



Pulp, paper and board

Sodium and potassium contents

Atomic Absorption Spectroscopy (AAS) using a flame

0 Introduction

This SCAN-test Method replaces SCAN-CM 63:00/P 83:00 from which it differs in that a number of withdrawn SCAN-test Methods, referred to in this method, have been replaced by the corresponding ISO standards.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.

This SCAN-test Method describes a procedure for the determination of the contents of acid-soluble sodium and potassium using Atomic Absorption Spectroscopy (AAS) using a flame. Two alternative digestion techniques are specified:

- ignition at 525 °C and
- wet digestion in an autoclave or microwave oven.

Note – The determination can also be made by inductively coupled plasma spectroscopy (ICP-AES) or flame atomic emission spectroscopy (AES).

1 Scope

The Method is applicable to most types of pulp, paper and board having sodium and potassium contents that are acid-soluble by using one of the wet digestion procedures described in this Method.

The method is not suitable for samples containing kaolin as coating or filler pigment because of the difficulty in dissolving sodium and potassium quantitatively.

Wet digestion in an open system is not included in this method. The technique is however applicable to most types of samples. It is not recommended for potassium determination in samples containing clay because it gives too low results.

2 References

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| 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Note – SCAN-test has withdrawn a number of test methods and refers instead to the corresponding ISO and/or EN Standards.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 *Sodium content, acid-soluble* – The sodium content in the pulp, paper or board obtained after either:
- Ignition the material at 525 °C and treating the residue with 6 mol/l hydrochloric acid as specified in this method, or
 - Wet digestion of the material with concentrated nitric acid in a closed vessel as specified in this method.

3.2 *Potassium content, acid-soluble* – The potassium content in the pulp, paper or board obtained after either:

- Ignition the material at 525 °C and treating the residue with 6 mol/l hydrochloric acid as specified in this method, or
- Wet digestion of the material with concentrated nitric acid in a closed vessel as specified in this method.

4 Principle

4.1 *Alternative A – ignition*

The material is ignited at (525 ± 25) °C. The residue is treated with 6 mol/l hydrochloric acid (HCl) and the sodium and potassium contents in the solution are determined by Atomic Absorption Spectroscopy (AAS) using a flame.

4.2 *Alternative B – wet digestion (closed system)*

The material is treated with concentrated nitric acid (HNO₃) in a closed vessel at elevated temperature and pressure. The resulting solution is diluted and the sodium and potassium contents are determined by Atomic Absorption Spectroscopy (AAS) using a flame.

The method specifies two alternative wet-digestion techniques:

- digestion in an autoclave;
- digestion in a laboratory microwave oven.

5 Reagents and chemicals

Use only chemicals of analytical grade.

5.1 *Water*, of high purity, distilled or deionized.

5.2 *Hydrochloric acid*, $c(\text{HCl}) = 6$ mol/l. Dilute 500 ml of concentrated hydrochloric acid, (37 %, density 1,19 g/ml) in 500 ml of water (5.1).

5.3 *Concentrated nitric acid*, (HNO₃), 65 %, density 1,40 g/ml.

5.4 *Sodium stock solution*, 1000 mg/l. Ignite a portion of anhydrous sodium sulphate, Na₂SO₄, 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 (5.1). Dilute to 1 litre in a volumetric flask. Store in a polyethylene bottle.

5.4.1 *Sodium standard solution*, 50 mg/l. Dilute 5,00 ml of the sodium stock solution (5.4) to 100 ml in a volumetric flask.

5.5 *Potassium stock solution*, 1000 mg/l. Ignite a portion of anhydrous potassium sulphate, K₂SO₄, at 550 °C, in a crucible of platinum or porcelain. Allow to cool to room temperature in a desiccator.

Weigh $(2,228 \pm 0,005)$ g, using an analytical balance, and dissolve in water (5.1). Dilute to 1 litre in a volumetric flask. Store in a polyethylene bottle.

5.5.1 *Potassium standard solution*, 50 mg/l. Dilute 5,00 ml of the potassium stock solution (5.5) to 100 ml in a volumetric flask.

5.6 *Cesium solution*, $c(\text{Cs}) = 50$ g/l. In a 1000 ml volumetric flask, dissolve 63,5 g of cesium chloride, CsCl, in water (5.1) and fill up to the mark with water.

Note – Commercially available solutions may be used.

6 Apparatus

6.1 *Alternative A and B*

6.1.1 *Ordinary laboratory equipment*. Laboratory vessels made of plastics are recommended as well as ash-free and acid-washed filter paper. A suitable filter paper is Munktell No 00A but other similar qualities may be used.

Note 1 – Solutions can be diluted in acid-washed glassware bottles, but solutions should be stored in plastic bottles.

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

6.2 *Alternative A – ignition*

6.2.1 *Furnace*, capable of maintaining a temperature of (525 ± 25) °C. It is recommended the furnace be fitted with a hood or other means of evacuating smoke and fumes.

6.2.2 *Dishes* of platinum or quartz. Wash the dishes thoroughly. Remove any spots in the platinum dishes by cleaning with fine sand. Boil the dishes with hydrochloric acid (5.2) and avoid all contact with metals other than platinum.

6.3 *Alternative B – wet digestion*

Apparatus for wet digestion, either:

6.3.1 *Autoclave*, with an inner vessel of PTFE (polytetrafluoroethylene) provided with a lid of PTFE, and a heating block that can maintain the autoclave at a

temperature of (160 ± 5) °C. The block must be provided with safety arrangements that prevent it from being overheated.

Note 2 – The use of an oven instead of the heating block is not recommended because of the hazard involved in removing the hot autoclaves from the oven at the end of the heating period.

or

6.3.2 *Laboratory microwave oven* equipped with a rotating vessel holder and with programming facilities. The digestion vessels, made of PTFE, shall have a volume of at least 80 ml and either low-pressure or high-pressure vessels may be used. Follow the safety regulations given by the oven supplier. Since the test portion size influences the change of pressure and temperature during the wet digestion, the oven should preferably be equipped with temperature- and pressure-control facilities. The oven shall be able to keep the temperature constant at 175 °C.

7 Sample preparation

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

Carry out the determination in duplicate. Tear the air-dry sample into pieces of suitable size.

Weigh a separate test portion for the determination of dry matter content in accordance with ISO 638.

8 Ignition and wet digestion

8.1 *Alternative A – ignition*

8.1.1 *Weighing*. In a clean dish (6.2.2), weigh to the nearest 0,01 g a test portion of about 2 g to 5 g.

8.1.2 *Ignition*. Use a hot plate, a temperature-controlled oven or a low flame of a gas burner and char the test portion until it is well carbonised. The temperature shall be (525 ± 25) °C. If the dish is too small to hold the entire test portion, gently burn it off in smaller portions. Take care not to let any ash escape from the dish. Place the dish in a furnace and ignite it 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, since acid-insoluble compounds may then be formed.

8.1.3 *Dissolving the ignited test portion in acid*. To avoid splattering, cautiously moisten the ash with water (5.1) and add 5 ml of hydrochloric acid (5.2) to the dish.

Evaporate to dryness on a boiling water-bath or equivalent device. Repeat this procedure once.

Add 2,5 ml of the acid (5.2) to the dry ignited test portion and heat the dish, covered with a watch glass to prevent evaporation.

Filter the contents of the dish through a filter paper and collect the filtrate in a 25 ml volumetric flask. To ensure that the transfer is quantitative, add another portion of 2,5 ml of acid (5.2) 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 (5.1).

Wash the insoluble residue on the filter paper with water (5.1) and collect the filtrate in the volumetric flask. Fill to the mark and mix. The acid concentration in the solution is about 1,2 mol/l.

8.1.4 *Blank*. Run a blank with the same chemicals and the same procedure as in 8.1.3 but without any test portion.

8.2 *Alternative B – wet digestion (closed system)*

8.2.1 *Weighing*. Weigh to the nearest 1 mg a test portion of about 0,5 g to 2 g, or the maximum amount permissible within safety limits for the equipment used.

8.2.2 *Wet digestion*. Transfer the test portion to the PTFE vessel. Add 10 ml concentrated nitric acid (5.3) and wait 5 min. Close the vessel with its lid and place it in the autoclave or in the laboratory microwave oven as relevant.

Warning – Esters and alcohols can form explosive compounds with nitric acid. If the sample contains considerable amounts of such compounds, digestion with nitric acid should not be undertaken.

If an autoclave is used: Close the autoclave as instructed by the manufacturer and place it in the heating block. Heat it at a temperature of (160 ± 5) °C for 2 h. Allow the heating block and the autoclave to cool and, with caution, open the autoclave under a hood.

Follow the safety regulations for the equipment.

If a laboratory microwave oven is used: The exact power and time required may vary with the equipment used and the number of samples taken. Heat the closed digestion vessel with its contents, step by step and hold the temperature at (175 ± 5) °C for at least 5 min. It is essential that the organic content of the test portion is completely digested. Allow the vessel to cool and, with caution, open it under a hood.

Note 2 – Check the vessel and the sample after the wet digestion to ensure that no leakage has occurred.

Allow nitrous fumes to escape from the wet digestion vessel. If the solution contains any suspended matter remove it by filtration or centrifugation. Transfer the clear solution quantitatively into a 25 ml volumetric flask and fill to the mark with water (5.1) and mix by shaking. The acid concentration in the solution is about 3 mol/l. (As a rough estimate, half of the added acid is consumed in the oxidation of the organic matter).

8.2.3 *Blank*. Run a blank with the same chemicals as those added to the wet-digestion but without any test portion.

9 Atomic absorption procedure

9.1 Preparation of calibration solutions

It is important that the acid and the cesium concentrations are the same in the calibration and in the test solutions after the final dilution step, since the acid concentration influences the signal. This is particularly important when potassium is to be determined.

Use the same type of acid in the calibration and sample solutions, e.g.

- Hydrochloric acid after ignition;
- Nitric acid after wet digestion.

Prepare a series of at least 4 calibration solutions by diluting v ml of sodium standard solution (5.4.1) or of potassium standard solution (5.5.1) to 100 ml with water (5.1) in volumetric flasks. Before filling up to the mark, add 2 ml cesium solution (5.6) and either 10 ml hydrochloric acid (5.2) or 4 ml nitric acid (5.3). Select the volumes v so that the working range of the atomic absorption spectrometer is covered. Prepare also a zero solution ($v = 0$), similar to the calibration solutions, but containing no added elements. It should not be confused with the blank. An example of suitable calibration solutions is given in *Table 1*.

Note – A combined calibration solution with both sodium and potassium may be used.

Table 1. Suitable calibration solutions. By using the procedure described above and the recommendations given in this table, the cesium and acid concentrations in the solutions become 1 g/l and about 0,6 mol/l respectively.

	Calibration solutions				
	zero	No 1	No 2	No 3	No 4
Conc. of Na or K, mg/l	0	0,5	1,0	1,5	2,0
Standard solution, ml (5.4.1 or 5.5.1)	0	1,0	2,0	3,0	4,0

9.2 Determination of sodium and potassium

Dilute the sample solution until the sodium and potassium concentrations are within the range covered by the calibration solutions. In the final dilution stage, adjust the cesium concentration in the sample to 1 g/l by addition of an appropriate amount of cesium solution (5.6). Adjust the acid concentration in the sample to about 0,6 mol/l by addition of appropriate amounts of hydrochloric acid (5.2) or nitric acid (5.3). Notice that the acid concentration in the undiluted samples is about 1,2 mol/l after ignition (8.1.3) and 3 mol/l after wet digestion (8.2.2). This means that the sample solutions should be diluted at least twice and five times respectively to obtain the same acid concentration as in the calibration solutions.

Carry out the spectrometric measurements of the calibration solutions, of the sample solutions and of the blank solution. Adjust the instrument reading to zero by using the zero solution. Following the instructions of the spectrometer, measure the absorbance of sodium and potassium at 589,0 nm and 766,5 nm respectively 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 of the calibration solutions against the elemental content in these solutions. Correct the absorbance of sodium and potassium in the sample solutions for the blank. Note the concentration of sodium and potassium in the sample solutions, obtained from the calibration graph, as c mg/l.

10 Calculation

Calculate the acid-soluble sodium or potassium content from the expression:

$$X = \frac{c \cdot f \cdot V}{m} \quad [1]$$

where

- X is the sodium or potassium content of the pulp, paper or board, in milligrams per kilogram;
- c is the concentration of sodium or potassium in the sample solution, corrected for the blank, as obtained from the calibration graph, in milligrams per litre;
- f is the dilution factor (flask volume/aliquot);
- V is the volume of the sample solution in millilitres (standard 25 ml);
- m is the amount of sample taken, oven dry basis, in grams.

Calculate the mean of the parallel determinations for each element. Report the content 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.

11 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;
- any departure from the standard procedure and any other circumstances that may have affected the results.

12 Precision

The precision data given include results from the determination of the acid-soluble sodium and potassium content by both alternative digestion techniques, ignition and wet digestion.

12.1 *Repeatability.* Five samples were analysed six times in the same laboratory. The following results, mean value and coefficient of variation (CV), were obtained:

Repeatability for the determination of sodium

Sample type	Ignition		Wet digestion	
	mean, mg/kg	CV, %	mean, mg/kg	CV, %
Unbleached pulp	1860	1,0	1840	1,3
Bleached pulp	720	2,0	700	1,4
Kraft liner with recycled pulp	1080	1,0	1060	1,0
Copy paper with calcium carbonate	920	0,9	940	1,3
Paper with kaolin	1290	2,6	1390	2,1

Repeatability for the determination of potassium

Sample type	Ignition		Wet digestion	
	mean, mg/kg	CV, %	mean, mg/kg	CV, %
Unbleached pulp	26	1,6	25	2,6
Bleached pulp	4,4	9,3	5,1	26
Kraft liner with recycled pulp	106	3,2	129	3,2
Copy paper with calcium carbonate	40	3,8	44	2,9
Paper with kaolin	960	1,3	1140*	3,5

12.2 *Reproducibility.* Five samples were analysed at different laboratories. Results obtained after wet digestion include both digestion in a closed system and in some cases even digestion in an open system. The results, mean value and coefficient of variation (CV) between laboratories, were as follows (the figures in parentheses give the number of laboratories using each method):

Reproducibility for the determination of sodium

Sample type	Ignition		Wet digestion	
	mean, mg/kg	CV, %	mean, mg/kg	CV, %
Unbleached pulp	1990 (6)	6,3	1970 (5)	5,1
Bleached pulp	740 (6)	2,9	730 (5)	3,3
Kraft liner with recycled pulp	1110 (7)	3,7	1130 (7)	4,6
Copy paper with calcium carbonate	1000 (7)	6,0	970 (7)	4,5
Paper with kaolin	1310 (7)	18	1360 (7)	19

Reproducibility for the determination of potassium

Sample type	Ignition		Wet digestion	
	mean, mg/kg	CV, %	mean, mg/kg	CV, %
Unbleached pulp	26 (6)	11	27 (5)	4,9
Bleached pulp	4,8 (6)	22	5,0 (5)	9,1
Kraft liner with recycled pulp	110 (8)	11	114 (10)	13
Copy paper with calcium carbonate	44 (9)	18	41 (10)	7,8
Paper with kaolin	910 (7)	28	1260*(5)	15

* Only wet digestion in a closed system since the open system gives too low results.

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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