
**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.

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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, $c(\text{CyDTA}) = 0,05 \text{ mol/l}$.

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, $c(\text{Zn}) = 0,05 \text{ mol/l}$.

3.1.2 Standard volumetric CyDTA solution, $c(\text{CyDTA}) = 0,02 \text{ mol/l}$.

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, $c(\text{Zn}) = 0,02 \text{ mol/l}$.

3.1.3 Standard volumetric EDTA solution, $c(\text{EDTA}) = 0,012 5 \text{ mol/l}$.

Dissolve 5 g of EDTA Na_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, $c(\text{Zn}) = 0,05 \text{ mol/l}$.

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, $c(\text{Zn}) = 0,02 \text{ mol/l}$.

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:

$$F = \frac{m}{0,6539} \times \frac{A}{100} \quad (1)$$

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 $110\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ 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 $600\text{ }^\circ\text{C} \pm 25\text{ }^\circ\text{C}$ 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, SiO₂ 1 mg/ml.

Weigh 1,5 to 2 g of silicon(IV) oxide (purity, greater than 99,9 % by mass) in a platinum crucible (e.g. 30 ml) and heat for 30 min at $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$. 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, SiO₂ 0,2 mg/ml.

Pipette 40 ml of the standard silicon(IV) oxide solution (SiO₂ 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, SiO₂ 0,04 mg/ml.

Pipette 20 ml of the standard silicon(IV) oxide solution (SiO₂ 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, Na₂O 1 mg/ml.

Transfer 1 g to 1,5 g of sodium chloride into a platinum crucible (e.g. 30 ml) and ignite at $600\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ 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, TiO₂ 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, TiO₂ 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, TiO₂ 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, ZrO₂ 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 $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$ 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.

After cooling, put the platinum crucible in a 200 ml beaker, add 100 ml of sulfuric acid (1+9), and warm to dissolve. After further cooling, remove and wash the platinum crucible with water, transfer to a 200 ml volumetric flask, and dilute to the mark with water

3.2.23 Dilute standard zirconium oxide solution, ZrO_2 0,005 mg/ml.

Pipette 5 ml of the standard zirconium 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.

3.2.24 Standard scandium solution, Sc 1,0 mg/ml.

Dry about 0,2 g of scandium oxide at $110\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ for 60 min, then cool in a desiccator. Weigh 0,153 4 g of this, transfer to a 100 ml beaker, gradually add 10 ml of hydrochloric acid (1+1) to dissolve, and dilute precisely to 1 000 ml in a volumetric flask with water.

NOTE A suitable commercial standard solution may be used.

3.2.25 Standard yttrium solution, Y 1,0 mg/ml.

Dry about 0,2 g of yttrium oxide at $110\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ for 60 min, then cool in a desiccator. Weigh 0,127 0 g of this, and transfer to a 100 ml beaker. Dissolve by gradually adding 10 ml of hydrochloric acid (1+1) to dissolve, and dilute precisely to 1 000 ml in a volumetric flask with water.

NOTE A suitable commercial standard solution may be used.

3.2.26 Internal standard solution, Sc 0,1 mg/ml and Y 0,1 mg/ml.

Transfer 10 ml each of standard scandium solution and standard yttrium solution to a volumetric 100 ml flask and dilute to the mark with water. Prepare this solution immediately prior to use.

4 Dissolution and gravimetric silica

4.1 General decomposition techniques

Among the various techniques used in this standard method are traditional, 'wet' methods, flame photometry, atomic absorption spectrometry and ICP-AE spectrometry. To meet all these requirements, five separate decompositions are called for in the standard, but only those used in the particular techniques chosen will need to be prepared. The solutions that can be required are as follows:

- a) decomposition by fusion, followed by removal of the bulk of the silica present by dehydration (see 4.2.2);
- b) decomposition by fusion, followed by removal of the bulk of the silica present by coagulation (see 4.2.3);
- c) decomposition and removal of the silica by hydrofluoric acid for flame photometry (see 4.3.2);
- d) decomposition and removal of the silica by hydrofluoric acid for atomic absorption spectrometry (see 4.3.3);
- e) decomposition and removal of the silica by hydrofluoric acid for ICP-AES spectrometry (see 4.3.4).

4.2 Dissolution methods by fusion

4.2.1 General

A solution is prepared for the determination of residual silicon(IV) oxide in solution, ferric oxide, titanium oxide, manganese oxide, chromium(III) oxide, zirconium oxide, and phosphorus(V) oxide by one of the following two methods:

- a) fusion with alkali carbonate and boric acid, dissolution of the melt in hydrochloric acid and removal of the bulk of the silicon(IV) oxide by dehydration;
- b) fusion with alkali carbonate and boric acid, dissolution of the melt in hydrochloric acid and removal of the bulk of the silicon(IV) oxide by coagulation.

4.2.2 Preparing a solution by fusion and dehydration

4.2.2.1 Principle

The sample is fused with boric acid and either fusion mixture or anhydrous sodium carbonate. The melt is then dissolved in hydrochloric acid and evaporated to dryness for the dehydration of silicic acids. Soluble salts are dissolved in hydrochloric acid, and the solution filtered. The precipitate is ignited, and weighed before and after treatment with hydrofluoric and sulfuric acids. The difference in mass gives the main, or gravimetric silicon(IV) oxide content. This result is then added to that for residual silica in solution, to give the figure for the total silicon(IV) oxide content.

4.2.2.2 Mass of test portion to be weighed

Weigh, to the nearest 0,1 mg, 1,00 g of the test sample.

NOTE The sample used for the loss on ignition may be used if it has not sintered.

4.2.2.3 Procedure

Carry out the decomposition using the following procedure.

Weigh the dried sample into a platinum dish (e.g. 75 ml), add 3,0 g of fusion mixture or anhydrous sodium carbonate and 0,4 g of boric acid, and mix intimately. Cover the dish loosely with a lid. Heat over a burner, cautiously at first, then gradually raise the temperature to the full heat of the burner.

The sample should be heated slowly to avoid spurting caused by the dehydration of boric acid.

Alternatively, heat the sample from cold in an electric furnace, progressively raising the temperature. Finally, heat the dish and contents in an electric furnace at $1\,150\text{ °C} \pm 50\text{ °C}$ for as short a time as possible, until decomposition is complete

NOTE 15 min is usually adequate.

Remove the dish from the furnace and allow it to cool. Then add 5 ml of ethanol, 30 ml of hydrochloric acid (1+1) and 2 ml of sulfuric acid (1+1), cover with a lid and heat on a steam bath until the melt is completely dissolved.

Samples containing significant amounts of both zirconium oxide and phosphorus(V) oxide cannot be handled by the specified procedure. If, at this point, hydrochloric acid and sulfuric acid are added, a white precipitate of zirconium oxyphosphate occurs. In these circumstances, the following procedure should be adopted. To the cooled melt, add 50 ml of hot water, allow to stand on a steam bath until the melt is completely digested. Filter into a platinum dish (e.g. 200 ml) using filter paper (closed-pore) and wash 10 times with hot sodium carbonate solution (1 % by mass). Concentrate the solution of the filtrate and washings to 20 ml on a steam bath, then add ethanol, hydrochloric acid and sulfuric acid, and continue the procedure. Ash the paper

containing the filtered precipitate, After cooling, add 1,0 g of anhydrous sodium carbonate and 0,5 g of boric acid and fuse at a low temperature in a platinum crucible (e.g. 30 ml) in an electric furnace. Dissolve the melt with 10 ml of hydrochloric acid (1+1). Then transfer the solution to a 500 ml volumetric flask, diluting to the mark with water. In this solution, silicon(IV) oxide, aluminium oxide, iron(III) oxide, titanium(IV) oxide and phosphorus(V) oxide are determined by appropriate methods, as specified in the normal procedures. The content for each component is the sum of the "result obtained from filtered precipitate" and "result obtained from the solution of filtrate and washing mixture" in this paragraph.

Remove the lid, washing it with water and heat the dish and contents on a steam bath to apparent dryness. If necessary, a glass rod can be used occasionally to break up the salts. Cool and add 10 ml of hydrochloric acid (concentrated) and allow the whole to stand for 1 min. Add 30 ml of hot water and heat on a steam bath for about 5 min, with occasional stirring, until the solution of soluble salts appears to be complete. It is advantageous to add ashless filter-paper pulp at this stage to aid filtration. Filter through an ashless filter paper (close) into a 500 ml beaker, and wash several times with hot hydrochloric acid (1+50). Then, wash with hot water until free from chlorides. Reserve the filtrate and washings in the beaker, covered with a watch glass.

Transfer the precipitate with the filter paper to an ignited and weighed (mass m_0) platinum crucible (e.g. 30 ml), and add a drop of sulfuric acid (1+1). Heat over a burner or an electric furnace at low temperature, completely ashing the filter paper, and then heat the crucible and contents in an electric furnace at $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$ for about 30 min. Cool in a desiccator and weigh (mass m_1). Then, moisten the contents in the crucible with water, add 5 drops of sulfuric acid (1+1) and 10 ml of hydrofluoric acid (concentrated) and heat on a sand bath to dryness. Heat at $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$ for about 5 min, cool in a desiccator, and weigh (mass m_2).

Calculate the difference between the mass (m_1) and this mass (m_2) to provide the 'main' or 'gravimetric silicon(IV) oxide mass.

If the residue weighs more than 5 mg, repeat the treatment with hydrofluoric and sulfuric acids to ensure that all the silicon (IV) oxide has been removed.

Add 1,0 g of fusion mixture or anhydrous sodium carbonate and 0,3 g of boric acid to the crucible and fuse the residue. After cooling, add 10 ml of hydrochloric acid (1+1), warm to dissolve, and then add the solution to the reserved filtrate. If necessary, condense the reserved filtrate in the 500 ml beaker, transfer to a 500 ml volumetric flask and dilute to the mark with water.

This solution is referred to as the stock solution (S1).

4.2.2.4 Blank test

Carry out the procedure given in 4.2.2.3 without the sample, but omit the fusion of the flux.

The resulting blank solution is designated (B1).

4.2.3 Preparing a solution by fusion and coagulation

4.2.3.1 Principle

The sample is fused with boric acid and fusion mixture or anhydrous sodium carbonate, and the melt is dissolved in hydrochloric acid. After coagulation of silicic acids by the addition of poly(ethylene oxide) as coagulant, the precipitate is filtered. The precipitate is ignited in a platinum crucible and weighed. After removing the silicon(IV) oxide with hydrofluoric acid, the crucible is ignited and weighed again. The difference between the first and second masses gives the main quantity of the silicon(IV) oxide. The residue after hydrofluoric acid treatment is fused with boric acid and fusion mixture or anhydrous sodium carbonate, the melt is dissolved in the reserved filtrate, and the solution is diluted to a standard volume to obtain the stock solution.

NOTE This procedure results in smaller residues after the hydrofluoric treatment, thus reducing the risk of errors from any change in state of the materials remaining, and can therefore be considered preferable.

4.2.3.2 Mass of test portion

Weigh, to the nearest 0,1 mg, 1,00 g of the test sample.

NOTE The sample used for the loss on ignition may be used if it has not sintered.

4.2.3.3 Procedure

Carry out the decomposition using the following procedure.

Weigh the dried sample in a platinum dish (e.g. 75 ml), add 3,0 g of fusion mixture or anhydrous sodium carbonate and 0,4 g of boric acid and mix thoroughly. Cover the dish loosely with a lid. Heat over a burner or in an electric furnace, cautiously at first, then gradually raise the temperature to the full heat of the burner. Finally, heat the dish and contents in the electric furnace at $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$ for as short a time as possible, until completely decomposed (15 min is usually adequate).

The sample should be heated slowly to avoid spurting caused by the dehydration of boric acid.

Remove the dish from the furnace and allow it to cool. Then, add 5 ml of ethanol, 15 ml of hydrochloric acid (concentrated), 1 ml of sulfuric acid (1+1) and 10 ml of water. Cover the dish with the platinum lid, and heat on a steam bath to dissolve the melt. If the solution gels before dissolution is complete, stir gently with a glass rod. When dissolution is complete, remove the lid and wash any spray adhering to it into the dish with a minimum of water.

Allow the dish and contents to remain on the steam bath until a stiff paste has formed. Then add an adequate amount of paper filter powder and stir thoroughly. Add slowly, while stirring, 10 ml of polyethylene oxide solution (2,5 g/l) and mix intimately. It is essential that any gel adhering to the sides of the dish be brought into contact with the coagulant. Add 10 ml of water and allow the solution to stand for 5 min. Filter with filter paper (closed-pore) into a 500 ml beaker and wash several times with hot hydrochloric acid (1+50). Then, wash with hot water until free from chlorides. Reserve the filtrate and washings in the beaker, covered with a watch glass.

Transfer the paper and precipitate to an ignited and weighed platinum crucible (e.g. 30 ml) (mass m_0), and add a drop of sulfuric acid (1+1). Heat over a burner or an electric furnace at a low temperature until the precipitate is completely free from carbonaceous matter, then heat the crucible and contents in an electric furnace at $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$ for approximately 30 min. Cool in a desiccator and weigh (mass m_1). Then moisten the contents of the crucible with water, add 3 drops of sulfuric acid (1+1) and 10 ml of hydrofluoric acid, and heat on a sand bath to dryness. Heat at $1\ 150\ ^\circ\text{C} \pm 50\ ^\circ\text{C}$ for approximately 5 min, cool in a desiccator, and weigh (mass m_2). Calculate the difference between the first mass and this mass. Add 1,0 g of fusion mixture or anhydrous sodium carbonate and 0,3 g of boric acid to the residue in the crucible and fuse. After cooling, add 5 ml of hydrochloric acid (1+1), warm to dissolve, and then add to the reserved filtrate. If necessary, condense the reserved filtrate in the 500 ml beaker, transfer to a 500 ml volumetric flask, and dilute to the mark with water.

This solution is referred to as the stock solution (S'1).

4.2.3.4 Blank test

Carry out the procedure given in 4.2.3.3 without the sample, but omit the fusion of the flux.

The resulting blank solution is designated (B'1).

4.3 Dissolution methods by hydrofluoric acid attack

4.3.1 General

The following techniques are used:

- a) decomposition and removal of the silica by hydrofluoric acid for EDTA titrimetry and flame photometry (see 4.3.2);

- b) decomposition and removal of the silica by hydrofluoric acid for atomic absorption spectrometry (see 4.3.3);
- c) decomposition and removal of the silica by hydrofluoric acid for ICP-AES spectrometry (see 4.3.4).

4.3.2 Decomposition by hydrofluoric acid for EDTA titrimetry and flame photometry

4.3.2.1 Principle

A portion of the sample is decomposed using hydrofluoric acid, the remaining fluorides being removed by evaporation to dryness with sulfuric acid. The residue is dissolved in hydrochloric acid and the solution is made up to volume. This becomes the stock solution (S2).

4.3.2.2 Mass of test portion to be weighed

Weigh, to the nearest 0,1 mg, 0,25 g of the test sample.

4.3.2.3 Procedure

Carry out the decomposition using the following procedure.

Weigh the sample into a platinum dish (e.g. 75 ml) and ignite gently over a burner to remove carbonaceous matter. Allow the dish to cool and moisten the residue with water, add 2 ml of sulfuric acid (1+1), 2 ml of nitric acid, and 10 ml of hydrofluoric acid. Transfer the dish and contents to a sand bath, cover with a lid and allow the reaction to proceed for 15 min. Remove the lid, rinsing it with water into the dish, and then evaporate to dryness, being careful to avoid spurling. After cooling, rinse the inner wall of the platinum dish with a small quantity of water. Then add 1 ml of sulfuric acid (1+1), and 2 ml of nitric acid, and repeat the evaporation to dryness. After cooling, add 5,0 ml of hydrochloric acid (1+1) and approximately 20 ml of water, and warm on a steam bath to dissolve. Filter, if necessary, using a filter paper (closed-pore) into a 200 ml beaker, washing thoroughly with hot water.

After cooling, transfer to a 250 ml volumetric flask and dilute to the mark with water.

This solution is referred to as the stock solution (S2).

4.3.2.4 Blank test

Carry out the procedure given in with 4.3.2.3 without the sample. The resulting blank solution is designated (B2).

4.3.3 Decomposition by hydrofluoric acid for atomic absorption spectrometry

4.3.3.1 Principle

A portion of the sample is decomposed using hydrofluoric acid, the remaining fluorides being removed by evaporation to dryness with sulfuric acid. The residue is dissolved in hydrochloric acid, lanthanum solution is added and the solution is made up to volume. This becomes the stock solution (S3).

4.3.3.2 Reagent

Lanthanum solution, 50 g/l.

Weigh 50 g of lanthanum(III) oxide into a 1 l beaker. Add 200 ml of hydrochloric acid (1+1), and warm to dissolve the oxide. Dilute with water to 1 l, in a volumetric flask.

4.3.3.3 Mass of test portion to be weighed

Weigh, to the nearest 0,1 mg, 0,20 g of the test sample.

4.3.3.4 Procedure

Weigh the sample into a platinum dish (e.g. 75 ml) and ignite gently over a burner to remove carbonaceous matter. Allow the dish to cool and moisten the residue with water, add 2 ml of sulfuric acid (1+1), 2 ml of nitric acid, and 10 ml of hydrofluoric acid. Transfer the dish and contents to a sand bath, cover with a lid and allow the reaction to proceed for about 15 min. Remove the lid, rinsing it with water into the dish and then evaporate to dryness, being careful to avoid spurting. After cooling, rinse the inner wall of the platinum dish with a small quantity of water. Then add 1 ml of sulfuric acid (1+1), and 2 ml of nitric acid, and repeat the evaporation to dryness. After cooling, add 5,0 ml of hydrochloric acid (1+1) and approximately 20 ml of water, and warm on steam bath to dissolve. Filter, if necessary, using a filter paper (closed-pore) into a 200 ml beaker, washing thoroughly with hot water.

After cooling, add 10 ml of lanthanum solution, transfer to a 100 ml volumetric flask and dilute to the mark with water. Transfer immediately to a dry plastic bottle.

This solution is designated as the stock solution (S3).

4.3.3.5 Blank test

Carry out the procedure given in with 4.3.3.4 without the sample.

The resulting blank solution is designated (B3).

4.3.4 Decomposition by hydrofluoric acid for ICP-AE spectrometry

4.3.4.1 Principle

A portion of the sample is decomposed using hydrofluoric acid, the remaining fluorides being removed by evaporation to dryness with sulfuric acid. The residue is dissolved in hydrochloric acid and the solution is made up to volume. This becomes the stock solution (S4).

4.3.4.2 Mass of test portion to be weighed

Weigh, to the nearest 0,1 mg, 0,20 g of the test sample.

4.3.4.3 Procedure

Prepare a solution of the sample as in (4.3.3.4) but omitting the addition of 10 ml of lanthanum solution.

This solution is designated as stock solution (S4).

4.3.4.4 Blank test

Carry out the procedure given in 4.3.4.3 without the sample.

The resulting blank solution is designated (B4).

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