



*Black liquor*

## Acid-soluble metals

*Method for determining Al, Ba, Ca, Fe, Mg, Mn, P, S and Si using either inductively coupled plasma optical emission spectrometry (ICP-OES) or Atomic Absorption Spectroscopy (AAS) with a flame detector*

### 0 Introduction

This SCAN-test Method describes a procedure for the determination of the contents of acid-soluble metals in black liquors by ICP-OES or AAS using a flame (not for all elements).

The Method replaces SCAN-N 38:01 from which it differs in that several new elements are included (Ba, P and S) and that the ICP-OES method has been included.

### 1 Scope

This SCAN-test Method is applicable to all types of black liquor from the kraft process (sulphate process). The method has not been evaluated for non-wood-based black liquor.

*Note* – Other elements such as Cu, Cr, Ni, Zn or V can also be measured according to this method if the sensitivity of the measuring instrument used meets the requirements. However, this is not within the scope of this Method.

### 2 Reference

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest

edition of the referenced document (including any amendments) applies.

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

### 3 Definition

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

#### 3.1 Acid-soluble metals

contents of the respective elements in the solution obtained after wet-combustion of the sample in nitric acid as specified in this Method.

### 4 Principle

The material is wet-combusted in hydrogen peroxide and nitric acid in a microwave oven. The solution is then analysed and the different metals determined by one of two alternative methods. The solution is analysed in method A by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and in method B by Atomic Absorption Spectroscopy (AAS) using a flame detector.

*Note* – Wet-combustion can also be carried out in an open system by boiling the material in nitric acid and hydrogen

peroxide on a hot plate. This procedure is not however suitable for the determination of sulphur (volatile sulphur compounds evaporates easily) or silicon.

## 5 Reagents and chemicals

Use only chemicals of analytical grade.

### 5.1 Water

Distilled or deionised of high purity for use in the preparation of reagents and in the dilution of samples.

**5.2 Concentrated nitric acid,  $HNO_3$ ,**  
(65-69 %, density 1,40 -1,42 g/ml).

**5.3 Hydrogen peroxide,  $H_2O_2$ , 30 %.**

**5.4 Concentrated hydrochloric acid,  $HCl$**   
(37 %, density 1,19 g/ml).

### 5.5 Standard solutions

Commercially available standard solutions containing one or more of the various metals to be analysed with concentrations of the order of 1000 mg/l known to an accuracy of  $\pm 2$  mg/l. These solutions are required for use as stock solutions for calibration.

### 5.6 Lanthanum-caesium solution

$c(La) = 100$  g/l and  $c(Cs) = 10$  g/l. Dissolve with caution 117,3 g of lanthanum oxide,  $La_2O_3$ , in 230 ml of concentrated hydrochloric acid (5.4). Add the acid in small portions since the reaction is violent in its initial stages. Add 500 ml of water (5.1) and 12,7 g of cesium chloride,  $CsCl$ . Transfer the cooled solution to 1000 ml volumetric flask and fill up to the mark with water.

*Note 1* – Commercially available lanthanum-caesium solutions may be used.

*Note 2* – The lanthanum-caesium solution is used to eliminate interference ionisation and to eliminate disturbances from different anions in the AAS technique but it is not needed in the ICP-OES technique. The lanthanum-caesium solution is used in the determination of calcium, magnesium and aluminium.

### 5.7 Stock solution for matrix modification.

The calibration standards should have the same composition as the samples. Since black liquors contain large amounts of Na- and S-compounds after digestion, these compounds shall also be added to the calibration standards in order to ensure the same physical and chemical matrix composition.

Weigh

11,8 g  $Na_2SO_4$

22,9 g  $NaNO_3$

0,25 g  $NaCl$

0,50 g  $K_2SO_4$

1,6 g  $KNO_3$

into a 1000 ml volumetric flask. Add 200-400 ml water (5.1) and 70 ml nitric acid (5.2). Dilute to the mark with water (5.1). Filter before use.

The content of this solution is similar to that of an ordinary kraft mill black liquor after wet digestion with nitric acid as described in this Method.

### 5.8 Solution for sample dilution

Dilute 400 ml of the stock solution (5.7) to 1000 ml with water (5.1) in a volumetric flask.

### 5.9 Quality control solutions

An independent calibration standard from an outside source is required for the initial verification of the calibration standards. Use commercially available standard solutions containing one or more of the various metals to be analysed with concentrations of the order of 1000 mg/l known to an accuracy of  $\pm 2$  mg/l. To ensure their independence, use other manufactures products provided by a manufacturer other than the supplier of the standard solutions (5.5).

## 6 Apparatus

6.1 *Balance*, having an accuracy of 0,001 g.

6.2 *Water-bath* capable of maintaining a temperature of 90 °C.

6.3 *ICP-OES* in **Method A**

6.4 *AAS*, with a burner for air-acetylene and for nitrous oxide-acetylene, and with hollow-cathode lamps for the elements to be determined (multi-element lamps may be used) in **Method B**.

6.5 *Microwave oven* for laboratory-use, programmable and equipped with a rotating disk.

Follow the safety instructions given by the manufacturer of the oven.

Since the amount of sample will influence the pressure and temperature changes during the wet-combustion, the oven should, if possible, be equipped with a device for recording the temperature and the pressure. The oven shall be capable of maintaining a constant temperature of  $(175 \pm 5) ^\circ\text{C}$ .

6.6 *Combustion bottles*, made of PTFE (polytetrafluoroethylene), of a volume of at least 80 ml. Low-pressure bottles as well as high-pressure bottles may be used.

6.7 *Apparatus needed for open air combustion*: 100 ml conical quartz flask and a hot plate.

## 7 Test material preparation

The sampling procedure is not covered by this Method.

### 7.1 Determination of the dry matter content

Determine the dry matter content of the black liquor sample in accordance with SCAN-N 22.

### 7.2 Homogenisation of the sample

If the sample has a dry matter content less than 50 %, as determined in 7.1, proceed to 7.4.

If the sample has a dry matter content greater than 50 %, as determined in 7.1, heat the sample in a water-bath (6.2) at  $90 ^\circ\text{C}$  for approximately 20 min or in an ordinary microwave oven and keep the sample bottle closed (not too tightly) during the heating period.

Mix the sample carefully so that any sediment on the bottom of the sample bottle is mixed and is homogenised with the rest of the sample.

### 7.3 Dilution of the black liquor

Place a 100 ml beaker on the balance (6.1) and tare the balance. Weigh into the beaker with an accuracy of 0,005 g an amount of the homogenized sample (7.2), corresponding to approx. 5 g of dry substance, see Table 1. Add water (5.1) to a volume of 20-30 ml, mix and cool to room temperature. Transfer this solution quantitatively to a 100 ml volumetric flask using water (5.1) and fill up to the mark with water.

Transfer this diluted sample to a plastic bottle.

Table 1. Recommended sample size in the dilution of black liquor. The sample sizes correspond approximately to a dry substance of 5 g.

	Dry matter content of the black liquor (%)	Sample size (g)
Weak liquor	15-20	33-25
Medium liquor	30-50	17-10
Concentrated liquor	50-80	10-6

### 7.4 Selection of test portions

Different alternative procedures for transferring the sample to the wet-combustion bottle are given below depending on whether the result is to be reported per unit weight or per unit volume.

#### 7.4.1 Result per unit weight

If the dry matter content of the sample is above 50 % and the black liquor has been diluted, transfer 10,0 ml of the diluted liquor (7.3) to the wet-combustion bottle (6.6). This volume contains approximately 0,5 g dry substance.

If the dry matter content of the sample is below 50 %, the dilution procedure can be omitted (7.2). In such cases, weigh a test portion of the homogenised liquor, corresponding to 0,5 g dry substance, directly into the wet-combustion bottle (7.2). Finally, add water (5.1) to a volume of approximately 10 ml.

#### 7.4.2 Result per unit volume

This procedure shall be used only if the dry matter content of the sample is below 50 %. Using a pipette, transfer a test portion of the original black-liquor sample corresponding to 0,5 g dry substance in the wet-combustion bottle (6.6) and add water (5.1) to an approximate volume of 10 ml. (If, for example, the liquor has a dry matter content of approximately 20 %, 2,5 ml of liquor and 7,5 ml of water are suitable volumes.)

*Note* – It is normally recommended to use 0,5 g of dry substance in the wet-combustion. If however, aluminium and silica are to be determined, the amount of the test portion sometimes has to be increased since these elements have a low sensitivity in the atomic absorption determination.

To avoid matrix disturbances, not more than approximately 0,5 g of dry

substance shall be used in the wet-combustion.

### 7.5 *Wet-combustion*

#### 7.5.1 *In a microwave oven*

To avoid any formation of elemental sulphur or hydrogen sulphide in the addition step, add hydrogen peroxide before adding the acid.

To the test portion in the wet-combustion bottle, carefully add 2 ml of hydrogen peroxide (5.3). Mix and allow the mixture to stand for 10 minutes, then add with caution 1 ml of concentrated nitric acid (5.2).

**WARNING** – There is a risk of foaming.

Close the wet-combustion bottle and place the bottle in the microwave oven (6.5). Perform the wet-combustion in accordance with a program where the temperature is gradually increased to 175 °C, and then kept at 175 °C for 20 minutes. Allow the wet-combustion bottle to cool and open it with caution under a hood. Transfer quantitatively to a 25 ml volumetric flask and fill up to the mark with water (5.1). Normally, no particles are present in the solution after wet-combustion, but if particles are present, remove the particles by filtration (use acid-washed paper filter, e.g. Munktell 00A) or by centrifugation.

#### 7.5.2 *In an open system*

Transfer the test material to a 100 ml conical quartz flask (6.7). Carefully add 2 ml of hydrogen peroxide (5.3). Mix and allow the mixture to stand for 10 minutes, then add with caution 2 ml of concentrated nitric acid (5.9). Place a watch-glass over the conical flask. Heat the sample to just below the boiling point for 1 hour on a hot plate (6.7) under a fume-hood. Increase the temperature to boiling and boil the sample to near dryness. Allow the conical flask to cool and add 1 ml of concentrated nitric acid. Transfer the solution quantitatively to a 25 ml volumetric flask and fill up to the mark with water (5.1).

Note- This method is not suitable for samples containing volatile sulphur compounds which may evaporate during digestion

### 7.6 *Blank*

Run a blank following the instructions for wet-combustion in section 7.4, but without any sample.

## 8 **Determination**

Two different analytical techniques are available for determining the element concentrations. With the ICP-OES technique more elements can be easily measured.

AAS is not suitable for some elements (like P, S). The sensitivity of the AAS method is also low for aluminium, silica and barium, and it is therefore sometimes difficult to determine these elements.

It is important that the acid and salt concentrations are the same in the calibration solutions and in the test-solutions, since the concentrations influence the measurement signal. The matrix modification should therefore be used.

### 8.1 **METHOD A based on the use of ICP-OES**

#### 8.1.1 *Preparation of calibration solutions*

Multi-element standard solutions can be used (standard solution 1). Some elements (like Ba) are known to cause problems by precipitation under certain circumstances, and it is recommended that a separate standard solution for Ba be prepared (standard solution 2). For the determination of sulphur, a separate standard solution (standard solution 3) is needed (no matrix solution).

Prepare a series of at least three calibration solutions for each element by dilution of the respective standard solutions (5.5). Also prepare a zero-solution. This solution is similar to the calibration solutions, but contains no added elements. This solution shall not be confused with the blank. Examples of suitable concentrations in the calibration solutions for certain wavelengths are given in *Table 2*. These concentrations may however vary from case to case, since different instruments and different wavelengths may have different sensitivities. If the linear part of the calibration has been properly established, it may be possible to use one calibration solution (the highest) instead of three different solutions.

Pipette the required amounts of the standard solutions into a 1000 ml volumetric flask. Add 400 ml of the solution for matrix modification (5.7) and dilute to the mark with water (5.1) or use the dilution solution (5.8).

For sulphur measurement, pipette the required amount of the standard solution into a 1000 ml volumetric flask, add 28 ml conc. HNO<sub>3</sub> (5.2) and dilute to the mark with water (5.1).

Standard solutions 1 and 3 have a shelf life of several months, but solution 2 should be prepared daily.

### 8.1.2 Preparation of quality control solutions

Prepare suitable solutions as indicated in 5.9. Multi-element solutions may be used. The concentration of the elements in this solution should be at the same level as the concentration of the test material. If the concentration is not constant, choose the concentration in the middle of the calibration range.

For example: The highest calibration standard in aluminium is 10 mg/l. The quality control sample could be 5 mg/l.

### 8.1.3 Determination

Most of the elements can be determined directly after the wet-combustion. The sulphur content of black liquor is however so high that a further dilution is needed. The dilution factor is about 1:25 ...1:50 depending on the sample and the calibration range. Dilute the wet-combusted sample with water (5.1) and add 2,8 ml/100 ml of nitric acid (5.2) and dilute to the mark.

Follow the instructions provided by the manufacturer of the instrument. Some useful emission lines (wavelengths) are shown in Table 2 but other lines may also be available.

*Note* – Sensitivity, instrumental detection limit, precision, linear dynamic range and interference effects should be investigated and established for each individual analyte line on that particulate instrument.

Table 2. Examples of measurement range (highest calibration standard) in some useful wavelength

Element	Concentration of the highest standard solutions (mg/l)	Wavelengths (nm)
Standard solution 1		
Al	10	396,1
Ca	50	315,8
Fe	2,0	238,2
Mg	20	285,2
Mn	4,0	257,6
P	20	213,6
Si	20	251,6
Standard solution 2		
Ba	2,0	455,4
Standard solution 3		
S	50	182,0

Calibrate the instrument according to the instrument manufacturer's recommended procedure.

Before beginning the test-portion run, analyse the highest-concentration mixed reference standard as though it were a sample. Ensure that the values determined do not deviate from the true values by more than  $\pm 5\%$  (or the established control limits).

Analyse the quality control sample (QC) and the zero sample before and after each batch of 10 tests. Ensure that the values determined do not deviate from the true values by more than  $\pm 5\%$  (or the established control limits).

Analyse the blank and the test portions. The concentration in the test portion should be between those of the lowest and highest standard solutions. If the concentrations in the test material exceed that of the highest standard, dilute the sample with the dilution solution (5.8).

*Note* – Do not use matrix solution when diluting the sample for sulphur measurement. Use water (5.1) instead. Add the same amount of conc. HNO<sub>3</sub> (5.2) as in the calibration solution before the final dilution.

## 8.2 METHOD B based on the use of AAS

### 8.2.1 Preparation of calibration solutions

Prepare a series of at least three calibration solutions for each element by dilution of the respective standard solutions (5.5). Also prepare a zero-solution. This solution is similar to the calibration solutions, but contains no added elements. The solution shall not be confused with the blank. Examples of suitable concentrations in the calibration solutions are given in Table 3. These concentrations may however vary from case to case, since different instruments may have different sensitivities. Multi-element standard solutions can also be used.

Table 3. Examples of calibration solutions for some elements. All concentrations are given in milligram per litre.

Element	Zero-solution	Solution 1	Solution 2	Solution 3
Ca	0	0,5	1,0	2,0
Mg	0	0,1	0,3	0,5
Fe	0	1,0	3,0	5,0
Mn	0	1,0	3,0	5,0
Al	0	5	10	20
Si	0	5	10	20

To each calibration solution, add solution for matrix modification (5.7) and, if required,

lanthanum-cesium solution (5.6) to the calibration and zero solutions as indicated in Table 4. The concentrations of lanthanum and cesium will be 10 g/l and 1 g/l, respectively.

Table 4. Addition of lanthanum-cesium solution and matrix solution in a total volume of 100 ml of calibration solution.

Element	Lanthanum-cesium solution (5.6) (ml)	Matrix solution (5.7), (ml)
Ca	10	40
Mg	10	40
Fe	0	40
Mn	0	40
Al	10	40
Si	0	40

### 8.2.2 Measurement

Dilute the test solution (7.4) step by step until the concentrations of the respective elements are within the range covered by the calibration solutions. If required, add lanthanum-cesium solution (5.6) (see Table 4). Use the dilution solution (5.8) for matrix modification.

After wet-combustion, the acid concentration in 25 ml of the sample solution (7.4) is approximately 2,8 mol/l, since the consumption of acid in the oxidation of organic material is negligible. Thus the sample solution can be analysed without further dilution if iron, manganese or silica are to be determined. If calcium, magnesium or aluminium are to be determined, the sample solutions have to be diluted since lanthanum-cesium will be added. The sample solution has to be diluted at least once to yield an acid concentration in agreement with that of the calibration solutions.

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, the sample solutions and the blank for the element required. Suitable types of flame and recommended wavelengths are given in Table 5.

Table 5. Recommended types of flame and wavelengths in the atomic absorption determination.

Element	Type of flame	Wavelength, (nm)
Ca	Nitrous oxide-acetylene	422,7
Mg	Air-acetylene	285,2
Fe	Air-acetylene	248,3
Mn	Air-acetylene	279,5
Al	Nitrous oxide-acetylene	309,3
Si	Nitrous oxide-acetylene	251,6

Note 2 – Calcium can also be determined using an air-acetylene flame but the signal is more sensitive to disturbances than when a nitrous oxide-acetylene flame is used.

Magnesium can also be determined using a nitrous oxide-acetylene flame.

Most instruments have a system for automatic evaluation of the results. If the instrument has no such device, plot the absorbance against the element content of the calibration solutions. From this calibration curve, calculate the concentration, corrected for the blank, for each element in the sample solutions. Record the concentration as *c* mg/l.

The sensitivity may vary between different elements in the determination using atomic absorption. The sensitivity is low for aluminium, barium and silica, and it is therefore sometimes difficult to determine these elements.

## 9 Calculation

Calculate the contents of the different elements in the black liquor, in milligram per kilogram dry substance, from the expression:

$$X_1 = \frac{c f V_1 V_2 100}{m_1 V_3 T} \quad (1)$$

or in milligram per litre from the following expression:

$$X_2 = \frac{c f V_2}{V_4} \quad (2)$$

where

- $X_1$  is the element content in the original black liquor, in milligram per kilogram dry substance;
- $X_2$  is the element content in the original black liquor, in milligram per litre;
- $c$  is the element content in the sample solution obtained from the calibration curve, corrected for the blank, in milligram per litre;
- $f$  is the dilution factor in the dilution of the combusted sample ( $f = 1$  if no dilution has been made);
- $V_1$  is the volume (normally 100 ml) of the sample solution after dilution (7.2), in millilitre;
- $V_2$  is the volume (normally 25 ml) of the sample solution after combustion (7.4), in millilitre;
- $m_1$  is the mass of the original black liquor taken to analysis, in gram;
- $V_3$  is the volume (normally 10 ml) of the diluted black liquor (7.2) taken to combustion, in millilitre;
- $V_4$  is the volume of the original black liquor taken to analysis, in millilitre;
- $T$  is the dry matter content of the black liquor, as a percentage.

For each element, calculate the mean of the parallel determinations. The results of the parallel determinations should not differ by more than 5 % from their mean.

## 10 Report

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

- a) date and place of testing;
- b) identification of the sample tested;
- c) The Method used;
- d) the results, given with two significant figures;
- e) any departure from the standard procedure and any other circumstances that may have affected the results.

## **Annex A Precision**

### **A1 Precision**

Three black liquor samples were tested in six laboratories according to this method. The precision data given include results from the determination of the element content by both alternative measuring techniques, ICP-OES and AAS after digestion in microwave oven. Sulphur was also determined according to method SCAN-N 35:96 (titrimetric method).

### **A2 Repeatability and reproducibility**

The pooled repeatability was calculated according to TAPPI T1200 sp-00 Interlaboratory evaluation of test methods to determine TAPPI repeatability and reproducibility. The repeatability and reproducibility were calculated and the results are shown in Table A1. These results include ICP-OES and AAS results (ICP+AAS). ICP-OES was used in all laboratories. Some of these laboratories used also AAS. The number of results show the total number of the results (ICP+AAS) and also how many of the results have been measured by AAS (AAS).

Table A1 Precision data

	Sample 1	Sample 2	Sample 3		Sample 1	Sample 2	Sample 3
<b>Fe</b>				<b>Al</b>			
Average, mg/kg DS	17,0	22,8	22,8	Average, mg/kg DS	18,8	26,6	25,9
Repeatability, r	1,5	0,7	0,8	Repeatability, r	1,6	1,4	6,3
CoV (r), %	8,7	2,9	3,3	CoV (r), %	8,6	5,1	24
Reproducibility, R	4,8	5,1	4,2	Reproducibility, R	5,2	2,9	9,1
CoV (R), %	10	8,1	6,7	CoV (R), %	9,9	3,9	13
Number of results (ICP+AAS/AAS)	8/2	8/2	8/2	Number of results (ICP+AAS/AAS)	7/1	7/1	7/1
<b>Mn</b>				<b>S</b>			
Average, mg/kg DS	80,7	77,5	76,1	Average, g/kg DS	52,4	52,9	51,7
Repeatability, r	3,5	2,3	1,9	Repeatability, r	1,8	1,4	1,9
CoV (r), %	4,4	3,0	2,5	CoV (r), %	3,5	2,7	3,7
Reproducibility, R	7,4	9,5	9,3	Reproducibility, R	4,8	7,9	8,4
CoV (R), %	3,3	4,4	4,4	CoV (R), %	3,3	5,4	5,9
Number of results (ICP+AAS/AAS)	8/2	8/2	8/2	Number of results (ICP+titrimetric/titrimetric)	7/2	7/2	7/2
<b>Ca</b>				<b>P</b>			
Average, mg/kg DS	175	205	193	Average, mg/kg DS	53,0	117	106
Repeatability, r	2,0	6,5	18,1	Repeatability, r	4,2	9,0	1,8
CoV (r), %	1,1	3,2	9,4	CoV (r), %	7,9	7,7	1,7
Reproducibility, R	30,6	59,2	42,6	Reproducibility, R	5,5	18,5	22,2
CoV (R), %	6,3	10	8,0	CoV (R), %	3,7	5,7	7,6
Number of results (ICP+AAS/AAS)	8/2	8/2	8/2	Number of results (ICP/AAS)	5/-	5/-	6/-
<b>Mg</b>				<b>Ba</b>			
Average, mg/kg DS	335	342	337	Average, mg/kg DS	4,0	6,7	6,2
Repeatability, r	10,7	6,9	12,8	Repeatability, r	0,3	0,2	0,3
CoV (r), %	3,2	2,0	3,8	CoV (r), %	7,4	3,1	4,1
Reproducibility, R	18,4	29,3	28,9	Reproducibility, R	1,3	1,8	2,1
CoV (R), %	2,0	3,1	3,1	CoV (R), %	12	9,7	12
Number of results (ICP+AAS/AAS)	8/2	8/2	8/2	Number of results (ICP/AAS)	5/-	5/-	4/-
<b>Si</b>							
Average, mg/kg DS	335	342	337				
Repeatability, r	16,9	16,4	17,3				
CoV (r), %	5,2	3,6	4,1				
Reproducibility, R	97,6	221	128				
CoV (R), %	11	18	11				
Number of results (ICP+AAS/AAS)	6/1	7/1	7/1				

CoV = Coefficient of variation

