



Mechanical and chemical pulps

Total sulphur content

0 Introduction

This SCAN-test Method is based on the so-called Schöniger combustion and the end-determination is based on ion chromatography.

1 Scope

This SCAN-test Method describes a procedure for the determination of the total sulphur content in all kinds of pulp. It is intended for pulps with a total sulphur content exceeding 20 mg/kg oven-dried pulp.

Note – The method has not been evaluated for pulp consisting of recovered fibres.

2 Reference

ISO 638 Pulps – Determination of dry matter content (EN ISO 638)

Note – SCAN-test has withdrawn a number of test methods and refers instead to the corresponding ISO and/or EN Standards

3 Definition

For the purpose of this Method, the following definition applies:

3.1 *Total sulphur, TotS* – The total amount of the element sulphur present in the pulp.

4 Principle

A sample is combusted with oxygen in a Schöniger flask in the presence of hydrogen peroxide. The sulphur is converted into sulphate, which is determined by ion chromatography (IC).

5 Reagents

5.0 All chemicals must be of analytical grade. Use only distilled and/or deionized water.

5.1 *Concentrated nitric acid*, $c(\text{HNO}_3) = 14 \text{ mol/l}$ (approximately 65 %) for washing the platinum basket.

5.2 *Concentrated eluent*. The composition is given by the manufacturer of the ion chromatograph. This eluent may be needed, depending on the instrument, to adjust the ionic strength of the sample solution prior to ion chromatography.

5.3 *Concentrated sulphate standard solution*, $c(\text{SO}_4^{2-}) = 1000 \text{ mg/l}$. Dry a portion of anhydrous sodium sulphate, Na_2SO_4 , at 105 °C for at least 1 hour. Weigh 1,479 g of the dried salt in a 1000 ml volumetric flask, dissolve and fill to the mark with water (5.0).

Note – A commercially available standard solution may be used.

5.4 *Sulphate standard solution.* Transfer 1,00 ml of the concentrated standard solution (5.3) to a 250 ml volumetric flask. Add concentrated eluent (5.2) if prescribed by the ion chromatograph manual. Fill to the mark with water (5.0).

5.5 *Eluent for ion chromatography.* The composition of this solution is highly variable depending on the type of ion chromatography column to be used. Therefore, follow the recommendations given by the IC column supplier. Filter the eluent through a membrane of cellulose acetate or nitrate.

5.6 *Compressed gas.* Oxygen is used for the combustion. It is essential that the compressed gas used is free from sulphur compounds.

5.7 *Hydrogen peroxide, H₂O₂,* concentration between 30 % and 40 %.

6 Apparatus

Ordinary laboratory equipment and the item listed below. Wash all equipment with water (5.0).

6.1 *Schöniger flask,* volume between 750 ml and 1000 ml. The flask is made of thick, heat-resistant glass and is provided with a ground-in stopper. A basket or net made of platinum is attached to the stopper. An automatic ignition device may also be fitted (12.2).

Check the flask carefully before using it. A flask with a suspected crack must not be used.

Clean the platinum basket or net with nitric acid (5.1). Rinse with water (5.0). Clean the basket or net in a flame if any contamination is suspected.

6.2 *Ion chromatograph,* with a fractionating column suitable for the determination of sulphate and a conductivity detector. The chromatography column must be able to withstand peroxides.

6.3 *Absorption paper,* sulphur-free paper such as Whatman chromatography paper No 3 or Munktells filter paper No 3, with a diameter between 30 mm and 70 mm.

7 Sampling and sample pretreatment

Use protective gloves. Keep the sample wrapped in aluminium foil or in a black polyethylene bag. Protect it from sulphur-contaminated air.

The sampling procedure is not covered by this Method. Make sure that the test pieces taken to analyse are representative of the sample received.

Determine the dry matter content of the sample as described in ISO 638.

8 Procedure

8.1 Run the procedure at least in duplicate. Weigh out two different amounts (between 250 mg and 500 mg) of the sample. The optimal amount depends on the expected sulphur content and the size of the apparatus. See Note in 8.3.

If the sample is in sheet form, cut pieces of suitable size so that they can be placed in the platinum basket.

If the sample is a fluff pulp or a finely divided pulp, compress the sample to form a tablet or wrap the sample in absorption paper (6.3) before ignition.

If the flask has no device for ignition it is recommended to use a strip of adsorption paper (6.3), of about 3 mm to 5 mm x 40 mm to 55 mm, as a wick.

8.2 *Blank.* Carry out the whole determination without any sample. If a paper (6.3) is used as a wick in the ignition or as wrapping paper for the sample, a paper of the same size must be used in the blank.

8.3 *Combustion.* Using a pair of forceps, place the strip in the basket or on the net (6.1) together with the weighed sample. Add 25,0 ml of water (5.0) and 500 µl of hydrogen peroxide (5.7) to the Schöniger flask.

Warning – It has been reported that Schöniger flasks can explode during the combustion step. Use protective spectacles. If the combustion is carried out in the open, use a face shield.

Flush the inside of the flask with oxygen (5.6) for about 1 minute. Ignite the strip for example with a spirit lamp. Quickly insert the basket or the net with the burning strip and the sample into the Schöniger flask. Close the flask immediately. Turn the flask upside down and keep it in this position during the combustion.

For electric ignition follow the instructions provided by the manufacturer of the Schöniger apparatus. If an automatic ignition device is fitted on the Schöniger flask, the ignition procedure can be modified and no paper strip is needed.

Watch the combustion carefully. If the combustion is not complete (some carbon remains) repeat it with a new sample.

Do not open the flask when the combustion is complete. Shake the Schöniger flask and allow it to cool. Shake again vigorously for 15 seconds and leave the flask to cool for 45 min. It is important that all mist (smoke) has disappeared before the flask is opened.

Note – A larger amount of sample is needed if the sulphur content is low (see 8.1). In this case, make several combustions consecutively in the same flask. Shake the flask and let it stand without opening it for at least 45 min between the combustions.

8.4 *Ion chromatographic determination.* The optimum conditions depend on the apparatus and the column. Use the conditions recommended by the manufacturer or determine the conditions empirically.

Transfer the content of the Schöniger flask to a 50 ml volumetric flask. Rinse the Schöniger flask carefully (shake it) twice with 10 ml portions of water (5.0). Transfer the rinsings to the volumetric flask and make up to the mark with water (5.0).

Note – Some ion-chromatographs require the addition of concentrated eluent (5.2). Make this addition before filling the volumetric flask to the mark.

Perform the chromatography with the sulphate standard solution (5.4). Check from the chromatogram that the separation is adequate. Measure either the area or the height of the sulphate peak.

Perform the chromatography with the sample solution and measure the area or the height of the sulphate peak.

9 Calculation

9.1 Calculate the total sulphur content in the pulp from the expression:

$$X = \frac{V(A_x - A_o) CD}{m A_{st}} \frac{32}{96} \quad [1]$$

where

X is the total sulphur content in the dry sample, in milligrams per kilogram;

V is the volume of the sample solution (here 50 ml), in millilitres;

A_x is the area or the height of the sulphate peak for the sample solution;

A_o is the area or the height of the sulphate peak for the blank solution;

A_{st} is the area or the height of the sulphate peak for the standard solution;

C is the content of sulphate in the standard solution (5.4);

m is the mass of the test portion taken, as dry, in grams;

D is the dilution factor (=1, if no dilutions have been made);

32 is the atomic mass of sulphur;

96 is the molar mass of sulphate.

9.2 *Mean.* Calculate the mean of the parallel determinations. The results of the parallel determinations should not deviate by more than 5 % from their mean. For means below 50 mg/kg deviations up to 5 mg/kg are acceptable.

10 Report

The test report shall include reference to this SCAN-test Method and the following particulars:

- date and place of testing;
- identification mark of the sample tested;
- the result given to two significant figures;
- any departure from the standard procedure and any other circumstances that may have affected the result.

11 Precision

11.1 Repeatability

Two pulp samples were investigated in one laboratory. Six parallel determinations were made in each case. The results were as follows:

Sample type	Mean, mg/kg	Coeff of variation, %
Bl. eucalyptus pulp	67	3,1
CTMP	1171	1,7

11.2 Reproducibility

Two samples of pulp were investigated in five laboratories. The results were as follows:

Sample type	Mean, mg/kg	Coeff of variation, %
Bl. eucalyptus pulp	70	10,5
CTMP	1156	2,9

12 Literature

- Schöniger, W., *Microchimica Acta* 1(1995) 123
- Douek, M. and Ing, J., *Journal Pulp Paper Science*, 15:2 (1989) J72

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.