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**Chemical analysis of refractories  
containing alumina, zirconia, and silica —  
Refractories containing 5 % to 45 %  
of ZrO<sub>2</sub> (alternative to the X-ray  
fluorescence method) —**

**Part 2:  
Wet chemical analysis**

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*Analyse chimique des matériaux réfractaires contenant de l'alumine,  
de la zirconie et de la silice — Matériaux réfractaires contenant de 5 %  
à 45 % de ZrO<sub>2</sub> (méthode alternative à la méthode par fluorescence  
de rayons X)*

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



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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 21079-2 was prepared by Technical Committee ISO/TC 33, *Refractories*.

ISO 21079 consists of the following parts, under the general title *Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 % to 45 % of ZrO<sub>2</sub> (alternative to the X-ray fluorescence method)*:

- *Part 1: Apparatus, reagents and dissolution* [ISO 21079-2:2008](https://standards.iteh.ai/catalog/standards/sist/b35efa0b-3f54-4b78-9ece-0fed3ee57534/iso-21079-2-2008)
- *Part 2: Wet chemical analysis* <https://standards.iteh.ai/catalog/standards/sist/b35efa0b-3f54-4b78-9ece-0fed3ee57534/iso-21079-2-2008>
- *Part 3: Flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma emission spectrometry (ICP-AES)*

# Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 % to 45 % of ZrO<sub>2</sub> (alternative to the X-ray fluorescence method) —

## Part 2: Wet chemical analysis

### 1 Scope

This part of ISO 21079 specifies methods for the chemical analysis of AZS (alumina, zirconia, and silica) refractory products (containing 5 % to 45 % of ZrO<sub>2</sub>) and raw materials, using traditional (“wet”) methods.

This part of ISO 21079 is not applicable to MgO-based refractories.

This part of ISO 21079 gives alternatives to the X-ray fluorescence (XRF) method given in ISO 12677.

### 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 10058-2:—<sup>1)</sup>, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

ISO 21079-1:2008, *Chemical analysis of refractories containing alumina, zirconia and silica — Refractories containing 5 % to 45 % of ZrO<sub>2</sub> (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents and dissolution*

ISO 21079-3:2008, *Chemical analysis of refractories containing alumina, zirconia and silica — Refractories containing 5 % to 45 % of ZrO<sub>2</sub> (alternative to the X-ray fluorescence method) — Part 3: Flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma emission spectrometry (ICP-AES)*

ISO 21587-2:2007, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

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*

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1) To be published.

### 3 Determination of silicon(IV) oxide

#### 3.1 General

The determination of silicon(IV) oxide is carried out 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 8 % by mass of silicon(IV) oxide.

#### 3.2 Combined use of dehydration or coagulation and molybdenum blue methods

##### 3.2.1 Principle

An aliquot portion of stock solution (S1) or (S'1) 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 accordance with 9.2.2.3 or 9.2.3.3 of ISO 21079-1:2008 gives the total silicon(IV) oxide content.

##### 3.2.2 Procedure

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

Transfer a 10,0 ml aliquot portion of stock solution (S1) or (S'1) (see Annex A of ISO 21079-1:2008) to a 100 ml plastic beaker, add 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, 2 ml of ammonium molybdate solution while swirling at a temperature of about 25 °C, and allow to stand for 10 min. Add 5 ml of L (+)-tartaric acid solution while swirling and after 1 min add 2 ml of L (+)-ascorbic acid solution while shaking. Transfer a solution to a 100 ml plastics volumetric flask, dilute to the mark with water 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 reference.

##### 3.2.3 Plotting the calibration graph

Transfer 0 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml aliquot portions of diluted silicon(IV) oxide solution (0 mg to 0,4 mg as silicon(IV) oxide) into six 100 ml plastic beakers and, to each, add 10 ml of blank solution (B1) or (B'1) (see Annex A of ISO 21079-1:2008). Treat these solutions and measure the absorbance as described 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 Calculation

Calculate the mass fraction of silicon(IV) oxide,  $w(\text{SiO}_2)$ , expressed as a percentage, using Equation (1) with the absorbances obtained in 3.2.2 and the calibration graph.

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

where

$m_1$  is the mass from 9.2.2.3 or 9.2.3.3 of ISO 21079-1:2008, in grams;

$m_2$  is the mass from the blank prepared in accordance with 9.2.2.4 or 9.2.3.4 of ISO 21079-1:2008, in grams;

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

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

$m$  is the mass of the test portion prepared in accordance with ISO 21079-1:2008, in grams.

### 3.3 Molybdenum blue method

#### 3.3.1 Principle

An aliquot portion of the stock solution (S'1) 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 the specified volume of stock solution (S'1) (see Annex A of ISO 21079-1:2008) to two plastic beakers and add, to each, the specified volume of blank solution (B'1) (see Annex A of ISO 21079-1:2008). 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 and dilute to about 80 ml with water. Add 5 ml of ammonium molybdate solution while mixing at a temperature of 20 °C to 30 °C and allow to stand for 10 min. Add 20 ml of tartaric acid solution while stirring. After 1 min, add 10 ml of L (+)-ascorbic acid solution while stirring. Transfer each solution to two 200 ml plastics volumetric flasks, 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. Take the mean value of the two measurements for the calculation of silica content.

The volume of the aliquot portions from stock solution (S'1) and the blank solution are given in Table 1 depending on the mass fraction of silicon(IV) oxide.

Table 1 — Aliquot volume of stock solution (S'1) and blank solution (B'1)

Mass fraction of SiO <sub>2</sub> %	Volume of stock solution (S'1) ml	Volume of blank solution (B'1) ml
< 4	20	0
≥ 4, ≤ 8	10	10

When the difference between two measurements exceeds 0,005 absorbance units, repeat the procedure given in 9.2.4.3 of ISO 21079-1:2008.

The spectrophotometer should give a value of less than 0,002 absorbance units as the difference between two repeated measurements of identical solutions at an absorbance level of about 1,00.

#### 3.3.3 Blank test

Carry out the procedure described in 3.3.2 using blank solution (B'1) (see Annex A of ISO 21079-1:2008).

#### 3.3.4 Plotting of calibration graph

Transfer 0 ml (as reference), 2 ml, 4 ml, 6 ml, 8 ml and 10 ml aliquot portions of silicon(IV) oxide standard solution into six 100 ml plastic beakers and add, to each, 10 ml of blank solution. Treat these solutions as described in 3.3.2, measure the absorbance against the reference solution and plot the absorbance against the amounts of silica.

### 3.3.5 Calculation

Calculate the mass fraction of silicon(IV) oxide,  $w(\text{SiO}_2)$ , expressed as a percentage, using Equation (2).

$$w(\text{SiO}_2) = \frac{(m_s - m_b)}{m} \times \frac{500}{V} \times 100 \quad (2)$$

where

- $m_s$  is the silica in the aliquot portion of stock solution (S''1), in grams;
- $m_b$  is the silica in the aliquot portion of blank solution (B''1), in grams;
- $V$  is the volume of the aliquot portion taken from stock solution (S''1), in millilitres;
- $m$  is the mass of the test portion, in grams.

## 4 Determination of aluminium oxide

### 4.1 General

The determination of aluminium oxide is carried out using one of the following methods.

- a) Cation-exchange column separation: trans-1,2-Cyclohexanediamine-N,N,N',N'-tetraacetic acid (hydrate) (CyDTA) – Zinc back titration method;
- b) Cupferron separation: CyDTA – Zinc back titration method.

### 4.2 Cation-exchange column separation: CyDTA – Zinc back titration method

#### 4.2.1 Principle

An aliquot portion of stock solution (S1), (S'1) or (S''1) is pipetted into a cation-exchange resin column and cation, such as aluminium ion, is absorbed into the ion-exchange resin. 0,8 mol/l hydrofluoric acid and 0,65 mol/l boric acid solution is poured into the column, so that the zirconium and titanium flows out. Hydrofluoric acid (1+200) is poured into the column in order to elute the aluminium. The eluate is evaporated with the addition of sulfuric acid. The boric acid and hydrofluoric acid are removed and then dissolved into the hydrochloric acid. CyDTA solution is added and 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 excess amount of CyDTA is back-titrated by zinc standard solution using xylenol orange as an indicator.

#### 4.2.2 Procedure

**4.2.2.1** Pour a 50 ml aliquot portion of stock solution (see Annex A of ISO 21079-1:2008) into a cation-exchange resin column (see ISO 26845). Pour 10 ml of eluent A (see 5.1.25 of ISO 26845:2008) on the inner side of the column twice, followed by a further 60 ml of eluent A.

Up to this point, eluate is unnecessary.

**NOTE** It is not until the former solution ceases to drip out of the end of the column that further additions can be poured. The same applies to the following procedure.

**4.2.2.2** Place a platinum dish (e.g. 150 ml) below the lower end of the column and pour 10 ml of eluent B (see 5.1.26 of ISO 26845:2008) on the inner side of the column twice. Pour 80 ml of eluent B into the column to elute aluminium.



Regenerate the column as follows. Prepare a 100 ml plastic beaker below the end of the column and pour 10 ml of hydrochloric acid (1+2) on the inner side of the column twice. Pour 100 ml of hydrochloric acid (1+2) on the inner side of the column to elute iron, calcium, magnesium, etc.

This solution can be used for the determination of calcium oxide if the procedure is carried out using the following steps. Transfer the solution to a 150 ml platinum dish and evaporate until dry on a steam bath in a fume cupboard. Add 5 ml of hydrochloric acid (1+2) 30 ml of water and transfer to a steam bath to facilitate the dissolution of the melt. Cool and dilute the solution to 100 ml in a volumetric flask. In the case of FAAS, add 10 ml of lanthanum solution before diluting to 100 ml.

**4.2.2.3** Pour 70 ml of water into the column. Add 50 ml of sulfuric acid (1+1) to the eluate obtained in accordance with 4.2.2.2, evaporate by heating on a hot plate until the white smoke of the sulfuric acid appears. Cool and wash the inner side of the beaker with a small quantity of water and heat until the white smoke of sulfuric acid appears. When the amount of the solution is about 2 ml, allow to cool and add 10 ml of hydrochloric acid (1+1). Dissolve by heating and transfer to a 300 ml beaker.

**4.2.2.4** Allow to cool and add of 2 ml of hydroxylammonium chloride while mixing. Add a precisely known amount of 0,02 mol/l CyDTA standard solution and drop in ammonia solution (1+1) and ammonia solution (1+9) between pH 2,9 and pH 3,1 using a pH meter. If excessive ammonia water is added, the pH is adjusted to less than 3 by adding hydrochloric acid (1+1), and, subsequently, the identical adjustment procedure is carried out. Add hexamethylenetetramine between pH 5,5 and pH 5,8 using a pH meter, add 4 to 5 drops of xylene orange solution as an indicator and titrate with 0,02 mol/l of zinc standard solution. When the colour starts to change from yellow to the first appearance of a permanent reddish colour, carry out titration gently while mixing.

NOTE The relation between the volume of the aliquot portion of 0,02 mol/l CyDTA standard solution and the mass fraction of aluminium oxide is given in Table 2.

Table 2 — Volume of 0,02 mol/l CyDTA standard solution

Mass fraction of aluminium oxide	CyDTA standard solution
< 15	10
≥ 15, < 35	20
≥ 35, < 55	30
≥ 55, < 75	40
≥ 75	50

#### 4.2.3 Blank test

Transfer 200 ml aliquot portion of blank solution B1, B'1 or B''1 (see Annex A of ISO 21079-1:2008) and carry out the procedure given in 4.2.2.

#### 4.2.4 Calculation

Calculate the mass fraction of aluminium oxide,  $w(\text{Al}_2\text{O}_3)$ , expressed as a percentage, in the sample using Equation (3).

$$w(\text{Al}_2\text{O}_3) = \frac{(V_2 - V_1) \times F \times 0,0010196}{m} \times \frac{500}{50} \times 100 \quad (3)$$

where

$V_1$  is the used quantity of 0,02 mol/l zinc standard solution in 4.2.2.4 in millilitres;

- $V_2$  is the used quantity of 0,02 mol/l zinc standard solution in 4.2.3 in millilitres;
- $F$  is the factor of 0,02 mol/l zinc standard solution (see 5.2.17 of ISO 21079-1:2008);
- 0,001 019 6 is the mass equivalent of  $Al_2O_3$ ;
- $m$  is the mass of the sample in grams.

### 4.3 Cupferron separation-CyDTA-Zinc back titration method

#### 4.3.1 Principle

Hydrochloric acid is added to an aliquot portion of stock solution (S1), (S'1) or (S''1) 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 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 zinc solution using dithizone as an indicator and the content of aluminium oxide calculated.

#### 4.3.2 Procedure

Transfer a 200 ml aliquot portion of the stock solution (S1), (S'1) or (S''1) (see Annex A of ISO 21079-1:2008) to a beaker (500 ml), add 20 ml of hydrochloric acid, cool to under 5 °C and keep at this temperature using iced water. Add powdery filter paper (e.g. 0,05 g), then drop in 25 ml of cupferron solution and cool to under 5 °C while mixing. After complete mixing, allow to stand for 5 min. Filter the solution with medium filter paper into a beaker (500 ml), and wash the precipitate 10 times with hydrochloric acid (1+9) which has been cooled to under 5 °C, as above. Use the precipitate together with the filter paper for the determination of zirconium oxide (including hafnium oxide).

The temperature should be kept as low as possible.

Evaporate the filtrate and washing solutions to about 20 ml on a steam bath, then cover with a watch glass, add 10 ml of nitric acid and 5 ml of sulfuric acid (1+1), and boil gently for about 10 min on a sand bath. Remove the watch glass, rinse the watch glass with water, and continue the evaporation carefully, then evaporate until the white smoke of sulfuric acid appears.

Allow to cool, add 10 ml of hydrochloric acid (1+1) and about 100 ml of water, then heat to dissolve the salts. Allow to cool, and dilute to 250 ml in a volumetric flask. Transfer a 100 ml aliquot portion of the solution and add 2 ml of hydroxylammonium chloride while mixing. Add a precisely known amount of 0,02 mol/l CyDTA standard solution and drop in ammonia solution (1+1), and ammonia solution (1+9) of between pH 2,9 and 3,1 using a pH meter. If ammonia water is added excessively, the pH is adjusted to less than 3 by adding hydrochloric acid (1+1), then, subsequently, the identical adjustment procedure is carried out. Add hexamethylenetetramine of between pH 5,5 and 5,8 using a pH meter, add 4 to 5 drops of xylenol orange solution as an indicator, and titrate with 0,02 mol/l zinc standard solution. When the colour starts to change from yellow to the first appearance of a permanent reddish colour, carry out titration gently while mixing.

NOTE The relation between the volume of the aliquot portion of 0,02 mol/l CyDTA standard solution and the mass fraction of aluminium oxide is shown in Table 3.

Table 3 — Volume of 0,02 mol/l CyDTA solution

Mass fraction of aluminium oxide %	CyDTA solution ml
< 20	20
≥ 20, < 35	30
≥ 35, < 60	50
≥ 60	70

#### 4.3.3 Blank test

Carry out the procedure described in 4.3.2 using the blank test solution (B1), (B'1) or (B''1) (see Annex A of ISO 21079-1:2008).

#### 4.3.4 Calculation

Calculate the mass fraction of aluminium oxide,  $w(\text{Al}_2\text{O}_3)$ , expressed as a percentage, in the sample using Equation (4).

$$w(\text{Al}_2\text{O}_3) = \frac{(V_2 - V_1) \times F \times 0,001\,019\,6}{m} \times \frac{500}{200} \times \frac{250}{100} \times 100 \quad (4)$$

where

$V_1$  is the used quantity of 0,02 mol/l zinc standard solution in 4.3.3, in millilitres;

$V_2$  is the used quantity of 0,02 mol/l zinc standard solution in 4.3.2, in millilitres;

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

0,001 019 6 is the mass equivalent of  $\text{Al}_2\text{O}_3$ ;

$m$  is the mass of the sample obtained in accordance with 9.2.2.2, 9.2.3.2 or 9.2.4.2 of ISO 21079-1:2008, in grams.

## 5 Determination of iron(III) oxide

### 5.1 Principle

Stock solution (S1), (S'1), or (S''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. The colour of iron develops and absorbance is measured.

### 5.2 Procedure

**5.2.1** Transfer an appropriate aliquot portion of stock solution (S1), (S'1) or (S''1) (see Annex A of ISO 21079-1:2008) into a 100 ml volumetric flask.

The aliquot volume of stock solution (S1), (S'1), or, (S''1) corresponding to the mass fraction of iron(III) oxide in the sample is shown in Table 4.