
**Chemical analysis of aluminosilicate
refractory products (alternative to the
X-ray fluorescence method) —**

**Part 2:
Wet chemical analysis**

*Analyse chimique des produits réfractaires d'aluminosilicates (méthode
alternative à la méthode par fluorescence de rayons X) —
Partie 2: Méthodes d'analyse chimique par voie humide*

ISO 21587-2:2007

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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.

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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 21587-2 was prepared by Technical Committee ISO/TC 33, *Refractories*.

ISO 21587 consists of the following parts under the general title *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method)*:

- Part 1: *Apparatus, reagents, dissolution and gravimetric silica*
- Part 2: *Wet chemical analysis* [ISO 21587-2:2007](https://standards.iteh.ai/catalog/standards/sist/5cbacdf7-a99b-440c-a293-568e9d5a33c6/iso-21587-2-2007)
- Part 3: *Inductively coupled plasma and atomic absorption spectrometry methods*

Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) —

Part 2: Wet chemical analysis

1 Scope

This part of ISO 21587 specifies traditional ("wet") methods for the chemical analysis of aluminosilicate refractory products and raw materials.

The methods are applicable to the determination of the following:

- silicon(IV) oxide (SiO_2)
- aluminium oxide (Al_2O_3)
- iron(III) oxide (total iron oxide calculated as Fe_2O_3)
- titanium(IV) oxide (TiO_2)
- manganese(II) oxide (MnO)
- calcium oxide (CaO)
- magnesium oxide (MgO)
- sodium oxide (Na_2O)
- potassium oxide (K_2O)
- chromium(III) oxide (Cr_2O_3)
- zirconium oxide (ZrO_2)
- phosphorous(V) oxide (P_2O_5)

This part of ISO 21587 gives alternatives to the X-ray fluorescence (XRF) method given in ISO 12677:2003, *Chemical analysis of refractory products by XRF — Fused cast bead method*.

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 21587-1:2007, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and gravimetric silica*

ISO 26845, *Chemical analysis of refractories — General requirements for wet chemical analysis, atomic absorption spectrometry and inductively coupled plasma methods*

3 Determination of residual silicon(IV) oxide in solution

3.1 Principle

An aliquot portion of the stock solution (S1) or (S'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 ($m_1 - m_2$) derived in ISO 21587-1:2007, 4.2.2.3 or 4.2.3.3, gives the total silicon(IV) oxide content.

3.2 Procedure

This determination should be commenced with little delay after the stock solution (S1) or (S'1) is prepared, as prolonged standing can allow polymerization of silica to occur, leading to low results.

Transfer 10 ml of stock solution (S1) or (S'1) obtained in 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007 to a 100 ml plastic beaker, and add 2 ml of hydrofluoric acid (1+9), mix with a plastic rod and allow to stand for 10 min. Then 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 to it 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 using water as the reference.

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3.3 Plotting the calibration graph (standards.iteh.ai)

Transfer 0, 2, 4, 6, 8 and 10 ml aliquot portions (0 mg to 20,4 mg as silicon(IV) oxide) of dilute standard silicon(IV) oxide solution (SiO_2 : 0,04 mg/ml) into several 100 ml plastic beakers, and to each add 10 ml of blank solution (B1) or (B'1) obtained in 4.2.2.4 or 4.2.3.4 of ISO 21587-1:2007. Treat these solutions and measure the absorbance as given in 3.2, 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.

3.4 Calculation

Calculate the mass fraction of silicon(IV) oxide, w_{SiO_2} , as a percentage, using the following equation, with the absorbances obtained by the procedure in 3.2 and the plotting of the calibration graph by the procedure in 3.3.

$$w_{\text{SiO}_2} = \frac{(m_1 - m_2) + (m_3 - m_4) \times \frac{500}{10}}{m} \times 100 \tag{1}$$

where

m_1 is the mass, in g, from 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007;

m_2 is the mass, in g, from 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007;

m_3 is the mass, in g, of silicon(IV) oxide in the aliquot portion of stock solution (S1) or (S'1) as applicable;

m_4 is the mass, in g, of silicon(IV) oxide in the aliquot portion of blank solution (B1) or (B'1) as applicable;

m is the mass, in g, of the test portion from 4.2.2.2 or 4.2.3.2 of ISO 21587-1:2007.

4 Determination of aluminium oxide

4.1 General

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

- separation by cupferron-CyDTA-zinc back titration method;
- CyDTA-zinc back titration method (without separation method).

4.2 Separation by cupferron-CyDTA-zinc back titration method

4.2.1 Principle

Hydrochloric acid is added to an aliquot portion of stock solution (S1) or (S'1), obtained in 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007, to adjust the acidity. Iron, titanium, manganese and zirconium are separated from the solution by solvent extraction with cupferron solution and the precipitate removed by dissolution in chloroform. The organic phase is discarded. Excess standard volumetric CyDTA solution is added to the aqueous solution after adjusting the pH with ammonia solution, and a chelate compound of aluminium CyDTA is formed. The pH is further adjusted by the addition of ammonium acetate buffer solution and an equivalent volume of ethanol is added to the solution. The amount of excess CyDTA is determined by back-titration with standard volumetric zinc solution using dithizone as an indicator and the content of aluminium oxide calculated.

4.2.2 Procedure

Transfer a 100 ml aliquot portion of the stock solution (S1) or (S'1), obtained in 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007, to a 500 ml separating funnel and add 20 ml of hydrochloric acid (concentrated) To the solution, add 20 ml of chloroform and 10 ml of 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 a little water. Allow the layers to separate and withdraw the chloroform layer. Confirm that extraction is complete by checking that the addition of a few drops of the cupferron solution to the aqueous solution does not produce a permanent coloured precipitate. Add further 10 ml portions of the chloroform and repeat the extraction until the chloroform layer is colourless. Wash the stem of the funnel, inside and out, with chloroform, using a polyethylene wash bottle. Discard the chloroform extracts; do not allow them to dry as there can be an explosion risk. Transfer the aqueous solution and washings from the funnel into a 1 l conical flask. Add a few drops of bromophenol blue indicator and ammonia solution (concentrated) until the solution is just alkaline. Re-acidify quickly with hydrochloric acid (concentrated) and add 5 to 6 drops in excess. Cool to room temperature. Add sufficient standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,05 \text{ mol/l}$] to combine with the aluminium oxide present, and a few millilitres in excess.

NOTE 1 1 ml of standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,05 \text{ mol/l}$] is equivalent to 1,275 % Al_2O_3 for a 100 ml aliquot portion.

Add ammonium acetate buffer solution until the indicator turns blue, followed by 10 ml in excess. Add a volume of the ethanol equal to the total volume of the solution. If sulfates are precipitated by the alcohol, add just enough water to re-dissolve them. Add 20 ml of hydroxyammonium chloride and 1 ml to 2 ml of dithizone indicator, and titrate with standard volumetric zinc solution [$c(\text{Zn}) = 0,05 \text{ mol/l}$] from green to the first appearance of a permanent pink colour.

NOTE 2 The end point is often improved by the addition of a little naphthol green B solution (1 g/l) to eliminate any pink colour which can be formed in the solution on addition of the indicator.

4.2.3 Blank test

Transfer an aliquot portion of blank solution (B1) or (B'1) obtained in 4.2.2.4 or 4.2.3.4 of ISO 21587-1:2007 and carry out the procedure given in 4.2.2. Use the same volumes of the aliquot portion of blank solution (B1) or (B'1) and standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,05 \text{ mol/l}$] as those for the corresponding stock solution (S1) or (S'1).

4.2.4 Calculation

Calculate the mass fraction of aluminium oxide in the sample as follows.

If the standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,05 \text{ mol/l}$] is not exactly 0,05 mol/l, calculate the equivalent volume of standard volumetric CyDTA solution.

Calculate the mass fraction of aluminium oxide, $w_{\text{Al}_2\text{O}_3}$, as a percentage, using the equation

$$w_{\text{Al}_2\text{O}_3} = 1,275 (V - V_1) \tag{2}$$

where

V is the volume of standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,05 \text{ mol/l}$] added, in ml;

V_1 is the volume of standard volumetric zinc solution [$c(\text{Zn}) = 0,05 \text{ mol/l}$] used in the back-titration, in ml, for a 1 g test sample.

4.3 CyDTA-Zinc back titration method (without separation method)

4.3.1 Principle

Excess standard volumetric CyDTA solution is added to an aliquot of stock solution (S1) or (S'1). A chelate compound of aluminium CyDTA is formed by adjusting the pH with ammonia water. The pH is further adjusted by the addition of hexamethylenetetramine. The amount of remaining CyDTA is determined by back-titration with standard volumetric zinc solution, using xylenol orange as an indicator. The content of aluminium oxide is calculated by adjusting the content of iron(III) oxide, titanium(IV) oxide, manganese(II) oxide and zirconium oxide by other methods.

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4.3.2 Procedure

Determination is carried out in accordance with the following procedure.

Transfer precisely 50 ml of stock solution (S1) or (S'1), obtained in 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007, to a beaker (300 ml), and add 2 ml of hydrochloric acid (1+1). Then add a precisely known amount of standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,02 \text{ mol/l}$], and dilute to 100 ml with water.

NOTE The relation between the volume of the aliquot of standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,02 \text{ mol/l}$] and the mass fraction of aluminum oxide, iron(III) oxide, and titanium(IV) oxide are shown in Table 1.

Table 1 — Aliquots of stock solution (S1) or (S'1) and volume of standard volumetric CyDTA solution

Sum of mass fractions of aluminum oxide, iron(III) oxide and titanium(IV) oxide %	Volume of standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,02 \text{ mol/l}$] ml
less than 10	20
10 to 20	30
20 to 30	40
30 to 50	50

Add 1 g of hexamethylenetetramine and a drop of methyl orange solution as an indicator. Then, drop in ammonia water (1+1), and ammonia water (1+9) of up to pH 3 indicating a slightly orange colour. If ammonia

water is added excessively, the pH is adjusted to less than 3 (showing a red colour) by adding hydrochloric acid (1+1). Then, subsequently, carry out the identical adjustment. Add 5 g of hexamethylenetetramine of up to pH 5,5 to 5,8, add 4 or 5 drops of xylenol orange solution as an indicator, and titrate with standard volumetric zinc solution [$c(\text{Zn}) = 0,02 \text{ mol/l}$]. In the vicinity of the end point, titration is carried out gently while mixing, and the end point is decided when the colour changes from yellow to the first appearance of a permanent reddish colour.

4.3.3 Blank test

Transfer an aliquot of blank solution (B1) or (B'1), obtained in 4.2.2.4 or 4.2.3.4 of ISO 21587-1:2007, and carry out the procedure in accordance with 4.3.2. The volumes of the aliquot of blank solution (B1) or (B'1) and standard volumetric CyDTA solution [$c(\text{CyDTA}) = 0,02 \text{ mol/l}$] are the same as those for the corresponding stock solution (S1) or (S'1).

4.3.4 Calculation

Calculate the mass fraction of aluminum oxide in the sample, $w_{\text{Al}_2\text{O}_3}$, as a percentage, using the following equation:

$$w_{\text{Al}_2\text{O}_3} = \frac{(V_2 - V_1) \times F \times 0,0010196}{m} \times \frac{500}{50} \times 100 - \left[0,638 \times (w_{\text{Fe}_2\text{O}_3} + w_{\text{TiO}_2}) + 0,729 \times w_{\text{MnO}} + 0,414 \times w_{\text{ZrO}_2} \right] \quad (3)$$

where

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- V_1 is the used quantity, in ml, of standard volumetric zinc solution [$c(\text{Zn}) = 0,02 \text{ mol/l}$] in 4.3.2;
- V_2 is the used quantity, in ml, of standard volumetric zinc solution [$c(\text{Zn}) = 0,02 \text{ mol/l}$] in 4.3.3;
- F is the factor of standard volumetric zinc solution [$c(\text{Zn}) = 0,02 \text{ mol/l}$];
- m is the mass, in g, of sample in 4.2.2.2 or 4.2.3.2 in ISO 21587-1:2007;
- $w_{\text{Fe}_2\text{O}_3}$ is the mass fraction, in %, of iron(III) oxide determined in Clause 5 or ISO 21587-3:2007 (Clause 4);
- w_{TiO_2} is the mass fraction, in %, of titanium(IV) oxide determined in Clause 6 or ISO 21587-3:2007 (Clause 5);
- w_{MnO} is the mass fraction, in %, of manganese(II) oxide determined in Clause 7 or ISO 21587-3:2007 (Clause 6 or 18);
- w_{ZrO_2} is the mass fraction, in %, of zirconium oxide determined in Clause 13 or ISO 21587-3:2007 (Clause 12).

5 Determination of iron(III) oxide

5.1 Principle

Two methods are given, using alternative reducing agents for the ferric oxide in solution. The iron in stock solution (S1) or (S'1) is reduced with L(+)-ascorbic acid or hydroxyammonium chloride, 1,10-phenanthroline is added, and the pH is adjusted by adding ammonium acetate. The absorbance is measured.

5.2 Procedure

Transfer 5 ml of stock solution (S1) or (S'1) obtained in 4.2.2.3 or 4.2.3.3 in ISO 21587-1:2007 into a 100 ml volumetric flask.

5 ml of aliquot volume is a typical amount. An aliquot volume of stock solution (S1) or (S'1) should be adjusted according to the mass fraction of iron(III) oxide in the sample as shown in Table 2.

Table 2 — Aliquot volume of stock solution (S1) or (S'1)

Mass fraction of iron(III) oxide %	Aliquot volume of stock solution (S1) or (S'1) ml
Less than 0,5	25
0,5 to 1,5	10
More than 1,5	5

Reduce the solution by one of the following methods.

- a) Reduce with ascorbic acid by diluting to about 60 ml with water, and adding 5 ml of L(+)-tartaric acid solution and 2 ml of L(+)-ascorbic acid solution while shaking. Add 10 ml of 1,10-phenanthroline chloride solution (1 g/l) and 10 ml of ammonium acetate solution (20 %). Dilute to the mark with water, then allow to stand for 30 min.
- b) Reduce with hydroxyammonium chloride by adding 2 ml of hydroxyammonium chloride solution or L(+)-ascorbic acid solution (100 g/l), 5 ml of 1,10-phenanthroline solution (10 g/l) and 5 ml of ammonium acetate solution (100 g/l). Allow the solution to stand for 15 min, dilute to the mark and mix. The colour is stable between 15 min and 75 min after the addition of the ammonium acetate solution.

Measure the absorbance of the solution in a 10 mm cell at a wavelength of 510 nm or a colour filter against water in a suitable instrument.

5.3 Blank test

Transfer the same volume of the blank solution (B1) or (B'1), obtained in 4.2.2.4 or 4.2.3.4 of ISO 21587-1:2007, as that of stock solution (S1) or (S'1), and carry out the appropriate procedure given in 5.2 a) or b), as applicable.

5.4 Plotting the calibration graph

Transfer 0 (as reference), 5,0, 10,0 and 15,0 ml portions [0 mg to 0,6 mg as iron(III) oxide] of the dilute standard iron(III) oxide solution (Fe₂O₃ 0,04 mg/ml) into several 100 ml volumetric flasks. Treat these solutions in accordance with 5.2 a) or b) and measure the absorbance against the reference solution. Then plot the relation between the absorbances and mass of iron(III) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

5.5 Calculation

Calculate the mass fraction of iron(III) oxide in the sample, $w_{Fe_2O_3}$, as a percentage, using the following equation. Use the amount of iron(III) oxide that is derived from the absorbance in 5.2 and the calibration in 5.4.

$$w_{Fe_2O_3} = \frac{m_1 - m_2}{m} \times \frac{500}{V} \times 100 \tag{4}$$

where

m_1 is the mass, in g, of iron(III) oxide in the aliquot portion of stock solution (S1) or (S'1);

m_2 is the mass, in g, of iron(III) oxide in the aliquot portion of blank solution (B1) or (B'1);

m is the mass, in g, of the test portion in 4.2.2.3 or 4.2.3.3 in ISO 21587-1:2007;

V is the volume, in ml, of the aliquot portion taken from stock solution (S1) or (S'1) in 5.2, i.e. 5 ml.

6 Determination of titanium(IV) oxide

6.1 General

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

- di-antipyrylmethane (DAM) absorption spectrophotometric method;
- hydrogen peroxide absorption spectrophotometric method.

6.2 DAM absorption spectrophotometric method

6.2.1 Principle

An aliquot portion of stock solution (S1) or (S'1) is adjusted for acidity. The iron is reduced with an addition of L(+)-ascorbic acid and diantipyrylmethane. The absorbance of the colour produced is then measured.

6.2.2 Procedure

Carry out the determination using the following procedure.

Transfer 5 ml of stock solution (S1) or (S'1), obtained in 4.2.2.3 or 4.2.3.3 of ISO 21587-1:2007, into a 50 ml volumetric flask.

5 ml of aliquot volume is a typical amount. An aliquot volume of stock solution (S1) or (S'1) should be adjusted according to the mass fraction of titanium(IV) oxide in the sample as shown in Table 3.

Table 3 — Aliquot taken from stock solution (S1) or (S'1)

Mass fraction of titanium(IV) oxide %	Aliquot taken ml
Less than 0,5	25
0,5 to 1,5	10
More than 1,5	5

Add 5 ml of hydrochloric acid (1+1) and 2 ml of L(+)-ascorbic acid solution, and allow to stand for 1 min, then add 15 ml of DAM solution, and dilute to the mark with water. Allow the solution to stand for approximately 90 min. Measure the absorbance of the solution in a 10 mm cell at a wavelength of 390 nm against water.