INTERNATIONAL STANDARD

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

Part 1: Apparatus, reagents, dissolution and gravimetric silica

Analyse chimique des produits réfractaires d'aluminosilicates (méthode alternative à la méthode par fluorescence de rayons X) —

Partie 1: Appareillage, réactifs, dissolution et teneur en silice par gravimétrie

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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 21587-1 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*

— *Part 3: Inductively coupled plasma and atomic absorption spectrometry methods*

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

Part 1: Apparatus, reagents, dissolution and gravimetric silica

1 Scope

This part of ISO 21587 specifies reagents, dissolution and gravimetric silica analysis for the chemical analysis of aluminosilicate refractory products and raw materials.

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*.

This part of ISO 21587 should be used in conjunction with ISO 21587-2 and ISO 21587-3, which give the analytical procedures for 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)

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

ISO 21587-3, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 3: Inductively coupled plasma and atomic absorption spectrometry methods*

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

3 Reagents

Standard solutions specified in ISO 26845 and the following reagents.

3.1 Standard volumetric solutions

3.1.1 Standard volumetric CyDTA solution, c(CyDTA) = 0,05 mol/l.

Dissolve 18 g of 1,2 cyclohexanediamine-N,N,N',N'-tetraacetic acid monohydrate (CyDTA) in 500 ml of water by the progressive addition of the minimum amount of potassium hydroxide solution.

NOTE Approximately 25 ml is required. Determine the exact strength of this solution by titration against the standard volumetric zinc solution, c(Zn) = 0,05 mol/l.

3.1.2 Standard volumetric CyDTA solution, c(CyDTA) = 0,02 mol/l.

Add 16 ml of sodium hydroxide solution (100 g/l) and approximately 150 ml of water to 7,30 g of 1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid monohydrate (CyDTA), and dissolve by heating. After cooling, dilute to 1 000 ml with water.

NOTE Approximately 25 ml is required. Determine the exact strength of this solution by titration against the standard volumetric zinc solution, c(Zn) = 0,02 mol/l.

3.1.3 Standard volumetric EDTA solution, c(EDTA) = 0,012 5 mol/l.

Dissolve 5 g of $EDTANa_2$ (ethylenediamine-tetraacetic acid disodium salt, dihydrate) in water and dilute to 1 000 ml in a volumetric flask. Store in a plastic bottle.

Standardize against calcium as follows.

Pipette 25 ml of standard calcium oxide solution (1 mg/ml), into a 500 ml conical flask, add 10 ml of potassium hydroxide solution, and dilute to about 200 ml. Add about 0,015 g of screened Calcein indicator, and titrate with the standard volumetric EDTA solution, from a fluorescent green colour to pink.

Standardize against magnesium as follows.

Pipette 25 ml of standard magnesium oxide solution (1 mg/ml), into a 500 ml conical flask, add 20 drops of hydrochloric acid (concentrated) and 20 ml of ammonia solution (concentrated), and dilute to about 200 ml. Add about 0,04 g of methylthymol blue complexone indicator, and titrate with the standard volumetric EDTA solution.

3.1.4 Standard volumetric zinc solution, c(Zn) = 0,05 mol/l.

Wash the surface of about 5 g of pellets of metallic zinc in about 50 ml of hydrochloric acid (1+1) to remove oxide, then wash successively with water, ethanol and diethyl ether. Weigh 3,269 g of the dried pellets, dissolve in 10 ml of hydrochloric acid (concentrated) and 50 ml of water, cool and dilute to the mark in a 1 000 ml volumetric flask. 1 ml of this zinc solution (0,05 mol/l) is equivalent to 2,55 mg of Al_2O_3.

3.1.5 Standard volumetric zinc solution, c(Zn) = 0,02 mol/l.

Wash the surface of the zinc (purity, more than 99,9 % by mass) with hydrochloric acid (1+3) and dissolve the oxidized layer. Subsequently, wash with water, ethanol and diethyl ether in succession, then dry in a desiccator. Weigh 0,66 g (recorded to 0,1 mg) of zinc, transfer it to a 300 ml beaker, and cover with a watch glass. Add 20 ml of water and 10 ml of nitric acid carefully, and heat to dissolve on a steam bath. After cooling, dilute to 1 000 ml in a volumetric flask with water.

Calculate the factor of this zinc solution using the following equation:

$$F = \frac{m}{0{,}653\,9} \times \frac{A}{100} \qquad (1)$$

where

F is the factor of this zinc solution;

m is the mass, in grams, of the weighed zinc;

A is the purity, in percentage by mass, of the zinc.

3.2 Standard solutions

3.2.1 Standard aluminium oxide solution, Al_2O_3 1 mg/ml.

Wash the surface of a sufficient amount of aluminum metal (purity more than 99,9 % by mass) with hydrochloric acid (1+4) to dissolve the oxidized layer. Then wash with water, ethanol and diethyl ether in succession, and dry in a desiccator. Weigh 0,529 2 g of aluminium and transfer to a 250 ml beaker. Cover with a watch glass, add 20 ml hydrochloric acid (1+1), and heat to dissolve. After cooling, dilute to 1 000 ml in a volumetric flask with water.

3.2.2 Standard calcium oxide solution, CaO 1 mg/ml.

Dissolve 1,785 g of pure calcium carbonate, previously dried at 150 °C, in a slight excess of dilute hydrochloric acid (1 + 4) in a 250 ml beaker, covered with a watch glass. Boil to expel carbon dioxide, cool and dilute to 1 000 ml in a volumetric flask.

3.2.3 Standard chromium(III) oxide solution, Cr_2O_3 1 mg/ml.

Dry about 2 g to 3 g of potassium dichromate at 110 °C for at least 2 h. Weigh 1,935 g of this and dissolve in water, diluting to 1 000 ml in a volumetric flask.

3.2.4 Dilute standard chromium(III) oxide solution, Cr_2O_3 0,025 mg/ml.

Pipette 25 ml of the standard chromic oxide solution (1 mg/ml) to a 1 000 ml volumetric flask and dilute to the mark with water. Prepare this solution freshly when required.

3.2.5 Standard iron(III) oxide solution, Fe_2O_3 1 mg/ml.

Wash the surface of a sufficient amount of iron metal (purity greater than 99,9 %) with hydrochloric acid (1+4). Then dissolve the oxidized layer, and wash with water, ethanol and diethyl ether in succession. Then dry in a

desiccator. Weigh 0,699 4 g of this, transfer to a beaker (200 ml), and cover with a watch glass. Add 40 ml of hydrochloric acid (1+1), and heat on a steam bath until it is dissolved. After cooling, dilute to 1 000 ml in a volumetric flask with water.

3.2.6 Diluted standard iron(III) oxide solution, Fe_2O_3 0,2 mg/ml.

Pipette 20 ml of the standard iron(III) oxide solution (Fe_2O_3 1 mg/ml) into a 1 000 ml volumetric flask and dilute to the mark with water. Prepare this solution freshly when required.

3.2.7 Dilute standard iron (III) oxide solution, Fe_2O_3 0,04 mg/ml.

Pipette 4 ml of the standard iron(III) oxide solution (Fe_2O_3 1 mg/ml) into a 1 000 ml volumetric flask and dilute to the mark with water. Prepare this solution freshly when required.

3.2.8 Standard magnesium oxide solution, MgO, 1 mg/ml.

Wash the surface of a sufficient amount of magnesium metal (purity more than 99,9 % by mass) with hydrochloric acid (1+1) to dissolve the oxidized layer. Then wash with water, ethanol and diethyl ether in succession, and dry in a desiccator. Weigh 0,301 5 g of the washed magnesium, transfer to a 200 ml beaker and cover with a watch glass. Add 20 ml of hydrochloric acid (1+1), and heat on a steam bath until dissolved. After cooling, transfer to a 500 ml volumetric flask, and dilute to the mark with water.

3.2.9 Standard manganese(II) oxide solution, MnO 1 mg/ml.

Wash the surface of a sufficient mass of manganese metal (purity more than 99,9 % by mass) with hydrochloric acid (1+3) to dissolve the oxidized layer. Then wash with water, ethanol and diethyl ether in succession and dry in a desiccator. Weigh 0,774 5 g of this metal, transfer to a 200 ml beaker and cover with a watch glass. Add 40 ml of nitric acid (1+1) and heat to dissolve. After cooling, transfer to a 1 000 ml volumetric flask.

3.2.10 Dilute standard manganese(II) oxide solution, MnO 0,04 mg/ml.

Transfer 40 ml of the standard manganese(II) oxide solution (MnO 1 mg/ml) into a 1 000 ml volumetric flask and dilute to the mark with water. Prepare this solution freshly as required.

3.2.11 Standard phosphorus(V) oxide solution, P_2O_5 1 mg/ml.

Heat about 3 g of potassium dihydrogen phosphate at 110 °C ± 5 °C for 3 h, and allow to cool in a desiccator. Weigh 1,917 6 g, transfer to a beaker and dissolve with approximately 300 ml of water. Dilute to 1 000 ml in a volumetric flask with water.

3.2.12 Dilute standard phosphorus(V) oxide solution, P_2O_5 0,04 mg/ml.

Transfer precisely 40 ml of the standard phosphorus(V) oxide solution (P_2O_5 1 mg/ml) to a 1 000 ml volumetric flask, and dilute to the mark with water.

3.2.13 Dilute standard phosphorus(V) oxide solution, P_2O_5 0,01 mg/ml.

Pipette 10 ml of the standard phosphorus(V) oxide solution (P_2O_5 1 mg/ml) into a 1 000 ml volumetric flask, and dilute to the mark with water. Prepare this solution freshly when required.

3.2.14 Standard potassium oxide solution, K_2O 1 mg/ml.

Transfer 1 g to 1,5 g of potassium chloride to a platinum crucible (e.g. 30 ml) and ignite at 600 °C ± 25 °C for approximately 60 min. Allow the crucible and contents to cool in a desiccator. Weigh 0,791 4 g of this and transfer to a 200 ml beaker. Dissolve in 100 ml of water, transfer to a 500 ml volumetric flask, and dilute to the mark with water.

3.2.15 Standard silicon(IV) oxide solution, SiO_2 1 mg/ml.

Weigh 1,5 to 2 g of silicon(IV) oxide (purity, greater that 99,9 % by mass) in a platinum crucible (e.g. 30 ml) and heat for 30 min at 1 150 °C ± 50 °C. Cool in a desiccator and then weigh 1,000 g of this silicon(IV) oxide into a platinum crucible (e.g. 50 ml). Fuse the silicon(IV) oxide with 5,0 g of anhydrous sodium carbonate. Cool and wipe the outside of the crucible, and dissolve in warm water (150 ml) in a plastic 200 ml beaker, while stirring with a plastic rod. Cool and dilute without heating to 1 000 ml in a volumetric flask. Transfer this solution to a plastics bottle immediately.

3.2.16 Dilute standard silicon(IV) oxide solution, SiO_2 0,2 mg/ml.

Pipette 40 ml of the standard silicon(IV) oxide solution (SiO_2 1 mg/ml) into a 200 ml volumetric flask, and dilute to the mark with water. Prepare this solution freshly when required.

3.2.17 Dilute standard silicon(IV) oxide solution, SiO_2 0,04 mg/ml.

Pipette 20 ml of the standard silicon(IV) oxide solution (SiO_2 1 mg/ml) into a 500 ml volumetric flask and dilute to the mark with water. Prepare this solution freshly when required.

3.2.18 Standard sodium oxide solution, Na_2O 1 mg/ml.

Transfer 1 g to 1,5 g of sodium chloride into a platinum crucible (e.g. 30 ml) and ignite at 600 °C ± 25 °C for approximately 60 min. Allow the crucible and contents to cool in a desiccator. Weigh 0,942 9 g of the contents and transfer to a 200 ml beaker. Dissolve in 100 ml of water, transfer to a 500 ml volumetric flask, and dilute to the mark with water.

3.2.19 Standard titanium(IV) oxide solution, TiO_2 1 mg/ml.

Wash the surface of a sufficient amount of titanium metal (purity more than 99,9 % by mass) with hydrochloric acid (1+3) and dissolve the oxidized layer. Subsequently, wash with water, ethanol and diethyl ether in succession, then dry in a desiccator. Weigh 0,599 4 g of this titanium metal, and transfer to a platinum dish. Cover with a watch glass made of ethylene 4-fluoride resin, then add 40 ml of hydrofluoric acid, 15 ml of sulfuric acid (1+1), and 2 ml of nitric acid, and heat to dissolve on a steam bath. Remove the watch glass, rinse the watch glass with water, and heat the solution on a sand bath until the appearance of strong sulfuric acid fumes. After cooling, rinse the inner wall of the platinum dish with a small amount of water, and heat again until fumes are seen. After cooling, add water, and dilute to 1 000 ml in a volumetric flask with water.

3.2.20 Dilute standard titanium(IV) oxide solution, TiO_2 0,1 mg/ml.

Pipette 20 ml of the standard titanium(IV) oxide solution (1 mg/ml) into a 200 ml volumetric flask, and dilute to the mark with water. Prepare this solution freshly when required.

3.2.21 Dilute standard titanium(IV) oxide solution, TiO_2 0,01 mg/ml.

Pipette 10 ml of the standard titanium(IV) oxide solution (1 mg/ml) into a 1 000 ml volumetric flask, and dilute to the mark with water. Prepare this solution freshly when required.

3.2.22 Standard zirconium oxide solution, ZrO_2 1 mg/ml.

Transfer about 0,3 g of zirconium oxide (purity more than 99,9 % by mass) into a platinum crucible (e.g. 30 ml), heat strongly at 1 150 °C ± 50 °C for approximately 30 min, and allow to cool in a desiccator. Weigh 0,200 0 g of this into a platinum crucible (e.g. 30 ml), add 4 g of potassium disulfate, and fuse, covering with a platinum lid.

Fuse over a gas burner at as low a temperature as possible, otherwise sulfur trioxide will be lost before the attack is complete.