INTERNATIONAL STANDARD

ISO 21869

Second edition
2022-06

Rubber compounding ingredients — Magnesium oxide — Methods of test

Ingrédients de mélange du caoutchouc — Oxyde de magnésium — Méthodes d'essai

Reference number
ISO 21869:2022(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

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

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 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 21869:2006), which has been technically revised.

The main changes are as follows:

— a new Clause 6, Loss on ignition, and a new Clause 7, Magnesium oxide content, have been added;

— information on the determination of copper and manganese content have been moved to Annex B;

— a 75 µm sieve opening has been added as an alternative in 9.2;

— a new Clause 12, Ash of hydrochloric acid-insoluble matter, Clause 13, Water–soluble matter content and Clause 14, Bulk density have been added;

— a new Annex A, Determination of calcium oxide content, has been added;

— high, medium and low activity for α, β, and γ, respectively, have been specified in Annex B.

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

Magnesium oxide is used in the rubber industry as a stabilizer, as an agent for modifying the vulcanization process and to enhance the heat resistance of rubber articles. The performance of magnesium oxide in these roles is dependent on its particle size, surface properties and purity. This document specifies the methods used to determine these properties.

Rubber compounding ingredients — Magnesium oxide — Methods of test

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

1 Scope

This document specifies the test methods to be used for magnesium oxide intended for use in the rubber industry as a stabilizer and vulcanizing agent.

The choice of the properties to be determined and the values required are subject to agreement between the interested parties.

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 3819, *Laboratory glassware — Beakers*

ISO 4652, *Rubber compounding ingredients — Carbon black — Determination of specific surface area by nitrogen adsorption methods — Single-point procedures*

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

ISO 18852, *Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)*

3 Terms and definitions

No terms and definitions are listed in this document.

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 https://www.electropedia.org/

4 Sampling

Sampling shall be carried out in accordance with ISO 15528.

5 Moisture, magnesium hydroxide and magnesium carbonate content

Two methods are included: thermogravimetry and oven heating.

5.1 Thermogravimetry

5.1.1 Procedure

The tests are performed on a thermogravimetric analyser capable of controlling temperature at 105 °C ± 10 °C, 390 °C ± 20 °C and 750 °C ± 50 °C.

The tests are performed in either an air or a nitrogen flow of 100 cm^3/min ± 20 cm^3/min. The temperature increase rate should be between 20 °C/min and 40 °C/min while the temperature sweep shall go from ambient to 800 °C.

5.1.2 Expression of the results

5.1.2.1 Moisture content (mass loss from ambient to 105 °C)

The moisture content, M, is given by Formula (1):

$$M = \frac{(m_1 - m_2)}{m_1} \times 100 \quad (1)$$

where

M is the moisture content, in mass fraction %;

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

m_2 is the mass after heating to within the 95 °C to 115 °C temperature range, in grams.

5.1.2.2 Magnesium hydroxide content (mass loss from 105 °C to 390 °C)

The magnesium hydroxide content, w_h, is given by Formula (2):

$$w_h = 3{,}2 \times \frac{(m_2 - m_3)}{m_1} \times 100 \quad (2)$$

where

w_h is the magnesium hydroxide content, in mass fraction %;

m_1 as defined in 5.1.2.1;

m_2 as defined in 5.1.2.1;

m_3 is the mass after heating to within the 370 °C to 410 °C temperature range, in grams;

3,2 is the ratio between 58, the molecular mass of magnesium hydroxide, and 18, the molecular mass of water, calculated on the basis of the following reaction:

$Mg(OH)_2 \Rightarrow MgO + H_2O$

5.1.2.3 Magnesium carbonate content (mass loss from 390 °C to 750 °C)

The magnesium carbonate content, w_c, is given by Formula (3):

$$w_c = 1{,}9 \times \frac{(m_3 - m_4)}{m_1} \times 100 \quad (3)$$

where

w_c is the magnesium carbonate content, in mass fraction %;

m_1 as defined in 5.1.2.1;

m_3 as defined in 5.1.2.2;

m_4 is the mass after heating to above 700 °C, in grams;

1,9 is the ratio between 84, the molecular mass of magnesium carbonate, and 44, the molecular mass of carbon dioxide, calculated on the basis of the following reaction:

$MgCO_3 \Rightarrow MgO + CO_2$

5.2 Loss in mass on oven heating

5.2.1 Moisture content

5.2.1.1 Apparatus

5.2.1.1.1 Weighing dish, low form, approximately 70 mm diameter and 30 mm high (tared).

5.2.1.1.2 Oven, capable of controlling temperature at 115 °C ± 10 °C.

5.2.1.1.3 Analytical balance, accurate to 0,1 mg.

5.2.1.2 Procedure

Weigh into the tared weighing dish 5 g of magnesium oxide sample to the nearest 1 mg.

Spread the test portion to form an even layer in the bottom of the weighing dish. Place the dish, without its cover, in the oven with the temperature previously set at 115 °C ± 10 °C and dry to constant mass (to the nearest 1 mg).

On removal from the oven, always place the cover on the weighing dish. Allow to cool in a desiccator and weigh, the mass loss represents the moisture content.

5.2.1.3 Expression of the results

The moisture content, ω_m, is given by Formula (4):

$$\omega_m = \left(\frac{\Delta m_1}{m_{01}} \right) \times 100 \quad (4)$$

where

ω_m is the moisture content, in mass fraction %;

Δm_1 is the mass loss after heating, in grams;

m_{01} is the original mass of the test portion, in grams.

5.2.2 Magnesium hydroxide content

5.2.2.1 Apparatus

5.2.2.1.1 Crucible (tared), platinum or porcelain. If a porcelain crucible is used, it shall be heated to 390 °C ± 20 °C and cooled in a desiccator before the test.

5.2.2.1.2 Furnace, capable of reaching 450 °C ± 20 °C.

5.2.2.1.3 Analytical balance, accurate to 0,1 mg.

5.2.2.1.4 Desiccator, with desiccating agents (silica gel) inside.

5.2.2.2 Procedure

Weigh into the tared crucible 2 g of magnesium oxide sample to the nearest 1 mg.

Place the crucible containing the magnesium oxide sample in the furnace and set at 390 °C ± 20 °C.

If a porcelain crucible is used, raise the temperature gradually. When 390 °C is reached, maintain it for 2 h in an oxidative atmosphere. Remove the crucible from the furnace, allow to cool in a desiccator and weigh.

Repeat the calcination to verify that a constant mass has been reached.

It is preferable to allow a porcelain crucible to cool slowly in the furnace before placing it in the desiccator.

The mass loss represents the moisture plus magnesium hydroxide content.

5.2.2.3 Expression of the results

The magnesium hydroxide content, ω_h, is given by Formula (5):

$$\omega_h = 3{,}2 \times \left[\frac{\Delta m_2}{m_{02}} \times 100 - \omega_m \right] \quad (5)$$

where

ω_h is the magnesium hydroxide content, in mass fraction %;

Δm_2 is the loss in mass after heating to 390 °C, in grams;

m_{02} is the original mass of the test portion, in grams;

ω_m is the moisture content (determined as specified in 5.2.1.3), in mass fraction %;

3,2 is the ratio between 58, the molecular mass of magnesium hydroxide, and 18, the molecular mass of water, calculated on the basis of the following reaction:

$Mg(OH)_2 \Rightarrow MgO + H_2O$

5.2.3 Magnesium carbonate content

5.2.3.1 Apparatus

5.2.3.1.1 Crucible (tared), platinum or porcelain.

5.2.3.1.2 **Furnace**, capable of reaching over 700 °C.

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

5.2.3.1.4 **Desiccator**, with desiccating agents (silica gel) inside.

5.2.3.2 Procedure

Weigh into the tared crucible 2 g of magnesium oxide sample to the nearest 1 mg.

Place the crucible containing the magnesium oxide sample in a furnace and set at over 700 °C.

If a porcelain crucible is used, raise the temperature gradually. When 700 °C is reached maintain it for 2 h in an oxidative atmosphere. Remove the crucible from the furnace, allow to cool in a desiccator and weigh.

Repeat the calcination to verify that a constant mass has been reached.

The mass loss represents the moisture plus magnesium hydroxide plus magnesium carbonate content.

5.2.3.3 Expression of the results

The magnesium carbonate content, w_c, is given by Formula (6):

$$w_c = 1,9 \times \left[\left(\frac{\Delta m_3}{m_{03}} \right) \times 100 - \omega_m - \omega_h \right] \quad (6)$$

where

w_c is the magnesium carbonate content, in mass fraction %;

Δm_3 is the loss in mass after heating to over 700 °C, in grams;

m_{03} is the original mass of the test portion, in grams;

ω_m is the moisture content (determined as specified in 5.2.1.3), in mass fraction %;

ω_h is the magnesium hydroxide content (determined as specified in 5.2.2.3), in mass fraction %;

1,9 is the ratio between 84, the molecular mass of magnesium carbonate, and 44, the molecular mass of carbon dioxide, calculated on the basis of the following reaction:

$MgCO_3 \Rightarrow MgO + CO_2$

6 Loss on ignition

6.1 Principle

Ignite a test portion at 900 °C to 1 000 °C for more than 2 h and measure the amount of loss. The test portion after ignition is used for the measurement of magnesium oxide content in Clause 7.

NOTE Although loss on ignition measurement is one of the steps in the magnesium oxide content test procedure, it is described in an independent clause in consideration for its importance as an index for burning degree in a manufacturing calcination process.

6.2 Apparatus

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

6.2.2 Crucible, platinum or porcelain, nominal capacity of 15 cm^3.

6.2.3 Desiccator, with desiccating agents (silica gel) inside.

6.2.4 Electric furnace, capable of controlling the temperature accurately to within ±25 °C in the range of 900 °C to 1 000 °C.

6.3 Test procedure

The procedure is as follows:

a) Ignite the crucible (6.2.2) for 30 min at the ignition temperature for testing.

b) Allow the crucible to cool to room temperature in the desiccator (6.2.3) and weigh the mass of the crucible to the nearest 0,1 mg. Record the mass as m_5.

c) Take a test portion of the sample and put it into the crucible up to about 2/3 of its capacity and weigh the mass of the crucible including the test portion to the nearest 0,1 mg. Record the mass as m_6.

NOTE The mass of the test portion to be weighed in this procedure, which differs according to the bulk density, is approximately 2 g to 3 g.

d) Place the crucible in an electric furnace (6.2.4) and ignite at a selected temperature between 900 °C and 1 000 °C. Recommendation for the ignition time at the temperature between 900 °C and 1 000 °C is more than 2 h.

e) Remove the crucible from the electric furnace, allow to cool in a desiccator and weigh the mass to the nearest 0,1 mg. Record the mass as m_7.

f) Preserve the test portion in the desiccator to prevent moisture absorption and use it in the measurement specified Clause 7.

6.4 Calculation

Calculate loss on ignition, I, using Formula (7), with the result rounded to one decimal place.

$$I = \frac{m_6 - m_7}{m_6 - m_5} \times 100 \tag{7}$$

where

m_5 is the mass of the crucible, in grams;

m_6 is the mass of the crucible including the test portion before ignition, in grams;

m_7 is the mass of the crucible including the test portion after ignition, in grams.

7 Magnesium oxide content

7.1 Principle

The test portion prepared in 6.3 f) after the measurement of loss on ignition in Clause 6 is dissolved in hydrochloric acid. The solution is titrated with disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA) aqueous solution and the total content of magnesium oxide and calcium oxide corresponding to the amount of EDTA titration is determined. Then, the calcium oxide content is determined by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES), and converted into the titration volume of EDTA corresponding to the content.

The magnesium oxide content is calculated by subtracting the converted content of the calcium oxide from the total of magnesium oxide and calcium oxide content.

7.2 Determination of total magnesium oxide and calcium oxide contents

7.2.1 Reagents

7.2.1.1 Water, of grade 1 or higher as specified in ISO 3696.

7.2.1.2 Hydrochloric acid, ρ_{20} = 1,19 Mg/m^3.

7.2.1.3 Hydrochloric acid (1+1), prepared by adding one volume of water (7.2.1.1) to one volume of hydrochloric acid (7.2.1.2).

7.2.1.4 Sodium hydroxide, of analytical reagent grade.

7.2.1.5 Sodium hydroxide aqueous solution, 40 g/l prepared by weighing out about 4 g of sodium hydroxide (7.2.1.4) and adding about 50 cm^3 of water to dissolve. Dilute with water (7.2.1.1) to a total volume of 100 cm^3.

7.2.1.6 Sodium hydroxide aqueous solution, 0,8 g/l prepared by diluting 40 g/l sodium hydroxide aqueous solution (7.2.1.5) 50-fold with water (7.2.1.1).

7.2.1.7 Aqueous ammonia, of analytical reagent grade, 28 % mass fraction.

7.2.1.8 Ammonium chloride, of analytical reagent grade.

7.2.1.9 Ammonia-ammonium chloride buffer solution, pH 10,7 prepared by adding water (7.2.1.1) to 67,5 g of ammonium chloride (7.2.1.8) to dissolve, add 570 cm^3 of 28 % mass fraction aqueous ammonia (7.2.1.7) and further add water to a total volume of 1 000 cm^3.

7.2.1.10 Eriochrome black T (EBT), of analytical reagent grade.

7.2.1.11 Hydroxylammonium chloride, of analytical reagent grade.

7.2.1.12 Methanol, of analytical reagent grade.

7.2.1.13 EBT indicator, prepared by dissolving 0,6 g of EBT (7.2.1.10) and 4,0 g of hydroxylammonium chloride (7.2.1.11) in 100 cm^3 of methanol (7.2.1.12). Store in dark place.

7.2.1.14 Zinc electrolytic, minimum purity: 99,9 %.

7.2.1.15 Acetone, of analytical reagent grade and 99,5 % or more in purity.

7.2.1.16 Zinc aqueous solution, 0,01 mol/l prepared as follows.

a) Preparation: wash zinc (7.2.1.14) with diluted hydrochloric acid and then with water (7.2.1.1) and acetone (7.2.1.15), and dry. Weigh about 0,65 g of dried zinc to the nearest 0,1 mg and record the zinc mass as m_8. Dissolve completely with 5 cm^3 of hydrochloric acid (1+1) (7.2.1.3) and dilute with water (7.2.1.1) to 1 000 cm^3.

b) Calculation: calculate the factor (f_1) of 0,01 mol/l zinc aqueous solution by Formula (8). Round off the result to three decimal places.

$$f_1 = \frac{m_8}{0{,}653\ 8} \times \frac{Z}{100} \tag{8}$$

where

f_1 is the factor of 0,01 mol/l zinc aqueous solution;

m_8 is the mass of zinc, in grams;

Z is the purity of zinc, in mass fraction %;

0,653 8 is the mass of zinc contained in 1 000 cm^3 of 0,01 mol/l zinc aqueous solution, grams.

A commercially available 0,01 mol/l zinc aqueous solution may be used.

7.2.1.17 Disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA), of analytical reagent grade.

7.2.1.18 0,01 mol/l EDTA aqueous solution, prepared as follows:

a) Preparation: Weigh about 3,72 g of EDTA (7.2.1.17), dissolve in water and add water to obtain a total volume of 1 000 cm^3. Put into airtight container made of resin such as polyethylene to store.

b) Standardization: take 20 cm^3 of 0,01 mol/l zinc aqueous solution (7.2.1.16) with a pipette, add 80 cm^3 of water and then adjust the pH to about 7 with 0,8 g/l sodium hydroxide aqueous solution (7.2.1.6). Add 2 cm^3 of ammonia-ammonium chloride buffer solution of pH 10,7 (7.2.1.9) to this adjusted aqueous solution, titrate with 0,01 mol/l EDTA aqueous solution prepared in 7.2.1.18 a) using EBT (7.2.1.13) indicator, and determine its volume to the equivalence point when the reddish purple turns into a non-reddish blue colour. Record the volume as V.

c) Calculation: Calculate the factor (f_2) of 0,01 mol/l EDTA aqueous solution by Formula (9). Round off the result to three decimal places.

$$f_2 = \frac{f_1 \times 20}{V} \tag{9}$$

where

f_2 is the factor of 0,01 mol/l EDTA aqueous solution;

f_1 is the factor of 0,01 mol/l zinc aqueous solution, calculated using Formula (8);

V is the titration volume of 0,01 mol/l EDTA aqueous solution required for standardization in cm^3.

7.2.2 Apparatus

7.2.2.1 Analytical balance, accurate to 0,1 mg.

7.2.2.2 Volumetric flask, one-mark, with ground-glass stoppers and with capacity 500 cm^3.

7.2.2.3 Pipette, with capacity 10 cm^3.

7.2.2.4 Burette, with capacities of 25 cm^3 or 50 cm^3.

7.2.3 Test procedure

The procedure is as follows.

a) Weigh about 500 mg of the test portion prepared in 6.3 f) after the measurement of loss on ignition into a beaker to the nearest 0,1 mg. Record the portion mass as m_9.

b) Gradually add 10 cm^3 of hydrochloric acid (1+1) (7.2.1.3) to the beaker in 7.2.3 a), and heat to dissolve.

c) After cooling, transfer to a 500 cm^3 volumetric flask (7.2.2.2), wash the original beaker with a small amount of water, add the washings to the volumetric flask, further add water to a total volume of 500 cm^3 and take this as a test solution.

d) Take 10 cm^3 of the test solution into a beaker with a pipette (7.2.2.3). Add 80 cm^3 of water and adjust the pH to about 7 with 0,8 g/l sodium hydroxide aqueous solution (7.2.1.6). Add 2 cm^3 of ammonia-ammonium chloride buffer solution (7.2.1.9), titrate with 0,01 mol/l EDTA aqueous solution (7.2.1.18) with a burette (7.2.2.4) using EBT indicator (7.2.1.13). Determine the volume of titrant to the equivalence point when the reddish purple turns into a non-reddish blue colour. Record the volume as A which is the total amount of magnesium oxide and calcium oxide content [calculated with Formula (11)].

7.3 Determination of calcium oxide content

7.3.1 Determination of the content by AAS or ICP-AES

The content by AAS ($C1$) or by ICP-AES ($C2$) is determined in accordance with Annex A.

7.3.2 Conversion of the content by AAS or by ICP-AES into the titration volume of EDTA

The volume of 0,01 mol/l EDTA solution corresponding the content by AAS or ICP-AES, expressed as B, is calculated by Formula (10). Round off the result to two decimal places.

$$B = m_9 \times \frac{10}{500} \times \frac{C}{100} \times \frac{1}{0{,}560\ 8} \tag{10}$$

where

m_9 is the mass of the test portion weighed in 7.2.3 a), in milligrams;

C is the calcium oxide content C_1 by AAS or the calcium oxide content C_2 by ICP-AES in Annex A;

0,560 8 is the mass of calcium oxide equivalent to 1 cm^3 of 0,01 mol/l EDTA aqueous solution, in milligrams.

7.4 Calculation of magnesium oxide content

The magnesium oxide content, M, is calculated by Formula (11). Round off the result to one decimal place.

$$M = \frac{0{,}403\ 0 \times (A \times f_2 - B)}{m_9 \times \frac{10}{500}} \times 100 \tag{11}$$

where

M is the magnesium oxide content, in mass fraction %;

A is the titration volume, in cm^3, of 0,01 mol/l EDTA corresponding to total of magnesium oxide and calcium oxide content from 7.2.3 d);

f_2 is the factor of 0,01 mol/l EDTA aqueous solution used for total amount of magnesium oxide and calcium oxide content from Formula (9);

B is the volume from 7.3.2, in cm^3;

m_9 is the mass of the test portion weighed in 7.2.3 a), in milligrams;

0,403 0 is the mass of magnesium oxide equivalent to 1 cm^3 of 0,01 mol/l EDTA aqueous solution, in milligrams.

8 Determination of the specific surface area

The determination of the specific surface area shall be carried out by the method described in ISO 4652 or ISO 18852. The typical values of specific surface area are given in Annex B.

9 Determination of the sieve residue

9.1 Reagents

9.1.1 Sodium alkyl-aryl sulfonate, 0,5 % solution in water.

NOTE If it allows the determination to be carried out satisfactorily, water alone can be used.

9.2 Apparatus

9.2.1 Beaker, 400 cm^3, tall form, in accordance with ISO 3819.

9.2.2 Sieve, with openings of 45 µm or 75 µm, in accordance with ISO 565.

9.2.3 Stirrer, with glass blades.

9.2.4 Glass rod, with a rounded end 6 mm in diameter.

9.2.5 Desiccator, with desiccating agents (silica gel) inside.

9.2.6 Analytical balance, accurate to 0,1 mg.

9.2.7 Oven, capable of controlling temperature at 105 °C ± 2 °C.

9.3 Procedure

To prepare the test portion, weigh, to the nearest 1 mg, 10 g of magnesium oxide into a 400 cm^3 beaker.

The testing is the following. Wash and dry the sieve in an oven at 105 °C ± 5 °C. Tare it. Pour 300 cm^3 of sodium alkyl-aryl sulfonate solution (9.1.1) or water into a beaker containing the test portion. Mix for 5 min with a stirrer turning at 260 rad/s (2 500 r/min). Pour the mixture onto the sieve. Rinse the beaker and pour the rinsing onto the sieve. Spray the sieve with a stream of water at a rate of 2,5 l/min. Using the rounded end of the glass rod, lightly scrape the bottom of the sieve until no more magnesium oxide is seen in the water flowing through the sieve. Dry the sieve in an oven at 105 °C ± 5 °C, for 30 min. Allow to cool to room temperature in a desiccator. Weigh to the nearest 1 mg.

Continue the drying operation until constant mass is reached.

9.4 Expression of the results

The sieve residue, *ω(sr)*, is calculated from Formula (12):

$$\omega(sr) = 100\frac{(m_{t2} - m_{t1})}{m_t} \tag{12}$$

where

$\omega(sr)$ is the sieve residue, in %;

m_{t1} is the mass of the sieve, in grams;

m_{t2} is the mass of the sieve and the residue, in grams;

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

10 Determination of chloride

10.1 Principle

The chloride ion in a test portion are replaced by sulfate ion from magnesium sulfate. They are then precipitated from solution using silver nitrate. The end of the reaction is indicated by the precipitation of silver chromate caused by the presence of potassium chromate (argentometric titration).

10.2 Reagents

10.2.1 Hydrated magnesium sulfate ($MgSO_4 \cdot 7H_2O$).

10.2.2 Silver nitrate solution ($AgNO_3$), 0,02 mol/l.

10.2.3 Potassium chromate (K_2CrO_4), 10 % solution in water.

10.3 Apparatus

Conventional laboratory equipment and the following.

10.3.1 Analytical balance, accurate to 0,1 mg.

10.4 Procedure

Weigh, to the nearest 1 mg, 2 g of magnesium oxide sample into a 200 cm^3 beaker. Add 15 cm^3 to 30 cm^3 of distilled water and 6 drops of potassium chromate solution (10.2.3). Then add 200 mg of hydrated magnesium sulfate (10.2.1).

Before titrating, boil the solution in order to accelerate the extraction of the chloride ions.

Titrate with 0,02 mol/l silver nitrate solution (10.2.2) until the colour turns reddish-yellow.

10.5 Expression of the results

The chloride content of the test portion, w_{Cl^-}, is given by Formula (13):

$$w_{Cl^-} = 2 \times \frac{0{,}0355 V_{Ag}}{m_c} \quad (13)$$

where

w_{Cl^-} is the chloride content of the test portion, in mass fraction %;

V_{Ag} is the volume of 0,02 mol/l silver nitrate solution used, in cubic centimetres;

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

11 Determination of the sulfate content

11.1 Principle

Barium chloride solution is added to a test portion dissolved in hydrochloric acid, and the sulfate ions precipitate in the form of barium sulfate which is weighed (gravimetric method).

11.2 Reagents

11.2.1 Hydrochloric acid, 18 %.

11.2.2 Barium chloride solution, 10 %.

11.3 Apparatus

Conventional laboratory equipment and the following.

11.3.1 Tared platinum or porcelain crucible.

11.3.2 Analytical balance, accurate to 0,1 mg.

11.4 Procedure

Weigh, to the nearest 1 mg, 2 g of magnesium oxide sample into a 250 cm^3 beaker and wet it with distilled water. Dissolve it in 20 cm^3 of 18 % hydrochloric acid (11.2.1). Bring to the boil and remove the insoluble matter by filtering through a filter paper, washing with 20 cm^3 of hot distilled water. Make up the volume of the filtrate plus washing water to approximately 250 cm^3.

Bring to the boil and add dropwise 15 cm^3 of 10 % barium chloride solution (11.2.2) from a pipette so that boiling does not stop. Boil for two more minutes and then keep for 2 h on a steam bath.

Filter through a filter paper and wash with 20 cm^3 of hot distilled water.

Dry and incinerate the filter paper in a tared platinum or porcelain crucible for 30 min at 600 °C. Allow to cool to room temperature in a desiccator and weigh.

11.5 Expression of the results

The sulfate content of the test portion, w_s, is given by Formula (14):

$$w_s = 41,0\frac{m_r}{m_s} \quad (14)$$

where

w_s is the sulfate content of the test portion, in mass fraction %;

m_r is the difference in mass between the crucible with the calcined barium sulfate and the tare, in grams;

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

12 Ash of hydrochloric acid-insoluble matter

12.1 Principle

Dissolve the sample in hydrochloric acid under the specified conditions, filter out insoluble matters, wash with water, ash, and measure the mass of the residue.

12.2 Reagents

12.2.1 Water, of grade 1 or higher as specified in ISO 3696.

12.2.2 Hydrochloric acid, ρ_{20} = 1,19 Mg/m^3.

12.2.3 Hydrochloric acid (1+1), prepared by diluting 1 volume of hydrochloric acid (12.2.2) with 1 volume of water (12.2.1).

12.2.4 Ashless filter paper.

12.3 Apparatus

12.3.1 Analytical balance, accurate to 0,1 mg.

12.3.2 Electric furnace, capable of controlling temperature at 900 °C ± 25 °C.

12.3.3 Electric heater or electric hotplate.

12.3.4 Desiccator, with desiccating agents (silica gel) inside.

12.3.5 Crucible, platinum or porcelain 10 cm^3 capacity.

12.4 Procedure

Weigh 2 g to 5 g of the portion from the magnesium oxide sample into a beaker to the nearest 0,1mg. Record the mass of the test portion as m_{t3}.

Add a small amount of water to the beaker to moisten the test portion, add hydrochloric acid (1+1) (12.2.3) to dissolve and boil for 5 min. The amount of hydrochloric acid (1+1) (12.2.3) to be used shall be 10 cm^3 to 12 cm^3 per 1 g of test portion.

Filtrate the insoluble matter using an ashless filter paper (12.2.4) and wash thoroughly with warm water.

Dry the residue together with the filter paper using an electric heater or electric hotplate.

Weigh the mass of the crucible (12.3.5) to the nearest 0,1 mg. Record the mass as m_{t4}.

Put the dried filter paper into the crucible and ignite it in an electric furnace until ashed.

Take out the crucible, allow the crucible to cool down to room temperature in a desiccator (12.3.4) and weigh the mass to nearest 0,1 mg. Record the mass as m_{t5}.

12.5 Expression of the results

Insoluble matter content in hydrochloric acid, $m_{(is)}$, is calculated from Formula (15):

$$m_{(is)} = \frac{100(m_{t5} - m_{t4})}{m_{t3}} \quad (15)$$

where

$m_{(is)}$ is the insoluble matter content in hydrochloric acid, in mass fraction %;

m_{t3} is the mass, in grams, of the original test portion;

m_{t4} is the mass, in grams, of tared crucible;

m_{t5} is the mass, in grams, of residue and crucible after ignition.

13 Water-soluble matter content

13.1 Principle

Extract the water-soluble matter from the sample with water under specified conditions, evaporate the water extract after removing insoluble matter dry and weigh the mass of the residue.

NOTE The soluble content in water contains chloride, sulfate and magnesium bicarbonate, etc. For the measurement of chloride content and sulfate content, see Clauses 10 and 11.

13.2 Reagents

During the analysis, unless stated otherwise, use only analytical-quality reagents and distilled water or water of equivalent purity.

13.3 Apparatus

13.3.1 Analytical balance, accurate to 0,1 mg.

13.3.2 Weighing bottle, 50 mm in diameter and 30 mm in height.

13.3.3 Water bath.

13.3.4 Oven, capable of controlling temperature at 105 °C ± 5 °C.

13.3.5 Desiccator, with desiccating agents (silica gel) inside.

13.3.6 Volumetric flask, one-mark, with ground-glass stoppers and with capacity 100 cm^3.

13.3.7 Pipettes, with a capacity of 25 cm^3.

13.4 Procedure

Weigh about 2,0 g of the portion from the magnesium oxide sample into a beaker to the nearest 0,1 mg. Record the mass as m_{t6}.

Add 100 cm^3 of water to the beaker cover the beaker with a watch glass and boil for 5 min.

Filtrate the solution immediately and take the filtrate into a 100 cm^3 volumetric flask (13.3.6).

After cooling, add water to make 100 cm^3.

Weigh the mass of the weighing bottle (13.3.2) to the nearest 0,1 mg. Record the mass as m_{t7}.

Take 25 cm^3 of the solution into the weighing bottle using a pipette (13.3.7), evaporate the water on a water bath (13.3.3) and dry the residue at 105 °C for 1 h.

Allow the residue to cool in a desiccator (13.3.5) and weigh the mass to the nearest 0,1 mg. Record the mass as m_{t8}.

13.5 Expression of the results

Soluble content in water, $m_{(sc)}$, is calculated from Formula (16):

$$m_{(sc)} = \frac{(m_{t8} - m_{t7})}{m_{t6} \times \frac{25}{100}} \times 100 \quad (16)$$

where

$m_{(sc)}$ is the soluble content in water, in mass fraction %;

m_{t6} is the mass, in grams, of the test portion;

m_{t7} is the mass, in grams, of empty weighing bottle;

m_{t8} is the mass, in grams, of residue and weighing bottle.

14 Bulk density

14.1 Principle

The bulk density is determined according to the volume of sample obtained when the specified force is applied to the sample in a container.

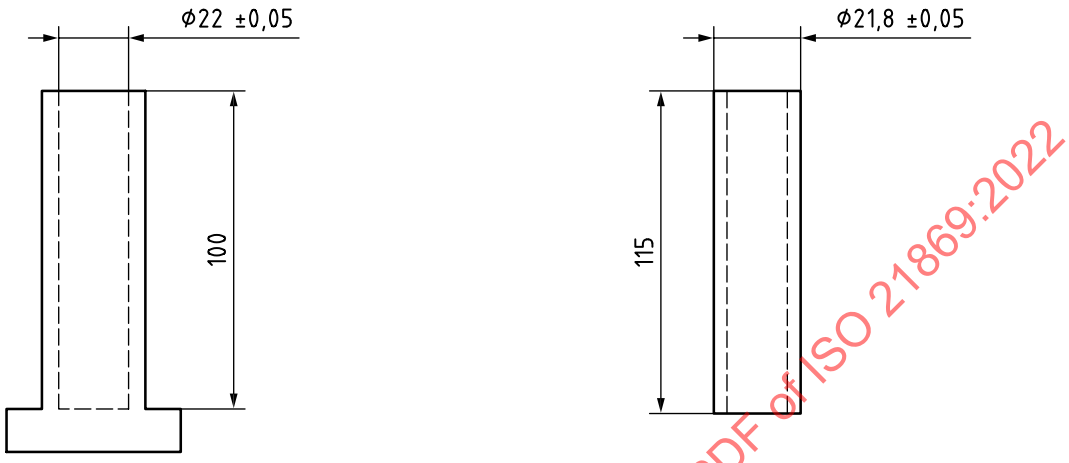
14.2 Apparatus

14.2.1 Analytical balance, accurate to 0,01 g.

14.2.2 Bulk density measuring apparatus, composed of a cylinder and a piston and made of ordinary steel with dimensions indicated in Figure 1.

The cylinder shall have an inside diameter of 22,00 mm ± 0,05 mm and an inside depth of 100 mm. The piston shall be hollow and have an outside diameter of 21,80 mm ± 0,05 mm, a length of 115 mm and a mass of 190 g.

Dimensions in millimetres



a) Cylinder **b) Piston**

Figure 1 — Bulk density measuring apparatus

14.3 Procedure

The procedure is as follows.

a) Insert the piston into a cylinder appropriately, allow the piston to sink with its own weight and measure the dimension of the upper projecting part to the nearest 0,01 cm. Take this difference in height between the piston and the cylinder as l_{h1}.

b) Weigh 1 g to 5 g of sample to the nearest 0,01 g. Take the sample mass as m_{t9}.

c) Draw out the piston from the cylinder, pour the sample gently into the cylinder, lightly shake or pat the cylinder to dislodge any sample adhering to the cylinder wall and level the upper surface of the sample.

d) Drop the piston from the upper part of the cylinder correctly and gradually with fingers placed on it. As a general rule, the time taken for the piston to reach the sample surface shall be 5 s. At this time, the contact with the sample surface by the piston shall be sensed with fingers.

e) When the piston reaches the sample surface, revolve the piston once lightly with fingers or tap the cylinder wall with a piece of wood to settle the piston.

f) Measure the length of the projecting part of the piston above the cylinder to the nearest 0,01 cm. Take this difference in height between the piston and the cylinder as l_{h2}.

14.4 Expression of the results

Bulk density, $\omega_{(bd)}$, is calculated from Formula (17):

$$\omega_{(bd)} = \frac{m_{t9}}{0{,}785\ 4(l_{h1} - l_{h2})\ l_d{}^2} \tag{17}$$

where

$\omega_{(bd)}$ is the bulk density, expressed as g/cm^3;

l_{h1} is the length of the part of the piston which projects from the cylinder when there is no test portion in the cylinder, in centimetres;

l_{h2} is the length of the part of the piston which projects from the cylinder with the test portion in the cylinder, in centimetres;

m_{t9} is the mass of the test portion, in grams;

l_d is the length of the diameter of cylinder, in centimetres;

0,785 4 is the factor for converting diameter of cylinder into area.

15 Test report

The test report shall contain the following information:

a) a reference to this document, i.e. ISO 21869:2022;

b) all information necessary to identify the product tested;

c) the method of sampling used;

d) the method(s) used;

e) the instrument type(s) used;

f) the results and the units in which they have been expressed;

g) any unusual observations noted during testing;

h) details of any operations not included in this document, or in the referenced standards, which may have influenced the results;

i) the date of testing.

Annex A
(normative)

Determination of calcium oxide content

A.1 General

The following two methods are available to determine calcium oxide content.

a) Atomic absorption spectrometry (AAS): with an atomic absorption spectrometer, the calcium concentration is determined by dissociating calcium contained in the sample to ground-state atoms with flame and by measuring the absorbance of the atomic vapour layer.

b) Inductively coupled plasma atomic emission spectrometry (ICP-AES): with an ICP atomic emission spectrometer, the calcium concentration is determined by gasifying and exciting calcium contained in the sample with radio-frequency inductively coupled plasma and by measuring the emission intensity of the atomic spectral line obtained.

A.2 Atomic absorption spectrometry (AAS)

A.2.1 Reagents

A.2.1.1 Water, of grade 1 or higher as specified in ISO 3696.

A.2.1.2 Hydrochloric acid, ρ_{20} = 1,19 Mg/m^3.

A.2.1.3 Hydrochloric acid (1+1), prepared by adding one volume of water (A.2.1.1) to one volume of hydrochloric acid (A.2.1.2).

A.2.1.4 Lanthanum oxide, La_2O_3 (not less than 99,5 % in mass fraction).

A.2.1.5 Lanthanum oxide solution, 0,2 mol/l prepared by dissolving 6,5 g of lanthanum oxide (A.2.1.4) dissolved in hydrochloric acid (1+1) (A.2.1.3) to make total 100 cm^3.

A.2.1.6 Calcium carbonate.

A.2.1.7 Calcium standard stock solution (Ca 1 000 mg/l), prepared by weighing about 1,249 g of calcium carbonate (A.2.1.6), which has been dried at 150 °C to 180 °C for 1 h, to the nearest 0,1 mg, add 110 cm^3 of hydrochloric acid (1+1) (A.2.1.3) to dissolve and add water to a total volume of 500 cm^3

A commercially available calcium standard stock solution may be used.

A.2.1.8 Calcium standard solution (Ca 100 mg/l), prepared by diluting one volume of the calcium standard stock solution (A.2.1.7) with 9 volumes of water (A.2.1.1).

A commercially available calcium standard stock solution may be used.

A.2.2 Apparatus

A.2.2.1 Analytical balance, accurate to 0,1 mg.

A.2.2.2 Volumetric flask, one-mark, with ground-glass stoppers and with capacities of 25 cm^3 and 100 cm^3.

A.2.2.3 Pipette, with capacity 1 cm^3.

A.2.2.4 Pipette, with capacities of between 0,5 cm^3 and 2,5 cm^3.

A.2.2.5 Atomic absorption spectrometer, fitted with a burner fed with acetylene and compressed air and equipped with a calcium hollow-cathode lamp capable of emitting radiation of the required wavelengths. A high-brightness lamp is advisable. The instrument shall be operated in accordance with the manufacturer's instructions for optimum performance. Alternatively, an electrothermal atomization device (graphite furnace) may be used. It shall be operated by a competent person in accordance with the manufacturer's instructions for optimum performance

A.2.3 Test procedure

The procedure is as follows.

a) Weigh about 1 g of test portion prepared in 6.3 f) after the measurement of loss on ignition in Clause 6 into a beaker to the nearest 0,1 mg. Record the sample mass as $m_{10.}$

b) Gradually add 20 cm^3 of hydrochloric acid (1+1) (A.2.1.3) to the beaker in A.2.3 a) and heat to dissolve.

c) After cooling, transfer to a 100 cm^3 volumetric flask (A.2.2.2), wash the original beaker with a small amount of water, add the washing to the volumetric flask and further add water to a total volume of 100 cm^3. Measure out 2,5 cm^3 of this solution into a 25 cm^3 volumetric flask (A.2.2.2) using a pipette (A.2.2.4) and add 1 cm^3 of 0,2 mol/l lanthanum oxide solution (A.2.1.5) using a pipette (A.2.2.3). Further, add water to a total volume of 25 cm^3 and use this as the test solution.

d) Take 0,5 cm^3 of calcium standard solution (Ca 100 mg/l) (A.2.1.8) in a 25 cm^3 volumetric flask using the pipette (A.2.2.4) and add 1 cm^3 of 0,2 mol/l lanthanum oxide (A.2.1.5) solution using a pipette (A.2.2.3). Add water to a total volume of 25 cm^3 and use this as the Ca 2,0 mg/l calibration standard solution. Furthermore, take the solution prepared in the same way with 1,5 cm^3 and 2,5 cm^3 of calcium standard solution (Ca 100 mg/l) (A.2.1.8) to use as the Ca 6,0 mg/l and Ca 10,0 mg/l calibration standard solutions, respectively.

e) Take the solution prepared in the same way without adding calcium standard solution (Ca 100 mg/l) as the blank solution.

f) Attach a calcium hollow cathode lamp to the atomic absorption spectrometer (A.2.2.5), set the wavelength at 422,7 nm and set the pressure and flow rate of air and acetylene at values suitable for measurement.

g) Spray the blank solution and the standard solutions on the device in the atomic absorption spectrometer and measure the absorbance to create the calibration curve by plotting the absorbance as a function of calcium concentration. Measure the absorbance of calcium of the test solution to determine the concentration and record as E_1.

h) Calculate the calcium oxide content by Formula (A.1) and Formula (A.2).

NOTE The determination range of the calibration standard solutions is a mass fraction of 0 % to 1 % of calcium oxide.

i) Record the calcium oxide content calculated as C_1 in Formula (A.2) and C in Formula (10).