INTERNATIONAL STANDARD

ISO 777

Third edition
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Paper, board and pulp — Determination of acid-soluble calcium

Papier, carton et pâte — Détermination de la teneur en calcium soluble dans l'acide

Reference number
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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 777 was prepared by Technical Committee ISO/TC 6, *Paper, board and pulps*.

This third edition cancels and replaces the second edition (ISO 777:2001), of which it constitutes a minor revision. Apart from minor editorial modifications, only the title has been changed, to be consistent with ISO 1830:2005, and to make a distinction with ISO 17812 (to be published) which specifies the method to determine the total mass fraction of calcium, manganese, iron and copper.

The first edition of this International Standard included the titrimetric procedure as well as the procedure based on atomic absorption spectroscopy. In the second edition, the titrimetric procedure was deleted, as it is now seldom used, and the scope was enlarged to include paper and board in addition to pulp.

Introduction

This International Standard corresponds to ISO 778 [1] and ISO 779 [2] in order to make it possible to perform the final measurement of all three elements on the same solution.

Paper, board and pulp — Determination of acid-soluble calcium

WARNING — The method specified in this International Standard involves the use of some hazardous chemicals and of gases that can form explosive mixtures with air. Care must be taken to ensure that the relevant precautions are observed.

1 Scope

This International Standard specifies the procedure for the determination of acid-soluble calcium by atomic absorption spectrometry or by plasma emission spectrometry.

It is applicable to all kinds of paper, board and pulp.

It specifies a method to determine the acid-soluble part of the incineration residue, i.e. that part of the ignition residue obtained after incineration that is soluble in hydrochloric acid. If the residue is completely soluble, the result obtained by the procedure specified in this International Standard is taken as the total amount of calcium in the sample.

2 Normative references

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.

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

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

ISO 638, *Pulps — Determination of dry matter content*

ISO 1762, *Paper, board and pulps — Determination of residue (ash) on ignition at 525 °C*

ISO 7213, *Pulps — Sampling for testing*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
mass fraction of calcium
amount of the element calcium in the solution obtained after incineration of the specimen at 525 °C and treating the residue with 6 mol/l hydrochloric acid, as specified in this International Standard

4 Principle

A test portion is incinerated at 525 °C and the residue is treated with 6 mol/l hydrochloric acid. The test solution is aspirated into an acetylene/dinitrogen monoxide or acetylene/air flame and the mass fraction of calcium is determined by one of the following procedures:

— measurement of the absorption of the 422,7 nm line emitted by a calcium hollow-cathode lamp, or

— measurement of the absorption of the 422,7 nm line emitted by plasma emission spectrometry.

5 Reagents and materials

Use only chemicals of recognized analytical grade and only distilled or deionized water.

5.1 Hydrochloric acid, about 6 mol/l.

Dilute 500 ml of hydrochloric acid (density 1,19 g/ml) in 500 ml of water.

5.2 Calcium stock solution, 500 mg/l of Ca.

Weigh 1,249 g ± 0,001 g of calcium carbonate, dried to constant mass at a temperature not exceeding 200 °C, into a 1 000 ml volumetric flask. Add 50 ml of water. Add a minimum volume of hydrochloric acid (5.1) (approximately 10 ml), drop by drop, to effect the complete dissolution of the calcium carbonate. Dilute with water to the mark and mix.

1 ml of this stock solution contains 0,500 mg of Ca.

5.3 Calcium standard solution, 50 mg/l of Ca.

Transfer 100 ml of the stock solution (5.2) to a 1 000 ml volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,05 mg of Ca.

Commercially available, certified standard solutions may be used.

5.4 Lanthanum solution, 50 g/l of La.

Moisten 59 g of lanthanum oxide (La_2O_3) with water. Slowly and cautiously, add 250 ml of hydrochloric acid (density 1,19 g/ml) to dissolve the lanthanum oxide. Dilute to the mark in a 1 000 ml volumetric flask and mix.

This solution is used to eliminate interference from phosphate when determining calcium in an air/acetylene flame. It is normally not required when the dinitrogen oxide/acetylene flame is used.

5.5 Caesium solution, 50 g/l of Cs.

In a 1 000 ml volumetric flask, dissolve 63,5 g of ultra-pure caesium chloride (CsCl) in water and fill up to the mark with water.

This solution is used to suppress ionization of calcium in the dinitrogen monoxide/acetylene flame. It is normally not required when an air-acetylene flame is used.

NOTE Caesium chloride may be replaced by the corresponding amount of potassium chloride, unless potassium is to be determined in the same solution.

5.6 Acetylene gas and/or **dinitrogen monoxide gas**, of a grade suitable for atomic absorption spectrometry.

WARNING — Acetylene gas forms explosive mixtures with air.

5.7 Appropriate gas for the plasma spectrometer (6.4). Argon is usually recommended as a carrier gas.

6 Apparatus and equipment

Ordinary laboratory equipment. Clean all equipment in 0,1 mol/l hydrochloric acid.

6.1 Filter paper, ash free, particle retention 20 μm to 25 μm.

6.2 Dishes, of platinum or quartz.

6.3 Atomic absorption spectrometer, with a burner for nitrogen monoxide/acetylene or air/acetylene and with a hollow-cathode lamp for calcium.

NOTE A multi-element lamp may be used.

6.4 Inductively coupled plasma spectrometer.

7 Sampling and preparation of sample

If the analysis is being made to evaluate a lot of paper, board or pulp, the sample shall be selected in accordance with ISO 186 or ISO 7213, as relevant. If the analysis is made on another type of sample, report the source of the sample, and, if possible, the sampling procedure. Select the specimens so that they are representative of the sample received. A sufficient amount of sample shall be collected to allow for at least duplicate determinations. Avoid cut edges, punched holes and other parts where metallic contamination may have occurred.

Prepare a test specimen by tearing at least 30 g of small pieces from various parts of the sample. This amount is sufficient for the duplicate determinations mentioned in Clause 8.

8 Procedure

8.1 Incineration and dissolution of the residue

Carry out the procedure in duplicate.

Air-dry the specimen in the laboratory atmosphere until it reaches moisture equilibrium.

Determine the moisture content on a separate air-dried portion as specified in ISO 287 or ISO 638, as relevant. Weigh this portion at the same time as the test portion used for incineration.

Carry out ashing of the test portion, as described in ISO 1762. A portion of 2 g to 5 g is usually sufficient.

Carry out the dissolution of the ash under a fume hood. To avoid splattering, carefully moisten the ash with water 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 twice.

For samples with a high carbonate content, more than 10 ml of acid (2×5 ml) may be needed.

Add 2,5 ml of the hydrochloric acid (5.1) to the dry residue. If necessary, heat the dish covered by a watch glass for a few minutes.

Using the filter paper (6.1), filter the contents of the dish into a 25 ml volumetric flask. To ensure that the transfer is complete, add another portion of 2,5 ml of acid to the dish and heat again. Filter this last portion of

acid into the main portion in the volumetric flask with the aid of some water. Fill up to the mark and mix. This is the test solution.

8.2 Blank

Run a blank with the same quantity of each of the chemicals as those added to the incineration residue, but without any residue.

9 Preparation of calibration solutions

It is important that the acid concentration is the same in the calibration solutions as in the test solution since the acid concentration influences the signal.

From the calcium standard solution (5.3), prepare at least three calibration solutions, and in addition one zero solution, for the construction of the calibration graph. (The zero solution is similar to the calibration solutions, but contains no added calcium. Do not confuse it with the blank.)

NOTE Not more than two calibration solutions are needed for plasma emission spectrometry.

10 Determination

If a dinitrogen monoxide/acetylene flame is used, add caesium solution (5.5) so that the caesium concentration of the solution is 1 g/l to prevent ionization. If an air/acetylene flame is used, add lanthanum solution (5.4) so that the lanthanum concentration is 5 g/l.

Carry out the spectrometric measurement of the calibration solutions, including the zero solution, the test solution and 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 shall be repeated with a more dilute test solution. Add acid, caesium solution or lanthanum solution as required.

Most instruments have a system for automatic evaluation of results. If the instrument has no automatic evaluation system, construct the calibration graph by plotting the absorbance, corrected for the blank, against the concentration of calcium in milligrams per litre. Then read the calcium concentration in the test solution from the calibration graph.

11 Calculation

Calculate the mass fraction of calcium from the expression

$$\omega_{\mathrm{Ca}} = \frac{f \cdot \rho_{\mathrm{Ca}} \cdot V}{m}$$

where

ω_{Ca} is the mass fraction of calcium in the sample, in milligrams per kilogram;

ρ_{Ca} is the calcium concentration in the test solution, as obtained from the calibration plot corrected for the blank, in milligrams per litre;

V is the volume, in millilitres, of the original test solution (standard volume = 25 ml);

m is the mass of sample taken, oven-dry basis, in grams;

f is the dilution factor; $f = 1$, unless the original test solution has been diluted.

Calculate the mean with two significant figures.

12 Precision

12.1 General

A study [1)] gave the following results.

12.2 Repeatability

A sample of uncoated paperboard was analysed in one laboratory nine times. The mean found was 730 mg/kg, and the coefficient of variation (CV) was 10 %.

NOTE As the above study comprises only one sample and one laboratory, the result is only a rough estimation of the repeatability.

12.3 Reproducibility

Four samples were analysed in eight laboratories. The results in Table 1 were obtained for the mean and the coefficient of variation (CV).

Table 1

Sample type	Mean mg/kg	CV %
Bleached pulp	160	6
Coated paperboard	10 500	5
Uncoated paperboard	640	9
Copy paper	86 400	11

13 Test report

The test report shall include the following information:

a) reference to this International Standard;

b) date and place of testing;

c) complete identification of the sample tested;

d) the result, expressed as indicated in Clause 11;

e) any departure from the procedure described in this International Standard or any other circumstances which may have affected the result.

1) Study made by SCAN-test in 1996.

Bibliography

[1] ISO 778, *Paper, board and pulp — Determination of acid-soluble copper*

[2] ISO 779, *Paper, board and pulp — Determination of acid-soluble iron*

ICS 85.040; 85.060

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