



Pulps, papers and boards

Cadmium and lead content

Atomic absorption spectrometry - graphite furnace technique

1 Scope

This SCAN-test Method specifies a method for the determination of traces of cadmium and lead in all types of pulps, papers and boards, including products containing recycled fibre, that can be wet-digested in nitric acid as specified in this Method.

Two alternative wet digestion techniques are specified:

- digestion in an autoclave and
- digestion in a microwave oven.

The limit of determination depends upon the amount of sample and upon the type of atomic absorption spectrometer used. The lower limit of determination is normally from 0,002 mg/kg to 0,01 mg/kg for cadmium and from 0,02 mg/kg to 0,1 mg/kg for lead, depending on the sample size and the instrument used.

Note – Lead present in coating and filler pigments that do not dissolve in nitric acid under the conditions specified in this Method will not be determined in a low-pressure vessel unless hydrofluoric acid is used.

2 References

ISO 638 Pulp – Determination of dry matter content

Note – SCAN-test has withdrawn a number of test methods and refers instead to the corresponding ISO and/or EN Standards.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 *Cadmium content* – The ratio of the mass of the element cadmium in the sample to the mass of the dry sample.

3.2 *Lead content* – The ratio of the mass of the element lead in the sample to the mass of the dry sample.

4 Principle

The sample is treated with nitric acid in a closed vessel at elevated temperature and pressure. The resulting solution is diluted, and the cadmium and lead contents are determined by atomic absorption spectrometry using the graphite furnace technique.

5 Reagents

All reagents shall be of highest possible purity. The usual analytical grade is often not sufficiently pure.

5.0 *Water*, only freshly distilled or deionized water, of the highest possible purity.

5.1 *Concentrated nitric acid*, $c(\text{HNO}_3) = 15 \text{ mol/l}$. Use a quality specially made for use in the determination of trace elements.

5.2 *Dilute nitric acid*, $c(\text{HNO}_3) = 0,15 \text{ mol/l}$. Dilute 10 ml of the concentrated nitric acid (5.1) to 1 litre with water (5.0).

5.3 *Cadmium stock solution*, $c(\text{Cd}) = 1,000 \text{ g/l}$, made by dissolving $(2,744 \pm 0,005) \text{ g}$ of cadmium nitrate tetrahydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per litre of nitric acid, $c(\text{HNO}_3) = 0,5 \text{ mol/l}$. The solution is commercially available.

5.4 *Cadmium standard solution*, $c(\text{Cd}) = 1,00 \text{ mg/l}$. Using a precision pipette, dilute 1,00 ml of the cadmium stock solution (5.3) to 1000 ml with diluted nitric acid (5.2) in a volumetric flask. Mix by shaking the flask. The solution has a shelf-life of several months if it is stored in a polyethylene bottle.

5.5 *Lead stock solution*, $c(\text{Pb}) = 1,000 \text{ g/l}$, made by dissolving $(1,000 \pm 0,002) \text{ g}$ of lead in a mixture of 10 ml of concentrated nitric acid (5.1) and 10 ml of water (5.0), and diluting to 1000 ml with water. The solution is commercially available.

5.6 *Lead standard solution*, $c(\text{Pb}) = 1,00 \text{ mg/l}$. Using a precision pipette, dilute 1,00 ml of the lead stock solution (5.5) to 1000 ml with diluted nitric acid (5.2) in a volumetric flask. Mix by shaking the flask. The solution has a shelf-life of several months if stored in a polyethylene bottle.

5.7 *Matrix modifier solutions*. Several matrix modifier solutions are recommended in the literature. The three solutions given here are in common use. Matrix modifier solutions are commercially available.

5.7.1 *Palladium nitrate stock solution*. Dissolve 2,0 g of $\text{Pd}(\text{NO}_3)_2$ in 10 ml of concentrated nitric acid (5.1) and dilute with water (5.0) to 500 ml in a volumetric flask.

or

5.7.2 *Ammonium dihydrogen phosphate stock solution*. Dissolve 2,0 g of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ in water (5.0) and dilute to 100 ml.

or

5.7.3 *Magnesium nitrate stock solution*. Dissolve 0,5 g of magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, in water (5.0) and dilute to 100 ml.

Note – The solutions 5.7.1, 5.7.2 and 5.7.3 can be combined.

5.7.4 *Matrix modifier working solutions*. Prepare matrix modifier working solutions according to the instructions given by the instrument supplier.

6 Apparatus

6.0 *Ordinary laboratory equipment*. All equipment used shall be washed in nitric acid, approx. 1 mol/l, for at least 24 h and afterwards rinsed with water (5.0).

6.1 *Apparatus for wet digestion*, either:

6.1.1 *Autoclave*, with an inner vessel of PTFE (polytetrafluoroethylene), volume 250 ml, provided with a lid of PTFE, and a heating block that can maintain the autoclave at a temperature of $(160 \pm 5) \text{ }^\circ\text{C}$. The block must be provided with safety arrangements that prevent it from being overheated.

Note 1 – 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

6.1.2 *Microwave oven* for laboratory purposes, with programming facilities and equipped with a rotating vessel holder. The digestion vessels, made of PTFE, shall have a volume of at least 100 ml, and either low-pressure or high-pressure vessels may be used. Follow the safety regulations given by the oven supplier.

Since the sample size influences the change of pressure and temperature during the wet digestion, the oven should preferably be equipped with temperature and pressure facilities recording. The oven shall be able to keep the temperature constant at $(175 \pm 5) \text{ }^\circ\text{C}$.

Note 2 – If the amount of sample in all vessels placed in the oven at the same time is similar and of the same material character, it is sufficient to check the change in temperature and pressure in only one vessel.

6.2 *Atomic absorption spectrometer*, equipped with the graphite furnace technique and with pyrolytic coated tubes with a L'vov platform, and with lamps for the determination of cadmium and lead. The instrument shall have background correction (15.1).

7 Sample preparation

The sampling procedure is not covered by this Method. Make sure that the test pieces taken are representative of the sample received. In order to avoid contamination, keep the sample wrapped in high-density polyethylene until required.

From the sample, tear pieces about 10 × 10 mm in size to provide the amount required, taking approximately the same amount from each specimen. Use tools of plastics or ceramics. Do not use a knife or any other metal tool.

Split pieces of pulp sheets and board sheets to reduce their thickness. Keep the sample near the balance for moisture equilibration for at least 20 min.

Withdraw a sample for the determination of dry matter content in accordance with ISO 638 irrespectively of the kind of sample.

8 Wet digestion

Carry out the procedure in duplicate. Run also a blank, see Clause 9.

Note 1 – Hydrofluoric acid can be used for a total digestion of the cadmium and lead content present in the sample. The use of hydrofluoric acid in laboratory routines is not desirable since the acid is hazardous. If, however, hydrofluoric acid is used, it shall be reported.

8.1 Weigh to the nearest 1 mg a sample of about 1 g, or the maximum amount permissible within safety limits for the equipment used. Transfer the sample to the PTFE vessel. Add 10 ml of the concentrated nitric acid (5.1). Close the vessel with its lid and place it in the autoclave (6.1.1) or in the microwave oven (6.1.2) 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.*

Note 2 – If a microwave oven is used, the sample size has to be adjusted to the capacity of the digestion vessel. If the volume of the low-pressure digestion vessel is 120 ml, the maximum sample weight is 0,3 g. If more sample is taken, the safety disc will rupture with consequent loss of sample solution.

8.2.1 *If an autoclave is used:* Close the autoclave as instructed by the manufacturer and place it in the heating block (6.1.1). Heat it at a temperature of (160 ± 5) °C for (16 ± 1) h. Allow the heating block and the autoclave to cool and, with caution, open the autoclave in a hood. Proceed to Subclause 8.3.

Note 3 – Follow the safety regulations for the equipment.

8.2.2 *If a 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 (6.1.2), with its content, step by step, for about 45 min and hold the temperature at (175 ± 5) °C for at least 5 min. It is essential that the sample is completely digested. Allow the vessel to cool and, with caution, open it in a hood.

Note 4 – Check the vessel and the sample after the wet digestion to ensure that no leakage has occurred.

8.3 Allow nitrous fumes to escape from the wet digestion vessel and dilute the remaining solution in a graded vessel of, for example, 25 ml. The volume should be kept as small as possible.

Allow any suspended matter to settle.

9 Blank

Run a blank following the instructions in Clause 8, but using no sample.

Note – Determination of trace elements is always sensitive to contamination. The proper cleaning of the digestion vessels is therefore essential. To ensure accurate results, rinse the vessels before use with nitric acid in the same way as the blank is prepared. It is recommended that the absorbance of the rinsing solution is measured. If the absorbance exceeds 10 % of the expected value for the samples, the rinsing should be repeated.

10 Preparation of calibration solutions

Prepare the calibration solutions by diluting the standard solutions (5.4) and (5.6) with dilute nitric acid (5.2). The cadmium and lead contents selected for the final calibration solutions depend on the particular instrument to be used. In general, a calibration solution having a cadmium content of 5 µg/l (= 0,005 µg/ml) and a lead content of 20 µg/l (= 0,02 µg/ml) is appropriate. The acid concentration of the calibration solutions should be adjusted to that of the sample solutions by replacing part of the dilute nitric acid (5.2) with concentrated nitric acid (5.1).

As an independent check of the calibration, samples of known cadmium and lead contents should be analysed.

11 Determination

The procedure for the spectrometric determination of the cadmium and lead contents of the sample solutions depends on the design of the atomic absorption spectrometer and of the graphite furnace. Follow the manufacturer's instructions when operating the instrument.

Note – The procedure should be checked by means of standard reference materials of similar type.

12 Calculation

Calculate the cadmium or lead content of the original sample, taking into account the amount of sample taken to wet digestion, its dry matter content and the blank value:

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

where

- X is the concentration of trace metal in the sample, in milligrams per kilogram;
 c is the concentration of trace metal in the sample solution corrected for the blank, in micrograms per litre;
 f is the dilution factor;
 V is the volume of the sample solution, in litres;
 m is the mass of the dry sample, in grams.

Note – In trace element analysis the results from replicate determinations can be inconsistent due to inherent inhomogeneity of the material tested.

Calculate and report the mean trace metal content for each element in milligrams per kilogram, with two significant figures if the content exceeds 0,1 mg/kg and with one significant figure for a content less than 0,1 mg/kg.

13 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 wet-digestion procedure used (autoclave or microwave oven);
- the content of each element;
- any departure from the procedure described in this SCAN-test Method or any other circumstances that may have affected the test results.

14 Precision

14.1 *Repeatability*. One pulp sample and two paper samples were analysed six to eight times in the same laboratory using each of the two methods for wet digestion.

The repeatability of the cadmium content determination, measured by the coefficient of variation (CV) within a laboratory, was as follows (the figures in parentheses are the number of duplicates):

Sample	Autoclave		Microwave oven	
	mean Cd, mg/kg	CV, %	mean Cd, mg/kg	CV, %
Unbleached kraft	0,06 (6)	7,6	0,07 (6)	2,9
Uncoated paperboard	0,04 (7)	8	0,05 (5)	33
Copy paper	0,20 (7)	32	0,15 (8)	18

The repeatability of the lead content determination, measured by the coefficient of variation (CV) within one laboratory was as follows (the figures in parentheses are the number of duplicates):

Sample	Autoclave		Microwave oven	
	mean Pb, mg/kg	CV, %	mean Pb, mg/kg	CV, %
Unbleached kraft	0,15 (6)	3,4	0,14 (6)	4,9
Uncoated paperboard	0,04 (7)	27	0,07 (5)	19
Copy paper	0,71 (7)	16	0,60 (6)	6,4

14.2 *Reproducibility*. Seven laboratories analysed five samples of pulp and paper using the autoclave method and/or the microwave oven method for wet digestion. The reproducibility of the cadmium content determination, measured by the coefficient of variation (CV) between laboratories, was as follows (the figures in parentheses give the number of laboratories using each method):

Sample	Autoclave		Microwave oven	
	mean Cd, mg/kg	CV, %	mean Cd, mg/kg	CV, %
Bl. kraft	0,002 (4)	38	0,003 (4)	104
Coated paperboard	0,03 (4)	35	0,03 (4)	23
Uncoated paperboard	0,04 (5)	20	0,04 (4)	25
Copy paper	0,15 (5)	48	0,15 (4)	20

Recycled pulp	0,01 (5)	24	0,01 (5)	29
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The reproducibility of the lead content determination was as follows (the figures in parentheses give the number of laboratories using each method):

Sample	Autoclave		Microwave oven	
	mean Pb, mg/kg	CV, %	mean Pb, mg/kg	CV, %
Bl.	0,05 (4)	141	0,07 (3)	76
Coated paperboard	3,0 (4)	9	2,7 (4)	25
Uncoated paperboard	0,05 (5)	68	0,15 (3)	63
Copy paper	0,65 (5)	7	0,43 (5)	28
Recycled pulp	2,5 (5)	34	2,0 (5)	10

The contents of cadmium and lead in pulp and paper for some of the analysed samples are close to the detection limit. For these samples, the coefficient of variation becomes high.

15 Literature

15.1 Svensk Standard SS 02 81 83, Clause 5.2. Metal content of water, sludge and sediment – Determined by flameless atomic absorption spectrometry – Electro-thermal atomization in a graphite furnace – General principles and guidelines.