INTERNATIONAL STANDARD

**ISO 20565-2**

First edition
2008-12-01

# Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method) —

## Part 2: Wet chemical analysis

*Analyse chimique des produits réfractaires contenant du chrome et des matières premières contenant du chrome (méthode alternative à la méthode par fluorescence de rayons X) —*

*Partie 2: Méthodes d'analyse chimique par voie humide*



Reference number
ISO 20565-2:2008(E)



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Published in Switzerland

 

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# Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 20565-2 was prepared by Technical Committee ISO/TC 33, *Refractories*, in collaboration with Technical Committee CEN/TC 187, *Refractory products and materials*.

ISO 20565 consists of the following parts, under the general title *Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method)*:

— *Part 1: Apparatus, reagents, dissolution and determination of gravimetric silica*

— *Part 2: Wet chemical analysis*

— *Part 3: Flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES)*

# Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method) —

## Part 2:
## Wet chemical analysis



## 1 Scope

This part of ISO 20565 specifies traditional ("wet process") methods for the chemical analysis of chrome-bearing refractory products and raw materials.

It is applicable to components within the ranges of determination given in Table 1.

**Table 1 — Range of determination (% by mass)**

| Component | Range |
|---|---|
| $SiO_2$ | 0,5 to 10 |
| $Al_2O_3$ | 2 to 30 |
| $Fe_2O_3$ | 0,5 to 25 |
| $TiO_2$ | 0,01 to 1 |
| MnO | 0,01 to 1 |
| CaO | 0,01 to 3 |
| MgO | 15 to 85 |
| $Na_2O$ | 0,01 to 1 |
| $K_2O$ | 0,01 to 1 |
| $Cr_2O_3$ | 2 to 60 |
| $ZrO_2$ | 0,01 to 0,5 |
| $P_2O_5$ | 0,01 to 5 |
| LOI | −0,5 to 5 |
| NOTE These values are after the loss on ignition (LOI) has been taken into account. | |

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 20565-1:2008, *Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and determination of gravimetric silica*

ISO 26845:2008, *Chemical analysis of refractories — General requirements for wet chemical analysis, atomic absorption spectrometry (AAS) and inductively compled plasma atomic emission spectromety (ICP-AES) methods*

## 3 Determination of silicon(IV) oxide

### 3.1 General

Determine the silicon(IV) oxide content using one of the following methods.

a) Combined use of the dehydration or the coagulation and molybdenum blue methods

   This method is applied to samples consisting of more than 4 % by mass of silicon(IV) oxide.

b) Molybdenum blue method

   This method is applied to samples consisting of less than 10 % by mass of silicon(IV) oxide.

### 3.2 Combined use of the coagulation and molybdenum blue methods

#### 3.2.1 Principle

An aliquot portion of the stock solution (S1) (see ISO 20565-1), after pH adjustment, is treated with ammonium molybdate and the silicomolybdate is reduced to yield molybdenum blue, the absorbance of which is measured.

The sum of this residual silicon(IV) oxide in solution plus the mass of silicon(IV) oxide determined in ISO 20565-1:2008, 9.2.2.3.3, gives the total silicon(IV) oxide content.

#### 3.2.2 Procedure

This determination should be commenced with little delay after the stock solution (S1) is prepared, as prolonged standing may allow polymerization of silica to occur leading to low results.

Transfer 10 ml of stock solution (S1) (see ISO 20565-1) to a 100 ml plastic beaker, add 2 ml of hydrofluoric acid (1+9) and mix with a plastic rod. Allow to stand for 10 min and add 50 ml of boric acid solution. Add 2 ml of ammonium molybdate solution while mixing at a temperature of 25 °C and allow to stand for 10 min. Add 5 ml of L (+)-tartaric acid solution while stirring and, after 1 min, add 2 ml of L (+)-ascorbic acid solution. Transfer the solution to a 100 ml volumetric flask, dilute to the mark with water, mix and allow to stand for 60 min.

Measure the absorbance of the solution in a 10 mm cell at a wavelength of 650 nm against water as a reference.

### 3.2.3 Plotting calibration graph

Transfer 0 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml aliquot portions of diluted standard silicon(IV) oxide solution (0 mg to 0,4 mg as silicon(IV) oxide) to separate 100 ml plastic beakers and add to each 10 ml of blank solution (B1) (see ISO 20565-1). Treat these solutions and measure the absorbance as given in 3.2.2, and plot the absorbances against the amounts of silicon(IV) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 3.2.4 Blank test

Using blank solution (B1), carry out the procedure given in 3.2.2.

### 3.2.5 Calculation

Calculate the mass fraction of silicon(IV) oxide, $w_{SiO_2}$, expressed as a percentage, using Equation (1) with the absorbances obtained in 3.2.2 and 3.2.4 and the calibration in 3.2.3.

$$w_{SiO_2} = \frac{(m_1 - m_2) + (m_s - m_b) \times \frac{500}{10}}{m} \times 100 \quad (1)$$

where

$m_1$ is the mass from ISO 20565-1, in grams (g);

$m_2$ is the mass from ISO 20565-1, in grams (g);

$m_s$ is the mass of silicon(IV) oxide in the aliquot portion of stock solution (S1) as applicable, in grams (g);

$m_b$ is the mass of silicon(IV) oxide in the aliquot portion of blank solution (B1) as applicable, in grams (g);

$m$ is the mass of the test portion from ISO 20565-1, in grams (g).

## 3.3 Molybdenum blue method

### 3.3.1 Principle

An aliquot portion of the stock solution (S′1) (see ISO 20565-1), after pH adjustment, is treated with ammonium molybdate and the silicomolybdate is reduced to yield molybdenum blue, the absorbance of which is measured.

### 3.3.2 Procedure

Transfer precisely an aliquot portion of stock solution (S′1) (to two 100 ml plastic beakers and add to each an aliquot portion of blank solution obtained from 3.3.3. Add to each beaker 2 ml of hydrofluoric acid (1+9), mix with a plastic rod and allow to stand for 10 min. Add 50 ml of boric acid solution, dilute to 80 ml with water. Add 5 ml of ammonium molybdate solution while mixing at a temperature of 25 °C and allow to stand for 10 min. Add 5 ml of L (+)-tartaric acid solution while stirring and, after 1 min, add 10 ml of L (+)-ascorbic acid solution. Transfer each solution to a 200 ml volumetric flask, dilute to the mark with water and mix. Allow to stand for 60 min and measure the absorbance of the solutions in a 10 mm cell at a wavelength of 650 nm against water as a reference. Take the mean of the two measurements.

NOTE Aliquot volumes of stock solution and blank solution (B′1) are shown in Table 2, corresponding to the content of silicon(IV) oxide in the sample.

When the difference of the two absorbance measurements is greater than 0,005, repeat the procedure in 3.3.2. When measurements of the same sample with around 1,0 absorbance are repeated, it is necessary for the spectrophotometer to show the differences within 0,002.

**Table 2 — Aliquot volumes of stock and blank solutions**

| Mass fraction of silicon(IV) oxide<br>% | Aliquot portion of stock solution (S′1)<br>ml | Aliquot portion of blank solution (B′1)<br>ml |
|---|---|---|
| < 2 | 20 | 0 |
| 2 to 4 | 10 | 10 |
| 4 to 10 | 5 | 15 |

### 3.3.3 Blank test

Using the blank solution (B′1) (see ISO 20565-1), follow the procedure given in 3.3.2. The volume of the aliquot portion of blank solution is the same as that for the corresponding stock solution.

### 3.3.4 Plotting of calibration graph

Transfer 0 ml, 5 ml, 10 ml, 15 ml, 20 ml and 25 ml aliquot portions of diluted standard silicon(IV) oxide solution [0 mg to 1 mg as silicon(IV) oxide] to separate 100 ml plastic beakers and add to each 20 ml of blank solution (B′1) (see ISO 20565-1). Treat these solutions and measure the absorbance in accordance with the procedure for addition of hydrofluoric acid (1+9) in 3.3.2. Plot the absorbance against the amounts of silicon(IV) oxide and prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 3.3.5 Calculation

Calculate the mass fraction of silicon(IV) oxide, $w_{SiO_2}$, expressed as a percentage, using Equation (2) with the amount of silicon(IV) oxide derived from the absorbance measurements obtained in 3.3.2 and 3.3.3 and the calibration in 3.3.4.

$$w_{SiO_2} = \frac{m_s - m_b}{m} \times \frac{250}{V} \times 100 \qquad (2)$$

where

$m_s$ is the mass of silicon(IV) oxide in the aliquot portion of stock solution (S′1), in grams (g);

$m_b$ is the mass of silicon(IV) oxide in the aliquot portion of blank solution (B′1), in grams (g);

$V$ is the aliquot volume of stock solution (S′1), in millilitres (ml);

$m$ is the mass of the test portion, in grams (g).

# 4 Determination of aluminium oxide

## 4.1 General

Determine the aluminium oxide content using one of the following methods:

a) cation-exchange separation — CyDTA-zinc back-titrimetric method (see 4.2);

b) cupferron extraction separation — CyDTA-zinc back-titrimetric method (see 4.3).

## 4.2 Cation-exchange separation — (1,2-Cyclohexylenenitrilo)tetraacetic acid zinc [CyDTA-zinc] back-titrimetric method

### 4.2.1 Principle

An aliquot portion of stock solution (SE-a) is transferred. Excess CyDTA solution is added to it. A chelate compound of aluminium CyDTA is formed by adjusting the pH with ammonia solution. The pH is further adjusted by the addition of hexamethylenetetramine. The amount of remaining CyDTA is determined by back-titration with zinc standard volumetric solution using xylenol orange as an indicator. The content of aluminium oxide is calculated by adjusting the content of titanium(IV) oxide.

### 4.2.2 Procedure

**4.2.2.1** Transfer precisely an aliquot portion of stock solution (SE-a) (see ISO 20565-1 and the following paragraph) to a 300 ml beaker. Add an amount of 0,01 mol/l CyDTA solution, in accordance with Table 4, and dilute to 100 ml with water. Add 1 g of hexamethylenetetramine and a drop of methyl orange solution as an indicator. Drop in ammonia water (1+1) and ammonia solution (1+9) of up to pH 3 until it indicates a slightly orange colour (see the paragraph directly below Table 3). Allow to stand for 5 min.

In Table 3, the aliquot volume of stock solution (SE-a) is shown. It depends on the volume of the aliquot portion of stock solution (S5) used in ISO 20565-1.

**Table 3 — Aliquot volume of stock solution (SE-a)**

| Aliquot volume of stock solution (S5)<br>ml | Aliquot volume of stock solution (SE-a)<br>ml |
|---|---|
| 100 | 40 |
| 50 | 80 |

If ammonia solution is added to excess, add hydrochloric acid (1+1) until the colour is changed to red, then adjust in the same manner.

NOTE The volume of 0,01 mol/l of CyDTA solution added depends on the mass fraction of aluminium oxide as shown in Table 4.

**Table 4 — Aliquot volume of 0,01 mol/l CyDTA solution**

| Mass fraction of aluminium oxide<br>% | Volume of 0,01 mol/l CyDTA solution<br>ml |
|---|---|
| < 5 | 10 |
| 5 to 10 | 20 |
| 10 to 15 | 30 |
| 15 to 20 | 40 |
| 20 to 30 | 50 |

**4.2.2.2** Add 5 g of hexamethylenetetramine of pH 5,5 to 5,8, add 4 or 5 drops of xylenol orange solution as an indicator and titrate with 0,01 mol/l zinc standard volumetric solution. Titrate while mixing gently and when the colour changes from yellow to the first appearance of a permanent reddish colour, consider this as the end point.

### 4.2.3 Blank test

Using the blank solution (BE-a) (see ISO 20565-1), follow the procedure given in 4.2.2. The volumes of the aliquot portion of blank solution (BE-a) and 0,01 mol/l CyDTA solution are the same as those for the corresponding stock solution (SE-a).

### 4.2.4 Calculation

Calculate the mass fraction of aluminium oxide, $w_{Al_2O_3}$, expressed as a percentage, using Equation (3).

$$w_{Al_2O_3} = \frac{(V_2 - V_1) \times F \times 0{,}000\,509\,8}{m} \times \frac{100}{40} \times \frac{250}{100} \times 100 - w_{TiO_2} \times 0{,}638 \qquad (3)$$

where

$V_1$ is the volume of 0,01 mol/l zinc standard volumetric solution in 4.2.3, in millilitres (ml);

$V_2$ is the volume of 0,01 mol/l zinc standard volumetric solution in 4.2.2.2, in millilitres (ml);

$F$ is the factor of 0,01 mol/l zinc standard volumetric solution;

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g);

$w_{TiO_2}$ is the mass fraction of titanium(IV) oxide determined in 6.2.5 or 6.3.5, expressed as a percentage.

## 4.3 Cupferron extraction separation — (1,2-Cyclohexylenenitrilo)tetraacetic acid zinc [CyDTA-zinc] back-titrimetric method

### 4.3.1 Principle

An aliquot portion of the stock solution (S6) (see ISO 20565-1) is cleaned up using first diethyldicarbonate and then cupferron in a separating funnel. To the resulting solution an excess of CyDTA is added, then back-titrated with a standard zinc solution.

### 4.3.2 Procedure

**4.3.2.1** Transfer 100 ml of the stock solution (S6) to the 500 ml separating funnel. Add the ammonia solution drop by drop until the solution is faintly alkaline to bromophenol blue. Re-acidify with dilute hydrochloric acid (1+3) and add an extra 4 ml. Add 20 ml of chloroform and 10 ml of sodium diethyldithiocarbamate solution. Stopper the funnel and shake vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer.

If an emulsion has formed, it will be necessary to add a few drops of hydrochloric acid and reshake.

Add 10 ml portions of chloroform and 5 ml portions of the sodium diethyldithiocarbamate and repeat the extraction until a coloured precipitate (brown or pink) is no longer formed. Wash the aqueous phase with 20 ml of chloroform to remove iron and manganese.

**4.3.2.2** Add 25 ml of the hydrochloric acid, concentrated, 36 % by mass, followed by 2 ml to 3 ml of cupferron solution and 20 ml of chloroform. Stopper the funnel and shake vigorously. Remove the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Repeat the extraction with three 10 ml portions of chloroform to remove traces of cupferron and sodium diethyldithiocarbamate. Run the aqueous phase from the separating funnel to a 1 l conical flask. Add a few drops of bromophenol blue indicator, followed by the ammonia solution until the solution is just alkaline. Re-acidify quickly with the concentrated hydrochloric acid, add an extra 5 to 6 drops and cool the flask in running water.

**4.3.2.3** Ensure that the solution is cold. Add CyDTA standard solution (0,05 M approximately) to produce an excess of a few millilitres over the expected amount (1 ml = 1,275 % $Al_2O_3$). Add ammonium acetate buffer solution until the indicator turns blue, followed by an extra 15 ml. Add a volume of ethanol equal to the total volume of the solution, then add 20 ml of the hydroxyammonium chloride solution and 1 ml to 2 ml of the dithizone indicator. Titrate with zinc standard solution (0,05 M) from green to the first appearance of a permanent pink colour.

NOTE The end point is often improved by the addition of a little naphthol green solution to eliminate any early formation of pink colour that might have formed in the solution on the addition of the indicator.

### 4.3.3 Calculation

Calculate the mass fraction of aluminium oxide, $w_{Al_2O_3}$, expressed as a percentage, using Equation (4).

$$w_{Al_2O_3} = \frac{(V_1 \times F_1 - V_2 \times F_2) \times 0{,}001\ 019\ 6}{m} \times \frac{250}{100} \times 100 \qquad (4)$$

where

$V_1$ is the volume of the 0,05 mol/l CyDTA standard solution in 4.3.2.3, in millilitres (ml);

$F_1$ is the factor of the 0,05 mol/l CyDTA standard solution;

$V_2$ is the volume of 0,05 mol/l zinc standard solution used in the back-titration in 4.3.2.3, in millilitres (ml);

$F_2$ is the factor of 0,05 mol/l zinc standard solution;

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g).

# 5 Determination of total iron as iron(III) oxide

## 5.1 General

Determine the iron(III) oxide content using one of the following methods.

a) 1,10-Phenanthroline absorption method using stock solution (S6) or (S′6) (see ISO 20565-1)

This method is applied to samples consisting of less than 15 % by mass of iron(III) oxide (see 5.2).

b) 1,10-Phenanthroline absorption method using stock solution (SE-b) (see ISO 20565-1)

This method is applied to samples consisting of less than 15 % by mass of iron(III) oxide (see 5.3).

c) CyDTA-Zinc back-titrimetric method

This method is applied to samples consisting of 10 % by mass or more of iron(III) oxide (see 5.4).

## 5.2 1,10-Phenanthroline absorption method using stock solution (S6) or (S′6)

### 5.2.1 Principle

An aliquot portion of the stock solution (S6) (see ISO 20565-1) is reduced with hydroxylamine chloride to iron(II) oxide, coloured with 1,10 ortho-phenanthroline and its absorbance measured at 510 nm.

### 5.2.2 Procedure

**5.2.2.1** Dilute 25,0 ml of the stock solution (S6) (see ISO 20565-1) with water to 500 ml in a volumetric flask and mix. Transfer 25 ml of this diluted solution to a 100 ml volumetric flask and add 2 ml of the hydroxyammonium chloride solution followed by 5 ml of the phenanthroline solution. Add the ammonium acetate solution until a pink colour forms, then add an extra 2 ml. Allow to stand for 15 min, dilute the solution with water to 100 ml and mix. Use a spectrophotometer to measure the optical density of the solution against water in 10 mm cells at 510 nm.

NOTE The use of a filter-type absorptiometer is not appropriate to this test.

**5.2.2.2** Add ammonium acetate solution to stabilize the colour. Ensure that the colour is stable from 15 min to 75 min. Determine the iron(II) oxide content of the solution by reference to a calibration graph.

NOTE The dilution of the "stock" solution quoted will cover the range from 0 % to 20 % $Fe_2O_3$ by mass. For iron mass fractions considerably below 20 % $Fe_2O_3$, a decreased dilution of the "stock" solution needs to be made. The aliquot portion of the solution should not be diluted once the colour has developed.

### 5.2.3 Blank test

Using blank solution (B6) (see ISO 20565-1), carry out the procedure given in 5.2.2. The volume of the aliquot portion of blank solution is the same as those for the corresponding stock solution.

### 5.2.4 Plotting of calibration graph

Transfer a range from 0 ml to 15,0 ml aliquot portions of the diluted iron(III) oxide standard solution [0 mg to 0,6 mg as iron(III) oxide] to separate 250 ml volumetric flasks. Treat these solutions in accordance with 5.2.2.1 and measure the absorbance against the reference solution. Plot the relation between the absorbance and the mass of iron(III) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 5.2.5 Calculation

Calculate the mass fraction of iron(III) oxide, $w_{Fe_2O_3}$, expressed as a percentage, using Equation (5), using the amount of iron(III) oxide which is derived from the absorbance obtained in 5.2.2.2 and 5.2.3 and the calibration in 5.2.4.

$$w_{Fe_2O_3} = \frac{m_s - m_b}{m} \times \frac{100}{25} \times \frac{500}{25} \quad (5)$$

where

$m_s$ is the mass of iron(III) oxide in the aliquot portion of stock solution (S6), in grams (g);

$m_b$ is the mass of iron(III) oxide in the aliquot portion of blank solution (B6), in grams (g);

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g).

## 5.3 1,10-Phenanthroline absorption method using stock solution (SE-b)

### 5.3.1 Principle

Stock solution (SE-b) (see ISO 20565-1) is transferred and the iron is reduced with L (+)-ascorbic acid. 1,10-Phenanthroline chloride is added and the pH is adjusted by adding ammonium acetate when the colour of iron develops. The absorbance is measured.

### 5.3.2 Procedure

**5.3.2.1** Transfer precisely an appropriate aliquot portion obtained by the procedure used for stock solution (SE-b) (see ISO 20565-1) to two 250 ml volumetric flasks, respectively. Add 5 ml of L (+)-ascorbic acid solution to each while shaking. Add 25 ml of 1,10-phenanthroline chloride solution and 10 ml of ammonium acetate solution. Dilute to the mark with water and allow to stand for 30 min.

In Table 5, an aliquot volume of stock solution (SE-b) is shown. It depends on the volume of the aliquot portion (see ISO 20565-1:2008, Table 2) and the mass fraction of iron(III) oxide in the sample.

**Table 5 — Aliquot volume of stock solution (SE-b)**

| Mass fraction of iron(III) oxide % | Aliquot volume of stock solution (SE-b) taken in ISO 20565-1 | |
|---|---|---|
| | 100 ml | 50 ml |
| < 8 | 20 | 40 |
| > 8 | 10 | 20 |

**5.3.2.2** Transfer a portion of the solution obtained in 5.3.2.1 to two absorption cells. Measure the absorbance of each solution at the wavelength of 510 nm against water, and calculate the mean of the measured values.

### 5.3.3 Blank test

Using blank solution (BE-b) (see ISO 20565-1), carry out the procedure in accordance with 5.3.2. The volume of the aliquot portion of blank solution is the same as that for the corresponding stock solution.

### 5.3.4 Plotting of calibration graph

Transfer a range of 0 ml to 40,0 ml aliquot portions of the diluted iron(III) oxide standard solution [0 mg to 1,6 mg as iron(III) oxide] to several 250 ml volumetric flasks. Treat these solutions in accordance with 5.3.2.1 and measure the absorbance against the reference solution. Plot the relation between the absorbance and mass of iron(III) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 5.3.5 Calculation

Calculate the mass fraction of iron(III) oxide, $w_{Fe_2O_3}$, expressed as a percentage, using Equation (6), using the amount of iron(III) oxide which is derived from the absorbance obtained in 5.3.2.2 and 5.3.3 and the calibration in 5.3.4.

$$w_{Fe_2O_3} = \frac{m_s - m_b}{m} \times \frac{250}{V_1} \times \frac{100}{V_2} \times 100 \qquad (6)$$

where

$m_s$ is the mass of iron(III) oxide in the aliquot portion of stock solution (SE-b), in grams (g);

$m_b$ is the mass of iron(III) oxide in the aliquot portion of blank solution (BE-b), in grams (g);

$V_1$ is the volume of the aliquot portion taken for stock solution (SE-b), in millilitres (ml);

$V_2$ is the volume of aliquot portion taken for stock solution (SE-b), in grams (g);

$m$ is the mass of the test portion described in ISO 20565-1, in grams (g).

## 5.4 (1,2-Cyclohexylenenitrilo)tetraacetic acid-zinc [CyDTA*-zinc] back-titrimetric method

### 5.4.1 Principle

An appropriate amount of CyDTA solution is added to an aliquot portion of stock solution (SE-b). A chelate compound of iron CyDTA is formed by adjusting the pH with ammonia water. The pH is further adjusted by addition of hexamethylenetetramine. The amount of remaining CyDTA is determined by back-titration with zinc standard volumetric solution using xylenol orange as an indicator.

### 5.4.2 Procedure

**5.4.2.1** Transfer precisely an appropriate volume of stock solution (SE-b) (see ISO 20565-1) to a 300 ml beaker, add a precisely known amount of 0,01 mol/l of CyDTA solution and dilute to 100 ml with water.

In the case of 100 ml of the aliquot portion (in ISO 20565-1), use 50 ml of stock solution (SE-b).

In the case of 50 ml of the aliquot portion (in ISO 20565-1), use the entire stock solution (SE-b).

**5.4.2.2** Use a volume of 0,01 mol/l of CyDTA solution, added depending on the content percentages of iron(III) oxide, as shown in Table 6.

**5.4.2.3** Carry out titration in accordance with 4.2.2.2 and add 2 g of hexamethylenetetramine.

**Table 6 — Volume of 0,01 mol/l CyDTA solution**

| Mass fraction of iron(III) oxide<br>% | Volume of 0,01 mol/l CyDTA solution<br>ml |
|---|---|
| 10 to 15 | 20 |
| 15 to 20 | 30 |
| 20 to 25 | 40 |

#### 5.4.3 Blank test

Treat the blank solution (BE-b) (see ISO 20565-1) and carry out the procedure in accordance with 5.3.3. Use the same volumes of the aliquot portion of blank solution (BE-b) and 0,01 mol/l CyDTA solution as those for the corresponding stock solution (SE-b).

#### 5.4.4 Calculation

Calculate the mass fraction of iron(III) oxide, $w_{Fe_2O_3}$, expressed as a percentage, using Equation (7).

$$w_{Fe_2O_3} = \frac{(V_2 - V_1) \times F \times 0{,}000\,798\,5}{m} \times \frac{100}{50} \times \frac{250}{100} \times 100 \qquad (7)$$

where

$V_1$ is the volume of 0,01 mol/l zinc standard volumetric solution in 5.4.3, in millilitres (ml);

$V_2$ is the volume of 0,01 mol/l zinc standard volumetric solution in 5.4.2, in millilitres (ml);

$F$ is the factor of 0,01 mol/l zinc standard volumetric solution;

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g).

## 6 Determination of titanium(IV) oxide

### 6.1 General

The titanium(IV) oxide determination method is carried out using one of the following two methods:

a) diantipyrylmethane (DAM) method (see 6.2);

b) hydrogen peroxide method (see 6.3).

### 6.2 Diantipyrylmethane (DAM) method

#### 6.2.1 Principle

Stock solution (S1) or (S′1) (see ISO 20565-1) is transferred. After the adjustment of hydrochloric acidity, iron is reduced with the addition of L (+)-ascorbic acid. The titanium is coloured by the DAM and the absorbance is measured.

### 6.2.2 Procedure

**6.2.2.1** Transfer precisely 20 ml of stock solution (S1) (see ISO 20565-1) or (S′1) (see ISO 20565-1) to a 50 ml volumetric flask. Add 5 ml of hydrochloric acid (1+1) and 5 ml of L (+)-ascorbic acid and allow to stand for 1 min. Add 15 ml of DAM solution, shake the flask, dilute to the mark with water and allow to stand for 90 min.

**6.2.2.2** Transfer precisely 20 ml of stock solution (S1) or (S′1) to a 50 ml volumetric flask. Add 5 ml of hydrochloric acid (1+1) and 5 ml of L (+)-ascorbic acid and dilute to the mark with water.

**6.2.2.3** Measure the absorbance of the solution obtained in 6.2.2.1 or 6.2.2.2 in a 10 mm cell at the wavelength of 390 nm against water. Obtain the absorbance difference of the solutions obtained in 6.2.2.1 and 6.2.2.2.

### 6.2.3 Blank test

Using blank solution (B1) (see ISO 20565-1) or (B′1) (see ISO 20565-1), carry out the procedure described in 6.2.2. Use blank test solution (B1) corresponding to stock solution (S1) and blank test solution (B′1) corresponding to stock solution (S′1).

### 6.2.4 Plotting of calibration graph

Transfer 0 ml, 5 ml, 15 ml and 20 ml aliquot portions of diluted titanium(IV) oxide standard solution (0,01 mg/ml) [0 mg to 0,2 mg as titanium(IV) oxide] to separate 50 ml volumetric flasks and treat these solutions as in 6.2.2.1. Plot the relation between the absorbance and the amount of titanium(IV) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 6.2.5 Calculation

Calculate the mass fraction of titanium(IV) oxide, $w_{TiO_2}$, expressed as a percentage, using Equation (8) with the amount of titanium(IV) oxide derived from the absorbance obtained in 6.2.2.2 and 6.2.3 and the calibration in 6.2.4.

$$w_{TiO_2} = \frac{m_s - m_b}{m} \times \frac{250}{20} \times 100 \quad (8)$$

where

$m_s$ is the mass of titanium(IV) oxide in the aliquot portion of stock solution (S1) or (S′1), in grams (g);

$m_b$ is the mass of titanium(IV) oxide in the aliquot portion of blank solution (B1) or (B′1), in grams (g);

$m$ is the mass of the test portion used to prepare solution (S1 or S'1) in ISO 20565-1, in grams (g).

## 6.3 Hydrogen peroxide method

### 6.3.1 Principle

An aliquot portion is bleached with phosphoric acid, coloured with hydrogen peroxide and its absorbance measured at 398 nm

### 6.3.2 Procedure

**6.3.2.1** Transfer 20 ml of the stock solution (S6) (see ISO 20565-1) to each of the two 50 ml volumetric flasks A and B. To each flask, add 10 ml of dilute phosphoric acid (2+3) and, to flask A only, add 10 ml of the hydrogen peroxide solution.

**6.3.2.2** Dilute the solution in each flask with water to 50 ml and shake well. Measure A against B in 40 mm cells at 398 nm, or by using a colour filter or filter of similar band-pass in a suitable instrument. Ensure that the colour is stable from 5 min until 24 h after the addition of the hydrogen peroxide solution. Determine the titanium content of the solution by reference to a calibration graph.

### 6.3.3 Blank test

Using blank solution (B6) (see ISO 20565-1), carry out the procedure described in 6.3.2.

### 6.3.4 Plotting of calibration graph

Transfer 0 ml, 5 ml, 15 ml and 20 ml aliquot portions of diluted titanium(IV) oxide standard solution (0,2 mg/ml) [0 mg to 4 mg as titanium(IV) oxide] to separate 50 ml volumetric flasks. To each flask, add 10 ml of dilute phosphoric acid (2+3) and 10 ml of the hydrogen peroxide solution. Dilute the solution in each flask with water to 50 ml and shake well. Plot the relation between the absorbance and the amount of titanium(IV) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 6.3.5 Calculation

Calculate the mass fraction of titanium(IV) oxide, $w_{TiO_2}$, expressed as a percentage, using Equation (9) with the amount of titanium(IV) oxide derived from the absorbance obtained in 6.3.2.2 and 6.3.3 and the calibration in 6.3.4.

$$w_{TiO_2} = \frac{m_s - m_b}{m} \times \frac{500}{20} \times 100 \qquad (9)$$

where

$m_s$ is the mass of titanium(IV) oxide in the aliquot portion of stock solution (S6), in grams (g);

$m_b$ is the mass of titanium(IV) oxide in the aliquot portion of blank solution (B6), in grams (g);

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g).

## 7 Determination of manganese(II) oxide

### 7.1 Principle

An aliquot portion of the stock solution (S6) prepared for titanium(IV) oxide is treated with sulfuric and nitric acid to destroy the resin, coloured by oxidation to permanganate with potassium periodate and its absorbance measured at 524 nm.

### 7.2 Procedure

**7.2.1** Transfer 50 ml of the stock solution (S6), (see ISO 20565-1) to a 250 ml beaker. Add 10 ml of dilute sulfuric acid (1+1), 10 ml of dilute nitric acid (1+1) and heat on a water bath until evaporated to destroy traces of resin. Allow to cool, add 20 ml of nitric acid, concentrated, 70 % by mass, 10 ml of dilute phosphoric acid (1+9) and 50 ml of water. Boil to dissolve the salts and to remove nitrous fumes, filtering if necessary. Add 0,5 g of potassium periodate, boil until the colour develops and then boil for a further 2 min. Transfer to a steam bath for 10 min. Allow to cool and transfer to a 100 ml volumetric flask. Dilute the solution with water to 100 ml and mix.

**7.2.2** Measure the absorbance of the solution against water in 40 mm cells at 524 nm, or by using a colour filter or filter of similar band-pass in a suitable instrument. Determine the manganese oxide content of the solution by reference to a calibration graph.

### 7.3 Blank test

Using blank solution (B6) (see ISO 20565-1), carry out the procedure described in 7.2.

### 7.4 Plotting of calibration graph

Transfer 0 ml (as reference), 5 ml, 10 ml, 15 ml, 20 ml and 25 ml aliquot portions of the diluted manganese(II) oxide standard solution (MnO 0,04 mg/ml) [0 mg to 1,00 mg as manganese(II) oxide] to 250 ml beakers. Treat each of these as in 7.2.1. Then measure the absorbance against the reference solution. Plot the relation between the absorbance and the mass of manganese(II) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 7.5 Calculation

Calculate the mass fraction of manganese(II) oxide, $w_{MnO}$, expressed as a percentage, using Equation (10) with the amount of manganese(II) oxide that is derived from the absorbance in 7.2.1 and 7.3, and the calibration in 7.4.

$$w_{MnO} = \frac{m_s - m_b}{m} \times \frac{500}{50} \times 100 \qquad (10)$$

where

$m_s$ is the mass of manganese(II) oxide in the aliquot portion of stock solution (S6), in grams (g);

$m_b$ is the mass of manganese(II) oxide in the aliquot portion of blank solution (B6), in grams (g);

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g).

## 8 Determination of calcium oxide

### 8.1 Principle

Excess EGTA [ethylene glycol-*O*,*O*′-bis(2-aminoethyl)-*N*,*N*,*N*′,*N*′-tetraacetic acid] is added to an aliquot portion of the stock solution (S6). The MgO is precipitated out with potassium hydroxide solution and a precipitating agent. After making up to volume, an aliquot portion is back-titrated with calcium oxide standard solution.

### 8.2 Procedure

Transfer 100 ml of the stock solution (S6) to a 250 ml separating funnel. Add 5 ml of dilute triethanolamine (1+1), 5,0 ml of EGTA standard solution (approximately 0,05 mol/l) and dilute with water to 150 ml. Add the potassium hydroxide solution until no further precipitation takes place, then add 10 ml in excess, followed by 10 ml of the Magflok solution (20 g/l). Dilute with water to 250 ml, shake and allow to stand for 10 min. Filter through a 150 mm dry coarse filter paper into a dry beaker. Add 200 ml of the filtrate using a pipette into a 500 ml conical flask and add 15 ml of the potassium hydroxide solution. Add approximately 0,03 g of screened calcein indicator and titrate with the calcium oxide standard solution (CaO 1 mg/ml) until the first appearance of a green fluorescence. Carry out the titration in good daylight but not in direct sunlight.

### 8.3 Calculation

Calculate the mass fraction of calcium oxide, $w_{CaO}$, expressed as a percentage, using Equation (11).

$$w_{CaO} = \frac{0{,}002\,804 \times 5 \times F_1 - F_2 \times V}{m} \times \frac{500}{100} \times \frac{250}{200} \times 100 \qquad (11)$$

where

0,002 804 is the mass of calcium oxide equivalent to 1 ml of 0,05 mol/l EGTA standard solution, in grams (g);

$F_1$ is the factor of 0,05 mol/l EGTA standard solution;

$F_2$ is the factor of calcium oxide standard solution (CaO 1 mg/ml);

$V$ is the volume of calcium oxide standard solution (CaO 1 mg/ml) needed for titration, in millilitres (ml);

$m$ is the mass of the test portion used to prepare (S6) (see ISO 20565-1), in grams (g).

# 9 Determination of magnesium oxide

## 9.1 General

The magnesium oxide determination method is carried out in accordance with either one of the following two methods:

a) EDTA titration method (see 9.2);

b) CyDTA titration method (see 9.3).

## 9.2 Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid [EDTA] titration method

### 9.2.1 Principle

Ammonia solution is added to an aliquot portion of stock solution (SE-c) and it is filtered. 2,2′,2″-nitrilotriethanol and buffer is added to the filtrate. Potassium cyanide is added to it and the content of calcium oxide and magnesium oxide is determined by EDTA (ethylenediaminetetraacetic acid) titration using Eriochrome Black T as an indicator, and is corrected by the content of calcium oxide obtained in Clause 8. The precipitate is dissolved in hydrochloric acid and the content of the residual magnesium oxide is determined by ICP-AES.

### 9.2.2 Procedure

**9.2.2.1** Transfer 50 ml of stock solution (SE-c) (see ISO 20565-1) to a 200 ml beaker. Heat on a water bath and concentrate to 20 ml by evaporation. Add 1 ml of iron(III) chloride solution and one drop of methyl red solution as an indicator. Add ammonia solution (1+1) until the colour changes to yellow and immediately add hydrochloric acid (1+3) dropwise until the colour changes to red. Cover with a watch glass, heat to boiling and add ammonia water (1+9) dropwise. Add 10 excess drops of ammonia water (1+9), cover with a watch glass and boil for 1 min. Heat on a water bath for 15 min.

**9.2.2.2** Filter using filter paper (medium-pore) and wash twice with hot ammonium chloride solution. Collect the filtrate and washings in a 300 ml beaker.

**9.2.2.3** Dilute the solution from 9.2.2.2 to 200 ml with water. Add 5 ml of 2,2′,2″-nitrilotriethanol (1+1), 10 ml of buffer (pH 10) and 3 or 4 drops of Eriochrome Black T as an indicator. Titrate the stirred solution with 0,02 mol/l EDTA solution. Carry out titration gently while mixing and when the colour changes from reddish purple to blue, consider this as being the end point.

NOTE The judgement of the end point is easier if the titration is carried out on milk-white glass or a plastic plate with light transmission by tungsten lamp.

**9.2.2.4** Transfer the precipitate prepared in 9.2.2.2 to the original 200 ml beaker by using a small amount of water. Add 20 ml of hydrochloric acid (1+3) and dissolve completely by heating. Put this solution into the filter paper used in 9.2.2.2 and dissolve the remaining precipitate in it. Wash the beaker and the filter paper, transfer the filtrate and washings to a 200 ml volumetric flask and dilute to the mark with water.

**9.2.2.5** Spray a portion of the solution prepared in 9.2.2.4 into the Ar plasma flame of an ICP-AE spectrometer and measure the emission intensities of magnesium at wavelengths of 279,55 nm.

NOTE AAS can be used. In this case, gather the solution prepared in 9.2.2.4 in a 100 ml volumetric flask, add 10 ml of lanthanum solution and dilute to the mark with water. Spray a portion of this solution into a flame of dinitrogen oxide-acetylene, or, air-acetylene, and measure the absorbance of magnesium at the wavelength of 285,2 nm.

### 9.2.3 Blank test

Carry out the procedure described in 9.2.2 with the blank solution (BE-c) (see ISO 20565-1).

### 9.2.4 Plotting of calibration graph

Transfer 0 ml, 2,0 ml, 4,0 ml, 6,0 ml, 8,0 ml and 10,0 ml of each diluted standard solution (0 mg to 1 mg as magnesium oxide) to six separate 200 ml volumetric flasks, add 20 ml of hydrochloric acid (1+3), respectively, and dilute to the mark with water. Treat these solutions in accordance with 9.2.2.5, plot the relation between the emission intensity and magnesium oxide and prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

NOTE If AAS is applied in 9.2.2.5, prepare a solution series for calibration by adding the reagent in 9.2.2.5, 1 ml of iron(III) chloride solution and 10 ml of lanthanum solution. Carry out the procedure in the Note to 9.2.2.5 for solution for calibration and plot the relation between the absorbance and magnesium oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

### 9.2.5 Calculation

Calculate the mass fraction of magnesium oxide, $w_{MgO}$, expressed as a percentage, using Equation (12) with the mass of magnesium oxide derived from the emission intensity obtained in 9.2.2.5 and 9.2.3 and the calibration for the residual magnesium oxide prepared in 9.2.4.

$$w_{MgO} = \frac{(V_1 - V_2) \times F \times 0{,}008\,061 + (m_s - m_b)}{m} \times \frac{250}{V_3} \times \frac{100}{50} \times 100 - 0{,}719 \times w_{CaO} \qquad (12)$$

where

$V_1$ is the volume of the titration of 0,02 mol/l EDTA solution in 9.2.2.2, in millilitres (ml);

$V_2$ is the volume of the titration of 0,02 mol/l EDTA solution in 9.2.5, in millilitres (ml);

$V_3$ is the volume of the aliquot portion taken for stock solution (S5) (see ISO 20565-1), in millilitres (ml);

$F$ is the factor of 0,02 mol/l EDTA solution;

$m_s$ is the mass of the residual magnesium oxide in the precipitation of 9.2.2.5, in grams (g);

$m_b$ is the mass of the residual magnesium oxide in the precipitation of 9.2.3, in grams (g);

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g);

$w_{CaO}$ is the mass fraction of calcium oxide determined in Clause 8, expressed as a percentage.

## 9.3 (1,2-Cyclohexylenenitrilo)tetraacetic acid [CyDTA] titration method by stock solution (S6)

### 9.3.1 Principle

An aliquot portion of the stock solution (S6) is cleaned up using first diethyldithiocarbamate and the cupferron in a separating funnel. A proportion of CyDTA is added to prevent magnesium oxide precipitation. After adjusting the pH, the titration is completed by titrating with more CyDTA. This gives magnesium oxide plus calcium oxide, so the result is corrected for calcium oxide.

### 9.3.2 Procedure

**9.3.2.1** Transfer 100,0 ml of the stock solution (S6) to a 500 ml separating funnel and add the ammonia solution, drop by drop, until the solution is faintly alkaline to bromophenol blue. Re-acidify with dilute hydrochloric acid (1+3) and add an extra 4 ml. Add 20 ml of chloroform and 10 ml of the sodium diethyldithiocarbamate solution. Stopper the funnel and shake vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer.

NOTE If an emulsion has formed, it will be necessary to add a few drops of hydrochloric acid and reshake.

Add 10 ml portions of chloroform and repeat the extraction with 5 ml portions of diethyldithiocarbamate solution until a coloured precipitate is no longer formed. Wash the aqueous phase once with 10 ml of chloroform to remove iron and manganese.

**9.3.2.2** Add dilute ammonia solution (1+1), drop by drop, until the solution is alkaline to bromophenol blue. Re-acidify with dilute hydrochloric acid (1+9) and add 20 ml of the ammonium acetate buffer solution to determine the magnesia content. Add 20 ml chloroform and 10 ml of the cupferron solution. Stopper the funnel and shake vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Repeat the extraction with a further 10 ml of cupferron solution and wash the aqueous phase three times with 10 ml portions of chloroform to remove aluminium and titanium.

**9.3.2.3** Transfer the aqueous layer to a 500 ml conical flask and boil off traces of chloroform. Allow to cool and add 2 g of ammonium chloride and 5 ml of 2,2′,2″-nitrilotriethanol (1+1) while swirling followed by a known amount of CyDTA standard solution (approximately 0,05 mol/l).

NOTE 1 The addition of CyDTA standard solution is made to complex most of the magnesia before the solution is made alkaline so that the tendency for magnesium hydroxide to precipitate is greatly reduced.

Add 30 ml of the concentrated ammonia solution and 5 ml of the hydroxyammonium chloride solution to stabilize the indicator. Titrate with the CyDTA standard solution using Solochrome Black 6B indicator, monitoring the colour change from red to purple and finally to a clear blue.

NOTE 2 This titration also includes the titration for lime in the sample which is to be corrected for.

### 9.3.3 Calculation

Calculate the mass fraction of magnesium oxide, $w_{MgO}$, expressed as a percentage, using Equation (13).

$$w_{MgO} = \frac{0{,}002\,015 \times F \times V}{m} \times \frac{500}{100} \times 100 - 0{,}719 \times w_{CaO} \qquad (13)$$

where

0,002 015 is the mass of magnesium oxide equivalent to 1 ml of 0,05 mol/l CyDTA standard solution, in grams (g);

$F$ is the factor of 0,05 mol/l CyDTA standard solution;

$V$ is the volume of 0,05 mol/l CyDTA standard solution needed for titration, in millilitres (ml);

$m$ is the mass of the test portion used to prepare (S6) (see ISO 20565-1), in grams (g);

$w_{CaO}$ is the mass fraction of calcium oxide determined in Clause 8, expressed as a percentage.

## 10 Determination of sodium oxide by flame photometry

### 10.1 Principle

An aliquot portion of stock solution (S2) is transferred and sprayed into the flame of a flame photometer and the emission intensities of sodium are measured.

### 10.2 Reagents

Use reagents described in ISO 20565-1:2008, Clause 5, and the following.

**10.2.1 Mixed standard solution 1**, $Na_2O$ 0,05 mg/ml, $K_2O$ 0,05 mg/ml.

Transfer 25 ml each of the sodium oxide and potassium oxide standard solutions to a 500 ml volumetric flask and dilute to the mark with water.

**10.2.2 Calibration solution series 1**.

Transfer a range of volumes from 0 ml to 40 ml of the mixed standard solution 1 to separate 100 ml volumetric flasks. Add an amount of magnesium oxide solution (MgO 10 mg/ml) corresponding to the magnesium oxide content in the samples (e.g. 12 ml of magnesium oxide solution in the case of 62 % by mass of magnesium oxide). Add 5,0 ml of hydrochloric acid (1+1) and dilute to the mark with water. An example is shown in Table 7.

NOTE The amount of magnesium oxide solution is approximately 5 ml per 10 % by mass of the magnesium oxide content.

**Table 7 — Example of calibration solution series 1**

| Calibration solution series 1 | Magnesium oxide solution (MgO 10 mg/ml) | Hydrochloric acid (1+1) | Mixed standard solution 1 | Concentration of solution mg/100 ml | |
|---|---|---|---|---|---|
| No. | ml | ml | ml | $Na_2O$ | $K_2O$ |
| 1 | 8 | 5 | 0 | 0,00 | 0,00 |
| 2 | 8 | 5 | 1 | 0,05 | 0,05 |
| 3 | 8 | 5 | 2 | 0,10 | 0,10 |
| 4 | 8 | 5 | 3 | 0,15 | 0,15 |
| 5 | 8 | 5 | 4 | 0,20 | 0,20 |
| 6 | 8 | 5 | 5 | 0,25 | 0,25 |
| 7 | 8 | 5 | 6 | 0,30 | 0,30 |
| 8 | 8 | 5 | 8 | 0,40 | 0,40 |
| 9 | 8 | 5 | 10 | 0,50 | 0,50 |
| 10 | 8 | 5 | 15 | 0,75 | 0,75 |
| 11 | 8 | 5 | 20 | 1,00 | 1,00 |
| 12 | 8 | 5 | 25 | 1,25 | 1,25 |
| 13 | 8 | 5 | 30 | 1,50 | 1,50 |
| 14 | 8 | 5 | 40 | 2,00 | 2,00 |
| NOTE 1 ml of magnesium oxide solution corresponds to 5 % by mass. In this case, the mass fraction of magnesium oxide is 40 %. | | | | | |

## 10.3 Procedure

Spray a portion of stock solution (S2) (see ISO 20565-1) into the flame of a flame photometer and measure the emission intensity at the wavelength of 589,0 nm.

An optical filter for sodium may be used.

## 10.4 Blank test

Carry out the procedure described in 10.3 using blank solution (B2) (see ISO 20565-1).

## 10.5 Plotting of calibration graph

Transfer the calibration solution series 1, carry out the procedure described in 10.3 and plot the relation between the emission intensities and mass of sodium oxide.

NOTE The measurement of the solution for calibration is carried out simultaneously with the measurements for the stock and blank solutions. The calibration line is newly prepared for each measurement.

### 10.6 Calculation

Calculate the mass fraction of sodium oxide, $w_{Na_2O}$, expressed as a percentage, using Equation (14) with the mass of sodium oxide derived from the emission intensities obtained in 10.3 and 10.4 and the calibration graph prepared in 10.5.

$$w_{Na_2O} = \frac{m_s - m_b}{m} \times 100 \quad (14)$$

where

$m_s$ is the mass of sodium oxide in stock solution (S2), in grams (g);

$m_b$ is the mass of sodium oxide in blank solution (B2), in grams (g);

$m$ is the mass of the test portion (see ISO 20565-1), in grams (g).

## 11 Determination of potassium oxide by flame spectrophotometry

### 11.1 Principle

Stock solution (S2) is transferred and sprayed into the flame of a flame photometer and the emission intensity of potassium is measured.

### 11.2 Procedure

Spray a portion of stock solution (S2) (see ISO 20565-1) into the flame of a flame photometer and measure the emission intensity at the wavelength of 766,5 nm.

The filter for potassium can be used.

### 11.3 Blank test

Using blank solution (B2) (see ISO 20565-1), carry out the procedure given in 11.2.

### 11.4 Plotting of calibration graph

Transfer series 1 solution for calibration in accordance with Table 7. Carry out the procedure given in 11.2 and plot the relation between the emission intensity and mass of potassium oxide as the calibration graph.

### 11.5 Calculation

Calculate the mass fraction of potassium oxide, $w_{K_2O}$, expressed as a percentage, using Equation (15) with the mass of potassium oxide derived from the emission intensity obtained in 11.2 and 11.3 and the calibration prepared in 11.4.

$$w_{K_2O} = \frac{m_s - m_b}{m} \times 100 \quad (15)$$

where

$m_s$ is the mass of potassium oxide in stock solution (S2), in grams (g);

$m_b$ is the mass of potassium oxide in blank solution (B2), in grams (g);

$m$ is the mass of the test portion used to prepare (S2) (see ISO 20565-1), in grams (g).

# 12 Determination of chromium(III) oxide

## 12.1 General

The determination of chromium(III) oxide is carried out using one of the following methods:

a) sodium carbonate-boric acid fusion–potassium dichromate titrimetry (see 12.2);

b) fusion mixture–boric acid fusion–potassium dichromate titrimetry (see 12.3);

c) mixed acids–potassium dichromate titrimetry (see 12.4).

NOTE Method c) does not always result in total decomposition. Methods a) and b) are preferred.

## 12.2 Sodium carbonate-boric acid fusion — Potassium dichromate titrimetry

### 12.2.1 Principle

A sample is fused with sodium carbonate and boric acid. It is dissolved in sulfuric acid, phosphoric acid is added and it is then oxidized to dichromic acid by peroxodisulfuric acid using a silver nitrite catalyst. Permanganate is decomposed with hydrochloric acid. By adding of a small excess of ammonium iron(II) sulfate, dichromate is reduced, and then the remaining ammonium iron(II) sulfate is titrated with potassium dichromate solution.

### 12.2.2 Procedure

**12.2.2.1** Weigh 0,250 g of the dried sample, prepared in accordance with Clause 7 of ISO 26845:2008, in a 75 ml platinum dish, add 4,0 g of sodium carbonate and 2,7 g of boric acid. Fuse in accordance with ISO 20565-1:2008, 9.2.2.3.1. Cover with a watch glass, add 25 ml of sulfuric acid (1+1) and heat on a steam bath until the melt is completely dissolved while occasionally stirring. Transfer to an Erlenmeyer flask (500 ml), add 10 ml of phosphoric acid and dilute to 200 ml with water.

NOTE See ISO 20565-1:2008 (Note 1 and Note 2 to 9.2.2.3.1).

**12.2.2.2** Add 0,5 ml of potassium permanganate solution, 10 ml of silver nitrate solution and 30 ml of ammonium peroxodisulfate solution and heat while stirring using a magnetic rotating bar coated by ethylene-4-fluoride resin. Boil until a red colour of permanganate appears and continue boiling for a further 5 min in order to decompose excess peroxodisulfate. Add 10 ml of hydrochloric acid (1+3). Heat until the red colour of the permanganate disappears in order to remove the yielding chlorine. Cool to room temperature.

**12.2.2.3** Add 0,1 mol/l of ammonium iron(II) sulfate solution to reduce dichromate. Add in excess of 5 ml to 10 ml of the ammonium iron(II) sulfate solution and 0,5 ml of sodium diphenylamine-4-sulfonate as an indicator and titrate with 1/60 mol/l potassium dichromate solution while stirring. Determine the end point as being when the colour of the solution changes to purple.

### 12.2.3 Blank test

Carry out the procedure in 12.2.2 without the sample and omit the fusion of sodium carbonate and boric acid. The volume of 0,1 mol/l of ammonium iron(II) sulfate solution is the same as that for the corresponding sample solution.