INTERNATIONAL STANDARD

ISO 17812

First edition
2007-12-01

Paper, board and pulps — Determination of total magnesium, total calcium, total manganese, total iron and total copper

Papier, carton et pâtes — Détermination de la teneur en magnésium total, en calcium total, en manganèse total, en fer total et en cuivre total

Reference number
ISO 17812:2007(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

COPYRIGHT PROTECTED DOCUMENT

© ISO 2007

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 17812 was prepared by Technical Committee ISO/TC 6, *Paper, board and pulps*.

Introduction

This International Standard combines the determination of magnesium (Mg), calcium (Ca), manganese (Mn), iron (Fe) and copper (Cu) into one single standard. The scope of this International Standard includes the acid-soluble part of the elements plus that part of the elements that may remain insoluble after dissolution of the incineration residue with hydrochloric acid. This International Standard is complementary to the following International Standards, which measure only the acid-soluble part of the element.

ISO 777, *Paper, board and pulp — Determination of acid-soluble calcium*

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

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

ISO 1830, *Paper, board and pulps — Determination of acid-soluble manganese*

Paper, board and pulps — Determination of total magnesium, total calcium, total manganese, total iron and total copper

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 should be taken to ensure the relevant precautions are observed.

1 Scope

This International Standard specifies the procedure for the determination of total magnesium, total calcium, total manganese, total iron and total copper by atomic absorption spectrometry or by plasma emission spectrometry. The total content comprises the acid-soluble part of the element plus the acid-insoluble part of the element.

It is applicable to all types of paper, board and pulps.

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 of a lot — Oven drying method*

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

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

ISO 7213, *Pulps — Sampling for testing*

3 Principle

A test specimen is incinerated at 525 °C and the residue is dissolved in 6 mol/l hydrochloric acid. If the resulting solution contains insoluble material, originating, for example, from fillers and coating formulations, these shall be destroyed. Two alternative methods for destroying the insoluble material are included in this International Standard: hydrofluoric acid digestion (7.3.2) and fusion with alkali metal salts (7.3.3). This insoluble part should be combined with the original solution. This is to ensure complete recovery of elements that may be occluded in the residue or combined with silicates. The concentration of each element in the test solution is then determined by atomic absorption or plasma emission spectrometry, as specified in this International Standard.

4 Reagents and materials

4.1 General

All chemicals shall be of reagent grade or better, unless otherwise indicated. Water shall be distilled or deionized with a maximum conductivity of 1,0 μS/cm at 25 °C.

4.2 Hydrochloric acid (HCl), about 6 mol/l.

Dilute 500 ml of concentrated hydrochloric acid (specific gravity 1,19 g/ml) to 1 000 ml with water.

4.3 Hydrofluoric acid (HF), 48 % to 52 % solution.

4.4 Sulfuric acid (H_2SO_4), concentrated (specific gravity 1,84 g/ml).

4.5 Lanthanum chloride ($LaCl_3$), solution, $c(\mathrm{La}) = 50$ g/l. In a volumetric flask, dissolve 59 g of lanthanum oxide (La_2O_3) in small portions, in 200 ml of hydrochloric acid (4.2) and dilute to 1 000 ml with water.

NOTE This lanthanum solution is used to eliminate chemical interference when determining magnesium in an air/acetylene flame. The solution is not required when the nitrous oxide/acetylene flame or inductively coupled plasma (ICP) technique is used.

4.6 Nitric acid (HNO_3), concentrated (specific gravity 1,4 g/ml).

4.7 Standard stock solutions of each element, commercially available Certified Atomic Absorption or Atomic Emission standard solutions can be used. Standard stock solutions can also be prepared as follows:

- **Magnesium,** 1 000 mg/l standard solution. Dissolve 1,000 g of magnesium metal ribbon in 100 ml of 1:4 nitric acid (4.6) and dilute to 1 000 ml with water.
- **Calcium,** 1 000 mg/l standard solution. Dissolve 2,497 g of primary standard calcium carbonate ($CaCO_3$) in a minimum volume of 1:4 nitric acid (4.6) and dilute to 1 000 ml with water.
- **Manganese,** 1 000 mg/l standard solution. Dissolve 1,000 g of manganese metal strip or wire in a minimum volume of 1:1 nitric acid (4.6) and dilute to 1 000 ml with water.
- **Iron,** 1 000 mg/l standard solution. Dissolve 1,000 g of iron metal strip or wire in 20 ml of hydrochloric acid (4.2) and dilute to 1 000 ml with water.
- **Copper,** 1 000 mg/l standard solution. Dissolve 1,000 g of copper metal strip or wire in a minimum volume of 1:1 nitric acid (4.6) and dilute to 1 000 ml with water.

4.8 Acetylene gas and/or nitrous oxide gas, of a grade suitable for atomic absorption spectrometry. Nitrous oxide is used only when measuring calcium.

WARNING — Acetylene gas forms explosive mixtures with air.

4.9 Carrier gas, appropriate gas for the plasma emission spectrometer. Argon is usually recommended as a carrier gas.

4.10 Alkali metal salts, mix sodium carbonate (Na_2CO_3) and boric acid (H_3BO_3) in the required amounts in the weight portions 3:1.

NOTE Other alkali metal salts can also be used [for example lithium metaborate ($LiBO_2$)]

4.11 Cesium chloride (CsCl), solution, $\rho(\mathrm{Cs}) = 50$ g/l. In a 1 000 ml volumetric flask, dissolve 63,5 g of ultra-pure cesium chloride (CsCl) in water and fill up to the mark with water.

NOTE This cesium solution is used to suppress ionization of calcium in a nitrous oxide/acetylene flame. The solution is not required when an air/acetylene flame or ICP technique is used.

5 Apparatus and equipment

5.1 General

Ordinary laboratory equipment is used. All glassware and plasticware shall be rinsed with 0,1 mol/l hydrochloric acid prior to use.

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

5.3 Crucibles, platinum or fused silica, of minimum capacity 50 ml.

NOTE If treatment with hydrofluoric acid is required, only platinum crucibles can be used, since fused silica is attacked by HF.

5.4 Muffle furnace, capable of maintaining a temperature of 525 °C ± 25 °C.

5.5 Balance, of capacity 100 g, accurate to 0,1 mg.

5.6 Atomic absorption spectrometer, equipped with air/acetylene and/or nitrous oxide/acetylene burners and with hollow cathode lamps for Mg, Ca, Mn, Fe and Cu.

NOTE Multi-element lamps can also be used.

5.7 Inductively coupled plasma (ICP) spectrometer.

5.8 Disposable protective gloves.

6 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. Protective disposable gloves (5.8) shall be worn when handling samples, to avoid contamination.

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 as specified in Clause 7.

Since iron tends to be nonhomogeneous in the sample, it is recommended that a composite sample be used.

7 Procedure

7.1 General

Although dry ignition followed by acid treatment is described in this International Standard, other dissolution methods, such as wet ignition or microwave digestion using various acid combinations, can also be used, provided that the results have been validated.

WARNING — For samples with a high silicon content, microwave digestion with nitric acid will give lower results for magnesium and for some other elements.

7.2 Incineration of the test portion

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. For the determination of major elements, including magnesium and calcium, a 1 g to 2 g test portion (calculated as oven-dry) should be used. For minor elements, including manganese, iron and copper, test portions of 5 to 10 g should be used. If trace levels of elements are needed then use larger than 10 g sample sizes.

Carry out ignition of the test portion as specified in ISO 1762.

In order to avoid flames, the dish shall be covered with a lid. The lid shall only partially cover the dish to avoid reducing conditions occurring in the dish, in which case acid-insoluble compounds may be formed. Under reducing conditions, for example, copper may be lost due to the formation of a platinum alloy.

7.3 Dissolution of the residue

7.3.1 General

After ignition, allow the crucible to cool. To avoid splattering, carefully moisten the residue of ignition with water and add cautiously, in a fume hood, 5 ml of hydrochloric acid (4.2) to the crucible. Evaporate to dryness on a boiling-water bath, hotplate or infrared lamp. Repeat this procedure.

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

Add 5 ml of hydrochloric acid (4.2) to the residue. If some insoluble residue is visible, heat, without boiling, the crucible covered with a watch glass for a few minutes.

If there is no insoluble residue after this treatment, add another 5 ml of hydrochloric acid (4.2), transfer quantitatively with water to a 100 ml volumetric flask. Dilute to 100 ml.

If the sample contains insoluble material, two alternative procedures are described in 7.3.2 and 7.3.3.

7.3.2 Dissolution of the insoluble residue using hydrofluoric acid

CAUTION — Hydrofluoric acid is extremely irritating. It is readily absorbed through the skin, penetrating it to attack underlying tissues and bone. Disposable protective gloves shall be worn when handling this material to avoid all contact with exposed skin. Use only in a fumehood with adequate ventilation.

Filter off the residue remaining after the hydrochloric acid treatment through the filter paper (5.2) retaining the filtrate in the 100 ml flask. After drying, ash the residue in a platinum crucible (5.3) at 525 °C ± 25 °C. Cool and add between 2 drops and 3 drops of sulfuric acid (4.4), followed by 5 ml of hydrofluoric acid (4.3).

Heat in a fumehood on a hotplate at a medium setting until all the hydrofluoric acid is evaporated, as indicated by the appearance of white fumes of sulfuric acid. Continue heating for an additional 5 min, then add 5 ml of hydrochloric acid (4.2) and combine it with the filtrate in the 100 ml volumetric flask. Dilute to 100 ml.

If some insoluble material remains after addition of hydrochloric acid, the procedure shall be repeated. If the sample also contains titanium, this will remain insoluble after the hydrofluoric acid treatment and shall be removed by filtration through the filter paper (5.2).

7.3.3 Dissolution of the insoluble residue by sodium carbonate/boric acid fusion

Filter off the residue remaining after the hydrochloric acid treatment through the filter paper (5.2), retaining the filtrate in the 100 ml flask. Transfer the filter paper with the insoluble residue to the platinum crucible (5.3) and dry it. Ash the residue in a furnace at 525 °C ± 25 ºC. Cool and add 2 g of the melt mixture (4.10). The amount of the melt mixture shall not be less than 10 times the weight of the residue of ignition.

If the amount of residue of ignition 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 results.

After stirring, heat the mixture over a gas burner until it has melted. Do not cover the crucible. If the transparent melt is not obtained, place the crucible in a furnace at 900 ºC and keep it there for 15 min. Allow the crucible to cool.

Dissolve the melt in water using a magnetic stirrer and combine the solution in the 100 ml volumetric flask. If a melt larger than 2 g has been prepared, use a correspondingly larger volumetric flask in order to maintain the proportion between salts and water volume. Wash the crucible carefully with 2 ml hydrochloric acid (4.2) and transfer the washing solution to the sample solution. Carefully add 8 ml of hydrochloric acid and dilute to 100 ml.

The amount of hydrochloric acid (4.2) in the final sample volume (100 ml) should be 10 ml. 2 g of melt mixture (equivalent to carbonates) consume about 5 ml of added hydrochloric acid (4.2).

If the determination is to be carried out by the atomic absorption technique, add 1 ml of lanthanum solution (4.5). If a larger melt has been prepared, add these reagents in a corresponding proportion. Fill up to mark. Mix and let the solution stand until the remaining solid material has settled. Use the transparent solution for the measurements.

NOTE If the sample contains a large amount of silicon, silicic acid can precipitate. The elements remain in solution under acid conditions, if the precipitation is not too extensive.

8 Preparation of calibration solutions

It is important that the acid concentration in the calibration solutions is the same as in the test solution, since the acid and salt concentration affects the instrument signal.

If atomic absorption spectrometry is used for the analysis, prepare of at least three calibration solutions for each element in 100 ml volumetric flasks, each containing 10 ml of hydrochloric acid (4.2), by diluting the corresponding standard stock solutions (4.7). In addition, a blank solution, similar to the calibration solutions, but containing no added element, shall be included.

When preparing the magnesium calibration solutions, 4 ml of the lanthanum chloride solution (4.5) shall also be added [ρ(La) will be 2 g/l]. When preparing the calcium calibration solutions, 2 ml of the cesium solution (4.11) shall be added [ρ(Cs) will be 1 g/l].

If plasma emission spectrometry is used, no more than two calibration solutions are necessary, and no addition of lanthanum chloride or cesium chloride is required.

Several elements may be combined in the same flask, if desired.

If fusion is used for dissolution of the residue, it is important that the calibration and sample solutions are matrix-matched to each other. Accordingly, the calibration solution shall be prepared as follows.

Dissolve 5 g of boric acid (H_3BO_3) and 15 g of sodium carbonate (Na_2CO_3) in water in a 1 000 ml volumetric flask. Adjust the pH to 2–3 with hydrochloric acid (4.2). Add corresponding standard stock solutions (4.7) and a 100 ml excess of hydrochloric acid (4.2) and dilute to 1 000 ml with water.

Add 4 ml of lanthanum chloride solution (4.5) or cesium chloride solution (4.11) as described previously, and fill up to the mark with water if atomic absorption spectrometry is used.

If plasma emission spectrometry is used, no addition of lanthanum or cesium chloride is required.

Calibration solutions are unstable and shall only be prepared on the same day that they are to be used, and stored in plastic bottles.

9 Blank solution

A blank solution shall also be prepared, omitting the test element, and containing the same amount of hydrochloric acid (4.2), as well as the same amount of lanthanum chloride (4.5), if required, as the calibration solutions.

If fusion is used for dissolution of the residue, the blank solution shall also contain the fusion salts.

10 Determination

For each element to be determined, optimize the conditions of the atomic absorption or plasma emission spectrometer, and operate the instrument as recommended by the manufacturer.

For atomic absorption, the recommended wavelengths are as follows:

- Magnesium: 285,2 nm flame: air/acetylene
- Calcium: 422,7 nm flame: nitrous oxide/acetylene
- Manganese: 279,5 nm flame: air/acetylene
- Iron: 248,3 nm flame: air/acetylene
- Copper: 324,8 nm flame: air/acetylene

For plasma emission, the recommended emission lines are as follows:

- Magnesium: 279,55 nm (for low levels), 280,27 nm (for high levels)
- Calcium: 396,85 nm (for low levels), 317,93 nm (for high levels)
- Manganese: 257,61 nm
- Iron: 259,94 nm
- Copper: 324,75 nm

Carry out the measurement of the calibration solutions, the test solution and the blank solution. If the reading of the test solution is outside the range of the calibration curve corrected for the blank, dilute with water to bring it within this range. All final dilutions of the test solution shall contain the same acid concentration (10 ml/100 ml) as the corresponding calibration solution, as well as lanthanum chloride/cesium chloride and fusion salt concentrations, if required.

NOTE If the test solution is used without dilution, then further addition of hydrochloric acid (4.2) is not necessary since the dilution already contains acid added after the ignition step.

Once the test solution is within the calibration range, determine the concentration of the element in the solution, by referring to the appropriate calibration curve.

In microprocessor-controlled spectrometers, the concentration is determined automatically, and consequently plotting of calibration curves is not required.

11 Calculation

Calculate the mass fraction of each element in the test specimen from the following expression:

$$\omega_{\text{el}} = \frac{f \rho_{\text{el}} V}{m} \qquad (1)$$

where

ω_{el} is the mass fraction of the particular element in the sample, in milligrams per kilogram;

f is the dilution factor; if the test solution has not been diluted, then $f = 1$;

ρ_{el} is the concentration of the particular element in the test solution (the acid soluble part plus the acid-insoluble part), corrected for the blank, as obtained from the calibration plot, in milligrams per litre;

V is the volume, in millilitres, of the original test solution (standard volume = 100 ml);

m is the mass of test portion used for ignition, on an oven-dry basis, in grams.

Calculate the mean to two significant figures for values below 10 mg/kg, and to three significant figures for values above 10 mg/kg.

12 Precision

12.1 Repeatability

Different kinds of pulp, paper and board samples were tested in six different laboratories according to this International Standard. The pooled repeatability was determined and the results are shown in Table 1.

Table 1 — Repeatability for determination of Mg, Ca, Mn, Fe and Cu

Sample	Mg		Ca		Mn		Fe		Cu	
	Mean mg/kg	CV[a] %	Mean mg/kg	CV %	Mean mg/kg	CV %	Mean mg/kg	CV %	Mean mg/kg	CV %
Bleached softwood	254	5,5	35,9	2,6	0,15	4,7	20,1	6,3	0,21	19,1
Bleached hardwood	448	5,0	41,5	5,1	0,41	2,1	35,5	5,2	0,26	7,4
CTMP[b]	50,8	1,1	420	0,8	0,35	14,5	0,9	21,4	0,11	24,2
Uncoated paper	1 732	1,1	47 600	3,1	25,1	2,0	282	1,1	2,9	11,3
Coated paper	1 826	2,5	166 000	1,3	64,3	1,4	612	1,0	2,7	48,2
Board	1 015	4,3	55 900	1,4	9,6	2,7	269	4,0	2,2	43,7

[a] CV: Coefficient of variation.

[b] CTMP: Chemo-Thermo-Mechanical Pulp.

12.2 Reproducibility

Different kinds of pulp, paper and board samples were tested in six different laboratories according to this International Standard. Reproducibility was determined and the results are shown in Table 2.

Table 2 — Reproducibility for determination of Mg, Ca, Mn, Fe and Cu

Sample	Mg		Ca		Mn		Fe		Cu	
	Mean mg/kg	CV[a] %	Mean mg/kg	CV %	Mean mg/kg	CV %	Mean mg/kg	CV %	Mean mg/kg	CV %
Bleached softwood	254	15,3	35,9	17,9	0,15	15,7	20,1	35,1	0,21	103
Bleached hardwood	448	10,5	41,5	16,9	0,41	7,9	35,5	23,4	0,26	117
CTMP[b]	50,8	4,0	420	5,9	0,35	30,4	0,9	30,7	0,11	89,9
Uncoated paper	1 732	6,0	47 600	11,5	25,1	8,5	282	10,5	2,9	58,6
Coated paper	1 826	11,0	166 000	10,9	64,3	17,2	612	21,9	2,7	57,2
Board	1 015	6,6	55 900	10,3	9,6	12,1	269	13,6	2,2	61,9

[a] CV: Coefficient of variation.

[b] CTMP: Chemo-Thermo-Mechanical Pulp.

The reproducibility of Cu measurements is poor in some cases because the mass fraction of Cu is very low in some samples.

13 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) the date and place of testing;

c) all information necessary for complete identification of the sample;

d) the procedure used for dissolving the acid-insoluble part;

e) the technique used for element determination: inductively coupled plasma/flame atomic absorption spectroscopy (ICP/FAAS);

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

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

ICS 85.040; 85.060

Price based on 8 pages