SCAN-CM 38:05
SCAN-P 74:05
Revised 2005

SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

Pulps, papers and boards

Calcium, magnesium, iron, manganese and copper content

Atomic absorption spectroscopy

0 Introduction

This SCAN-test Method replaces SCAN-CM 38:96/P 74:96 from which it differs in that a number of withdrawn SCAN-test Methods, referred to in this Method, have been replaced by the corresponding ISO standards. In SCAN-C 6, the ignition temperature was 575 °C but in the replacing ISO 1762 the ignition temperature is 525 °C so for that reason the temperature has been changed.

The Method refers to the acid-soluble part of the ignition residue, i.e. that part of the ignition residue obtained after ignition that is soluble in hydrochloric acid. In an Annex, the analysis of the insoluble part of the ignition residue is described.

1 Scope

This Method describes the procedure for the determination of calcium, magnesium, iron, manganese and copper by atomic absorption spectroscopy. It is applicable to all types of pulp, paper and board.

Note 1 – The determination can also be made by plasma emission spectroscopy.

If the residue from the ignition is completely soluble in hydrochloric acid, the results are taken as the total amount of the element in the sample. If, after treatment with acid, an insoluble residue remains, the total amount can be determined only by applying both the procedure described in the Method and the procedure described in the Annex.

Note 2 – The reason for including in the Method the option of determining only the acid-soluble fraction of the elements in samples with an insoluble ignition residue is that in a number of cases the acid-soluble fraction is more informative than the total content. Elements bound so firmly that they are not leachable in acid often have no relevance in the use of the material. For example, they are not likely to contaminate food in food-packaging, to enhance the formation of odorous compounds or to promote yellowing.

2 References

ISO 638 Pulps – Determination of dry matter content
ISO 1762 Paper, board and pulps – Determination of residue (ash) on ignition at 525 °C

Note – SCAN-test has withdrawn a number of test Methods and refers instead to the corresponding ISO and/or EN Standards.

3 Definitions

For the purpose of this Method, the following definitions apply:

3.1 *Acid-soluble element content* – The element content in the solution obtained after incinerating the sample at 525 °C and treating the residue with 6 mol/l hydrochloric acid as specified in this Method.

3.2 *Total element content* – The sum of the acid-soluble element content and the acid-insoluble element content.

4 Principle

The sample is ignited and charred at 525 °C. The charred residue is treated with 6 mol/l hydrochloric acid and the acid-soluble element content in the solution is determined by flame atomic absorption spectroscopy.

5 Reagents and chemicals

Use only chemicals of analytical grade.

5.0 *Water,* of high purity, deionized or distilled water.

5.1 *Hydrochloric acid, c*(HCl) about 6 mol/l. Dilute 500 ml of hydrochloric acid (density 1,19 g/ml) in 500 ml of water (5.0).

5.2 *Reference solutions.* Reference solutions have a shelf-life of several months if stored in polyethylene bottles.

Commercially available reference solutions may be used.

5.2.1 *Calcium reference solution*, *c*(Ca) = (1000 ± 2) mg/l. In a 1000 ml volumetric flask, dissolve 2,497 g of dry $CaCO_3$ in 50 ml hydrochloric acid (5.1) and fill up to the mark with water (5.0).

5.2.2 *Magnesium reference solution, c*(Mg) = (1000 ± 2) mg/l. In a 1000 ml volumetric flask, dissolve 1,000 g of magnesium in 50 ml of hydrochloric acid (5.1) and fill up to the mark with water (5.0).

5.2.3 *Copper reference solution, c*(Cu) = (1000 ± 2) mg/l. Dissolve 1,000 g of electrolytically pure copper in a minimum volume of nitric acid (HNO_3, density 1,4 g/ml). Boil the solution to expel all nitrous gases and allow it to cool. Transfer the solution quantitatively to a 1000 ml volumetric flask and fill up to the mark with water (5.0).

5.2.4 *Iron reference solution, c*(Fe) = (1000 ± 2) mg/l. In a 1000 ml volumetric flask, dissolve 1,000 g of pure oxide-free iron wire in a minimum volume of hydrochloric acid (density 1,19 g/ml). Fill up to the mark with water (5.0).

5.2.5 *Manganese reference solution, c*(Mn) = (1000 ± 2) mg/l. In a 1000 ml volumetric flask, dissolve 2,748 g of manganese sulphate, $MnSO_4$, dried at 300 °C, in water (5.0). Add 5 ml of hydrochloric acid (5.1) and fill up to the mark with water (5.0).

5.3 *Cesium solution, c*(Cs) = 50 g/l. In a 1000 ml volumetric flask, dissolve 63,5 g of ultra-pure cesium chloride, CsCl, in water (5.0) and fill up to the mark with water.

Note 1 – This solution is used to suppress ionization of calcium and magnesium in the nitrous oxide/acetylene-flame.

The solution is normally not required when the air/acetylene-flame is used.

5.4 *Lanthanum solution, c*(La) = 50 g/l. In a 1000 ml volumetric flask, dissolve with caution 59 g of lanthanum oxide, La_2O_3, in 250 ml of hydrochloric acid (density 1,19 g/ml) and fill up to the mark with water (5.0).

Note 2 – This solution is used to eliminate interference from phosphates when determining calcium or magnesium in an air/acetylene-flame.

The solution is normally not required when the nitrous oxide/acetylene-flame is used.

6 Apparatus

6.1 *Ordinary laboratory equipment.* Laboratory vessels made of plastics are recommended as well as ash-free filter paper (particle retention 20 µm – 25 µm). Clean all equipment in 0,1 mol/l hydrochloric acid.

6.2 *Dishes* of platinum or quartz.

Note – Wash the dishes thoroughly. Remove any spots in the platinum dishes by cleaning with fine sand. Boil the dish with hydrochloric acid (5.1) and avoid any possible contact with metals other than platinum. If necessary, clean platinum dishes by melting sodium carbonate in them.

6.3 *Atomic absorption spectrometer*, with a burner for air/acetylene and/or for nitrous oxide/acetylene and with hollow-cathode lamps for the elements to be determined (multi-element lamps may be used).

7 Ignition and dissolution of the residue

7.1 *Sample preparation.* The sampling procedure is not covered by this Method. Make sure that the test pieces taken are representative of the sample received.

Carry out the determination at least in duplicate. Tear the air-dry sample into pieces of suitable size. Do not use cut edges, punched holes or other parts where metallic contamination may have occurred.

7.2 *Weighing.* Select the amount of sample with regard to the anticipated element content. Normally an amount of between 2 g to 5 g is suitable but, if copper is to be determined in pulp, a larger amount of sample is recommended (10 g – 20 g) because the copper content of such samples is normally very low.

In a clean dish (6.2) with known weight, weigh the sample to the nearest 0,01 g. At the same time, weigh – irrespective of sample type – a separate test portion for the determination of dry matter content in accordance with ISO 638.

7.3 *Ignition.* Use a hot plate, a program-controlled oven or a low flame of a gas burner and char the sample until it is well carbonized. The temperature must not exceed 525 °C.

If the dish is too small to hold the entire sample, gentle burn it off in portions. Take care not to let any ash blow from the dish. Then place the dish in a furnace and ignite at a temperature of (525 ± 25) °C for a period of 3 h, or longer if needed to burn away all the carbon.

> *Note 1* – In order to avoid flames, the dish can be covered by a lid. The lid must not be so tight that reducing conditions occur in the dish, in which case acid-insoluble compounds may be formed. Under reducing conditions, e.g. copper may be lost due to the formation of a platinum alloy.

Weigh the ignition residue (*a*). If the residue exceeds 0,5 g, after thoroughly mixing with a glass rod, take a fraction of the residue and weigh it (*b*).

7.4 *Blank.* Run a blank with the same chemicals as those added to the ignition residue but without any residue (see Clause 7.5).

7.5 *Dissolving the ignition residue in acid*. To avoid splattering, with caution moisten the residue (or the fraction of the residue) with water (5.0) and add 5 ml of hydrochloric acid (5.1) to the dish. Evaporate to dryness on a boiling water-bath or equivalent device. Repeat this procedure once.

> *Note 2* – In samples with a high carbonate content, more than 10 ml of acid (2 x 5 ml) may be required. In such a case, the blank should be run using the same amount of acid.

Add 2,5 ml of the acid (5.1) to the dry residue and heat the dish, if needed covered by a watch glass.

Use the filter (6.1) and filter the contents of the dish into a 25 ml volumetric flask. To ensure that the transfer is quantitative, add another portion of 2,5 ml of acid (5.1) to the dish and heat it again. Filter this last portion of acid to the main portion in the volumetric flask with the aid of some water (5.0).

Wash the insoluble residue with water (5.0) into the volumetric flask. Fill up to the mark and mix.

If the total content is to be determined, keep the filter with the insoluble residue for the analysis of the insoluble part of the residue, as described in the Annex. The insoluble residue should be treated in the same dish without intermediate cleaning. Further instructions are given in the Annex.

8 Determination

8.1 *Preparation of calibration solutions*. It is important that the acid concentration is the same in the calibration and in the sample solutions since the acid concentration influences the signal.

> *Note 1* – Usually it may be preferable to prepare multi-element calibration solutions. When required, add cesium or lanthanum solutions as specified in 8.2.

At least three calibration solutions and one zero solution should be used for the construction of the calibration graph. (The zero solution is similar to the calibration solutions, but contains no added elements. It should not be confused with the blank). An example of suitable calibration solutions is given in *Table 1*.

Table 1. Example of suitable calibration solutions. All concentrations are given in milligrams per litre.

	Zero	I	II	III
Ca	0	1,0	2,0	4,0
Mg	0	0,25	0,5	1,0
Cu	0	0,5	1,0	2,0
Fe	0	1,0	3,0	5,0
Mn	0	1,0	2,0	3,0

8.2 *Measurement*. Carry out the spectrometric measurements of the calibration solutions, of the sample solutions and of the blank solution. Operate the instrument as instructed by the manufacturer.

If any value obtained exceeds the range covered by the calibration solutions, the measurement must be repeated with a more dilute sample solution. Add acid (5.1), cesium (5.3) or lanthanum (5.4) as required.

> *Note 2* – Cesium (5.3) and lanthanum (5.4) solutions are not needed and shall therefore not be used in the determination of iron, copper and manganese. Cesium (5.3) and lanthanim (5.4) solutions shall only be used for the determination of calcium and magnesium.

If a nitrous oxide/acetylene-flame is used, add cesium solution (5.3) so that *c*(Cs) in the solution used for measurement will be 1 g/l to prevent ionization. If an air/acetylene-flame is used, add lanthanum solution (5.4) so that *c*(La) will be 5 g/l.

Most instruments have a system for automatic evaluation of results. If the instrument has no automatic evaluation of results, plot the absorbance, corrected for the blank, against the element content (in milligrams per litre).

9 Calculation

9.1 *Acid-soluble element content*. Calculate the acid-soluble element contents, *X,* from the expression:

$$X = \frac{c\ f\ V\ a}{m\ b} \qquad [1]$$

where

X is the element content, in milligrams per kilogram;
c is the concentration of the element in the sample solution, as obtained from the calibration plot corrected for the blank, in milligrams per litre;
f is the dilution factor (flask volume/aliquot);
V is the volume of the sample solution (standard 25 ml);
m is the amount of sample taken, oven dry basis, in grams;
a is the total weight of the residue, in grams;
b is the weight of the residue fraction taken, in grams.

Calculate the mean element content for each element, with two significant figures for values above 1 mg/kg and with one significant figure in the range 0,1 mg/kg to 1 mg/kg.

9.2 *Total element content.* To obtain the total amount of the element in the sample, add the amount of the element which is soluble in hydrochloric acid, *X*, determined as described in this Method, to the result, *Z*, obtained by the melt procedure described in the Annex.

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 mark of the sample tested;
(c) the results, element by element, and a statement as to whether acid-soluble element content or total element content is reported;
(d) any departure from the procedure described in this Method and any other circumstances that may have affected the test results.

11 Precision

The precision data given includes results for the determination of the acid soluble element content as well as results for the total element content. The precision of the results when measuring the total amount of the determinand is influenced by both the precision of the results for the acid-soluble part of the sample and the precision of the results for the melt-soluble part of the sample. The part of the elements which does not dissolve in acid sometimes remains in the melt-soluble part in such a way that the two parts compensate each other. In such situations, the deviation in the total amount of the determinand is often less than the deviations for the acid-soluble part and the melt-soluble part separately.

11.1 *Repeatability.* A sample of uncoated paperboard was analysed in one laboratory nine times. The following results, mean value and coefficient of variation (CV) were obtained:

Element	Acid-soluble element content	
	Mean, mg/kg	CV, %
Calcium	730	10
Magnesium	210	7
Iron	13	8
Manganese	33	2
Copper	0,5	24

11.2 *Reproducibility*. Four samples were analysed in eight laboratories. In the samples from bleached pulp and uncoated paperboard, 100 % of the total element content was found in the acid-soluble fraction. For the acid-insoluble residue, two different melt chemical mixtures were used (sodium carbonate-boric acid melt and sodium carbonate-potassium carbonate melt). The total element results presented here are based on the mean value for the two melt chemical procedures. The following results, mean value and coefficient of variation (CV), were obtained:

Results for the determination of calcium:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	160	6	160	6
Coated paperboard	10 500	5	11 000	6
Uncoated paperboard	640	9	640	9
Copy paper	86 400	11	88 000	3

Results for the determination of magnesium:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	16	11	16	11
Coated paperboard	58	15	67	4
Uncoated paperboard	190	9	190	9
Copy paper	1 600	16	2 100	5

Results for the determination of iron:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	3,6	45*	3,6	45*
Coated paperboard	430	19	590	13
Uncoated paperboard	13	28*	13	28*
Copy paper	180	4	210	8

* The high CV-value for iron is due to an uneven distribution of the element in the sample.

Results for the determination of manganese:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	0,2	19	0,2	19
Coated paperboard	7,4	18	8,1	14
Uncoated paperboard	32	10	32	10
Copy paper	19	15	21	16

Results for the determination of copper:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	0,4	73*	0,4	73*
Coated paperboard	2,2	29*	3,4	31*
Uncoated paperboard	0,4	63*	0,4	63*
Copy paper	1,6	28*	2,8	37*

* The high CV-value for cupper is due to an element content close to the lower limit of detection and to an uneven distribution of the element in the sample.

Note – The limit of detection in the acid-insoluble procedure (using a melt mixture) is higher than in the acid-soluble procedure due to the fact that the sample solution is more dilute in relation to the amount of sample weighed. This must be taken into consideration when the accuracy of the procedure is estimated, especially for copper, which usually occurs at a concentration lower than that of the other elements. For example, a deviation in the sample solution of 0,02 mg/l corresponds to a deviation in the final result of 0,1 mg/kg for a 20 g sample and a deviation in the final result of 1 mg/kg for a 2 g sample.

Annex – Content of elements in the insoluble ignition residue

A.1 Introduction

If an insoluble residue remains after the ignition residue has been dissolved in hydrochloric acid, the residue can be analysed using the procedure described in this Annex.

The procedure makes it possible to determine the total element content in pulps, papers and boards yielding a large ignition residue or an ignition residue which is difficult to dissolve.

A.2 Principle

The insoluble residue which remains after dissolution of the ignition residue in 6 mol/l hydrochloric acid is filtered, ignited together with the filter paper, and mixed with melt chemicals. The mixture is melted with the aid of a gas burner and then in an oven, and is then cooled and dissolved. After dissolution, the element content is determined by flame atomic absorption spectroscopy.

Two alternative melt mixtures are described;

A. Sodium carbonate-potassium carbonate melt;
B. Sodium carbonate-boric acid melt

Alternative A: Sodium carbonate-potassium carbonate melt;

A.3 Reagents and chemicals

All reagents and chemicals used in Clause 5 in this Method and the following *melt chemical mixture:*

A.3.1 *Sodium carbonate-potassium carbonate melt.* Mix sodium carbonate, Na_2CO_3, and potassium carbonate, K_2CO_3, in the required amounts in the proportions 106:138 (equimolar mixture). The mixture is commercially available.

A.4 Procedure

A.4.1 *Blank.* Run a blank with the same chemicals as those added to the sample but without any sample.

A.4.2 *Procedure for the insoluble residue.* Transfer the filter paper with the insoluble residue to a platinum dish (6.2) and dry it. Incinerate with a gas burner and ignite in a furnace at 525 °C. Let it cool in a desiccator. Add 2 g of the melt mixture (A.3.1). The amount of melt mixture must not be less than 10 times the weight of the ash.

> *Note 1* – If the amount of ash is too large, a weighed portion of it can be taken after thorough mixing with a glass rod. The proportion taken shall be considered when calculating the result.

Stir with a glass rod. Heat the mixture over a gas burner until it has melted. If a transparent melt is not obtained, place the dish in a furnace at 900 °C and keep it there for 15 minutes. Allow the dish to cool. Leach the melt with water by putting the dish including the melt in a 250 ml beaker with 50 ml – 100 ml water (5.0) and heating in a water bath. Sometimes a red-blue colour develops in the solution, caused by the formation of permanganate. The permanganate can be removed by reduction with ethanol. Add a few drops of ethanol until the colour disappears.

Filter the mixture, wash the dish and filter 3 to 5 times with 1 % sodium carbonate-potassium carbonate solution. This solution is used to reduce the solubility of carbonates in the precipitation on the filter. Do not use the filtrate.

Add 5 ml of hydrochloric acid (5.1) in the dish to dissolve the carbonates of the elements. Transfer the acid carefully to the filter and collect the filtrate in a 50 ml volumetric flask. Repeat the procedure once. Wash the filter with water acidified with hydrochloric acid. Fill up to the mark with water.

A.5 Measurement

A.5.1 *Preparation of calibration solutions.* When the above procedure is used, the sample solution does not contain any melt chemicals, since they have been removed by washing. Therefore use the calibration solutions described in Clause 8.1. The concentration of acid should be the same in the calibration and sample solution.

A.5.2 *Measurement.* Carry out the measurements as described in Clause 8.2, page 3.

If any value obtained exceeds the range covered by the calibration solutions, the measurements must be repeated with a more dilute sample solution.

Calculate the result as described in A.9.

Alternative B: Sodium carbonate-boric acid melt

A.6 Reagents and chemicals

All reagents and chemicals used in Clause 5 in this Method and the following *melt chemical mixture:*

A.6.1 *Sodium carbonate-boric acid melt.* Mix sodium carbonate, Na_2CO_3, and boric acid, H_3BO_3, in the required amounts in the weight proportions 3:1.

A.6.2 *Matrix solution*. Use the matrix solution for the preparation of calibration solutions and for dilution of the sample solutions. The matrix solution contains the same reagents, in the same concentrations as the sample solutions, when these are prepared as described in Clause 5.

A.6.2.1 *Sodium carbonate-boric acid melt.* Dissolve 5 g of boric acid, H_3BO_3, and 15 g of sodium carbonate, Na_2CO_3, in water in a 1000 ml volumetric flask. Add 100 ml of hydrochloric acid (5.1).

Add 20 ml of cesium solution (5.3) and 10 ml of lanthanum solution (5.4) and fill up to the mark with water (5.0).

A.7 Procedure

A.7.1 *Blank.* Run a blank with the same chemicals as those added to the sample but without any sample.

A.7.2 *Procedure for the insoluble residue.* Transfer the filter paper with the insoluble residue to a platinum dish (6.2) and dry it. Incinerate with a gas burner and ignite in a furnace at 525 °C. Let the dish and the residue cool in a desiccator. Add 2 g of the melt mixture (A.6.1). The amount of the melt mixture must not be less than 10 times the weight of the ash.

> *Note 1* – If the amount of ash is too large, a weighed portion of it can be taken after thorough mixing with a glass rod. The proportion taken shall be considered when calculating the result.

Stir with a glass rod. Heat the mixture over a gas burner until it has melted. If a transparent melt is not obtained, place the dish in a furnace at 900 °C and keep it there for 15 minutes. Allow the dish to cool. Dissolve the melt in water using a magnetic stirrer and transfer the solution to a 100 ml volumetric flask. If a larger melt than 2 g has been prepared, use a correspondingly larger volumetric flask in order to maintain the proportion between salts and water volume. Carefully add 10 ml of hydrochloric acid (5.1) to dissolve the carbonates. Add a part of the hydrochloric acid to the dish to dissolve remaining carbonates. Wash the dish carefully with hydrochloric acid. If the determination is to be carried out by the atomic absorption technique, add 2 ml of cesium solution (5.3) and 1 ml of lanthanum solution (5.4). If a larger melt has been prepared, add these reagents in a corresponding proportion. Fill up to the mark. Mix and let the solution stand until remaining solid material has settled. Use the transparent solution for the measurements.

> *Note 2* – If the sample contains a large amount of silicon, silicic acid may precipitate. The elements remain in solution under acid conditions, if the precipitation is not too extensive.

A.8 Measurement

A.8.1 *Preparation of calibration solutions.* Prepare the calibration solutions using the matrix solution described in A.6.2.1.

> *Note* – It is important that calibration and sample solutions are matrix matched to each other. It is usually practical to prepare multi-element standards. The matrix solution is used as zero-solution.

A.8.2 *Measurement.* Carry out the measurements as described in Clause 8.2, page 3.

If any value obtained exceeds the range covered by the calibration solutions, the measurements must be repeated with a more dilute sample solution. Use the matrix solution as zero-solution.

A.9 Calculation (alternatives A and B)

A.9.1 *Elements in the acid-insoluble residue*. Calculate the element content, *Z*, in the insoluble residue, from the expression:

$$Z = \frac{c\ f\ V\ a}{m\ b} \qquad [A1]$$

where

Z is the acid-insoluble element content in the original sample, in milligrams per kilogram;
c is the concentration of the element in the sample solution, as obtained from the calibration plot corrected for the blank solution, in milligrams per litre;
f is the dilution factor, if dilution is used;
V the volume of the sample solution (normally 100 ml);
m is the amount of original sample of pulp, paper or board taken (not residue), oven dry basis, in grams;
a is the total amount of the ash, in grams;
b is the weighed amount of the ash, in grams.

A.10 Report

Report the results according to instructions given in Clauses 9.2 and 10, page 4. The mean value of the acid-soluble part and the total amount of the element should be reported.

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.
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