

INTERNATIONAL STANDARD

ISO 5796

Second edition
2000-09-01

Rubber compounding ingredients — Natural calcium carbonate — Test methods

*Ingrédients de mélange du caoutchouc — Carbonate de calcium naturel —
Méthodes d'essai*



Reference number
ISO 5796:2000(E)

© ISO 2000

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.

© ISO 2000

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.ch
Web www.iso.ch

Printed in Switzerland

Contents

Page

Foreword.....	iv
1 Scope	1
2 Normative references	1
3 Sampling.....	2
4 Methods of test	2
5 Test report	10
Annex A (normative) Determination of total copper content — Atomic absorption method.....	11
Annex B (normative) Determination of total manganese content — Atomic absorption method.....	14
Annex C (normative) Determination of total iron content — Atomic absorption method.....	17
Annex D (informative) Classification of natural calcium carbonate and typical physical and chemical properties	20

Rubber compounding ingredients — Natural calcium carbonate — Test methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

1.1 This International Standard specifies the methods to be used for the evaluation of natural calcium carbonate (chalk or limestone) ground to a dry powder for use in the rubber industry.

NOTE 1 Classification of natural calcium carbonate according to fineness and chemical purity and typical physical and chemical properties for use in the rubber industry are given in informative annex D.

NOTE 2 This International Standard does not cover calcium carbonates prepared by precipitation from solution.

1.2 There are two sets of analytical methods listed in this International Standard. In the body of the text (4.8.2 to 4.8.4), the traditional spectrophotometric methods are given; these are obsolescent, time-consuming and use a chlorinated solvent. It is recommended that these methods be phased out and replaced by the atomic absorption methods listed in annexes A, B and C.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings.*

ISO 787-2:1981, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C.*

ISO 787-10:1993, *General methods of test for pigments and extenders — Part 10: Determination of density — Pyknometer method.*

ISO 3262-1:1997 *Extendors for paints — Specifications and methods of test — Part 1: Introduction and general test methods.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

ISO 15528:2000, *Paints, varnishes and raw materials for paints and varnishes — Sampling.*

3 Sampling

Sampling shall be carried out in accordance with ISO 15528.

4 Methods of test

4.1 General

During the analysis, all reagents used shall be of recognized analytical reagent quality. Distilled water or water of equal purity shall be used throughout the tests.

4.2 Residue on sieve

Determine the sieve residue in accordance with ISO 3262-1, using 45 μm and 125 μm opening test sieves as defined by ISO 565.

4.3 Calcium carbonate (on dry sample)

Determine the calcium carbonate content in accordance with ISO 3262-1.

4.4 Loss on heating at 105 °C

Determine the loss on heating at 105 °C in accordance with ISO 787-2.

4.5 Loss on ignition at 1 000 °C (on dry sample)

Determine the loss on ignition at 1 000 °C in accordance with ISO 3262-1.

4.6 Matter insoluble in hydrochloric acid

4.6.1 Reagent

4.6.1.1 Hydrochloric acid, 73 g/dm³ solution.

Dilute 170 cm³ of concentrated (35 % by mass) hydrochloric acid ($\rho = 1,18 \text{ g/cm}^3$) to 1 dm³ with water and mix.

4.6.2 Apparatus

4.6.2.1 **Beaker**, of capacity 250 cm³, **watch glass**, suitable for covering the beaker, and **glass rod** suitable for stirring.

4.6.2.2 **Analytical balance**, accurate to 0,1 mg.

4.6.2.3 **Sintered-glass crucible**, porosity grade P 40, in conformity with the requirements of ISO 4793.

4.6.2.4 **Oven**, capable of being maintained at a temperature of 105 °C \pm 2 °C.

4.6.2.5 **Desiccator**.

4.6.3 Procedure

4.6.3.1 Weigh, to the nearest 1 mg, approximately 2 g of sample into the beaker (4.6.2.1).

4.6.3.2 Pour 100 cm³ of hydrochloric acid (4.6.1.1) into the beaker and cover with a watch-glass.

4.6.3.3 Swirl the mixture gently at room temperature, avoiding the formation of foam. Boil the mixture gently for 5 min to 10 min, then leave to cool for 30 min to 60 min, stirring from time to time.

4.6.3.4 Filter off the insoluble matter through the crucible (4.6.2.3) which has previously been washed, dried at 105 °C and weighed. Wash with water until the washings are free from chloride. Discard the filtrate and the washings.

4.6.3.5 Dry the crucible containing the insoluble residue in the oven (4.6.2.4), maintained at 105 °C ± 2 °C, until constant mass is achieved, i.e. until further oven-drying, cooling and weighing yields a mass change of less than 1 mg.

4.6.3.6 Cool in the desiccator (4.6.2.5).

4.6.3.7 Weigh to the nearest 1 mg.

4.6.4 Expression of results

The matter insoluble in hydrochloric acid, M_{is} , is given, as a percentage by mass, by the following equation:

$$M_{is} = \frac{m_2 - m_1}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the empty dried crucible;

m_2 is the mass, in grams, of the crucible containing the insoluble matter.

Express the result to the nearest 0,1 % by mass.

4.7 Alkalinity

4.7.1 Reagents

4.7.1.1 **Distilled water**, boiled to remove carbon dioxide.

4.7.1.2 **Phenolphthalein**, 0,5 % by mass solution in 95 % by volume ethanol.

4.7.1.3 **Hydrochloric acid**, standard volumetric solution, $c(\text{HCl}) = 0,01 \text{ mol/dm}^3$.

4.7.2 Apparatus

4.7.2.1 **Analytical balance**, accurate to 0,1 mg.

4.7.2.2 **Conical flask**, narrow-mouth, of capacity 250 cm³.

4.7.2.3 **Filter paper**, fine grade.

4.7.2.4 **Burette**, accurate to 0,1 cm³.

4.7.3 Procedure

4.7.3.1 Weigh, to the nearest 1 mg, about 10 g of sample and place this test portion in the flask (4.7.2.2). Add 150 cm³ of distilled water (4.7.1.1). Leave the mixture for 1 h, shaking it from time to time.

4.7.3.2 Filter the mixture through the filter paper (4.7.2.3) and keep all the residue on the filter. Wash three times with a minimum amount of distilled water, adding the washings to the filtrate.

4.7.3.3 Add a few drops of phenolphthalein solution (4.7.1.2) as indicator to the filtrate and titrate with hydrochloric acid (4.7.1.3) until colourless. Read the volume used for the titration to the nearest 0,1 cm³.

4.7.4 Expression of results

The alkalinity, w , expressed in grams of sodium carbonate (Na₂CO₃) per 100 g of sample, is given by the following equation:

$$w = \frac{V \times c \times 0,000\ 53}{m} \times 100$$

where

V is the volume of HCl, in cubic centimetres, used for the titration;

c is the actual concentration, expressed in moles of HCl per cubic decimetre of hydrochloric acid (4.7.1.3);

m is the mass, in grams, of the test portion;

0,000 53 is the mass, in grams, of sodium carbonate corresponding to 100 cm³ of hydrochloric acid, $c(\text{HCl}) = 0,010 \text{ mol/dm}^3$.

4.8 Determination of total copper, total manganese and total iron

4.8.1 Preparation of stock test solution

4.8.1.1 Reagents

4.8.1.1.1 Nitric acid, $\rho = 1,42 \text{ g/cm}^3$.

4.8.1.1.2 Hydrofluoric acid, 40 % by mass solution.

4.8.1.1.3 Sulfuric acid, 50 % by volume solution.

4.8.1.1.4 Octyl alcohol (octan-1-ol).

4.8.1.1.5 Hydrochloric acid, $\rho = 1,18 \text{ g/cm}^3$ (35 % by mass).

4.8.1.2 Apparatus

4.8.1.2.1 Beaker, of capacity 250 cm³.

4.8.1.2.2 Volumetric flask, of capacity 250 cm³.

4.8.1.2.3 Platinum crucible, of capacity 20 cm³.

4.8.1.2.4 Muffle furnace.

4.8.1.2.5 Fume cupboard.

4.8.1.2.6 Quartz triangle.

4.8.1.2.7 Analytical balance, accurate to 0,1 mg.

4.8.1.3 Procedure

4.8.1.3.1 Weigh, to the nearest 1 mg, about 5 g of sample into the beaker (4.8.1.2.1). Dissolve this test portion carefully in 25 cm³ of water and 15 cm³ of nitric acid (4.8.1.1.1) and heat to boiling. If foam tends to rise during the dissolution of the test portion, break the foam by adding a drop of octyl alcohol (4.8.1.1.4).

4.8.1.3.2 Filter through a medium filter paper, wash the paper with hot water and allow the combined filtrate plus washings to cool. Then transfer the solution into the volumetric flask (4.8.1.2.2) and retain for 4.8.1.3.7.

4.8.1.3.3 Lift out the filter paper, fold it carefully to enclose any residue and place in the platinum crucible (4.8.1.2.3). Heat gently until dry, then heat more to char the paper. Then place the crucible in the muffle furnace (4.8.1.2.4) at 1 000 °C ± 50 °C for 30 min to oxidize and to remove all char.

4.8.1.3.4 Cool the crucible and add 2 cm³ of hydrofluoric acid (4.8.1.1.2), drop by drop, to the crucible in such a way that all the contents are wetted. Then add 0,5 cm³ of sulfuric acid (4.8.1.1.3) drop by drop.

Place the crucible on a hotplate in the fume cupboard (4.8.1.2.5) and evaporate to dryness, taking care to avoid overheating and consequent bumping or spitting. Then continue heating until white fumes appear.

4.8.1.3.5 Transfer the crucible, still in the fume cupboard, to a quartz triangle on a stand and heat to a dull red heat until all white fumes have been driven off.

4.8.1.3.6 Allow the crucible to cool. Add 5 cm³ of water and 1 cm³ of nitric acid (4.8.1.1.1) and warm on a hotplate. Stir with a glass rod to dissolve all salts.

4.8.1.3.7 Cool and transfer the solution quantitatively to the flask containing the original acid-soluble portion (see 4.8.1.3.2), rinsing the crucible thoroughly with water into the flask.

4.8.1.3.8 Finally, dilute with water to the 250 cm³ mark.

The flask now contains the stock test solution, aliquots of which will be required for determination of copper, manganese and iron.

4.8.2 Copper (total) — Spectrophotometric method

4.8.2.1 Reagents

4.8.2.1.1 Biquinolyl reagent, solution.

Dissolve 0,03 g of 2,2'-biquinoline in 100 cm³ of *n*-hexanol (4.8.2.1.8) that has been freshly distilled from solid sodium hydroxide.

4.8.2.1.2 Hydroxylammonium chloride, solution.

Dissolve 25 g of hydroxylammonium chloride in about 80 cm³ of water. Filter, if necessary, and dilute to 100 cm³ with water.

If any appreciable amounts of copper are present in the solution, extract with successive 10 cm³ portions of a 0,01 % by mass solution of dithizone in carbon tetrachloride until there is no more violet coloration due to copper, hence no change in the green colour of the dithizone solution. Then extract the solution with carbon tetrachloride until all colour has been removed from the aqueous solution.

4.8.2.1.3 Sodium acetate buffer solution.

Dissolve 136 g of sodium acetate trihydrate in water and dilute to 1 dm³ with water. If the reagent contains more than a trace of copper, purify this solution by extraction with 0,01 % by mass dithizone solution in carbon tetrachloride as for the hydroxylammonium chloride solution (4.8.2.1.2).

ISO 5796:2000(E)

4.8.2.1.4 Hydroquinone, solution.

Dissolve 1 g of hydroquinone in 100 cm³ of redistilled ethanol.

4.8.2.1.5 Copper, standard stock solution.

Dissolve exactly 0,1 g of pure copper in 3 cm³ of nitric acid (4.8.1.1.1), add 1 cm³ of sulfuric acid (4.8.1.1.3) and evaporate in the fume cupboard until white fumes appear. Allow to cool, dissolve the residue in water and dilute to 500 cm³.

1 cm³ of this solution contains 200 µg of Cu.

4.8.2.1.6 Copper, 4 µg/cm³ standard working solution.

Dilute exactly 5 cm³ of the stock solution (4.8.2.1.5) to 250 cm³ with water.

1 cm³ of this solution contains 4 µg of Cu. This solution is used for the calibration of the 1 cm spectrometer cells.

4.8.2.1.7 Copper, 1 µg/cm³ standard working solution.

For the calibration of 4 cm cells, dilute exactly 5 cm³ of the stock solution (4.8.2.1.5) to 1 000 cm³ with water, to give a solution containing 1 µg of copper per cubic centimetre.

4.8.2.1.8 *n*-hexyl alcohol (hexan-1-ol).

4.8.2.2 Apparatus

Ordinary laboratory apparatus, plus the following:

4.8.2.2.1 Analytical balance, accurate to 0,1 mg.

4.8.2.2.2 Spectrometer, capable of being operated at 540 nm, with 1 cm and/or 4 cm cells.

4.8.2.2.3 Separating funnels, of capacity 250 cm³.

4.8.2.2.4 One-mark volumetric flask, of capacity 10 cm³.

4.8.2.3 Procedure

4.8.2.3.1 Transfer a 100 cm³ aliquot portion of the stock test solution (see 4.8.1) to a separating funnel (4.8.2.2.3) and add 2,5 cm³ of hydroxylammonium chloride solution (4.8.2.1.2) and 25 cm³ of sodium acetate buffer solution (4.8.2.1.3).

4.8.2.3.2 Shake with 6 cm³ of biquinolyl reagent (4.8.2.1.1) for 5 min and allow the phases to separate.

4.8.2.3.3 Run the lower, aqueous, layer into another separating funnel, add 2 cm³ of hydroxylammonium chloride solution and extract again with 2,5 cm³ of biquinolyl reagent.

4.8.2.3.4 Separate the phases and again extract the aqueous layer with 2 cm³ of biquinolyl reagent.

4.8.2.3.5 Combine the three organic extracts in the one-mark volumetric flask (4.8.2.2.4) containing 0,5 cm³ of hydroquinone solution (4.8.2.1.4) and dilute the solution to volume with *n*-hexyl alcohol (4.8.2.1.8).

4.8.2.3.6 Measure the absorbance of the solution in 1 cm or 4 cm cells with the spectrometer (4.8.2.2.2) set at a wavelength of 540 nm.

4.8.2.3.7 Measure also the absorbance (at the same wavelength and in the same size cell) of a reagent blank solution prepared in the same way as the sample solution but omitting the stock solution. Subtract the absorbance of this blank solution from the absorbance found in 4.8.2.3.6.

4.8.2.3.8 Obtain the amount of copper in the aliquot portion taken in 4.8.2.3.1 by use of the calibration curve plotted in 4.8.2.4.4.

4.8.2.4 Calibration

4.8.2.4.1 Use the standard copper working solution containing 4 µg of copper per cm³ (4.8.2.1.6) to calibrate the 1 cm cell and the solution containing 1 µg of copper per cm³ (4.8.2.1.7) for the 4 cm cell, as follows:

4.8.2.4.2 Transfer aliquot portions from 0 to 25 cm³ into separating funnels (4.8.2.2.3). Add 1,5 cm³ of concentrated hydrochloric acid and dilute each solution to 100 cm³ with water.

4.8.2.4.3 Add hydroxylammonium chloride solution and buffer solution, extract the copper with biquinolyl reagent and measure the absorbances as described in 4.8.2.3.6.

4.8.2.4.4 Plot the relationship of the absorbance to the copper concentration for the range 0 to 25 µg of copper (4 cm cells) to obtain the calibration curve.

NOTE A solution containing 25 µg of copper in 10 cm³ of organic extract should have an approximate absorbance reading of 0,984 in 4 cm cells or 0,246 in 1 cm cells.

4.8.2.5 Expression of results

The total copper content in the sample, w_{Cu} , expressed in milligrams per kilogram, is given by the following equation:

$$w_{\text{Cu}} = \frac{2,5m_2}{m_1}$$

where

m_1 is the mass in grams, of the test portion;

m_2 is the mass, in micrograms, of copper found in the aliquot portion.

4.8.3 Manganese (total) — Spectrophotometric method

4.8.3.1 Reagents

4.8.3.1.1 Phosphoric acid, solution.

To 700 cm³ of water add 200 cm³ of orthophosphoric acid ($\rho = 1,75 \text{ g/cm}^3$). Cool and dilute to 1 dm³.

4.8.3.1.2 Manganese, standard solution.

Dissolve 0,1436 g of potassium permanganate in 250 cm³ of water, reduce with a very slight excess of sulfur dioxide gas dissolved in water and dilute to 500 cm³.

1 cm³ of this solution contains 100 µg of Mn.

4.8.3.1.3 Potassium periodate.

4.8.3.2 Apparatus

Ordinary laboratory apparatus, plus the following:

4.8.3.2.1 Analytical balance, accurate to 0,1 mg.

4.8.3.2.2 Spectrometer, capable of being operated at 520 nm to 525 nm, with 4 cm cells.

4.8.3.2.3 Volumetric flask, of capacity 100 cm³.

4.8.3.2.4 Beakers, of capacity 250 cm³.

4.8.3.3 Procedure

4.8.3.3.1 Transfer a 50 cm³ aliquot portion of the stock test solution (see 4.8.1) to a 250 cm³ beaker (4.8.3.2.4). Add 25 cm³ of phosphoric acid (4.8.3.1.1) and 0,5 g of potassium periodate (4.8.3.1.3).

4.8.3.3.2 Heat to boiling and simmer gently until the pink permanganate colour begins to develop.

4.8.3.3.3 Boil the solution gently for 3 min to 4 min, cool and dilute to 100 cm³ in the one-mark volumetric flask (4.8.3.2.3).

Fill a cell of the spectrometer (4.8.3.2.2) with this solution.

4.8.3.3.4 Measure the absorbance of the solution in the cell at a wavelength of 520 nm to 525 nm.

4.8.3.3.5 Measure the reagent blank in a similar manner and deduct this value from the absorbance of the test solution.

4.8.3.3.6 Read the mass of manganese, in micrograms, from the calibration curve (see 4.8.3.4).

4.8.3.4 Calibration

To a series of 250 cm³ beakers (4.8.3.2.4), add a range of accurately measured volumes of standard manganese solution (4.8.3.1.2) between 0 and 30 cm³. Treat them as described in 4.8.3.3 and construct a calibration curve by plotting the amount of manganese, in micrograms, against absorbance.

4.8.3.5 Expression of results

The total manganese content in the sample, w_{Mn} , is expressed, in milligrams per kilogram, by the following equation:

$$w_{\text{Mn}} = \frac{5m_3}{m_1}$$

where

m_1 is the mass, in grams, of the test portion;

m_3 is the mass, in micrograms, of manganese found in the aliquot portion.

4.8.4 Iron (total) — Spectrophotometric method

4.8.4.1 Reagents

4.8.4.1.1 Bipyridine, solution.

Dissolve 0,2 g of 2,2'-bipyridine in 100 cm³ of 7,3 g/dm³ hydrochloric acid.

4.8.4.1.2 Sodium acetate buffer solution.

Dissolve 136 g of sodium acetate trihydrate in water and dilute to 1 dm³ with water.

4.8.4.1.3 Iron, standard stock solution.

Dissolve exactly 0,5 g of pure iron in 15 cm³ of 73 g/dm³ hydrochloric acid (4.6.1.1), transfer to a 1 000 cm³ volumetric flask and dilute to the mark with water.

4.8.4.1.4 Iron, standard working solution.

Dilute exactly 25 cm³ of the stock solution (4.8.4.1.3) to 250 cm³ with water.

1 cm³ of this solution contains 50 µg of Fe.

4.8.4.1.5 Hydroxylammonium chloride, 5 g/100 cm³ solution in water.

4.8.4.2 Apparatus

Ordinary laboratory apparatus and:

4.8.4.2.1 Analytical balance, accurate to 0,1 mg.

4.8.4.2.2 Spectrometer, capable of being operated at 520 nm, with 1 cm cells.

4.8.4.2.3 Volumetric flasks, of capacity 50 cm³ and 1 000 cm³.

4.8.4.2.4 pH-meter or pH-indicator paper, sensitive to 0,1 pH units.

4.8.4.3 Procedure

4.8.4.3.1 Transfer a 10 cm³ aliquot of the stock test solution (4.8.1) to a 100 cm³ beaker and add sodium acetate buffer solution (4.8.4.1.2) until the pH is 4.8 to 5.0.

4.8.4.3.2 Add 1 cm³ of hydroxylammonium chloride solution (4.8.4.1.5) and 5 cm³ of bipyridine solution (4.8.4.1.1). Transfer quantitatively to a 50 cm³ volumetric flask (4.8.4.2.3) and dilute to 50 cm³ with water.

4.8.4.3.3 Measure the absorbance of the solution in the spectrometer (4.8.4.2.2) at a wavelength of 520 nm in a 1 cm cell.

4.8.4.3.4 Measure also the absorbance (at the same wavelength and in the same size cell) of a reagent blank solution prepared in the same way as the test solution but omitting the stock test solution. Subtract the absorbance of the reagent blank from that of the test solution obtained in 4.8.4.3.3.

Read the mass of iron, in micrograms, from the calibration curve (see 4.8.4.4).

4.8.4.4 Calibration

To a series of 50 cm³ graduated flasks (4.8.4.2.3), add a range of accurately measured volumes from 0 to 10 cm³ of the standard iron working solution (4.8.4.1.4). Treat them as described in 4.8.4.3 and construct a calibration curve by plotting the amount of iron, in micrograms, against absorbance.

4.8.4.5 Expression of results

The total iron content in the sample, w_{Fe} , expressed in milligrams per kilogram, is given by the following equation:

$$w_{\text{Fe}} = \frac{25m_4}{m_1}$$

where

m_1 is the mass, in grams, of the test portion;

m_4 is the mass, in micrograms, of iron found in the aliquot portion.

NOTE See annexes A, B and C for alternative, atomic absorption, test methods for copper, manganese and iron.

5 Test report

The test report shall include the following information:

- a) a reference to this International Standard;
- b) all details necessary for the complete identification of the sample;
- c) the test method used for the determination of the total copper, total manganese and total iron contents (i.e. spectrophotometric or atomic absorption);
- d) the test conditions;
- e) the mass of the test portion used;
- f) the results obtained;
- g) any deviation from this International Standard;
- h) the date of the test.

Annex A (normative)

Determination of total copper content — Atomic absorption method

A.1 Principle

A test portion is dissolved in hydrochloric acid and the insoluble residue is digested with hydrofluoric acid and sulfuric acid and the silicon is volatilized as silicon tetrafluoride (see 4.8.1).

Any metals in the digested test portion are dissolved in nitric acid, then the solutions are combined, diluted and aspirated into the flame of an atomic absorption spectrometer set at a wavelength of 324,7 nm.

A.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

A.2.1 Acetylene, compressed-gas supply.

A.2.2 Air, compressed-gas supply.

A.2.3 Hydrochloric acid, 10 % by mass solution.

Dilute 20 cm³ of 35 % by mass hydrochloric acid ($\rho = 1,18 \text{ g/cm}^3$) with 50 cm³ of water.

A.2.4 Hydrofluoric acid, 40 % by mass solution ($\rho = 1,13 \text{ g/cm}^3$).

A.2.5 Sulfuric acid, 98 % by mass solution ($\rho = 1,84 \text{ g/cm}^3$).

A.2.6 Nitric acid, 68 % by mass solution ($\rho = 1,42 \text{ g/cm}^3$).

A.2.7 Copper, standard solution corresponding to 1 g of Cu per cubic decimetre.

Dissolve 1,000 g \pm 0,001 g of high-purity copper turnings in a mixture of 10 cm³ of water and 5 cm³ of nitric acid (A.2.6) in a 100 cm³ beaker. Boil under a fume hood to expel oxides of nitrogen. Cool, transfer to a 1 dm³ volumetric flask, make up to the mark with water and mix.

1 cm³ of this standard solution contains 1 mg of copper.

A.2.8 Copper, standard solution corresponding to 50 mg of Cu per cubic decimetre.

Pipette 50,0 cm³ of the 1 g/cm³ standard copper solution (A.2.7) into a 1 dm³ volumetric flask, add 5 cm³ of nitric acid (A.2.6), make up to the mark with water and mix.

1 cm³ of this standard solution contains 50 μg of copper.

A.2.9 Copper, standard solution corresponding to 10 mg of Cu per cubic decimetre.

Pipette 50,0 cm³ of the 50 mg/dm³ standard copper solution (A.2.8) into a 250 cm³ volumetric flask, add 1 cm³ of nitric acid (A.2.6), make up to the mark with water and mix.

1 cm³ of this standard solution contains 10 µg of copper.

NOTE Commercially available standard copper solutions may be used, if preferred, instead of A.2.7, A.2.8 and A.2.9.

A.3 Apparatus

Ordinary laboratory apparatus, plus the following:

A.3.1 Platinum dish, of capacity approximately 35 cm³.

A.3.2 Atomic absorption spectrometer, fitted with an air/acetylene burner.

A.3.3 Analytical balance, capable of weighing to 0,1 mg.

A.4 Procedure

A.4.1 Blank test

Carry out a blank test simultaneously with the determination, using the same reagents and procedures, but omitting the test portion.

A.4.2 Preparation of the calibration graph

A.4.2.1 Preparation of standard calibration solutions

Into a series of six 50 cm³ volumetric flasks, transfer the volumes of 10 mg/dm³ standard copper solution (A.2.9) indicated in Table A.1, dilute to the mark with water and mix.

Table A.1 — Standard calibration solutions for determination of copper

Volume of standard copper solution (A.2.9) cm ³	Corresponding copper content µg/cm ³
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

A.4.2.2 Spectrometric calibration

Aspirate in turn each of the standard calibration solutions prepared in A.4.2.1 into the flame of the atomic absorption spectrometer (A.3.2) and record their absorbances at a wavelength of 324,7 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

A.4.2.3 Plotting the graph

Plot a graph having the copper content, in micrograms per cubic centimetre, as the abscissa and the corresponding values of absorbance as the ordinate.

A.4.3 Determination

A.4.3.1 Preparation of the test solution

See 4.8.1.

A.4.3.2 Spectrometric measurement

Aspirate the test solution prepared in 4.8.1 and the blank test solution (see A.4.1) into the flame of the atomic absorption spectrometer and measure their absorbances at 324,7 nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of the absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest copper content, dilute 5 cm³ of the test solution to 50 cm³ with water, repeat the measurements and take the dilution into account in the expression of results.

A.5 Expression of results

By reference to the calibration graph, determine the copper contents corresponding to the absorbances of the test solution and the blank test solution.

Calculate the total copper content of the test portion, w_{Cu} , expressed in milligrams per kilogram, from the equation:

$$w_{\text{Cu}} = \frac{100 (M_1 - M_2)}{m}$$

where

M_1 is the copper content, in micrograms per cubic centimetre, of the test solution;

M_2 is the copper content, in micrograms per cubic centimetre, of the blank solution;

m is the mass, in grams, of the test portion.

If the test solution was diluted as described in A.4.3.2, multiply the right hand side of the equation by 10.

Express the result to the nearest 0,1 mg/kg.

Annex B (normative)

Determination of total manganese content — Atomic absorption method

B.1 Principle

The principle is the same as for the determination of total copper content (see annex A), except that the absorbance of the test solution is measured at 279,5 nm and is compared with the absorbance of manganese standard calibration solutions.

The method is applicable to the determination of manganese contents up to 125 mg/kg, and there is provision for extending the range to 1 250 mg/kg

B.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

B.2.1 Acetylene.

See A.2.1.

B.2.2 Air.

See A.2.2.

B.2.3 Hydrochloric acid, solution.

See A.2.3.

B.2.4 Hydrofluoric acid, solution.

See A.2.4.

B.2.5 Sulfuric acid, solution.

See A.2.5.

B.2.6 Nitric acid, solution.

See A.2.6.

B.2.7 Manganese, standard solution corresponding to 1 g of Mn per cubic decimetre.

Dissolve 1,000 g \pm 0,001 g of high-purity, oxide-free manganese in a mixture of 50 cm³ of water and 5 cm³ of nitric acid (B.2.6) in a 400 cm³ beaker. Boil under a fume hood to expel oxides of nitrogen. Cool, transfer to a 1 dm³ volumetric flask, make up to the mark with water and mix.

1 cm³ of this standard solution contains 1 mg of manganese.

B.2.8 Manganese, standard solution corresponding to 50 mg of Mn per cubic decimetre.

Pipette 50,0 cm³ of the 1 g/dm³ standard manganese solution (B.2.7) into a 1 dm³ volumetric flask, add 5 cm³ of nitric acid (B.2.6), dilute to the mark with water and mix.

1 cm³ of this standard solution contains 50 µg of manganese.

B.2.9 Manganese, standard solution corresponding to 10 mg of Mn per cubic decimetre.

Pipette 50,0 cm³ of the 50 mg/dm³ standard manganese solution (B.2.8) into a 250 cm³ volumetric flask, add 1 cm³ of nitric acid (B.2.6), make up to the mark with water and mix.

1 cm³ of this standard solution contains 10 µg of manganese.

NOTE Commercially available standard manganese solutions may be used, if preferred, instead of B.2.7, B.2.8 and B.2.9.

B.3 Apparatus

As specified in A.3.

B.4 Procedure

B.4.1 Blank test

See A.4.1.

B.4.2 Preparation of the calibration graph

B.4.2.1 Preparation of standard calibration solutions

Into a series of six 50 cm³ volumetric flasks, transfer the volumes of 10 mg/dm³ standard manganese solution (B.2.9) indicated in Table B.1, dilute to the mark with water and mix.

Table B.1 — Standard calibration solutions for determination of manganese

Volume of standard manganese solution (B.2.9) cm ³	Corresponding manganese content µg/cm ³
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

B.4.2.2 Spectrometric measurements

Aspirate in turn each of the standard calibration solutions prepared in B.4.2.1 into the flame of the atomic absorption spectrometer and record their absorbances at a wavelength of 279,5 nm, following the instrument manufacturer's instructions.

Aspirate water into the flame after each measurement.

B.4.2.3 Plotting the graph

Plot a graph having the manganese contents, in micrograms per cubic centimetre, as the abscissa and the corresponding values of absorbance as the ordinate.

B.4.3 Determination

B.4.3.1 Preparation of the test solution

See 4.8.1.

B.4.3.2 Spectrometric measurements

Aspirate the test solution prepared in B.4.3.1 and the blank test solution (see B.4.1) into the flame of the atomic absorption spectrometer and measure their absorbances at 279,5 nm following the instrument manufacturer's instructions. Repeat this procedure and record the mean values of the absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest manganese content, dilute 5 cm³ of the test solution to 50 cm³ with water, repeat the measurements and take the dilution into account in the expression of results.

B.5 Expression of results

By reference to the calibration graph, determine the manganese contents corresponding to the absorbances of the test solution and the blank test solution.

Calculate the total manganese content of the test portion, w_{Mn} , expressed in milligrams per kilogram, from the equation:

$$w_{\text{Mn}} = \frac{100 (M_3 - M_4)}{m}$$

where

M_3 is the manganese content, in micrograms per cubic centimetre, of the test solution;

M_4 is the manganese content, in micrograms per cubic centimetre, of the blank test solution;

m is the mass, in grams, of the test portion.

If the test solution was diluted as described in B.4.3.2, multiply the right-hand side of the equation by 10.

Express the result to the nearest 0,1 mg/kg.

Annex C (normative)

Determination of total iron content — Atomic absorption method

C.1 Principle

The principle is the same as for the determination of total copper content (see annex A), except that the absorbance of the test solution is measured at a wavelength of 248,3 nm and is compared with the absorbances of standard calibration iron solutions.

The method is applicable to the determination of iron contents up to 125 mg/kg, and there is provision for extending the range to 2 500 mg/kg.

C.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

C.2.1 Acetylene.

See A.2.1.

C.2.2 Air.

See A.2.2.

C.2.3 Hydrochloric acid, solution.

See A.2.3.

C.2.4 Hydrofluoric acid, solution.

See A.2.4.

C.2.5 Sulfuric acid, solution.

See A.2.5.

C.2.6 Iron, standard solution corresponding to 1 g of Fe per cubic decimetre.

Dissolve $1,000 \text{ g} \pm 0,001 \text{ g}$ of high-purity iron in a mixture of 10 cm^3 of water and 5 cm^3 of hydrochloric acid (C.2.3) in a 100 cm^3 beaker. Boil under a fume hood until dissolution is complete. Cool, transfer to a 1 dm^3 volumetric flask, make up to the mark with water and mix.

1 cm^3 of this standard solution contains 1 mg of iron.

C.2.7 Iron, standard solution corresponding to 50 mg of Fe per cubic decimetre.

Pipette $50,0 \text{ cm}^3$ of the 1 g/dm^3 standard iron solution (C.2.6) into a 1 dm^3 volumetric flask, add 5 cm^3 of hydrochloric acid (C.2.3), dilute to the mark with water and mix.

1 cm^3 of this standard solution contains $50 \mu\text{g}$ of iron.

C.2.8 Iron, standard solution corresponding to 10 mg of Fe per cubic decimetre.

Pipette 50,0 cm³ of the 50 mg/dm³ standard iron solution (C.2.7) into a 250 cm³ volumetric flask, add 1 cm³ of hydrochloric acid (C.2.3), make up to the mark with water and mix.

1 cm³ of this standard solution contains 10 µg of iron.

NOTE Commercially available standard iron solutions may be used, if preferred, instead of C.2.6, C.2.7 and C.2.8.

C.3 Apparatus

See A.3.

C.4 Procedure

C.4.1 Blank test

See A.4.1.

C.4.2 Preparation of the calibration graph

C.4.2.1 Preparation of standard calibration solutions

Into a series of six 50 cm³ volumetric flasks, transfer the volumes of 10 mg/dm³ standard iron solution (C.2.8) indicated in Table C.1, dilute to the mark with water and mix.

Table C.1 — Standard calibration solutions for determination of iron

Volume of standard iron solution (B.2.9) cm ³	Corresponding iron content µg/cm ³
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

C.4.2.2 Spectrometric measurements

Aspirate each of the standard calibration solutions prepared in C.4.2.1 into the flame of the atomic absorption spectrometer and record their absorbances at a wavelength of 248,3 nm, following the instrument manufacturer's instructions.

Aspirate water into the flame after each measurement.

C.4.2.3 Plotting the graph

Plot a graph having the iron contents, in micrograms per cubic centimetre, as the abscissa and the corresponding values of absorbance as the ordinate.

C.4.3 Determination

C.4.3.1 Preparation of the test solution

See 4.8.1.

C.4.3.2 Spectrometric measurements

Aspirate the test solution prepared in C.4.3.1 and the blank test solution (see C.4.1) into the flame of the atomic absorption spectrometer and measure their absorbances at 248,3 nm, following the instrument manufacturer's instructions.

Repeat this procedure and record the mean values of the absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest iron content, dilute 5 cm³ of the test solution to 100 cm³ with water, repeat the measurements and take the dilution into account in the expression of results.

C.5 Expression of results

By reference to the calibration graph, determine the iron contents corresponding to the absorbances of the test solution and the blank test solution.

Calculate the total iron content of the test portion, w_{Fe} , expressed in milligrams per kilogram, from the equation:

$$w_{\text{Fe}} = \frac{100 (M_5 - M_6)}{m}$$

where

M_5 is the iron content, in micrograms per cubic centimetre, of the test solution;

M_6 is the iron content, in micrograms per cubic centimetre, of the blank test solution;

m is the mass, in grams, of the test portion.

If the test solution was diluted as described in C.4.3.2, multiply the right-hand side of the equation by 20.

Express the result to the nearest 0,1 mg/kg.

Annex D (informative)

Classification of natural calcium carbonate and typical physical and chemical properties

NOTE This annex is given purely for the purpose of information, and does not constitute part of the standard.

D.1 Classification according to fineness and chemical purity

Six grades of natural calcium carbonate are defined in Table D.1, in which

A and B represent degrees of fineness;

1, 2 and 3 represent degrees of purity.

D.2 Typical values of physical and chemical properties

Typical values of the physical and chemical properties measured using the methods described in clause 4 are given in Table D.1.

Table D.1 — Typical values of physical and chemical properties

Property	Unit	Typical values					
		A1	A2	A3	B1	B2	B3
Residue on 45 µm sieve, max.	% by mass	0,5	0,5	0,5	5	5	5
Residue on 125 µm sieve, max.	% by mass	0,005	0,005	0,005	0,1	0,1	0,1
Calcium carbonate (on dry sample), min.	% by mass	98	96	94	98	96	94
Loss on heating at 105 °C, max.	% by mass	0,4	0,4	0,4	0,4	0,4	0,4
Loss on ignition at 1 000 °C (on dry sample)	% by mass	43 to 44,5	42 to 44,5	41 to 44,5	43 to 44,5	42 to 44,5	41 to 44,5
Alkalinity (as Na ₂ CO ₃), max.	% by mass	0,03	0,03	0,03	0,03	0,03	0,03
Copper (total), max.	mg/kg	15	30	30	15	30	30
Manganese (total), max.	mg/kg	100	400	400	100	400	400
Iron (total), max.	mg/kg	250	1 000	2 500	250	1 000	2 500
Density (typical)	g/cm ³	2,7	2,7	2,7	2,7	2,7	2,7

