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Second edition
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Paper, board, pulps and cellulose nanomaterials — Determination of acid-soluble magnesium, calcium, manganese, iron, copper, sodium and potassium

Papiers, cartons, pâtes et nanomatériaux à base de cellulose — Détermination de la teneur en magnésium, calcium, manganèse, fer, cuivre, sodium et potassium soluble dans l'acide

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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.

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 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 12830:2011), which has been technically revised. The main changes to the previous edition are as follows:

— the scope has been changed to include cellulose nanomaterials in addition to paper, board and pulps;

— a definition of cellulose nanomaterial has been incorporated, along with additional instructions for sampling, sample preparation, incineration and dissolution of the residue for cellulose nanomaterials;

— additional instructions are given on how to express results when an element is not detected.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document combines the determination of the acid-soluble part of magnesium (Mg), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), sodium (Na) and potassium (K) into a single document. The scope of this document covers only the acid-soluble part of the elements.

ISO 17812[1] specifies the procedure for the determination of total magnesium, total calcium, total manganese, total iron and total copper by atomic absorption spectrometry (AAS) or by inductively coupled plasma emission spectrometry (ICP/ES).

In the context of this document, “cellulose nanomaterial” refers specifically to cellulose nano-objects (see 3.1 to 3.3). Owing to their nanoscale dimensions, these cellulose nano-objects can have intrinsic properties, behaviours or functionalities that are distinct from those associated with paper, board and pulps.

Paper, board, pulps and cellulose nanomaterials — Determination of acid-soluble magnesium, calcium, manganese, iron, copper, sodium and potassium

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

WARNING — The method specified in this document involves the use of nanomaterials. Care should be taken to ensure observation of the relevant precautions and guidelines for nanotechnology laboratory safety and best practices.

1 Scope

This document specifies the procedure for the determination of acid-soluble magnesium, calcium, manganese, iron, copper, sodium and potassium by atomic absorption spectrometry (AAS) or by inductively coupled plasma emission spectrometry (ICP/ES). The acid-soluble element comprises the acid-soluble part of the incineration residue, i.e. that part of the ignition residue obtained after incineration which is soluble in hydrochloric acid or nitric acid. In cases where the residue is completely soluble, the result obtained by the procedure specified in this document is a measure of the total amount of each element in the sample.

This document is applicable to all types of paper, board, pulps and cellulose nanomaterials.

The limit of determination depends on the element and on the instrument used.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 7213, *Pulps — Sampling for testing*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp/

— IEC Electropedia: available at http://www.electropedia.org/

3.1
cellulose nanomaterial
material composed predominantly of cellulose, with any external dimension between approximately 1 nm and 100 nm, or a material having internal structure or surface structure in the *nanoscale* (3.4), with the internal structure or surface structure composed predominantly of cellulose

Note 1 to entry: The terms nanocellulose and cellulosic nanomaterial are synonymous with cellulose nanomaterial.

Note 2 to entry: Some cellulose nanomaterials can be composed of chemically modified cellulose.

Note 3 to entry: This generic term is inclusive of cellulose nano-object and cellulose nanostructured material.

Note 4 to entry: See also definitions of cellulose, nanoscale, cellulose nano-object and cellulose nanostructured material in ISO/TS 20477:2017.

[SOURCE: ISO/TS 20477:2017, 3.3.1, modified — "1 nm to 100 nm" changed to "1 nm and 100 nm"; abbreviations deleted from Note 1 to entry; Note 4 to entry added.]

3.2
nano-object
discrete piece of material with one, two or three external dimensions in the *nanoscale* (3.4)

Note 1 to entry: The second and third external dimensions are orthogonal to the first dimension and to each other.

[SOURCE: ISO/TS 80004-1:2015, 2.5]

3.3
cellulose nano-object
nano-object (3.2) composed predominantly of cellulose

[SOURCE: ISO/TS 20477:2017, 3.3.2]

3.4
nanoscale
length range approximately from 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from larger sizes are predominantly exhibited in this length range.

[SOURCE: ISO/TS 80004-1:2015, 2.1]

4 Principle

A test specimen is incinerated at 525 °C and the residue is dissolved in hydrochloric acid or nitric acid. The concentration of each element in the test solution is then determined by AAS or ICP/ES. Techniques using other types of instrumentation, such as ICP-mass spectrometry (ICP/MS), may also be used provided that they give at least the same level of precision as AAS or ICP/ES, and that they have been properly validated. The use of any such instrumentation shall also be reported.

5 Reagents and materials

5.1 General

All chemicals shall be of reagent grade or better unless otherwise indicated. Water shall be distilled or deionized, of grade 2 or better in accordance with ISO 3696.

5.2 Hydrochloric acid (HCl), 6 mol/l, trace metal grade. Dilute 500 ml of concentrated hydrochloric acid (specific gravity 1,19 g/ml) to 1 000 ml with water.

5.3 Nitric acid (HNO_3), concentrated (specific gravity 1,4 g/ml), trace metal grade.

5.4 Lanthanum chloride ($LaCl_3$), solution, ρ(La) = 50 g/l. In a 1 000 ml volumetric flask, dissolve 59 g of lanthanum oxide (La_2O_3), in small portions, in 200 ml of hydrochloric acid (5.2) and dilute to 1 000 ml with water.

This lanthanum chloride solution is used to eliminate chemical interference when determining calcium and magnesium in an air/acetylene flame. The solution is not required for use with the nitrous oxide/acetylene flame or when the ICP/ES technique is used.

5.5 Cesium chloride (CsCl), solution, ρ(Cs) = 50 g/l. In a 1 000 ml volumetric flask, dissolve 63,5 g of ultrapure cesium chloride (CsCl) in water and dilute to 1 000 ml with water.

This cesium chloride solution is used to suppress ionization of sodium and potassium in an air/acetylene flame. It is also used to suppress ionization of calcium in a nitrous oxide/acetylene flame. The solution is not required when the ICP/ES technique is used.

5.6 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:

5.6.1 Magnesium, 1 000 mg/l standard solution. Dissolve 1,000 g of magnesium metal ribbon in 100 ml of 1:4 nitric acid (5.3) and dilute to 1 000 ml with water.

5.6.2 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 (5.3) and dilute to 1 000 ml with water.

5.6.3 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 (5.3) and dilute to 1 000 ml with water.

5.6.4 Iron, 1 000 mg/l standard solution. Dissolve 1,000 g of iron metal strip or wire in 20 ml of hydrochloric acid (5.2) and dilute to 1 000 ml with water.

5.6.5 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 (5.3) and dilute to 1 000 ml with water.

5.6.6 Sodium, 1 000 mg/l standard solution. Ignite a portion of anhydrous sodium sulfate (Na_2SO_4) at 550 °C in a crucible of platinum or porcelain. Allow to cool to room temperature in a desiccator. Dissolve 3,089 g of dried sodium sulfate in water and dilute to 1 000 ml with water. Store in a polyethylene bottle.

5.6.7 Potassium, 1 000 mg/l standard solution. Ignite a portion of anhydrous potassium sulfate (K_2SO_4) at 550 °C in a crucible of platinum or porcelain. Allow to cool to room temperature in a desiccator. Dissolve 2,228 g of dried potassium sulfate in water and dilute to 1 000 ml with water. Store in a polyethylene bottle.

5.7 Acetylene gas and/or **nitrogen oxide gas**, of a grade suitable for AAS. Nitrous oxide is used only when measuring calcium.

WARNING — Acetylene gas forms explosive mixtures with air.

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

6 Apparatus and equipment

6.1 General

Ordinary laboratory equipment is used. All glassware and plastic ware shall be cleaned thoroughly and rinsed with 0,1 mol/l hydrochloric acid or 10 % nitric acid, followed by reagent grade water, prior to use.

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

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

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

6.5 Balance, of capacity 100 g, with a scale division (readability) of 0,1 mg or better.

6.6 Atomic absorption spectrometer, equipped with air/acetylene and nitrous oxide/acetylene burners and with hollow cathode lamps for Mg, Ca, Mn, Fe, Cu, Na and K. Multi-element lamps can also be used.

6.7 Inductively coupled plasma/emission spectrometer.

6.8 Disposable protective gloves.

7 Sampling

7.1 General considerations

If the analysis is being made to evaluate a lot of paper, board, pulp or cellulose nanomaterial, 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 material to be tested so that it is representative of the sample received. A sufficient amount of material shall be collected from the sample to allow for at least duplicate determinations. Avoid cut edges, punched holes and other parts where metallic contamination may have occurred.

Disposable protective gloves (6.8) shall be worn when handling samples to avoid contamination.

Since iron tends to have a non-homogeneous distribution, it is recommended that a composite sample be used.

7.2 Paper, board and pulp sampling

In the case of paper, board and pulp, tear or remove at least 30 g of small pieces from various parts of the sample. This amount is sufficient for the duplicate determinations described in Clause 8.

7.3 Cellulose nanomaterial sampling

In some cases, it may not be practical or possible to obtain large quantities of solid material from a cellulose nanomaterial sample. In the case of solid cellulose nanomaterials, tear or remove sufficient material for duplicate determinations as described in Clause 8, in the form of small pieces, dry powder or flakes from various parts of the sample. If the sample is in aqueous suspension form, remove sufficient material for duplicate determinations as described in Clause 8 (calculated as oven-dry, i.e. water- and moisture-free) from various portions of the aqueous suspension, and dry to give a pre-dried sample in the form of flakes, powder or other solid, which shall be mixed to homogeneity, after which the test specimen shall be obtained from the pre-dried sample. Filtration to concentrate dilute samples prior to drying is not recommended as it may result in loss of dissolved material.

8 Procedure

8.1 General

Although dry ignition followed by acid treatment is described in this document, 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 high silicon content, microwave digestion with nitric acid will give lower results for magnesium and for some other elements.

8.2 Incineration of the test specimen — Paper, board and pulp

Carry out the procedure in duplicate.

Air-dry the test and dry matter specimens in the laboratory atmosphere until they reach moisture equilibrium.

Determine the dry matter content on the dry matter specimen, as specified in ISO 638. Weigh this specimen at the same time as the test specimen used for incineration.

For the determination of major elements, including magnesium, calcium, sodium and potassium, a 1 g to 2 g test specimen (calculated as oven-dry) is recommended. For minor elements, including manganese, iron and copper, test specimens of 5 g to 10 g are recommended. If trace levels of elements are needed, then it is recommended that test specimen masses larger than 10 g be used.

Carry out ashing of the test specimen as described in ISO 1762.

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

If the minimum test specimen mass cannot fit into the crucible for any reason, the digested sample may be reconstituted to a smaller final volume (see 8.4).

8.3 Incineration of the test specimen — Cellulose nanomaterials

Carry out the procedure in duplicate.

Air-dry the test and dry matter specimens in the laboratory atmosphere until they reach moisture equilibrium.

Determine the dry matter content on the dry matter specimen, as specified in ISO 638. Weigh this specimen at the same time as the test specimen used for incineration.

For the determination of major elements, including magnesium, calcium, sodium and potassium, a 1 g to 2 g test specimen (calculated as oven-dry) is recommended. For minor elements, including manganese, iron and copper, test specimens of 5 g to 10 g are recommended. If trace levels of elements are needed, then it is recommended that test specimen masses larger than 10 g be used. However, owing to the possible impracticality of obtaining such quantities of cellulose nanomaterial from certain samples such as dilute suspensions, smaller test specimen masses may be used, provided that the test specimen masses used are stated in the report in accordance with Clause 13. It is possible that the level of precision obtained will be lower than for larger test specimens.

Carry out ashing of the test specimen as described in ISO 1762.

In order to avoid flames, cover the crucible with a lid. The lid should only cover the crucible partially to avoid the occurrence of reducing conditions in the crucible, in which case acid-insoluble compounds

might be formed. Under reducing conditions, for example, copper might be lost due to the formation of a platinum alloy.

If the minimum test specimen mass cannot fit into the crucible for any reason, the digested sample may be reconstituted to a smaller final volume (see 8.5).

An additional ashing step at 525 °C is often needed for residue (ash content) determination in cellulose nanocrystals. This additional procedure is not recommended for determination of acid-soluble metals in cellulose nanocrystals, in order to avoid loss of metals during prolonged heating.

8.4 Dissolution of the residue — Paper, board and pulp

After ashing, 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 (5.2) or nitric acid (5.3) to the crucible. Evaporate to dryness on a boiling water bath or hotplate or using an infrared lamp. Repeat this procedure.

For samples with high carbonate content, more than 10 ml of acid (2 × 5 ml) might be needed; repeat the procedure as required.

Add a further 5 ml of hydrochloric acid (5.2) to the residue. If some insoluble residue is visible, heat, without boiling, the crucible covered with a watch glass for a few minutes. Using the filter paper (6.2), filter the contents of the crucible into a 100 ml volumetric flask. To ensure that the transfer is complete, add another portion of 5 ml of hydrochloric acid (5.2) to the crucible and heat again if necessary. Filter this last portion of acid into the main portion in the volumetric flask with the aid of some water (5.1). If required for AAS, add 4 ml of lanthanum chloride solution (5.4) or 2 ml of cesium chloride solution (5.5) to the volumetric flask. Fill up to the mark with water and mix. This is the test solution.

Microwave vessel size restrictions may limit the amount of sample which can be digested. If necessary, the digested sample may be heated to dryness and reconstituted to a final volume of 25 ml such that the proportions as described previously are respected.

8.5 Dissolution of the residue — Cellulose nanomaterials

After ashing, allow the crucible to cool. Nitric acid (5.3) is recommended for the dissolution of the residue from cellulose nanomaterials. To avoid splattering, carefully moisten the residue of ignition with water and add cautiously, in a fume hood, 5 ml of nitric acid (5.3) to the crucible. Evaporate to dryness on a boiling water bath or hotplate or using an infrared lamp. Repeat this procedure.

For cellulose nanomaterial samples, more than 10 ml of acid (2 × 5 ml) might be needed; repeat the procedure as required.

ISO 21400[2] provides a method for microwave dissolution of cellulose nanocrystal samples (using nitric acid), which may be followed for cellulose nanocrystals or any other samples for which the described microwave digestion procedure has been validated.

Add a further 5 ml of nitric acid (5.3) to the residue. If some insoluble residue is visible, heat, without boiling, the crucible covered with a watch glass for a few minutes. To ensure that the transfer is complete, add 5 ml of water (5.1) to the crucible and heat again if necessary. Transfer the contents of the crucible into a 100 ml volumetric flask with the aid of some water (5.1). If required for AAS, add 4 ml of lanthanum chloride solution (5.4) or 2 ml of cesium chloride solution (5.5) to the volumetric flask. Fill up to the mark with water and mix. If undissolved residue is present, the solution may be sonicated to dissolve it. If residue does not dissolve with sonication, the solution may be filtered or the precipitate allowed to settle and the supernatant used for analysis.

Microwave vessel size restrictions may limit the amount of sample which can be digested. If necessary, the digested sample may be heated to dryness and reconstituted to a final volume of 25 ml such that the proportions as described previously are respected.

9 Calibration solutions — Measurement considerations

9.1 General

It is important that the acid concentration and the lanthanum chloride/cesium chloride concentration in the calibration solutions are the same as in the test solution, since the acid and salt concentrations affect the instrument signal.

Calibration solutions are unstable and should only be prepared on the day they are to be used and stored in plastic bottles. The standard stock solutions are less unstable and can be stored for several months.

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

9.2 Calibration solutions for AAS

When AAS is used for the analysis, prepare at least three calibration solutions for each element in 100 ml volumetric flasks, each containing 10 ml of hydrochloric acid (5.2) or 5 ml of nitric acid (5.3), according to the acid used to dissolve the residue after ashing in 8.4 or 8.5, by diluting the corresponding standard stock solutions (5.6). In addition, a blank solution similar to the calibration solutions, but containing no added element, shall be included.

When preparing the calcium and magnesium calibration solutions, 4 ml to 20 ml of the lanthanum chloride solution (5.4) shall also be added [ρ(La) will be 2 g/l to 10 g/l] if an air/acetylene flame is used. The concentration of La required will be dependent on the concentration of interferents such as P in the sample solution. When preparing the sodium and potassium calibration solutions, 2 ml of the cesium chloride solution (5.5) shall be added [ρ(Cs) will be 1 g/l] if an air/acetylene flame is used. When preparing the calcium calibration solution, 2 ml of the cesium chloride solution (5.5) shall be added [ρ(Cs) will be 1 g/l] if a nitrous oxide/acetylene flame is used.

9.3 Calibration solutions for ICP/ES

When ICP/ES is used, prepare at least three calibration solutions for each element; no addition of lanthanum chloride or cesium chloride is required. Add 10 ml of hydrochloric acid (5.2) or 5 ml of nitric acid (5.3) before diluting the corresponding standard stock solutions (5.6) to 100 ml. In addition, a blank solution similar to the calibration solutions, but containing no added element, shall be included.

10 Blank solution

10.1 Blank solution for AAS

A blank solution shall be prepared, omitting the test element, and containing the same amount of hydrochloric acid (5.2) or nitric acid (5.3), according to the acid used to dissolve the residue after ashing in 8.4 or 8.5, as well as the same amount of lanthanum chloride (5.4) and/or cesium chloride (5.5) depending on the type of flame used, as the calibration solutions.

10.2 Blank solution for ICP/ES

A blank solution shall be prepared, omitting the test element, and containing the same amount of hydrochloric acid (5.2) or nitric acid (5.3), according to the acid used to dissolve the residue after ashing in 8.4 or 8.5, as the calibration solutions.

11 Determination

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

For AAS, the commonly recommended wavelengths are as follows:

— magnesium: 285,2 nm;

— calcium: 422,7 nm;

— manganese: 279,5 nm;

— iron: 248,3 nm;

— copper: 324,8 nm;

— sodium: 589,0 nm;

— potassium: 766,5 nm.

For ICP/ES, the commonly 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;

— sodium: 589,00 nm;

— potassium: 766,50 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 hydrochloric acid (5.2) or 5 ml/100 ml nitric acid (5.3)] as the corresponding calibration solution, as well as lanthanum chloride/cesium chloride concentrations, if required.

If the test solution is used without dilution, then further addition of hydrochloric acid (5.2) or nitric acid (5.3) is not necessary since the dilution already contains acid added after the ashing step.

ISO 21400[2] provides a method for ICP/ES determination of sulfur in cellulose nanocrystals, which may be followed in general for the determination of metals in cellulose nanocrystals or other samples for which the method has been validated.

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.

12 Expression of results

Calculate the acid-soluble content of each element in the test specimen using Formula (1):

$$w_e = \frac{f \rho_e V}{m} \quad (1)$$

where

w_e is the acid-soluble content of the particular element in the test specimen, in milligrams per kilogram (mg/kg);

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

ρ_e is the concentration of the particular element in the test solution, corrected for the blank, as obtained from the calibration plot, in milligrams per litre (mg/l);

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

m is the mass of test specimen used for ashing, on an oven-dry basis, in grams (g).

Calculate the mean of the replicate determinations and express it to two significant figures for values below 10 mg/kg, and to three significant figures for values of 10 mg/kg and above. When an element is not detected, the result shall be expressed as "below the detection limit (x mg/kg)", where x (mg/kg) is the detection limit of the instrument for that element.

NOTE Precision values are given in Annex A.

13 Test report

The test report shall include the following information:

a) a reference to this document;

b) the date and place of testing;

c) all information for complete identification of the sample;

d) the technique used for element determination (AAS or ICP/ES);

e) the result, expressed as indicated in Clause 12;

f) any departure from the procedure described in this document or any other circumstances which could have affected the result.

Annex A
(informative)

Precision

A.1 General — Pulp, paper and board

In December 2009, an international round-robin test was performed in which six laboratories from five different countries participated.

Six samples of different types of pulp, paper and board were tested. The samples were submitted to the participating laboratories for testing according to this document. In some cases, the results were considered as outliers and were not included in the precision statement. In particular, the acid-soluble copper content was quite low in many cases, and some laboratories were not able to measure the acid-soluble copper. Reproducibility and repeatability data (mean values and coefficients of variation) for each type of sample are shown in Tables A.1 to A.12.

The calculations were made in accordance with ISO/TR 24498[3].

The repeatability and reproducibility limits reported are estimates of the maximum difference which should be expected in 19 out of 20 instances when comparing two test results for materials similar to those described under similar test conditions. These estimates may not be valid for different materials or different test conditions.

NOTE Repeatability and reproducibility limits were calculated by multiplying the repeatability and reproducibility standard deviations by 2,77, where 2,77 = 1,96 √2.

A.2 Repeatability — Pulp, paper and board

Table A.1 — Bleached softwood: Estimation of the repeatability of the test method

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_r mg/kg	Coefficient of variation $C_{V,r}$ %	Repeatability limit r mg/kg
Magnesium (Mg)	6	213	6,7	3,3	19,3
Calcium (Ca)	6	38,5	2,4	6,1	6,5
Manganese (Mn)	6	0,32	0,05	16,9	0,2
Iron (Fe)	6	23,5	0,60	2,5	1,6
Copper (Cu)	5	0,37	0,04	12,3	0,1
Sodium (Na)	6	186	3,2	1,7	9,0
Potassium (K)	6	7,8	0,69	8,7	1,9

Table A.2 — Bleached hardwood: Estimation of the repeatability of the test method

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_r mg/kg	Coefficient of variation $C_{V,r}$ %	Repeatability limit r mg/kg
Magnesium (Mg)	5	331	3,4	1,0	9,5

Table A.2 *(continued)*

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Repeatability limit
			s_r	$C_{V,r}$	r
		mg/kg	mg/kg	%	mg/kg
Calcium (Ca)	6	45,7	1,4	3,2	4,0
Manganese (Mn)	6	0,64	0,01	1,8	0,03
Iron (Fe)	6	32,6	0,70	2,2	1,9
Copper (Cu)	4	0,15	0,02	11,5	0,05
Sodium (Na)	6	281	5,2	1,8	14,3
Potassium (K)	6	8,0	0,26	3,2	0,7

Table A.3 — Chemo-thermo-mechanical pulp (CTMP): Estimation of the repeatability of the test method

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Repeatability limit
			s_r	$C_{V,r}$	r
		mg/kg	mg/kg	%	mg/kg
Magnesium (Mg)	6	19,8	0,19	1,0	0,5
Calcium (Ca)	6	142	7,8	5,5	21,6
Manganese (Mn)	6	0,21	0,03	12,1	0,07
Iron (Fe)	5	1,1	0,13	11,6	0,4
Copper (Cu)	4	0,23	0,02	6,6	0,04
Sodium (Na)	6	1 070	14,5	1,4	40,3
Potassium (K)	5	6,8	0,23	3,5	0,6

Table A.4 — Uncoated paper: Estimation of the repeatability of the test method

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Repeatability limit
			s_r	$C_{V,r}$	r
		mg/kg	mg/kg	%	mg/kg
Magnesium (Mg)	6	328	7,0	2,1	19,3
Calcium (Ca)	5	39 900	454	1,1	1 260
Manganese (Mn)	6	13,1	0,26	2,0	0,7
Iron (Fe)	6	77,2	1,2	1,5	3,2
Copper (Cu)	5	0,35	0,06	18,4	0,2
Sodium (Na)	6	1 370	37,9	2,8	105
Potassium (K)	5	23,0	0,80	3,5	2,2

Table A.5 — Coated paper: Estimation of the repeatability of the test method

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Repeatability limit
			s_r	$C_{V,r}$	r
		mg/kg	mg/kg	%	mg/kg
Magnesium (Mg)	6	1 830	104	5,7	289
Calcium (Ca)	6	107 000	365	0,3	1 010

Table A.5 *(continued)*

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_r mg/kg	Coefficient of variation $C_{V,r}$ %	Repeatability limit r mg/kg
Manganese (Mn)	6	8,6	0,12	1,4	0,3
Iron (Fe)	6	267	10,3	3,9	28,6
Copper (Cu)	5	0,71	0,09	12,2	0,2
Sodium (Na)	6	1 560	54,4	3,5	151
Potassium (K)	6	42,7	1,3	3,0	3,5

Table A.6 — Board: Estimation of the repeatability of the test method

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_r mg/kg	Coefficient of variation $C_{V,r}$ %	Repeatability limit r mg/kg
Magnesium (Mg)	6	234	4,1	1,7	11,3
Calcium (Ca)	6	19 800	471	2,4	1 300
Manganese (Mn)	6	10,1	0,27	2,6	0,7
Iron (Fe)	6	155	7,1	4,5	19,6
Copper (Cu)	5	1,0	0,15	15,1	0,4
Sodium (Na)	6	620	8,5	1,4	23,6
Potassium (K)	6	21,0	0,51	2,4	1,4

A.3 Reproducibility — Pulp, paper and board

Table A.7 — Bleached softwood: Estimation of the reproducibility of the test method

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_R mg/kg	Coefficient of variation $C_{V,R}$ %	Reproducibility limit R mg/kg
Magnesium (Mg)	6	213	44,8	21,0	124
Calcium (Ca)	6	38,5	9,7	25,3	26,9
Manganese (Mn)	6	0,32	0,06	17,2	0,15
Iron (Fe)	6	23,5	3,4	14,6	9,49
Copper (Cu)	5	0,37	0,36	97,6	0,99
Sodium (Na)	6	186	15,4	8,3	42,8
Potassium (K)	6	7,8	6,6	84,3	18,3

Table A.8 — Bleached hardwood: Estimation of the reproducibility of the test method

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_R mg/kg	Coefficient of variation $C_{V,R}$ %	Reproducibility limit R mg/kg
Magnesium (Mg)	5	331	78,6	23,7	218
Calcium (Ca)	6	45,7	11,0	24,1	27,0

Table A.8 *(continued)*

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Reproducibility limit
			s_R	$C_{V,R}$	R
		mg/kg	mg/kg	%	mg/kg
Manganese (Mn)	6	0,64	0,08	12,7	0,23
Iron (Fe)	6	32,6	9,7	29,9	27,0
Copper (Cu)	4	0,15	0,13	84,0	0,36
Sodium (Na)	6	281	37,4	13,3	103
Potassium (K)	6	8,0	5,2	65,0	14,3

Table A.9 — Chemo-thermo-mechanical pulp (CTMP): Estimation of the reproducibility of the test method

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Reproducibility limit
			s_R	$C_{V,R}$	R
		mg/kg	mg/kg	%	mg/kg
Magnesium (Mg)	6	19,8	1,3	6,6	3,64
Calcium (Ca)	6	142	18,4	12,9	50,9
Manganese (Mn)	6	0,21	0,07	33,2	0,20
Iron (Fe)	5	1,1	0,40	35,3	1,12
Copper (Cu)	4	0,23	0,21	89,0	0,57
Sodium (Na)	6	1 070	118	11,1	328
Potassium (K)	5	6,8	2,4	35,2	6,59

Table A.10 — Uncoated paper: Estimation of the reproducibility of the test method

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Reproducibility limit
			s_R	$C_{V,R}$	R
		mg/kg	mg/kg	%	mg/kg
Magnesium (Mg)	6	328	38,6	11,8	107
Calcium (Ca)	5	39 900	3 450	8,6	9 550
Manganese (Mn)	6	13,1	2,9	22,1	8,0
Iron (Fe)	6	77,2	20,5	26,5	56,7
Copper (Cu)	5	0,35	0,17	49,0	0,5
Sodium (Na)	6	1 370	183	13,4	508
Potassium (K)	5	23,0	7,6	33,2	21,1

Table A.11 — Coated paper: Estimation of the reproducibility of the test method

Element	Number of laboratories	Mean value	Standard deviation	Coefficient of variation	Reproducibility limit
			s_R	$C_{V,R}$	R
		mg/kg	mg/kg	%	mg/kg
Magnesium (Mg)	6	1 830	288	15,8	799
Calcium (Ca)	6	107 000	11 600	10,8	32 200
Manganese (Mn)	6	8,6	2,4	27,5	6,6

Table A.11 *(continued)*

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_R mg/kg	Coefficient of variation $C_{V,R}$ %	Reproducibility limit R mg/kg
Iron (Fe)	6	267	102	38,1	282
Copper (Cu)	5	0,71	0,16	22,2	0,4
Sodium (Na)	6	1 560	286	18,3	791
Potassium (K)	6	42,7	29,4	68,7	81,3

Table A.12 — Board: Estimation of the reproducibility of the test method

Element	Number of laboratories	Mean value mg/kg	Standard deviation s_R mg/kg	Coefficient of variation $C_{V,R}$ %	Reproducibility limit R mg/kg
Magnesium (Mg)	6	234	25,2	10,8	69,9
Calcium (Ca)	6	19 800	2 890	14,6	8 000
Manganese (Mn)	6	10,1	1,5	14,7	4,1
Iron (Fe)	6	155	32,5	20,9	90,1
Copper (Cu)	5	1,0	0,37	37,4	1,0
Sodium (Na)	6	620	139	22,4	385
Potassium (K)	6	21,0	12,1	57,6	33,5

A.4 General — Cellulose nanomaterials

The acid-soluble metal content of four cellulose nanomaterial samples was determined in an international round-robin study in which nine laboratories from eight countries participated.

In some cases, the results were considered as outliers and were not included in the precision statement. In particular, acid-soluble manganese and copper, as well as acid-soluble iron and potassium to a lesser extent, were present at very low levels in all samples, such that it was difficult to obtain good repeatability for these elements. Some outlier data points were therefore eliminated from the calculations. Reproducibility and repeatability data (mean values and coefficients of variation) for each type of sample are shown in Tables A.13 to A.20.

The calculations were made in accordance with ISO/TR 24498[3].

The repeatability and reproducibility limits reported are estimates of the maximum difference which should be expected in 19 of 20 instances, when comparing two test results for materials similar to those described under similar test conditions. These estimates may not be valid for different materials or different test conditions.

NOTE Repeatability and reproducibility limits were calculated by multiplying the repeatability and reproducibility standard deviations by 2,77, where 2,77 = 1,96 √2.