



## Black liquor

# Sodium and potassium contents

## 1 Scope

This SCAN-test Method specifies different procedures for the determination of sodium and potassium contents in black liquors.

The Method is applicable to all kinds of black liquor obtained in a pulp mill using the kraft process.

## 2 Reference

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

## 3 Principle

The black liquor sample is diluted with water and, without further pretreatment, is analysed by atomic absorption spectrometry (AAS) or by flame photometry.

*Note* – Inductively coupled plasma emission (ICP) and atomic emission spectroscopy (AES) were used by some laboratories in the intercalibrations and these methods gave comparable results.

## 4 Reagents

All reagents shall be of analytical grade.

4.0 *Water*, of high purity, distilled or deionized, shall be used in the preparation of solutions and for diluting samples.

4.1 *Sodium stock solution*, 1000 mg/l. Ignite a portion of anhydrous sodium sulphate,  $\text{Na}_2\text{SO}_4$ , at 550 °C, in a crucible of platinum or porcelain. Allow to cool to room temperature in a

desiccator. Weigh ( $3,089 \pm 0,005$ ) g, using an analytical balance, and dissolve in water (4.0). Dilute to 1 litre in a volumetric flask. Store in a polyethylene bottle.

*Note 1* – Commercially available stock solution, having a concentration of ( $1000 \pm 2$ ) mg/l may be used.

4.1.1 *Sodium standard solution*, 50 mg/l. Dilute 5,00 ml of the sodium stock solution (4.1) to 100 ml in a volumetric flask.

4.2 *Potassium stock solution*, 1000 mg/l. Ignite a portion of anhydrous potassium sulphate,  $\text{K}_2\text{SO}_4$ , at 550 °C in a crucible of platinum or porcelain. Allow to cool in a desiccator. Weigh ( $2,228 \pm 0,005$ ) g, using an analytical balance, and dissolve in water (4.0). Dilute to 1 litre in a volumetric flask. Store in a polyethylene bottle.

*Note 2* – Commercially available stock solutions having a concentration of ( $1000 \pm 2$ ) mg/l may be used.

4.2.1 *Potassium standard solution*, 50 mg/l. Dilute 5,00 ml of the potassium stock solution (4.2) to 100 ml in a volumetric flask.

4.3 *Cesium solution*, 50 g/l. Dissolve 63,5 g of cesium chloride,  $\text{CsCl}$ , in water (4.0) and dilute to 1 litre.

*Note 3* – This solution shall be used only when sodium and potassium is determined by atomic

absorption spectrometry. Cesium is added in order to prevent ionisation reactions in the flame.

- 4.4 *Hydrochloric acid*, approx. 6 mol/l. Dilute concentrated hydrochloric acid, HCl, (37 %, density 1,19 g/ml) with an equal volume of water (4.0).

## 5 Apparatus

- 5.1 *Balance*, with a resolution of 0,001 g.
- 5.2 *Water bath*, thermostated at 90 °C.
- 5.3 *Atomic absorption spectrometer*, equipped for the determination of sodium at 589,0 nm and potassium at 766,5 nm.

*Note 1* – An atomic emission spectrometer (AES) may be used.

- 5.4 *Flame photometer (or a flame emission spectrometer)* equipped for the determination of sodium at 589,0 nm and potassium at 766,5 nm. Propane should be used as fuel for the flame.

*Note 2* – An acetylene flame is not recommended for flame photometry or flame emission spectroscopy since it has been found to give different results.

## 6 Sampling and sample preparation

The sampling procedure is not covered by this Method. Carry out the determination at least in duplicate.

Determine the dry matter content of the black liquor according to SCAN-N 22.

*Note 1* – There is no need to determine the dry matter content for weak black liquors if the results are to be reported per volume.

### 6.1 Dilution

Heat the sample in a water bath (5.2) at 90 °C for about 20 min. Keep a lid on the sample bottle during the heating period.

*Note 2* – Only liquors with a dry matter content exceeding 50 % need to be heated.

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

Place a 100 ml volumetric flask on the balance (5.1). Tare the balance. Weigh to the nearest 0,005 g into the volumetric flask an amount of the sample corresponding to about 5 g of dry substance. Add about 70 ml of water

(4.0) and mix. Cool to room temperature. Fill up to the mark with water (4.0).

*Note 3* – 5 g of dry substance is equivalent to approx. 30 g of weak black liquor (between 15 % and 17 % dry matter content) and to approx. 12,5 g of heavy black liquor (between 30 % and 50 % dry matter content).

*Note 4* – It may be convenient to weigh the black liquor in a plastic bottle with a lid and then transfer the liquor to the volumetric flask with the aid of water (4.0).

*Note 5* – Results for weak black liquor may be reported per volume, in which case a specific volume containing about 5 g of dry substance is taken.

## 7 Atomic absorption procedure

### 7.1 Preparation of calibration solutions

Prepare a series of at least 3 calibration solutions by diluting  $v$  ml of the sodium standard solution (4.1.1) to 100 ml with water (4.0) in volumetric flasks. Before filling up to the mark, add 2 ml of the cesium solution (4.3). Select the volumes  $v$  so that the working range of the atomic absorption spectrometer is covered; this range is normally between 0,5 mg/l and 2,0 mg/l. Also prepare a zero solution ( $v = 0$ ).

Prepare, in a similar way, a series of calibration solutions for potassium.

*Note 1* – A combined calibration solution with both Na and K can be used.

*Note 2* – Hydrochloric acid (1 ml per 100 ml) can be added to increase the durability of the calibration solutions.

### 7.2 Determination of sodium

Dilute the sample solution (6.1) stepwise until the sodium concentration is within the range covered by the calibration solutions. In the final dilution stage, add 2 ml of the cesium solution (4.3) per 100 ml and fill up to the mark with water.

*Note 3* – Example: From the sample solution, withdraw a portion of 1,00 ml with a pipette and transfer this to a 100 ml volumetric flask. Dilute to the mark with water (4.0). Transfer 1,00 ml of this solution to a 100 ml volumetric flask. Add 2 ml of the cesium solution (4.3) and dilute to the mark. Dilution factor ( $f$ ) in the example = 10 000.

*Note 4* – If hydrochloric acid has been added to the calibration solutions the same amount of hydrochloric acid should also be added to the samples.

Operate the instrument as instructed by the manufacturer. Adjust the instrument reading to zero using the zero solution. Measure the absorbance of the calibration solutions and the sample solution at 589,0 nm in an air-acetylene flame.

Most instruments have a system for automatic evaluation of results. If the instrument has no such system, plot the absorbance against the sodium content of the calibration solutions. Note the concentration of sodium in the sample solutions, obtained from the calibration graph, as  $a$  mg/l.

### 7.3 Determination of potassium

Dilute the sample solution stepwise until the potassium concentration is within the range covered by the calibration solutions. In the final dilution stage, add 2 ml of the cesium solution (4.3) per 100 ml and fill up to the mark with water.

*Note 5* – Example: From the sample solution, withdraw a portion of 2,00 ml with a pipette and transfer this to a 100 ml volumetric flask. Dilute to the mark with water (4.0). Transfer 5 ml of this solution to a 100 ml volumetric flask. Add cesium chloride as above and dilute to the mark. Dilution factor ( $f$ ) in the example = 1 000.

*Note 6* – If hydrochloric acid has been added to the calibration solutions, the same amount of hydrochloric acid should also be added to the samples.

Operate the instrument as instructed by the manufacturer. Adjust the instrument reading to zero using the zero solution. Measure the absorbance of the calibration solutions and the sample solution at 766,5 nm in an air-acetylene flame.

Most instruments have a system for automatic evaluation of results. If the instrument has no such system, plot the absorbance against the potassium content of the calibration solutions. Note the concentration of potassium in the sample solutions, obtained from the calibration graph, as  $b$  mg/l.

## 8 Flame photometric method

### 8.1 Preparation of calibration solutions

Prepare a series of at least 4 calibration solutions by diluting  $v$  ml of the sodium standard solution (4.1.1) to 100 ml with water (4.0) in volumetric flasks.

Select the volumes  $v$  so that the working range of the flame photometer is covered, this range is normally between 1 mg/l and 10 mg/l.

Use water (4.0) as a zero solution.

Prepare, in a similar way, a series of calibration solutions for potassium.

### 8.2 Determination of sodium

Dilute the sample solution (6.1) stepwise until the sodium concentration is within the range covered by the calibration solutions.

Operate the flame photometer as instructed by the manufacturer. Adjust the instrument reading to zero using water (4.0). Measure the emission of the calibration solutions and the sample solution at 589,0 nm.

Determine the sodium concentration of the sample solution, noted as  $a$  mg/l, from a calibration graph obtained by plotting the emission against the sodium content of the calibration solutions.

### 8.3 Determination of potassium

Dilute the sample solution (6.1) stepwise until the potassium concentration is within the range covered by the calibration solutions.

Operate the flame photometer as instructed by the manufacturer. Adjust the instrument reading to zero using water (4.0). Measure the emission of the calibration solutions and the sample solution at 766,5 nm.

Determine the potassium content of the sample solution, noted as  $b$  mg/l, from a calibration graph obtained by plotting the emission against the potassium content of the calibration solutions.

## 9 Calculation

### 9.1 Sodium content

Calculate the sodium content of the black liquor, in grams per kilogram dry matter, from the expression:

$$X_1 = \frac{a V f 100}{m_1 T} \quad [1]$$

or in grams per litre from the expression:

$$X_2 = \frac{a V f}{m_2} \quad [2]$$

where

$X_1$  is the sodium content of the original black liquor, in grams per kilogram dry matter;

$X_2$  is the sodium content of the original black liquor, in grams per litre;

$a$  is the concentration of sodium in the sample solution, obtained from the calibration graph, in milligrams per litre;

$V$  is the volume of the sample solution (6.1) in litres;

$m_1$  is the mass of black liquor taken for analysis, in grams;

$m_2$  is the volume of the original black liquor taken for analysis, in millilitres;

$T$  is the dry matter content of the black liquor, in per cent;  
 $f$  is the dilution factor.

Calculate the mean of the parallel determinations and report the sodium content to the nearest gram per kilogram. The results of the parallel determinations should not deviate by more than 5 % from their mean.

*Note 1* – The sodium content of the black liquor can be calculated in mol per kilogram dry matter or in mol per litre dry matter, by dividing the results by the factor 23,0.

**9.2 Potassium content**

9.2.1 Calculate the potassium content of the black liquor, in grams per kilogram dry matter, from the expression:

$$Y_1 = \frac{b V f 100}{m_1 T} \quad [3]$$

or in grams per litre from the expression:

$$Y_2 = \frac{b V f}{m_2} \quad [4]$$

where

- $Y_1$  is the potassium content of the original black liquor, in grams per kilogram dry matter;
- $Y_2$  is the potassium content of the original black liquor, in grams per litre;
- $b$  is the concentration of potassium in the sample solution, obtained from the calibration graph, in milligrams per litre;
- $V$  is the volume of the sample solution (6.1), in litres;
- $m_1$  is the mass of black liquor taken for analysis, in grams;
- $m_2$  is the volume of the original black liquor taken for analysis, in millilitres;
- $T$  is the dry matter content of the black liquor, in per cent;
- $f$  is the dilution factor.

Calculate the mean of the parallel determinations and report the potassium content to the nearest 0,1 gram per kilogram. The results of the parallel determinations should not deviate by more than 5 % from their mean.

*Note 2* – The potassium content of the black liquor can be calculated in mol per kilogram dry matter or in mol per litre dry matter, by dividing the results by the factor 39,1.

**10 Report**

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

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

**11 Precision**

**11.1 Repeatability**

For a weak black liquor sample, one laboratory analysed the sample nine times (AAS). For a strong black liquor, the coefficient of variation (CV) within the laboratory was calculated from the difference between double determinations for 17 samples (AAS). The following results were obtained:

Sample	Sodium content		Potassium content	
	mean	CV*, %	mean	CV*, %
Weak black liquor	45 g/l	3,2	2,8 g/l	1,4
Strong black liquor	191 g/kg	2,6	32,0 g/kg	2,7

**11.2 Reproducibility**

The same black liquor samples were analysed by ten laboratories and both AAS, AES, flame photometry and ICP emission were used. For the strong black liquor, the coefficient of variation also includes the determination of dry matter content. The following results were obtained:

Sample	Sodium content		Potassium content	
	mean	CV*, %	mean	CV*, %
Weak black liquor	44 g/l	3,4	2,5 g/l	4,9
Strong black liquor	192 g/kg	7,7	18,4 g/kg	7,1

\* CV is the coefficient of variation, i.e. the standard deviation divided by the mean value.

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