH value close to 4 with a few drops of the perchloric acid (4.4) and with the aid of a strip of a suitable pH indicator paper.

Place the beaker on the magnetic stirrer and place the electrodes in position in the solution.

Note – The lead-sensitive electrode will lose 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.

Fill the burette with lead perchlorate solution (4.6). Start the titration and record the titration curve.

Determine the end point of the titration from the inflexion point of the S-shaped curve. Note the consumption of lead perchlorate solution at this point as a ml.

Note – The titration may be performed with other volumes v ml of the oxidized solution than 20 ml, provided that all other volumes are changed in proportion.

6 Calculation

Calculate the total sulphur content of the liquor according to the expression:

$$X = \frac{32,06 \cdot a \cdot c \cdot f}{v \cdot 1000}$$

where

X is the total sulphur content in grams per litre,

a 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,

f is the dilution factor, normally 1 ml to 50 ml = 50 (see 5.1),

v is the volume of oxidized solution taken to titration in millilitres,

32,06 is the relative atomic mass of sulphur in g/mol,

1000 is the factor to convert mmoles to moles.

7 Precision

Four samples were analysed by six different laboratories. The following results were obtained:

	White liquor	White liquor	Green liquor	Oxidized white liquor
Mean, g/l of sulphur	22,6	23,4	23,4	24,7
95 % confidence limit, g/l	±0,4	±0,3	±0,3	±0,4
Relative standard deviation, %	2,1	1,2	1,2	1,5

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

8 Report

Report the total sulphur content of the original sample to the nearest 0,1 g/l. The report shall include reference to this SCAN-test Method and the following particulars:

**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.
Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604,
SE-114 86 Stockholm, Sweden.**