INTERNATIONAL STANDARD

ISO 10775

Second edition
2013-08-01

# Paper, board and pulps — Determination of cadmium content — Atomic absorption spectrometric method

*Papier, carton et pâtes — Détermination de la teneur en cadmium — Méthode par spectrométrie d'absorption atomique*

Reference number
ISO 10775:2013(E)

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Published in Switzerland

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# Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2. www.iso.org/directives

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The committee responsible for this document is ISO/TC 6, *Paper, board and pulps*.

This second edition cancels and replaces the first edition (ISO 10775:1995), of which it constitutes a minor revision.

# Paper, board and pulps — Determination of cadmium content — Atomic absorption spectrometric method

## 1 Scope

This International Standard specifies a method for the determination of traces of cadmium in all types of paper, board and pulp, including products containing recycled fibre, that can be wet-combusted in nitric acid as specified in this International Standard.

The lower limit of the determination depends on the equipment used and is normally about 10 µg/kg. Cadmium present in pigments and fillers that do not dissolve in nitric acid under the conditions of this test may not be determined quantitatively.

NOTE It has been claimed that the dissolution of cadmium from pigments other than calcium carbonate is incomplete by a few percent.

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 186, *Paper and board — Sampling to determine average quality*

ISO 287, *Paper and board — Determination of moisture content of a lot — Oven-drying method*

ISO 638, *Paper, board and pulps — Determination of dry matter content — Oven-drying method*

ISO 7213, *Pulps — Sampling for testing*

## 3 Principle

The sample is treated with nitric acid in a closed vessel. The resulting solution is diluted and cadmium content determined by atomic absorption spectrometry using the graphite furnace technique.

Wet combustion may be done either in an autoclave or microwave oven.

## 4 Reagents

All reagents shall be of the highest possible purity. The quality normally designated “pro analysi” or “analytical reagent (AR)” is often not sufficiently pure. Use only freshly distilled and deionized water or water of equivalent purity.

NOTE Commercially available solutions may also be used.

### 4.1 Concentrated nitric acid, $c(\text{HNO}_3) = 15$ mol/l

Use a quality specially made for use in the determination of trace metals.

### 4.2 Dilute nitric acid, $c(\text{HNO}_3) = 0{,}15$ mol/l

Dilute with water 10 ml of concentrated nitric acid (4.1) to one litre.

**4.3 Cadmium nitrate standard solution,** $\rho(\text{Cd}) = (1{,}000 \pm 0{,}002)$ g/l, made, for example, by dissolving 2,774 g of cadmium nitrate tetrahydrate, $\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O}$, per litre of nitric acid, $c(\text{HNO}_3) = 0{,}5$ mol/l.

### 4.4 Cadmium stock calibration solution, $\rho(\text{Cd}) = 1{,}00$ mg/lp

Using a precision pipette dilute 1,00 ml of the cadmium standard solution (4.3) to 1 000 ml with dilute nitric acid (4.2) in a volumetric flask. Mix by shaking the flask.

The solution has a shelf life of several months if stored in a polyethylene bottle.

### 4.5 Matrix modifier solution

Several matrix modifier solutions are recommended in the literature. The three solutions given in 4.5.1 to 4.5.3 are in common use. The choice among them depends on their performance in each particular laboratory, which is evaluated by running a blank.

### 4.5.1 Palladium nitrate solution

Dissolve 2,0 g of $\text{Pd(NO}_3)_2$ in 10 ml of nitric acid (4.1) and dilute with water to 500 ml in a volumetric flask. (Alternatively, the equivalent amount of palladium metal, i.e. 0,924 g, is dissolved in nitric acid.) Prepare a working solution by diluting 5 ml of this stock solution with water to 100 ml.

or

### 4.5.2 Ammonium dihydrogenphosphate solution

Dissolve 2 g of $\text{NH}_4\text{H}_2\text{PO}_4$ in water and dilute to 100 ml.

or

### 4.5.3 Magnesium nitrate solution

Dissolve 0,5 g of $\text{Mg(NO}_3)_2$ in water and dilute to 100 ml.

## 5 Apparatus

Ordinary laboratory equipment and the following.

**5.1 Apparatus for wet combustion,** either:

**5.1.1 Autoclave**, with an inner vessel of polytetrafluoroethylene (PTFE), capacity 250 ml, provided with a lid of PTFE, and a heating block that can maintain the autoclave at a temperature of 160 ± 5 °C.

The block shall be provided with an extra safety switch that prevents overheating.

NOTE 1 The PTFE vessels can be protected from corrosion from the outside by applying a film of silicone grease on all outside surfaces. The film is removed and renewed after each heating period. Vessels treated in this manner should not be used when silica has to be determined.

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

**5.1.2 Laboratory microwave oven**, with programming facilities, specially designed for wet combustion, with digestion vessels of PTFE, capacity at least 120 ml, having safety valves to release pressures over 830 kPa.

**5.2 Atomic absorption spectrometer**, equipped for the graphite furnace technique and with a so-called "L'vov" platform, and with a lamp for the determination of cadmium.

Preferably, the instrument should have background correction.

# 6 Sampling and sample preparation

Ensure that the sample is representative of the lot to be tested. If applicable, follow the instructions given in ISO 186 or in ISO 7213.

In order to avoid contamination, keep the samples wrapped in aluminium foil until required.

Tear from the sample enough pieces, about 10 mm x 10 mm in size, to provide the amount required, taking an approximately equal amount from each sample. Do not use a knife or any other metal tool. (Tools of plastics or ceramics may be used.) Split samples of pulp sheets or board to reduce their thickness.

Keep the sample near the balance for moisture equilibration for at least 20 min. Withdraw a specimen for the determination of dry matter content in accordance with ISO 287 or ISO 638, as applicable.

# 7 Wet combustion

Carry out wet combustion in duplicate; also run a blank (see Clause 8).

## 7.1 Test sample preparation

Weigh a test portion of 1 g to the nearest 1,0 mg and transfer it to the appropriate PTFE vessel (5.1). Add 10 ml of the concentrated nitric acid (4.1). Close the vessel with its lid and place it in the autoclave (5.1.1) or in the microwave oven (5.1.2), as applicable.

## 7.2 Combustion procedure

### 7.2.1 Autoclave procedure

If an autoclave is used, close the autoclave as instructed by the manufacturer and place it in the heating block (5.1.1). Heat it at 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 7.3.

### 7.2.2 Microwave oven procedure

If a microwave oven is used, the test portion size shall be adjusted to the capacity of the digestion vessel. If this is 120 ml, the maximum test portion mass shall be 0,3 g. If more test portion is taken, the safety valve of the digestion vessel will activate.

Set the power regulator to the predetermined value and heat the closed digestion vessel (5.1.2), with its contents for 10 – 20 min typically, 30 min maximum, depending on the microwave power. Allow the vessel to cool and, with caution, open it in a hood.

The correct setting of the power regulator shall be determined separately for each oven. A typical setting is 40 % of the maximum power. Also see 5.1.2.

## 7.3 Dilution

Allow nitrous fumes to escape from the wet combustion vessel and dilute the remaining solution to a known volume with water. The dilution volume depends on the equipment used, and should be kept as small as possible.

The dilution can be made in a disposable graduated plastic vessel. Volumetric flasks thoroughly cleaned, may also be used.

Alternatively, dilute the remaining solution directly in the digestion vessel by adding from a graduated pipette the required volume of water. In this case, the volume of the residual nitric acid shall be determined in a separate experiment.

Allow any suspended solids to settle.

## 8 Blank

Follow the instructions in Clause 7, but use no sample.

## 9 Preparation of calibration solutions

Prepare the calibration solution daily by diluting the stock calibration solution (4.4) with dilute nitric acid (4.2). The cadmium content selected for the final calibration solution depends on the particular instrument to be used. In general, a calibration solution having a cadmium mass concentration of 10 µg/l (0,01 µg/ml) is appropriate.

## 10 Determination of cadmium

**10.1** The procedure for the spectrometric determination of the cadmium content of the test solutions depends on the design of the atomic absorption spectrometer (5.2) and of the graphite furnace. The manufacturer's instructions should be followed when operating the instrument.

In general, the technique with standard additions (see 10.2) should be used. In practice, the normal calibration procedure, based on a calibration curve, may be used, provided that there is no interference from the matrix. This must be verified by analysing suitable reference materials.

Before using the normal calibration procedure, check that any matrix effects are under control by running the same type of sample by the standard addition technique. In particular, differences in acid concentration between standards and sample solutions affect the results. The acid concentration of the standard solutions should be adjusted to that of the sample solutions by replacing part of the diluent (4.2) by concentrated nitric acid (4.1).

**10.2** For the technique with standard additions, the following instructions are given as a guide.

Prepare the solutions for measurement directly in the graphite tube by means of a sampler. Typical solutions and volumes are given in Table 1 as an example.

**Table 1 — Example of the technique with standard additions**

| Solution to be measured | Calibration solution [a] | Sample [a] | Blank [a] | Matrix modifier solution [a](4.5) |
|---|---|---|---|---|
| Blank | 0 | 0 | 20 | 5 |
| Solution 1 | 2 | 10 | 8 | 5 |
| Solution 2 | 4 | 10 | 6 | 5 |
| Solution 3 | 6 | 10 | 4 | 5 |
| Sample | 0 | 10 | 10 | 5 |

[a] Volumes in microlitres.

**10.3** Prepare a plot on graph paper or using software such as an Excel spreadsheet. Use as $y$-values the readings from the spectrometer (peak area or absorbance values, corrected for the value obtained for the blank) and as the *x*-values the amounts, in units of mass, of cadmium added with the solutions 1, 2 and 3. The value obtained for the sample solution is plotted on the y-axis.

Draw a straight line through the four plotted points. This line intersects the *x*-axis on its negative side. The point of intersection represents the cadmium content in the sample solution.

NOTE If the four points do not fall on a straight line, it is acceptable to use a line of best fit. If it is obvious from the diagram that the precision of the result is poor, the analysis should be repeated. If the points still are widely scattered, there is some serious error or the level of the results is below the lower limit of detection. The laboratory should then report that it is unable to determine the cadmium content quantitatively.

## 11 Calculation

Calculate the cadmium content of the original sample, taking into account the amount of sample taken for wet combustion, its dry matter content and the blank value.

NOTE As an independent check of the procedure, it is advisable to analyse samples of known cadmium content and similar overall composition in parallel with unknown samples.

## 12 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) date and place of testing;

c) complete identification of the sample tested;

d) wet combustion procedure used (autoclave or microwave oven);

e) method of calibration (standard additions or normal calibration procedure);

f) mean result of the determinations, expressed in micrograms per kilogram to two significant figures. If more than two determinations were carried out, this should be stated;

g) any departure from the procedure specified, or any other circumstances that may have affected the test results.