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Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 % to 45 % of ZrO_2 (alternative to the X-ray fluorescence method) —

Part 2:
Wet chemical analysis

Analyse chimique des matériaux réfractaires contenant de l'alumine, de la zircone et de la silice — Matériaux réfractaires contenant de 5 % à 45 % de ZrO_2 *(méthode alternative à la méthode par fluorescence de rayons X) —*

Partie 2: Méthodes d'analyse chimique par voie humide

Reference number
ISO 21079-2:2008(E)

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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_2 *(alternative to the X-ray fluorescence method)*:

— *Part 1: Apparatus, reagents and dissolution*

— *Part 2: Wet chemical analysis*

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

INTERNATIONAL STANDARD **ISO 21079-2:2008(E)**

Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 % to 45 % of ZrO_2 (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_2) 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:—[1], *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_2 *(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_2 *(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, $w(\mathrm{SiO_2})$, expressed as a percentage, using Equation (1) with the absorbances obtained in 3.2.2 and the calibration graph.

$$w(\mathrm{SiO_2}) = \frac{(m_1 - m_2) + (m_\mathrm{s} - m_\mathrm{b}) \times \frac{500}{10}}{m} \times 100 \tag{1}$$

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 (S1) or (S'1), in grams;

m_b is the mass of silicon(IV) oxide in the aliquot portion of blank solution (B1) 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_2 %	Volume of stock solution (S''1) ml	Volume of blank solution (B''1) ml
< 4	20	0
$\geqslant 4, \leqslant 8$	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, $w(\mathrm{SIO_2})$, expressed as a percentage, using Equation (2).

$$w\left(\mathrm{SiO_2}\right) = \frac{\left(m_\mathrm{s} - m_\mathrm{b}\right)}{m} \times \frac{500}{V} \times 100 \tag{2}$$

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 xylenol 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 ml
< 15	10
$\geqslant 15, < 35$	20
$\geqslant 35, < 55$	30
$\geqslant 55, < 75$	40
$\geqslant 75$	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, $w(\mathrm{Al_2O_3})$, expressed as a percentage, in the sample using Equation (3).

$$w\left(\mathrm{Al_2O_3}\right) = \frac{\left(V_2 - V_1\right) \times F \times 0{,}001\,019\,6}{m} \times \frac{500}{50} \times 100 \qquad (3)$$

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
$\geqslant 20, < 35$	30
$\geqslant 35, < 60$	50
$\geqslant 60$	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, $w(\mathrm{Al_2O_3})$, expressed as a percentage, in the sample using Equation (4).

$$w\left(\mathrm{Al_2O_3}\right) = \frac{(V_2 - V_1) \times F \times 0{,}001\,019\,6}{m} \times \frac{500}{200} \times \frac{250}{100} \times 100 \qquad (4)$$

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 $\mathrm{Al_2O_3}$;

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.

Table 4 — Aliquot volume of the stock solution
(S1, S', or, S"1)

Mass fraction of iron(III) oxide %	Volume of aliquot portion ml
< 1	50
> 1	25

5.2.2 Dilute to about 60 ml with water, add 5 ml of L (+)-tartaric acid solution and 2 ml of L (+)-ascorbic acid while mixing. Add 10 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. Measure the absorbance of the solution in a 10 mm cell at the wavelength of 510 nm against water.

5.3 Blank test

Transfer the same aliquot volume used in 5.2.1 of blank solution (B1), (B'1), or (B''1) (see Annex A of ISO 21079-1:2008) and carry out the procedure in 5.2.2.

5.4 Plotting of calibration graph

Transfer 0 ml (as reference), 5 ml, 10 ml and 15 ml aliquot portions of diluted iron(III) oxide standard solution [0,0 mg to 0,75 mg as iron(III) oxide] into several 100 ml volumetric flasks. Treat these solutions as described in 5.2.2 and measure the absorbance against the reference solution. Plot the relation between the absorbances and mass of iron(III) oxide.

5.5 Calculation

Calculate the mass fraction of iron(III) oxide, $w(\mathrm{Fe_2O_3})$, in the sample, expressed as a percentage, using Equation (5). Use the amounts of iron(III) oxide derived from the absorbances in 5.2.2 and 5.3, and the calibration in 5.4.

$$w\left(\mathrm{Fe_2O_3}\right) = \frac{\left(m_\mathrm{s} - m_\mathrm{b}\right)}{m} \times \frac{500}{V} \times 100 \qquad (5)$$

where

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

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

m is the mass of the test portion from 9.2.2.2, 9.2.3.2 or 9.2.4.2 of ISO 21079-1:2008, in grams;

V is the volume of the aliquot portion taken for stock solution (S1, S'1, or, S''1) in 5.2.1, in millilitres.

6 Determination of titanium(IV) oxide

6.1 General

The determination of titanium(IV) oxide shall be carried out as described in one of the following two methods.

a) Di-antipyrylmethane (DAM) method.

b) Hydrogen peroxide absorption spectrophotometric method.

6.2 DAM method

6.2.1 Principle

A sample stock solution (S), (S'1), or (S''1) is transferred. CyDTA is added while heating after the adjustment of acidity, and the zirconium is masked. With an addition of L (+)-ascorbic acid, the iron is reduced and the titanium is coloured by the di-antipyrylmethane. The absorbance is then measured.

6.2.2 Procedure

6.2.2.1 Transfer an appropriate aliquot portion of stock solution (S1), (S'1), or (S''1) (see Annex A of ISO 21079-1:2008) into a 50 ml volumetric flask. While mixing, add 5 ml of hydrochloric acid (1+1) and 1 ml of CyDTA solution, place the flask in a water bath and heat for about 5 min. Cool in running water.

NOTE The aliquot portion taken from stock solution (S1), (S'1), or (S''1) is given in Table 5 corresponding to the mass fraction of titanium(IV) oxide in the sample.

Table 5 — Aliquot portion taken from the stock solution (S1, S'1, or, S''1)

Mass fraction of titanium(IV) oxide %	Aliquot portion taken ml
< 1	25
$\geqslant 1, < 2{,}5$	10
$\geqslant 2{,}5$	5

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

6.2.3 Blank test

Transfer the same volume aliquot portion used in 6.2.2.1 of blank solution (B1), (B'1), or (B''1) (see Annex A of ISO 21079-1:2008) and carry out the procedure described in 6.2.2.

6.2.4 Plotting of calibration graph

Transfer 0 ml (as reference), 5 ml, 10 ml, 15 ml, 20 ml and 25 ml aliquot portions of diluted titanium(IV) oxide standard solution [0 mg to 0,25 mg as titanium(IV) oxide] into six 50 ml volumetric flasks and treat these solutions as described in 6.2.2. Measure the absorbance against the reference solution and plot the relation between the absorbance and the amount of titanium(IV) oxide.

6.2.5 Calculation

Calculate the mass fraction of titanium(IV) oxide, $w(\mathrm{TiO_2})$, in the sample, expressed as a percentage, using Equation (6). Use the amount of titanium(IV) oxide derived from the absorbances in 6.2.2.2 and 6.2.3 and the calibration in 6.2.4.

$$w(\mathrm{TiO_2}) = \frac{m_\mathrm{s} - m_\mathrm{b}}{m} \times \frac{500}{V} \times 100 \qquad (6)$$

where

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

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

m is the mass of the test portion obtained in accordance with 9.2.2.2, 9.2.3.2 or 9.2.4.2 of ISO 21079-1:2008, in grams;

V is the volume of the aliquot portion taken for stock solution (S1), (S'1), or (S''1) of 6.2.2.1, in millilitres.

6.3 Hydrogen peroxide absorption spectrophotometric method

6.3.1 Principle

The colour from the iron content of the stock solution (S1), (S'1) or (S''1) is masked by an addition of phosphoric acid and the titanium is reacted with hydrogen peroxide. The absorbance is measured.

6.3.2 Procedure

Transfer 20 ml of stock solution (S1), (S'1) or (S''1) (see Annex A of ISO 21079-1:2008) into each of two 50 ml volumetric flasks, A and B.

To each flask, add 10 ml of phosphoric acid (2+3) and to flask A only add 10 ml of hydrogen peroxide solution (6 % by mass). Allow to stand for 10 min. Dilute each to the mark with water and shake vigorously. Measure the absorbance of the solution in flask A against that in flask B using a 10 mm cell at a wavelength of 398 nm or using a colour filter in a suitable instrument.

6.3.3 Blank test

Using the same volume of blank solution (B1), (B'1) or (B''1) as that of the aliquot portion of stock solution (S1), (S'1) or (S''1) carry out the procedure described in 6.3.2.

6.3.4 Plotting the calibration graph

Transfer 0 (as reference), 10 ml, 20 ml, 30 ml and 40 ml aliquot portions of the diluted titanium(IV) oxide standard solution (0 mg to 4,0 mg as titanium(IV) oxide) into five 100 ml volumetric flasks, and treat these solutions as in 6.3.2. Then measure the absorbance against the reference solution (0 ml). Plot the relation between the absorbance and the mass 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, $w(\mathrm{TiO_2})$, expressed as a percentage, using Equation (7) with the amount of titanium(IV) oxide that is derived from the absorbance in 6.3.2 and 6.3.3, and the calibration in 6.3.4.

$$w(\mathrm{TiO_2}) = \frac{m_s - m_b}{m} \times \frac{500}{20} \times 100 \qquad (7)$$

where

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

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

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

7 Determination of calcium oxide

7.1 Principle

To an aliquot portion of the solution prepared by hydrofluoric acid attack (S2) a solution of 2,2',2''-nitrilotriethanol is added to mask interference ions. After adjusting the pH to about 13, an EDTA titration is carried out using screened calcein as indicator.

7.2 Procedure

7.2.1 Take a quantity of solution (S2) prepared (see Annex A of ISO 21079-1:2008) and check the approximate level of manganese(II) oxide using the method given in Clause 7 of ISO 21587-2:2007.

This determination is semi-quantitative; a two point calibration will suffice but the calculation of manganese oxide content should be based on the mass of original sample in the aliquot portion of S2 taken.

In the event of the sample containing manganese(II) oxide at a level of more than about 0,1 % by mass, follow the procedure given in 7.2.3 first, followed by the procedure given in 7.2.2. In all other cases, follow the procedure given in 7.2.2.

7.2.2 Pipette 100 ml of the solution (S2) into a 500 ml conical flask. Add 5 ml of 2,2', 2''-nitrilotriethanol (1+1), and 10 ml of potassium hydroxide solution (250 g/l), dilute to about 200 ml with water. Add about 0,015 g of screened calcein indicator, and titrate with EDTA solution (5 g/l), from a semi-micro burette, the colour change being from fluorescent green to pink, with the end-point being the final change in colour.

7.2.3 Transfer precisely 100 ml of stock solution (S2) into a 200 ml beaker and add 5 ml of bromine water. Make the solution slightly alkaline with ammonia solution (1+1) maintaining this alkalinity by the addition of drops of ammonia solution (1+1) as required. After the precipitate has flocculated, filter through a filter paper (coarse) and wash thoroughly with warm water. Collect the filtrate and washings in a 300 ml beaker and acidify the solution with hydrochloric acid (1+1). Boil to completely remove any remaining bromine and evaporate to less than 80 ml. After cooling, carry out the procedure described in 7.2.2.

7.3 Blank test

Carry out the procedure in 7.2.2 using solution (B2) (see Annex A of ISO 21079-1:2008). Use an equivalent aliquot portion as used for the sample in 7.2.2.

7.4 Calculation

Calculate the mass fraction of calcium oxide, $w(\text{CaO})$, expressed as a percentage, using Equation (8).

$$w(\text{CaO}) = (V - v) \times F \times m \times \frac{250}{100} \times 100 \qquad (8)$$

where

V is the equivalent volume of EDTA solution in 7.2.3, in millilitres;

v is the equivalent volume of EDTA solution in 7.3, in millilitres;

F is the factor of 5 g/l EDTA solution;

m is the mass of the test portion obtained in accordance with 9.3.2.2 of ISO 21079-1:2008, in grams.

8 Determination of magnesium oxide

8.1 Principle

Hydroxyammonium chloride and 2,2', 2''-nitrilotriethanol are added to an aliquot portion of stock solution (S2) to mask interfering ions. Then a buffer solution is added to adjust the pH to about 10. The sum of the content of calcium oxide and magnesium oxide is determined by titration with EDTA solution. The content of magnesium oxide is calculated from this volume and that obtained in accordance with 7.2.

In the presence of significant amounts of chromium and manganese, sodium sulfide is added prior to the titration.

8.2 Procedure

8.2.1 Take a quantity of solution (S2) (see Annex A of ISO 21079-1:2008) and check the content of manganese(II) oxide in accordance with Clause 7 of ISO 10058-2 and/or chromium(III) oxide in accordance with subclause 3.2 or 4.2 of ISO 21079-3:2008.

If the solution (S2) contains a mass fraction of manganese(II) oxide and/or chromium(III) oxide more than 0,02%, follow the procedure given in 8.2.3. In all other cases, follow the procedure given in 8.2.2.

8.2.2 Pipette 100 ml of stock solution (S2) (see Annex A of ISO 21079-1:2008) into a 500 ml conical flask and dilute with water to about 200 ml. Add 10 drops of hydrochloric acid (concentrated), 20 ml of 2,2', 2''-nitrilotriethanol (1+1), and 25 ml of ammonia solution (concentrated). Add about 0,04 g of the methyl thymol blue complexone indicator and titrate with EDTA (5 g/l) solution from a semi-micro burette, until the colour changes from blue to colourless.

8.2.3 Pipette 100 ml of stock solution (S2) (see Annex A of ISO 21079-1:2008) into a 500 ml conical flask and dilute with water to about 200 ml. Add 5 ml of hydroxyammonium chloride solution (100 g/l), 20 ml of 2,2', 2''-nitrilotriethanol (1+1), 2 g ammonium chloride, 25 ml of ammonia solution (concentrated) and 1 ml of sodium sulfide solution. Add 0,04 g of the methyl thymol blue complexone as an indicator while stirring and titrate with EDTA (5 g/l) solution from a semi-micro burette, until the colour changes from blue to colourless.

8.3 Blank test

Carry out the procedure on an equivalent aliquot portion of blank solution (B2) (see Annex A of ISO 21079-1:2008).

8.4 Calculation

Calculate the mass fraction of magnesium oxide in the sample, expressed as a percentage, as follows.

Deduct the volume of EDTA used in the titration for the determination of calcium oxide from that used for the titration of the sum of calcium and magnesium oxide, after correcting for the volumes in the blank determinations.

Calculate the mass fraction of magnesium oxide, $w(\mathrm{MgO})$, expressed as a percentage, using Equation (9).

$$w(\mathrm{MgO}) = \frac{V \cdot F}{m} \times \frac{250}{100} \times 100 \tag{9}$$

where

V is the equivalent volume of EDTA solution used after deducting the volume of EDTA used in the determination of CaO and the blank determinations, in millilitres;

F is the factor for magnesium oxide of 5 g/l EDTA solution;

m is the mass of the test portion obtained in accordance with 9.3.2.2 of ISO 21079-1:2008, in grams.

9 Determination of sodium oxide by flame photometry

9.1 Principle

A portion of stock solution (S2) is sprayed into the flame of a flame photometer, and the emission intensity of sodium is measured.

9.2 Reagents

9.2.1 Reagents specified in ISO 21079-1:2008, as necessary, and those given in 9.2.2 to 9.2.3.

9.2.2 Mixed standard solution 1, 0,1 mg CaO/ml, 0,1 mg MgO/ml, 0,1 mg Na_2O/ml, 0,1 mg K_2O/ml.

Transfer 20 ml aliquot portions each of the calcium oxide, magnesium oxide, sodium oxide and potassium oxide standard solutions into a 200 ml volumetric flask and dilute to the mark with water.

9.2.3 Series 1 solution for calibration.

Transfer aliquot portions of mixed standard solution 1 to each of several 100 ml volumetric flasks. To each, add 5 ml of hydrochloric acid (1+1) and dilute to the mark with water. Typical examples of preparation are shown in Table 6.

The volume of aluminium oxide required is determined by the content of that oxide in the sample.

Table 6 — Example of series 1 solution for calibration

Solution No.	Hydrochloric acid (1+1)	Mixed standard solution 1	Concentration of solution mg/100 ml			
	ml	ml	CaO	MgO	Na_2O	K_2O
1	5	0	0	0	0	0
2	5	2	0,2	0,2	0,2	0,2
3	5	4	0,4	0,4	0,4	0,4
4	5	6	0,6	0,6	0,6	0,6
5	5	8	0,8	0,8	0,8	0,8
6	5	10	1,0	1,0	1,0	1,0
7	5	20	2,0	2,0	2,0	2,0
8	5	30	3,0	3,0	3,0	3,0
9	5	40	4,0	4,0	4,0	4,0
10	5	50	5,0	5,0	5,0	5,0
11	5	60	6,0	6,0	6,0	6,0

9.3 Procedure

Spray a portion of stock solution (S2) (see Annex A of ISO 21079-1:2008) into the flame of a flame photometer, as described in ISO 26845, and measure the emission intensity at a wavelength of 589,0 nm.

An optical filter for sodium may be used.

9.4 Blank test

Carry out the procedure described in 9.3 using blank solution (B2) (see Annex A of ISO 21079-1:2008).

9.5 Plotting the calibration graph

Prepare a calibration graph by using the series 1 solution described in 9.2.3. Carry out the procedure described in 9.3, and plot the relation between the emission intensity and mass of sodium oxide.

9.6 Calculation

Calculate the mass fraction of sodium oxide, $w(\mathrm{Na_2O})$, expressed as a percentage, using Equation (10) with the mass of sodium oxide derived from the emission intensity obtained as described in 9.3 and 9.4, and the calibration prepared as described in 9.5.

$$w(\mathrm{Na_2O}) = \frac{m_\mathrm{s} - m_\mathrm{b}}{m} \times 100 \qquad (10)$$

where

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

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

m is the mass of the test portion obtained in accordance with 9.3.2.2 of ISO 21079-1:2008, in grams.

10 Determination of potassium oxide by flame photometry

10.1 Principle

The emission intensity of potassium is measured on stock solution (S2) by spraying into the flame of a flame photometer.

10.2 Procedure

Spray a portion of stock solution (S2) (see Annex A of ISO 21079-1:2008) into the flame of a flame photometer, as described in ISO 26845, and measure the emission intensity at the wavelength of 766,5 nm.

An optical filter for potassium may be used.

10.3 Blank test

Carry out the procedure described in 10.2 using blank solution (B2) (see Annex A of ISO 21079-1:2008).

10.4 Plotting the calibration graph

Carry out the procedure described in 10.2 using Series 1 solution for calibration described in 9.2.3. Plot the relation between the emission intensity and mass of potassium oxide.

10.5 Calculation

Calculate the mass fraction of potassium oxide in the sample, $w(\mathrm{K_2O})$, expressed as a percentage, using Equation (11) with the mass of potassium oxide derived from the emission intensity obtained as described in 10.2 and 10.3, and the calibration prepared as described in 10.4.

$$w(\mathrm{K_2O}) = \frac{m_\mathrm{s} - m_\mathrm{b}}{m} \times 100 \qquad (11)$$

where

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

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

m is the mass of the test portion from 9.3.2.2 of ISO 21079-1:2008, in grams.

11 Determination of chromium(III) oxide using diphenylcarbazide

11.1 Principle

Ammonium ceric nitrate solution is added to a portion of the stock solution (S1) (S'1) or (S''1), previously evaporated with sulfuric acid to remove chlorides. Sodium azide solution is then added in order to destroy excess ceric ions, followed by diphenylcarbazide solution. The absorbance of the complex is measured at 540 nm.

11.2 Procedure

Transfer 5 ml of the stock solution (S1), (S'1) or (S''1) (see Annex A of ISO 21079-1:2008), into a 100 ml beaker, add 5 ml of the sulfuric acid (1+9) and evaporate to dryness. To the dry residue, add 2 ml of the sulfuric acid (1+9) and about 15 ml of water. Warm to dissolve as much of the residue as possible. Filter, if necessary, through a filter paper (fine) and wash the residue with warm water. Evaporate to 20 ml, add 2 ml of the ammonium ceric nitrate solution and allow the solution to stand on a steam bath for 25 min. Cool to 10 °C and add the sodium azide solution drop by drop, to destroy the colour of the excess ceric ion.

Transfer the solution to a 100 ml volumetric flask containing 3 ml of sulfuric acid (1+9) and dilute to about 90 ml with water. Add 2 ml of diphenylcarbazide solution, dilute to 100 ml with water and mix. Allow the solution to stand for 5 min. Measure the absorbance of the solution against water in 10 mm cells at 540 nm, or by using a colour filter in a suitable instrument.

11.3 Blank test

Carry out the procedure given in 11.2 using an aliquot portion of blank solution (B1), (B'1) or (B''1) (see Annex A of ISO 21079-1:2008). The volumes of the aliquot portion of blank solution used should be identical with those for the corresponding stock solution.

11.4 Plotting the calibration graph

Transfer 0 ml (as reference), 1 ml, 2 ml, 3 ml, 4 ml and 5 ml aliquot portions of diluted chromium(III) oxide standard solution [0 mg to 0,125 mg as chromium(III) oxide] into each of six 100 ml volumetric flasks. Treat each of these solutions as described in 11.2, but add 5 ml of sulfuric acid instead of 3 ml of sulfuric acid, and measure the absorbance against the reference solution. Plot the relation between the absorbances and mass of chromium(III) oxide. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

11.5 Calculation

Calculate the mass fraction of chromium(III) oxide , $w(\mathrm{Cr_2O_3})$, expressed as a percentage, using Equation (12). Use the amount of chromium(III) oxide which is derived from the absorbance in 11.2 and 11.3 and the calibration in 11.4.

$$w\left(\mathrm{Cr_2O_3}\right) = \frac{m_s - m_b}{m} \times \frac{500}{5} \times 100 \qquad (12)$$

where

m_s is the mass of chromium(III) oxide in the aliquot portion of stock solution (S1), (S'1) or (S''1), in grams;

m_b is the mass of chromium(III) oxide in the aliquot portion of blank solution (B1), (B'1) or (B''1), in grams;

m is the mass of the test portion from 9.2.2.2, 9.2.3.2 or 9.3.4.2 of ISO 21079:2008, in grams;

5 is the volume of the aliquot portion taken from stock solution (S1), (S'1) or (S''1) in 11.2, in millilitres.

12 Determination of zirconium oxide (including hafnium oxide) by mandelic acid (α-hydroxybenzeneacetic acid) gravimetric method

12.1 Principle

An aliquot portion of stock solution (S1), (S'1) or (S''1) (see Annex A of ISO 21079-1:2008) is transferred into a beaker and hydrochloric acid is added. Zirconium (hafnium) is precipitated by the addition of DL-mandelic acid and then filtered. The precipitate is ignited and the mass weight of the zirconium oxide (including hafnium oxide) is measured.

12.2 Reagent

12.2.1 Washing solution

Dissolve 10 g of DL-mandelic acid in 180 ml of water and add 20 ml of hydrochloric acid (see 5.1.32 of ISO 26845:2008).

12.3 Procedure

12.3.1 Precisely transfer a 200 ml aliquot portion of stock solution (S1), (S'1) or (S''1) (see Annex A of ISO 21079-1:2008), into a beaker, add 50 ml of hydrochloric acid and heat on a sand bath or hot plate. Boil the solution and carefully add 16 g to 18 g of DL-mandelic acid. When the solution starts bubbling, transfer onto a steam bath of more than 90 °C and add 0,2 g of powdery filter paper pulp while mixing thoroughly. Allow to digest on a steam bath for 30 min after the supernatant solution has become clear. Add 0,2 g of another filter paper pulp. Filtrate with filter paper while the beaker with the precipitate is kept warm on the steam bath during the course of filtration. Finally wash it 10 times with a hot washing solution (12.2.1).

For lower content samples, increase the aliquot portion of stock solution (S1, S'1, or, S''1) to more than 200 ml (e.g. 400 ml) and condense to 200 ml. If necessary, repeat the stock solution preparation (see ISO 21079-1:2008).

12.3.2 Remove the precipitate together with the filter paper into a platinum crucible and heat at a low temperature. Increase the temperature gradually to burn the filter paper to ash and ignite at 1 100 °C ± 25 °C for 30 min. Allow to cool in a desiccator and weigh the mass.

12.4 Blank test

Transfer a 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 described in 12.3.

12.5 Calculation

Calculate the mass fraction of zirconium oxide (including hafnium oxide), $w(\text{ZrO2} + \text{HfO}_2)$, in the sample, expressed as a percentage, using Equation (13) with the values obtained in accordance with 12.3 and 12.4.

$$w\left(\text{ZrO}_2 + \text{HfO}_2\right) = \frac{m_1 - m_2}{m_0} \times \frac{500}{200} \times 100 \qquad (13)$$

where

m_0 is the mass of the test portion from 9.2.2.2, 9.2.3.2 or 9.2.4.2 of ISO 21079-1:2008, in grams;

m_1 is the mass of the precipitate obtained as described in 12.3, in grams;

m_2 is the mass of the precipitate obtained as described in 12.4, in grams.

13 Calculation and expression of test results

Express the test results in accordance with ISO 26845.

14 Test report

Prepare a test report as described in ISO 26845.

Bibliography

[1] ISO 12677, *Chemical analysis of refractory products by XRF — Fused cast bead method*

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