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 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

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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 5796 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This second edition cancels and replaces the first edition (ISO 5796:1990), of which it constitutes a technical revision.

Annexes A, B and C form a normative part of this International Standard. Annex D is for information only.

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 *Extenders 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/dm^3 solution.

Dilute 170 cm^3 of concentrated (35 % by mass) hydrochloric acid (ρ = 1,18 g/cm^3) to 1 dm^3 with water and mix.

4.6.2 Apparatus

4.6.2.1 **Beaker,** of capacity 250 cm^3, **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 ± 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 cm^3 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(HCl) = 0,01 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 cm^3.

4.7.2.3 **Filter paper,** fine grade.

4.7.2.4 **Burette,** accurate to 0,1 cm^3.

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 cm^3 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 cm^3.

4.7.4 Expression of results

The alkalinity, w, expressed in grams of sodium carbonate (Na_2CO_3) 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 cm^3 of hydrochloric acid, c(HCl) = 0,010 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, ρ = 1,42 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, ρ = 1,18 g/cm^3 (35 % by mass).

4.8.1.2 Apparatus

4.8.1.2.1 Beaker, of capacity 250 cm^3.

4.8.1.2.2 Volumetric flask, of capacity 250 cm^3.

4.8.1.2.3 Platinum crucible, of capacity 20 cm^3.

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 cm^3 of water and 15 cm^3 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 cm^3 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 cm^3 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 cm^3 of water and 1 cm^3 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 cm^3 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 cm^3 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 cm^3 of water. Filter, if necessary, and dilute to 100 cm^3 with water.

If any appreciable amounts of copper are present in the solution, extract with successive 10 cm^3 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 dm^3 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).

4.8.2.1.4 Hydroquinone, solution.

Dissolve 1 g of hydroquinone in 100 cm^3 of redistilled ethanol.

4.8.2.1.5 Copper, standard stock solution.

Dissolve exactly 0,1 g of pure copper in 3 cm^3 of nitric acid (4.8.1.1.1), add 1 cm^3 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 cm^3.

1 cm^3 of this solution contains 200 μg of Cu.

4.8.2.1.6 Copper, 4 $\mu g/cm^3$ standard working solution.

Dilute exactly 5 cm^3 of the stock solution (4.8.2.1.5) to 250 cm^3 with water.

1 cm^3 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 $\mu g/cm^3$ standard working solution.

For the calibration of 4 cm cells, dilute exactly 5 cm^3 of the stock solution (4.8.2.1.5) to 1 000 cm^3 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 cm^3.

4.8.2.2.4 One-mark volumetric flask, of capacity 10 cm^3.

4.8.2.3 Procedure

4.8.2.3.1 Transfer a 100 cm^3 aliquot portion of the stock test solution (see 4.8.1) to a separating funnel (4.8.2.2.3) and add 2,5 cm^3 of hydroxylammonium chloride solution (4.8.2.1.2) and 25 cm^3 of sodium acetate buffer solution (4.8.2.1.3).

4.8.2.3.2 Shake with 6 cm^3 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 cm^3 of hydroxylammonium chloride solution and extract again with 2,5 cm^3 of biquinolyl reagent.

4.8.2.3.4 Separate the phases and again extract the aqueous layer with 2 cm^3 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 cm^3 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 cm^3 (4.8.2.1.6) to calibrate the 1 cm cell and the solution containing 1 μg of copper per cm^3 (4.8.2.1.7) for the 4 cm cell, as follows:

4.8.2.4.2 Transfer aliquot portions from 0 to 25 cm^3 into separating funnels (4.8.2.2.3). Add 1,5 cm^3 of concentrated hydrochloric acid and dilute each solution to 100 cm^3 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 cm^3 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:

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

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 cm^3 of water add 200 cm^3 of orthophosphoric acid (ρ = 1,75 g/cm^3). Cool and dilute to 1 dm^3.

4.8.3.1.2 Manganese, standard solution.

Dissolve 0,143 6 g of potassium permanganate in 250 cm^3 of water, reduce with a very slight excess of sulfur dioxide gas dissolved in water and dilute to 500 cm^3.

1 cm^3 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 cm^3.

4.8.3.2.4 **Beakers,** of capacity 250 cm^3.

4.8.3.3 Procedure

4.8.3.3.1 Transfer a 50 cm^3 aliquot portion of the stock test solution (see 4.8.1) to a 250 cm^3 beaker (4.8.3.2.4). Add 25 cm^3 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 cm^3 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 cm^3 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 cm^3. 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:

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

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 cm^3 of 7,3 g/dm^3 hydrochloric acid.

4.8.4.1.2 Sodium acetate buffer solution.

Dissolve 136 g of sodium acetate trihydrate in water and dilute to 1 dm^3 with water.

4.8.4.1.3 Iron, standard stock solution.

Dissolve exactly 0,5 g of pure iron in 15 cm^3 of 73 g/dm^3 hydrochloric acid (4.6.1.1), transfer to a 1 000 cm^3 volumetric flask and dilute to the mark with water.

4.8.4.1.4 Iron, standard working solution.

Dilute exactly 25 cm^3 of the stock solution (4.8.4.1.3) to 250 cm^3 with water.

1 cm^3 of this solution contains 50 μg of Fe.

4.8.4.1.5 Hydroxylammonium chloride, 5 g/100 cm^3 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 cm^3 and 1 000 cm^3.

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 cm^3 aliquot of the stock test solution (4.8.1) to a 100 cm^3 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 cm^3 of hydroxylammonium chloride solution (4.8.4.1.5) and 5 cm^3 of bipyridine solution (4.8.4.1.1). Transfer quantitatively to a 50 cm^3 volumetric flask (4.8.4.2.3) and dilute to 50 cm^3 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 cm^3 graduated flasks (4.8.4.2.3), add a range of accurately measured volumes from 0 to 10 cm^3 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:

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

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 cm^3 of 35 % by mass hydrochloric acid (ρ = 1,18 g/cm^3) with 50 cm^3 of water.

A.2.4 Hydrofluoric acid, 40 % by mass solution (ρ = 1,13 g/cm^3).

A.2.5 Sulfuric acid, 98 % by mass solution (ρ = 1,84 g/cm^3).

A.2.6 Nitric acid, 68 % by mass solution (ρ = 1,42 g/cm^3).

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

Dissolve 1,000 g ± 0,001 g of high-purity copper turnings in a mixture of 10 cm^3 of water and 5 cm^3 of nitric acid (A.2.6) in a 100 cm^3 beaker. Boil under a fume hood to expel oxides of nitrogen. 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 copper.

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

Pipette 50,0 cm^3 of the 1 g/cm^3 standard copper solution (A.2.7) into a 1 dm^3 volumetric flask, add 5 cm^3 of nitric acid (A.2.6), make up to the mark with water and mix.

1 cm^3 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 cm^3 of the 50 mg/dm^3 standard copper solution (A.2.8) into a 250 cm^3 volumetric flask, add 1 cm^3 of nitric acid (A.2.6), make up to the mark with water and mix.

1 cm^3 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 cm^3.

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 cm^3 volumetric flasks, transfer the volumes of 10 mg/dm^3 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 cm^3 of the test solution to 50 cm^3 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:

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

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 ± 0,001 g of high-purity, oxide-free manganese in a mixture of 50 cm^3 of water and 5 cm^3 of nitric acid (B.2.6) in a 400 cm^3 beaker. Boil under a fume hood to expel oxides of nitrogen. 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 manganese.

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

Pipette 50,0 cm^3 of the 1 g/dm^3 standard manganese solution (B.2.7) into a 1 dm^3 volumetric flask, add 5 cm^3 of nitric acid (B.2.6), dilute to the mark with water and mix.

1 cm^3 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 cm^3 of the 50 mg/dm^3 standard manganese solution (B.2.8) into a 250 cm^3 volumetric flask, add 1 cm^3 of nitric acid (B.2.6), make up to the mark with water and mix.

1 cm^3 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 cm^3 volumetric flasks, transfer the volumes of 10 mg/dm^3 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 cm^3 of the test solution to 50 cm^3 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:

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

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.