



## *Black liquors*

# Total sulphur content

### 1 Scope

This SCAN-test Method describes two methods for determining the total sulphur content in black liquors having a dry matter content exceeding 8 %.

The methods are based on Schöniger combustion followed either by potentiometric titration or by ion chromatography (IC).

The standard is intended for black liquors with a total sulphur content exceeding 0,5 gram of sulphur per kilogram of dry substance (0,016 mol/kg d s).

In Annex A, a method based on pyrolytic decomposition is described. In Annex B, a bomb calorimetric procedure, as an alternative to Schöniger combustion, is described.

The Schöniger combustion-based methods (IC or titration), the pyrolytic decomposition procedure described in Annex A, and the calorimetric bomb combustion procedure described in Annex B give comparable results, see Annex C.

### 2 Reference

SCAN-N 22 Black liquors – Dry matter content and fibre content

### 3 Definition

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

3.1 *Total sulphur, Tot S* – The total amount of the element sulphur present in the black liquor.

*Note* – The procedure may involve losses of sulphur due to volatile sulphur compounds.

### 4 Principle

A sample aliquot is transferred to a filter paper and combusted with oxygen in a Schöniger flask in the presence of hydrogen peroxide. The sulphur is converted into sulphate, which is determined either by potentiometric titration or by ion chromatography (IC).

*Note* – Alternative procedures are described in Annex A and Annex B.

## 5 Reagents

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

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

5.2 *Hydrogen peroxide*, concentration between 30 % and 40 %.

5.3 *Concentrated nitric acid*, 65 %.

5.4 *Concentrated sulphate standard solution*,  $c(\text{Na}_2\text{SO}_4) = 10 \text{ mmol/l}$ . Dissolve 1,42 g absolutely dry  $\text{Na}_2\text{SO}_4$  in water (5.0) in a 1000 ml volumetric flask and fill to the mark with water.

*Note* – A commercially available standard solution may be used.

5.5 *Sulphate standard solution*,  $c(\text{Na}_2\text{SO}_4) = 0,04 \text{ mmol/l}$ . Transfer 1,00 ml of the concentrated standard solution (5.4) to a 250 ml volumetric flask. Add concentrated eluent if prescribed by the ion chromatograph manual. Fill to the mark with water (5.0).

5.6 *Cobalt nitrate solution*,  $c(\text{Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}) = 5 \text{ mmol/l}$ . Dissolve 1,45 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$  in 1000 ml water (5.0).

5.7 *Acetone*,  $\text{CH}_3\text{COCH}_3$ .

5.8 *Perchloric acid*,  $c(\text{HClO}_4) = \text{approx. } 1 \text{ mol/l}$ . Add 10 ml concentrated  $\text{HClO}_4$  to a 100 ml volumetric flask and fill to the mark with water (5.0).

5.9 *Lead perchlorate solution*,  $c(\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}) = 10 \text{ mmol/l}$ . Dissolve 4,6 g of  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  in a 1000 ml volumetric flask and fill to the mark with water (5.0).

The concentration of the solution is determined as follows: Mix 2,0 ml solution (5.4), 20 ml water (5.0) and 50 ml acetone (5.7) in a 150 ml beaker. Adjust the pH value in the beaker to  $\text{pH} = 3,5 \pm 0,5$  using a few drops of perchloric acid (5.8). Determine the concentration of the lead perchlorate solution by titration according to the potentiometric titration procedure described in 8.3.1.

Calculate the lead perchlorate concentration  $c(\text{Pb}(\text{ClO}_4)_2)$  in mmol per litre, as follows:

$$c = \frac{d \cdot V}{a} \quad [1]$$

where

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

$a$  is the volume of the lead perchlorate solution used at the inflection point, in millilitres;

$d$  is the concentration of the sodium sulphate solution, in millimoles per litre (here 10 mmol per litre);

$V$  is the volume of sodium sulphate solution, in millilitres (here 2 ml).

5.10 *Eluent solution*, for ion chromatography. The composition of this solution is highly variable depending on the type of ion chromatography column used. Therefore, follow the recommendations given by the IC column supplier.

## 6 Apparatus

Ordinary laboratory equipment. Wash all equipment with nitric acid (5.3) and rinse with water (5.0).

6.1 *Micropipettes*, between 100  $\mu\text{l}$  and 1000  $\mu\text{l}$ .

6.2 *Pasteur pipettes*.

6.3 *Schöniger flask*, 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.

*Note 1* – Check the flask carefully before using it. A flask with a suspected crack must not be used.

*Note 2* – Clean the platinum basket or net with nitric acid (5.3). Rinse with water (5.0). Clean the basket or net in a flame if any contamination is suspected.

6.4 *Titration equipment*. An automatic device for potentiometric titration including a motorized burette (10 ml) and a recorder is recommended.

6.5 *Lead-sensitive electrode*. Store the electrode in a dry place when not in use.

*Note 3* – Before using the electrode for the first time, or after a long period out of use, it must first be polished according to the manufacturer's instructions.

6.6 *Reference electrode*. Calomel electrode or equivalent.

6.7 *pH meter with combined glass electrode or pH indicator paper* with an accuracy of  $\pm 0,5$  pH unit.

6.8 *Peroxide-sensitive indicator paper.*

6.9 *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.

6.10 *Absorption paper*, sulphur-free paper such as Whatman chromatography paper No 3 or Munktell filter paper No 3, with a diameter between 3 cm and 7 cm and with a 4 cm long wick attached.

## 7 Sampling and sample pretreatment

To obtain a representative sample from black liquors with dry matter content exceeding 40 %, a dilution procedure is necessary. The sample is to be diluted with distilled water to a dry matter content around 20 %.

Determine the dry matter content of the original sample according to SCAN-N 22.

Heat the sample in a water bath at 90 °C for 20 min, keeping the bottle closed during the heating period.

Mix the sample carefully with a glass rod, taking care to ensure that sediment on the bottom of the sample container is stirred and homogenized with the rest of the sample.

Place an empty, dry plastic bottle with lid (volume 100 ml) on the balance. Tare the balance.

*Note* – It may be convenient to weigh the black liquor, if a lid is used. Tare the balance with the plastic bottle and the lid.

Weigh into the plastic bottle 10 g of the homogenized sample to the nearest 0,01 g and add 50 g of hot, distilled water, weighed to the nearest 0,01 g.

Put a stirring magnet into the bottle and close the bottle. Tighten it well. Place the bottle on a magnetic stirrer and stir until the sample is totally homogenized, for approximately 10 min. Calculate the dilution factor of the original black liquor ( $D = 60/10$ ). The sample is now ready to be analysed.

## 8 Procedure

Carry out the procedure in duplicate. A reagent blank shall also be carried out through the entire procedure.

*Warning* – Use protective spectacles. If the combustion is carried out in the open, use a face shield.

8.1 Cut the absorption paper (6.10) and add a few drops of hydrogen peroxide (5.2) to the paper. Drop carefully an aliquot of the sample (between 0,1 g and 0,2 g if IC and approximately 1,0 g if titration) onto the paper with a pasteur pipette (6.2) while the paper is hanging. Weigh the pipette containing the black liquor sample before and after the addition. Dry the absorption paper with the sample in an oven at about 50 °C for 10 min to 20 min.

### 8.2 Schöniger combustion

Roll the absorption paper to form a roll and place the roll together with a wick (6.10) in a platinum basket. Use pincers.

Add 10 ml of water and between 200  $\mu$ l and 500  $\mu$ l of hydrogen peroxide (5.2) to the Schöniger flask (6.3). Flush the inside of the flask with the compressed gas (5.1) for about one minute. Ignite the wick, for example with a spirit lamp. Quickly insert the basket with the burning sample into the Schöniger flask. Close the flask immediately, turn it upside down and back again and keep it in this position during the combustion.

For automatic ignition, follow the instructions provided by the manufacturer of the Schöniger apparatus.

Do not open the flask until the combustion is complete and the flask has cooled to room temperature.

Watch the combustion carefully. If the combustion is not complete (some carbon remains) a new combustion is needed.

When the combustion is completed, shake the Schöniger flask and allow it to cool. Shake again vigorously for 15 min or leave the flask for at least 45 min. It is important that all mist has disappeared.

### 8.3 End determination

For the end determination, use either the potentiometric titration procedure described in 8.3.1 or the Ion Chromatographic (IC) procedure described in 8.3.2.

#### 8.3.1 Potentiometric titration

Operate the titration equipment (6.4) as instructed by the manufacturer.

*Note 1* – The lead-sensitive electrode (6.5) will lose its sensitivity 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.

Add 10 ml of water (5.0) to a 150 ml beaker. Keep the platinum basket or net in the beaker for a few minutes to dissolve salts. Rinse with a small amount of water (5.0).

Transfer the contents of the Schöniger flask to the same beaker. Rinse the Schöniger flask carefully (shake it) twice with 10 ml portions of water (5.0). Add the rinsings to the beaker. The total volume of the solution should now be about 50 ml.

To remove remaining peroxide, add 0,2 ml of cobalt nitrate solution (5.6) to the beaker. Boil the mixture for 2 min to 3 min covered with a watch glass. Rinse the beaker inside along the walls with water (5.0) and check with the peroxide-sensitive indicator paper (6.8) that no peroxide is left in the solution.

Let the solution cool and add 80 ml of acetone (5.7) to the mixture.

Acidify the solution with perchloric acid (5.8) until a pH value between 3 to 4 is reached.

Insert the lead-sensitive electrode (6.5) and the reference electrode (6.6) in the solution and stir with a magnetic stirrer. Titrate with lead perchlorate (5.9) past the inflection point so that an S-shaped curve is obtained. Read off the volume,  $a$  ml, of the lead perchlorate solution consumed at the inflection point. The change in the potential is approximately 100 mV and the consumption of the lead perchlorate (5.9) should be at least 0,4 ml.

*Note 2* – If the consumption of the perchlorate is less than 0,4 ml, more sample must be taken in the combustion (subclause 8.1 - 8.2).

*Note 3* – If an automatic device is not used, read the potentiometric value after each addition of lead perchlorate (5.9) and construct the titration curve by plotting each reading against the corresponding total volume of lead perchlorate solution (5.9) added. Read the volume of lead perchlorate solution at the inflection point,  $a$  ml.

8.3.2 *Ion chromatography.* The optimum conditions depend on the apparatus and on the column. Use the conditions recommended by the manufacturer or determine the optimum conditions empirically.

Transfer the contents of the Schöniger flask to a 50 ml volumetric flask. Rinse the Schöniger flask carefully (shake it) twice with 10 ml of water (5.0). Transfer the washings to the volumetric flask and fill to the mark with water (5.0) (here  $V = 50$  ml).

*Note 4* – Some chromatographs require the addition of concentrated eluent. If required, make this addition before filling the volumetric flask to the mark.

Perform the chromatography with one of the standard solutions (5.4 or 5.5). Check from the chromatogram that the separation is adequate. Measure either the area or the height of the sulphate peak of the standard solution,  $b$ . Perform the chromatography with the sample solution and measure the area or the height of the sulphate peak,  $a$ . Repeat with the blank solution.

Calculate the IC results for the sample solution and the blank solution respectively ( $C_1$  and  $C_0$ ) in millimoles per litre, as follows:

$$C = \frac{a \cdot c}{b} \quad [2]$$

where

- $C$  is the concentration of the sample solution, in millimoles per litre;
- $a$  is the peak area or height of the sample solution or the blank solution;
- $b$  is the peak area or height of the standard solution;
- $c$  is the concentration of the standard solution, in millimoles per litre.

## 9 Calculation

### 9.1 Potentiometric titration

Calculate the total sulphur content in the black liquor according to the following equation:

$$X_s = \frac{(a_1 - a_0) \cdot c \cdot D}{m \cdot f \cdot 10} \quad [3]$$

where

- $X_s$  is the total sulphur content in the original black liquor, in mol per kilogram dry substance;
- $a_1$  is the volume of the lead perchlorate solution used in the titration of the sample, in millilitres;
- $a_0$  is the volume of the lead perchlorate solution used in the titration of the blank, in millilitres;
- $c$  is the concentration of the lead perchlorate solution, in millimoles per litre;
- $D$  is the dilution factor of the original black liquor ( $D = 1$  if there is no dilution);
- $m$  is the amount of the black liquor sample used for Schöniger combustion, in grams.
- $f$  is the dry matter content of the original black liquor, in per cent;
- 10 is the numerical factor (100/1000) which contains the factor 1000 to convert millimoles to moles and the factor 100 to bring the result to dry substance.

Calculate the total sulphur content in grams per kilogram dry substance according to the equation:

$$X_2 = 32,06 X_s \quad [4]$$

where

- $X_2$  is the amount of sulphur in the original black liquor, in grams per kilogram dry substance;
- 32,06 is the relative atomic mass of sulphur, in grams per mol.

### 9.2 Ion Chromatography

Calculate the total sulphur content in the black liquor from the equation:

$$X_s = \frac{(C_1 - C_0) \cdot V \cdot D}{m \cdot f \cdot 10} \quad [5]$$

where

- $X_s$  is the total sulphur content in the original black liquor, in mol per kilogram dry substance;  
 $C_1$  is the IC result for the sample, in millimoles per litre;  
 $C_0$  is the IC result for the blank, in millimoles per litre;  
 $V$  is the volume of the sample solution after Schöniger combustion (here 50 ml), in millilitres;  
 $D$  is the dilution factor of the original black liquor ( $D = 1$  if there is no dilution);  
 $m$  is the amount of black liquor used for the Schöniger combustion, in grams;  
 $f$  is the dry matter content of the original black liquor, in per cent;  
 10 is the numerical factor (100/1000) which contains the factor 1000 to convert millimoles to moles and the factor 100 to bring the result to dry substance.

Calculate the total sulphur content in grams per kilogram dry substance according to the equation:

$$X_2 = 32,06 X_s \quad [6]$$

where

- $X_2$  is the amount of sulphur, in gram per kilogram dry substance;  
 32,06 is the relative atomic mass of sulphur, in grams per mol.

9.3 *Mean value.* Calculate the mean of the parallel determinations. The results of the parallel determinations should not deviate by more than 5 % from their mean.

## 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 sampled tested;
- the end-determination procedure used;
- the result given to two significant figures;
- any departure from this Method and any other circumstances that may have affected the result.

## 11 Precision

11.1 *Repeatability.* One laboratory analysed two different black liquor samples ten times. The results were as follows:

| Sample         | Mean total sulphur content, mol per kilogram | CV*, % |
|----------------|--|--------|
| Black liquor 1 | 1,20   | 1,4    |
| Black liquor 2 | 1,54   | 1,3    |

11.2 *Reproducibility.* Three samples of black liquor were analysed in four laboratories. The results were as follows:

| Sample                    | Mean total sulphur content, mol per kilogram | CV*, % |
|---------------------------|--|--------|
| Spent liquor              | 1,72   | 6,3    |
| Weak liquor               | 1,45   | 4,7    |
| Concentrated waste liquor | 1,60   | 1,4    |

\*) CV = coefficient of variation

## Annex A – Pyrolytic decomposition procedure

### A.1 Sampling and sample pretreatment

Sampling and sample pretreatment are described in section 7 in this Method.

### A.2 Procedure

Weigh a suitable amount of sample as recommended by the manufacturer of the pyrolysis instrument. Dry the sample in an oven at 50 °C for 10 min to 20 min before placing it in the instrument. Follow the instructions given in the instrument manual. The decomposition temperature shall be at least 1350 °C.

#### *Combustion*

To decompose all bound sulphur, the oxidation substance vanadium oxide ( $V_2O_5$ ) must be used. Therefore, use an amount of 0,2 g  $V_2O_5$  to 0,6 g sample. The signal registration time shall be 10 min.

### A.3 Calculation

Calculate the total sulphur content in the black liquor according to the following equation:

$$X_s = \frac{A \cdot 10}{32,06} \quad [A1]$$

where

$X_s$  is the total sulphur content in the black liquor, in mol per kilogram of dry substance;

$A$  is the total sulphur content in the dry sample, in per cent (g sulphur/100 g dry sample);

10 is the numerical factor, which brings the result into mol per kilogram dry sample;

32,06 is the relative atomic mass of sulphur, in gram per mol.

## Annex B – Calorimetric bomb combustion procedure

### B.1 Principle

A weighed portion of the black liquor sample mixed with an auxiliary material (propanediol) is burned in high-pressure oxygen in a calorimetric bomb under specified conditions.

### B.2 Reagents

B.2.1 *Oxygen*, at a pressure high enough to fill the bomb to 3 MPa, at least 99,5 % pure.

B.2.2 *Propanediol*, C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>, analytical grade.

B.2.3 *Water*. Use only distilled or deionized water.

### B.3 Apparatus

B.3.1 *Combustion bomb*, inner volume between 200 ml and 400 ml, intended for combustion of organic materials in oxygen at elevated pressure (3 MPa), equipped with a pressure regulation to control the pressure when filling the bomb with oxygen.

B.3.2 *Ignition circuit* connected to the bomb electrodes suitable for igniting the sample.

B.3.3 *Conducting wire*, made of platinum.

B.3.4 *Cotton fuse*.

### B.4 Procedure

Weigh approximately 0,5 g of the sample to the nearest 0,1 mg in a platinum crucible. Add approximately 0,4 g of propanediol (B.2.2). Fill the bomb (B.3.1) with 5 ml of water (B.2.3) and follow the instructions for combustion given in the manual. At the end, examine the interior of the bomb for any sign of incomplete combustion.

Wash with water (B.2.3) the contents of the bomb into a beaker. Make sure to wash also the underside of the bomb lid and the electrodes. Put a small magnet in a crucible filled with water (B.2.3) and place it in the beaker. Warm up under stirring to dissolve the solids in the crucible.

Determine the sulphate content of the solution either by potentiometric titration or by ion chromatography (IC).

### B.5 Literature

B.5.1 ISO 1928:1995 Solid mineral fuels – Determination of gross calorific value by the calorimeter bomb method and calculation of net calorific value

B.5.2 Operative Instruction for 126 Isoperibol Calorimeter. Parr Instrument Company

## Annex C – Comparison between specified procedures

A comparison test between different alternative procedures, carried out within the SCAN-test working group "Black liquor", showed that three alternative procedures were acceptable. These procedures are:

- Schöniger combustion;
- High temperature pyrolytic combustion, at 1350 °C, in an oxygen atmosphere.
- Calorimetric bomb decomposition.

The Schöniger combustion technique was chosen as the standard method because the same apparatus is used in the SCAN-test methods for the determination of sulphur in pulp and for the determination of total chlorine in pulp and paper, and that equipment is thus already available at the pulp mills.

Table 1. Comparison between results achieved from the three alternative procedures

| Sample             | Schöniger + titration |          | Schöniger + IC        |          | Pyrolytic decomposition |         | Calorimetric bomb combustion |          |
|--------------------|-----------------------|----------|-----------------------|----------|-------------------------|---------|------------------------------|----------|
|                    | $\bar{X}$ ,<br>mol/kg | CV,<br>% | $\bar{X}$ ,<br>mol/kg | CV,<br>% | $\bar{X}$ ,<br>mol/kg   | CV<br>% | $\bar{X}$ ,<br>mol/kg        | CV,<br>% |
| Spent liquor       | 1,68                  | 2,3      | 1,72                  | 6,1      | 1,79                    | 11,8    | 1,82                         | 1,4      |
| Weak liquor        | 1,55                  | 2,8      | 1,47                  | 5,0      | -                       | -       | 1,66                         | 4,8      |
| Conc. waste liquor | 1,59                  | 1,4      | 1,60                  | 1,7      | 1,59                    | 1,5     | 1,60                         | 8,9      |

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.