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

Part 2:

Wet chemical analysis

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*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) —*

ISO 20565-2:2008
Partie 2: Méthodes d'analyse chimique par voie humide

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Foreword

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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 ₂ O ₃ | 2 to 30 |
| Fe ₂ O 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 ₂ O | 0,01 to 1 |
| K ₂ O | 0,01 to 1 |
| Cr ₂ O ₃ | 2 to 60 |
| ZrO ₂ | 0,01 to 0,5 |
| P ₂ O 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 coupled plasma atomic emission spectrometry (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.

$$w_{\text{SiO}_2} = \frac{(m_1 - m_2) + (m_s - m_b) \times \frac{500}{10}}{m} \times 100 \quad (1)$$

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 % | Aliquot portion of stock solution (S'1) ml | Aliquot portion of blank solution (B'1) 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.

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3.3.5 Calculation

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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.

$$w_{\text{SiO}_2} = \frac{m_s - m_b}{m} \times \frac{250}{V} \times 100 \quad (2)$$

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-Cyclohexylenitrilo)tetracetic 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) ml | Aliquot volume of stock solution (SE-a) 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 % | Volume of 0,01 mol/l CyDTA solution 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

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

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

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-Cyclohexylenitrilo)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 % Al₂O₃). 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.

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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, $w_{\text{Al}_2\text{O}_3}$, expressed as a percentage, using Equation (4).

$$w_{\text{Al}_2\text{O}_3} = \frac{(V_1 \times F_1 - V_2 \times F_2) \times 0,001\,019\,6}{m} \times \frac{250}{100} \times 100 \quad (4)$$

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 % Fe₂O₃ by mass. For iron mass fractions considerably below 20 % Fe₂O₃, 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.