INTERNATIONAL STANDARD

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Fine ceramics (advanced ceramics, advanced technical ceramics) — Methods for chemical analysis of fine silicon nitride powders

Céramiques techniques — Méthodes pour l'analyse chimique de poudres de nitrure de silicium

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 206, *Fine ceramics*.

Introduction

This International Standard has been developed from Japanese Industrial Standard JIS R 1603:2007 with reference to CEN ENV 14226:2002 and ASTM C1494-01:2007, and is applicable to the chemical analysis of silicon nitride raw powders for fine ceramics use. This International Standard covers both major and minor constituents such as total silicon, total nitrogen, and some of trace metallic and non-metallic elements.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Methods for chemical analysis of fine silicon nitride powders

1 Scope

This International Standard specifies the methods for the chemical analysis of fine silicon nitride powders used as the raw material for fine ceramics.

This International Standard stipulates the determination methods of total silicon, total nitrogen, aluminium, iron, calcium, oxygen, carbon, fluorine, and chlorine in fine silicon nitride powders.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2828, *Aluminium oxide primarily used for the production of aluminium — Determination of fluorine content — Alizarin complexone and lanthanum chloride spectrophotometric method*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 6353-1, *Reagents for chemical analysis — Part 1: General test methods*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

ISO 6353-3, *Reagents for chemical analysis — Part 3: Specifications — Second series*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

ISO 21068-2, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon*

ISO 21068-3, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 3: Determination of nitrogen, oxygen and metallic and oxidic constituents*

ISO 21438-2, *Workplace atmospheres — Determination of inorganic acids by ion chromatography — Part 2: Volatile acids, except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid)*

ISO 21438-3, *Workplace atmospheres — Determination of inorganic acids by ion chromatography — Part 3: Hydrofluoric acid and particulate fluorides*

ISO 26845, *Chemical analysis of refractories — General requirements for wet chemical analysis, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) methods*

EN 12698-1, *Chemical analysis of nitride bonded silicon carbide refractories - Part 1: Chemical methods*

EN 12698-2, *Chemical analysis of nitride bonded silicon carbide refractories - Part 2: XRD methods*

3 Analytes and ranges

Analytes and ranges specified in this International Standard shall be as follows.

a) Total silicon (T. Si), range of 30 % to 70 % (mass fraction)

b) Total nitrogen (T. N), range of 30 % to 45 % (mass fraction)

c) Aluminium (Al), range of 0,001 % to 0,6 % (mass fraction)

d) Iron (Fe), range of 0,001 % to 0,6 % (mass fraction)

e) Calcium (Ca), range of 0,001 % to 0,03 % (mass fraction)

f) Oxygen (O), range of 0,05 % to 5 % (mass fraction)

g) Carbon (C), range of 0,01 % to 6 % (mass fraction)

h) Fluorine (F), range of 0,001 % to 0,2 % (mass fraction)

i) Chlorine (Cl), range of 0,001 % to 0,2 % (mass fraction)

4 Preparation of test sample

The method of preparing samples shall be in accordance with ISO 8656-1 unless otherwise mutually agreed upon between the analyser and the customer.

4.1 Sampling

Take the sample in accordance with ISO 8656-1.

4.2 Drying

Take about 10 g of the sample into a flat-type weighing bottle (60 mm × 30 mm) and spread it uniformly over the bottom of the bottle. Place the bottle in an air bath at 110 °C ± 5 °C for 2 h without a lid, and then cool in a desiccator (desiccant: magnesium perchlorate for drying) with a lid for 1 h.

4.3 Weighing

Weigh the sample of the required quantity to the nearest 0,1 mg using a balance.

5 Apparatus and reagents

Unless otherwise specified in each determination, use ordinary laboratory apparatus for chemical analysis listed in ISO 26845, Clause 4, as necessary. Reagents should conform to the requirements of ISO 6353-1, ISO 6353-2, and ISO 6353-3, as appropriate. Unless otherwise specified in each determination, use corresponding reagents of analytical grade listed in ISO 26845, Clause 5, as necessary.

6 Blank test

Blank test shall be carried out by using identical quantities of reagents, conditions, and procedures throughout each determination to correct the analytical values obtained.

7 Determination of total silicon

7.1 Classification of determination methods

Total silicon shall be determined by either of the following methods. If analytical results with four figures are required, use the method A. If analytical results with two or three figures are required, the method B can be used.

— Method A: Fusion–dehydration/insolubilization separation–gravimetry and ICP-OES

— Method B: XRF using fused cast-bead method

7.2 Fusion-dehydration/insolubilization separation-gravimetry and ICP-OES

7.2.1 Principle

A sample is fused with alkaline carbonate and the melt is treated with an acid to separate into two parts of silicon, insoluble silicon and soluble silicon, by filtration. Insoluble silicon is determined using gravimetry as silicon dioxide converted after ignition, whereas soluble silicon in the filtrate is determined using ICP-OES. The sum of them represents the total silicon.

7.2.2 Reagents

Reagents of analytical grade shall be used. Reagent solutions shall be preserved in plastic bottles.

7.2.2.1 Water, of grade 1 or superior specified in ISO 3696.

7.2.2.2 Sodium carbonate, anhydrous, specified in ISO 6353-3 or that of higher grade.

7.2.2.3 Hydrochloric acid (1+1), (1+4), (1+50), prepared by diluting hydrochloric acid with water, respectively.

7.2.2.4 Sulfuric acid (1+1), (1+4), prepared by diluting sulfuric acid with water, respectively.

7.2.2.5 Cellulose powder.

7.2.2.6 Polyethylene oxide solution [0,05 % (m/V)], prepared by dissolving polyethylene oxide with water.

7.2.2.7 Hydrofluoric acid, concentration of 48 %.

7.2.3 Apparatus and instruments

Use ordinary laboratory apparatus and instruments for chemical analysis in accordance with ISO 26845, Clause 4.

7.2.3.1 Platinum dish.

7.2.3.2 Platinum crucible.

7.2.3.3 Burner, capable of heating at 1 100 °C.

7.2.3.4 Muffle furnace, capable of being operated at 1 100 °C.

7.2.3.5 Balance, readable to 0,1 mg.

7.2.3.6 Inductively coupled plasma optical emission spectrometer (ICP-OES).

7.2.4 Procedure

The procedure shall be as follows. The procedure described in ISO 21068-2, Clause 8 can be alternatively used.

7.2.4.1 Fusion of sample

Weigh 0,30 g of the sample and 2,0 g of sodium carbonate, anhydrous into a platinum dish and mix well. Start to heat carefully and increase the temperature gradually to 1 000 °C to completely fuse the sample using a burner or in a muffle furnace.

7.2.4.2 Separation of silicon

Add 20 ml of hydrochloric acid (1+1) to dissolve the melt on a hot plate. Silicon dioxide will appear to be jellified and precipitated at this stage. There are two methods to separate the precipitated silicon dioxide.

a) Dehydrate carefully the precipitate to dryness in order to prevent it from spattering and add 5 ml of hydrochloric acid and 20 ml of water to dissolve any salt mixed with the precipitate. Filtrate the precipitate with a filter paper and wash with hot hydrochloric acid (1+50) several times and then with hot water sufficiently until it contains no salt. Receive the filtrate and washings together in a volumetric flask and make constant volume. Preserve this precipitate for gravimetry of insoluble silicon and the solution for the ICP-OES determination of soluble silicon, respectively.

b) After eduction of jellified silicon dioxide, add 0,05 g of cellulose powder and 10 ml of polyethylene oxide solution to agglomerate silicon dioxide for easy filtration. Filtrate and wash in the same procedure, and then preserve this precipitate for gravimetry of insoluble silicon and the solution for the ICP-OES determination of soluble silicon, respectively.

7.2.4.3 Gravimetry for insoluble silicon

Transfer the precipitate embedded in the filter paper together into a platinum crucible and ignite at 1 100 °C after charring and ashing the paper. Weigh the crucible. Moisten the precipitate in the crucible with a few drops of water and sulfuric acid (1+1) and add 10 ml of hydrofluoric acid. Then evaporate to dryness on a hot plate to remove all of silicon dioxide, ignite it at 1 100 °C and weigh the crucible again. The loss of mass after hydrofluoric acid treatment shall be the amount of insoluble silicon dioxide.

7.2.4.4 ICP-OES for soluble silicon

Aspirate an aliquot of the preserved solution into an Ar plasma of ICP-OES to determine soluble silicon in the sample.

7.2.5 Blank test

Run blank determinations according to the operations of 7.2.4.1 to 7.2.4.4 without taking a sample.

7.2.6 Drawing calibration curve

For ICP-OES, prepare calibration solutions to span the range of concentration of silicon in the test solution. Each calibration solution shall have a similar matrix to the test solution.

With those calibration solutions, draw calibration curves for soluble silicon to establish the relation between the emission intensity and the amount of silicon.

7.2.7 Calculation

With the amount of insoluble silicon in 7.2.4.3, soluble silicon in 7.2.4.4 and the blank test in 7.2.5, calculate the content of total silicon according to Formula (1).

$$T.Si = [\{(m_1 - m_0) + (A_1 - A_0)\} / m\ ] \times 0{,}4674 \times 100 \quad (1)$$

where

$T.Si$ is the content of total silicon in the sample, % (mass fraction);

m_1 is the amount of insoluble silicon dioxide in the sample, g;

m_0 is the amount of insoluble silicon dioxide in the blank test, g;

A_1 is the amount of soluble silicon dioxide in the sample, g;

A_0 is the amount of insoluble silicon dioxide in the blank test, g;

m is the weighed amount of the sample, g.

7.3 XRF using fused cast-bead method

The procedure shall be in accordance with EN 12698-2.

8 Determination of total nitrogen

8.1 Classification of determination methods

Total nitrogen shall be determined by either of the following methods. If analytical results with four figures are required, use the method A or C. If two figures are required, the method B can be used.

— Method A: Acid pressure decomposition–distillation separation–acidimetric titration method

— Method B: Inert gas fusion–thermal conductivity method

— Method C: Fusion–ammonia separation–acidimetric titration method

8.2 Acid pressure decomposition-distillation separation-acidimetric titration method

8.2.1 Principle

A sample is decomposed in a pressure decomposition vessel with a mixture of hydrofluoric acid and sulfuric acid to convert nitrogen into ammonia. Add boric acid and transfer the solution into a distillation flask. Add sodium hydroxide and perform steam distillation. React the distilled ammonia with a known amount of amidosulfuric acid and back-titrate the excess of amidosulfuric acid with a standardized sodium hydroxide solution.

8.2.2 Reagents

Reagents of analytical grade shall be used. Reagent solutions shall be preserved in plastic bottles.

8.2.2.1 Water, of grade 1 or superior specified in ISO 3696.

8.2.2.2 Hydrofluoric acid.

8.2.2.3 Sulfuric acid.

8.2.2.4 Sodium hydroxide, more than 97,0 % (mass fraction) of purity.

8.2.2.5 Sodium hydroxide solution (500 g/l), prepared by dissolving sodium hydroxide in water.

8.2.2.6 Amidosulfuric acid, more than 99,0 % (mass fraction) of purity.

8.2.2.7 0,1mol/l amidosulfuric acid solution, prepared by weighing 10,0 g of amidosulfuric acid and dissolving in water to make 1 000 ml. Calculate the factor of this solution according to Formula (2).

$$F = m \times P/(9{,}7095 \times 100) \quad (2)$$

where

F is the factor of the 0,1 mol/l amidosulfuric acid solution;

m is the weighed amount of amidosulfuric acid, g;

P is the purity of amidosulfuric acid, % (mass fraction).

8.2.2.8 0,1 mol/l sodium hydroxide solution, prepared by dissolving sodium hydroxide in water in accordance with ISO 21068-3, 5.2.2.8. Take exactly 50 ml of the 0,1 mol/l amidosulfuric acid solution in a beaker (200 ml) and dilute with water to about 100 ml. Titrate this solution with the 0,1 mol/l sodium hydroxide solution using a pH meter. Take the end point as pH 5,5 and determine the volume of the titrant consumed. Calculate the factor of this solution according to Formula (3).

$$F_1 = F \times 50{,}00/V \quad (3)$$

where

F_1 is the factor of the 0,1 mol/l sodium hydroxide solution;

F is the factor of the 0,1 mol/l amidosulfuric acid solution;

V is the titration volume of the 0,1 mol/l sodium hydroxide solution, ml.

8.2.2.9 Boric acid.

8.2.2.10 Ammonium sulfate, more than 99,9 % (mass fraction) of purity.

8.2.3 Apparatus

Use ordinary laboratory apparatus for chemical analysis and the following.

8.2.3.1 Platinum crucible.

8.2.3.2 Pressure decomposition vessel, on the market.

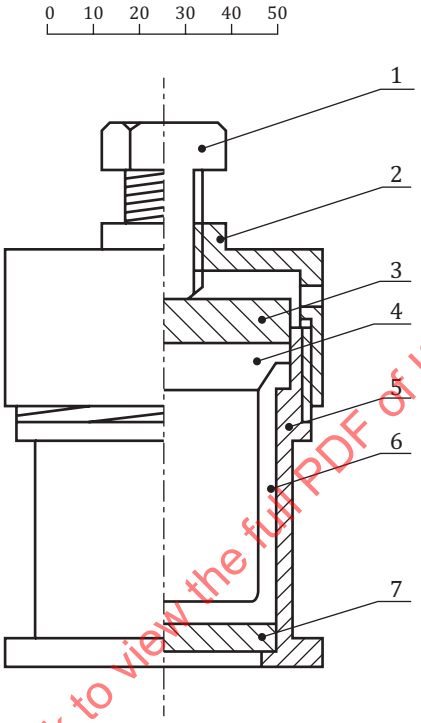
An example is shown in Figure 1. Use the vessels for the exclusive use in this analysis only to avoid cross-contamination by nitrogen. If the vessel which has ever contacted with nitric acid is used, the lower values of nitrogen can be obtained.

8.2.3.3 **Air bath**, capable of heating at 160 °C ± 5 °C.

8.2.3.4 **Steam distillation apparatus**, consisting of the components listed below.

An example of the apparatus is shown in Figure 2. Each component shall be made of hard glass coupled by common ground joints and fixed by springs or clamps just as per ISO 21068-3, Figure 1.

Dimensions in millimetres

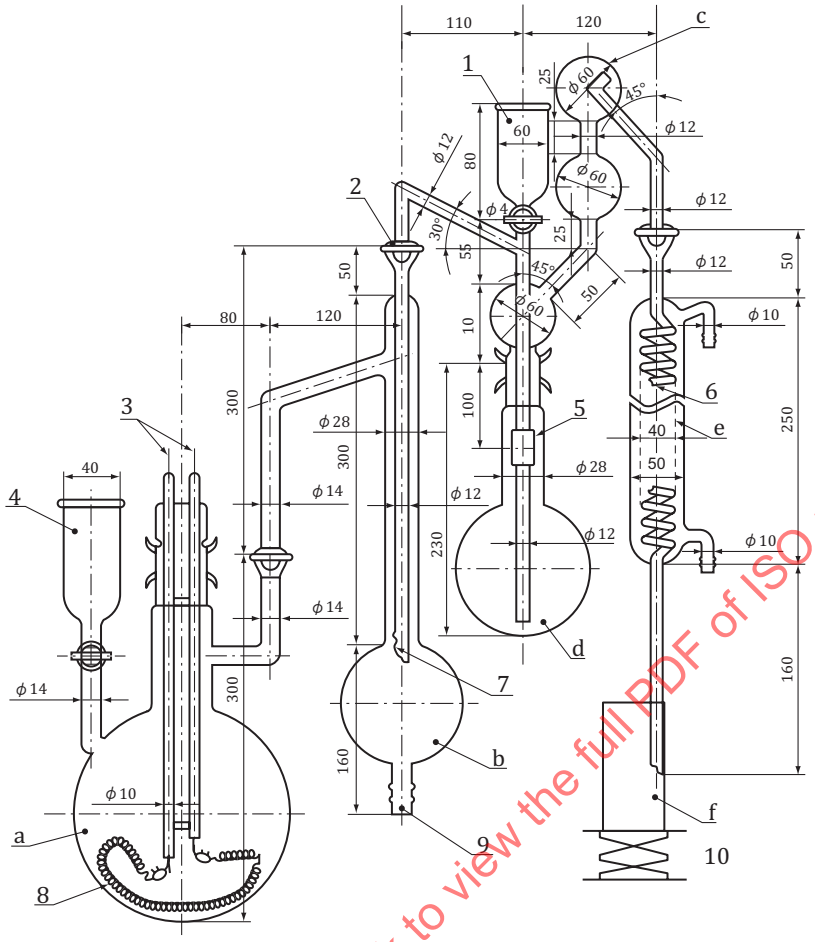


Key

1 centre screw
2 screw cap
3 top plate
4 PTFE cap
5 cylinder
6 PTFE bottle
7 bottom plate

Figure 1 — An example of sealed decomposition vessel

Dimensions in millimetres



Key

a	flask (2,5 l) for generation of steam	3	Dumet wire
b	trap (500 ml)	4	funnel with stopcock
c	sphere and tube	5	rubber tube
d	distillation flask (750 ml)	6	13 to15 coils
e	Graham condenser	7	small holes
f	receiver	8	electric heater
1	funnel	9	connection of rubber tube with pinchcock
2	ball joint	10	jack

Figure 2 — An example of steam distillation apparatus

8.2.3.5 Steam generation flask (2,5 l), equipped with a funnel with a cock, a throw-in heater (with 1 kW Nichrome wire), and a steam outlet tube.

8.2.3.6 Trap, the bottom of a bulb shall be connected to a rubber tube with a pinch cock for a drain.

The tip of steam leading-out tube shall have several small holes.

8.2.3.7 Bulb, equipped with a steam leading-in tube, a funnel with a cock, a splash-proof trap, etc.

The steam leading-in tube shall be cut in the middle enabling the exchange of the tip by connecting to a rubber tube.

8.2.3.8 Distillation flask (750 ml).

8.2.3.9 Coiled condenser.

8.2.3.10 Receiver, a tall beaker (300 ml) shall be used.

8.2.3.11 pH meter, readable to the smallest value of 0,1 equipped with a glass electrode.

8.2.4 Procedure

a) **Acid pressure decomposition of sample.** Weigh 0,15 g of the sample in a platinum crucible (20 ml) and add 5 ml of sulfuric acid (1+1) and 5 ml of hydrofluoric acid. Position the crucible into a pressure decomposition vessel and close according to the manufacturer's instructions. Place the vessel into an air bath and heat at 160 °C ± 5 °C for 16 h. Acid pressure decomposition under microwave irradiation can be performed if available.

b) **Preparation of sample solution.** After cooling, disassemble the vessel. Transfer the solution into a 100 ml plastic beaker by washing the crucible with water. Add 5 g of boric acid and mix well.

c) **Preparation of steam distillation apparatus.** After transferring the solution into a distillation flask, assemble a distillation apparatus and add exactly 50 ml of the 0,1 mol/l amidosulfuric acid solution to the receiver. Fix the coiled condenser so that the tip is immersed in the solution. Pour 50 ml of the sodium hydroxide solution (500 g/l) through the funnel of the flask by washing the funnel with water, make the solution volume about 150 ml and close the funnel cock.

d) **Steam distillation.** Perform the steam distillation with a steam flow of 4,5 ml to 5,0 ml per minute. When the distillate reaches about 170 ml, lower the receiver to expose the tip of the condenser above the liquid surface and continue distillation until the distillate reaches about 200 ml. Wash the outside of the tip with a small amount of water. When using a new distillation apparatus or the apparatus which has not been used for a long time, perform preliminary distillation for washing inside of it for 2 h to 3 h.

e) **Titration.** Titrate the distillate with the 0,1 mol/l sodium hydroxide solution using the pH meter. Take the end point as pH 5,5 and record the volume of the titrant.

8.2.5 Recovery measurement

Weigh 0,280 g of ammonium sulfate to the nearest 0,1 mg in a platinum crucible (20 ml), perform operations of 8.2.4 and calculate the recovery according to Formula (4). The recovery shall be not less than 99 %.

$$R = [\{(50{,}00 \times F) - (V \times F_1)\} \times 0{,}0014007/(m \times 0{,}2120)] \times 100 \quad (4)$$

where

R is the recovery, %;

F is the factor of the 0,1 mol/l amidosulfuric acid solution;

V is the titration volume of the 0,1 mol/l sodium hydroxide solution, ml;

F_1 is the factor of the 0,1 mol/l sodium hydroxide solution;

m is the weighed amount of ammonium sulphate, g.

8.2.6 Calculation

Calculate the content of total nitrogen in the sample according to Formula (5).

$$T.N = [\{[(50{,}00 \times F) - (V \times F_1)] \times [(0{,}0014007 \times 100/R)]\}/m] \times 100 \quad (5)$$

where

$T.N$ is the content of total nitrogen in the sample, % (mass fraction);

F is the factor of the 0,1 mol/l amidosulfuric acid solution;

V is the titration volume of the 0,1 mol/l sodium hydroxide solution, ml;

F_1 is the factor of the 0,1 mol/l sodium hydroxide solution;

R is the recovery (%) in 8.2.5;

m is the weighed amount of the sample, g.

8.3 Inert gas fusion-thermal conductivity method

8.3.1 Principle

A sample is fused together with a flux in a graphite crucible under inert gas flow to extract nitrogen and other gases from the sample. The elemental nitrogen is determined using a thermal conductivity detector after the removal of concomitants such as carbon monoxide, carbon dioxide, other gases, and moisture.

8.3.2 Reagents

Reagents shall be as follows.

8.3.2.1 Helium, more than 99,99 % (volume fraction) of purity.

8.3.2.2 Flux, in shot or basket form made of tin or nickel.

Use a combination of metals which is different from a capsule.

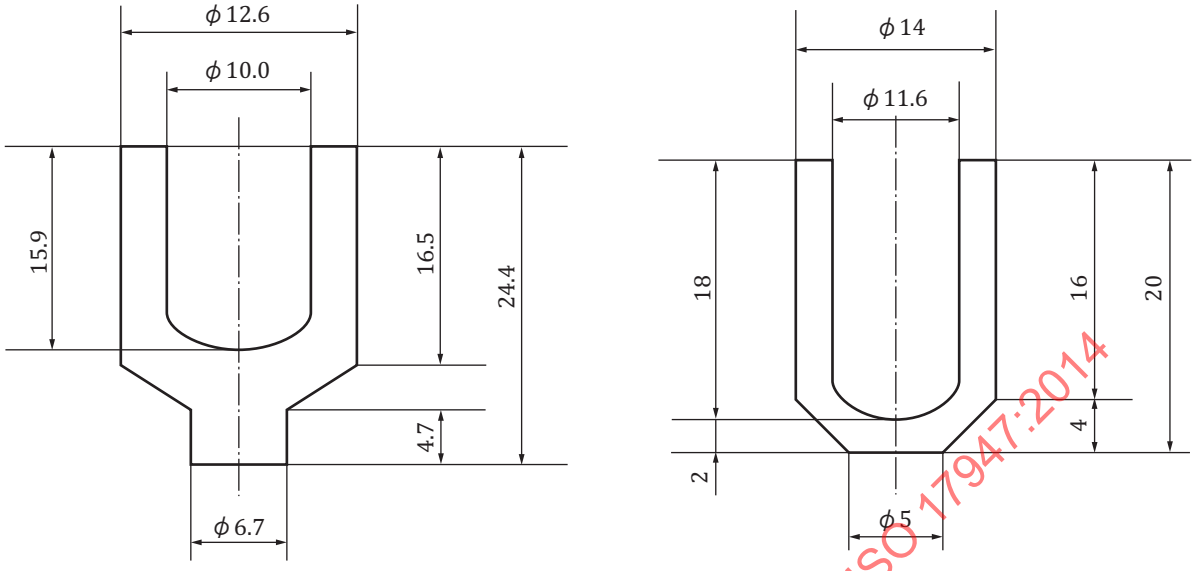
8.3.3 Apparatus

8.3.3.1 Capsule, made of nickel or tin designated for each apparatus.

8.3.3.2 Graphite crucible, suitable for impulse furnace.

An example is shown in Figure 3 a) and Figure 3 b).

Dimensions in millimetres



a) b)

Figure 3 — An example of graphite crucible

8.3.4 Instrument

A commercial nitrogen analyser is available. It consists of the components listed below. The block diagram is shown in Figure 4.

8.3.4.1 Inert gas refiner, consisting of a deoxidation tube (reduced copper) with an electric furnace, a carbon dioxide absorption tube (sodium hydroxide shots for gas analysis), a dehydration tube (magnesium perchlorate for drying), etc.

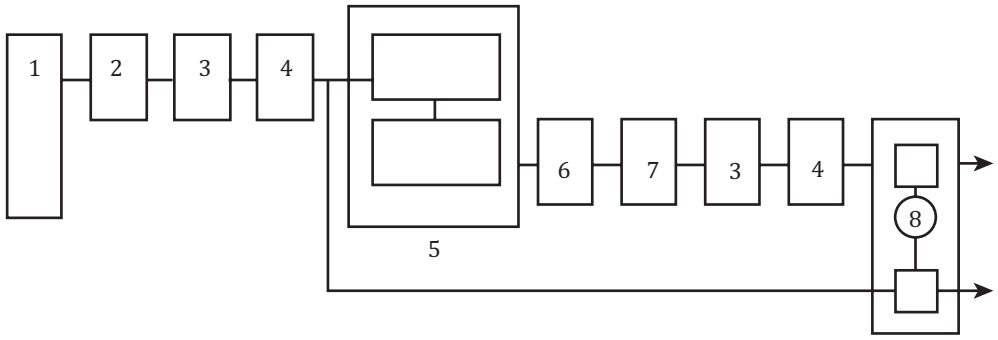
A denitrification tube (sponge titanium) is attached in some instruments.

8.3.4.2 Gas extractor, consisting of a sample feeder, an impulse furnace, etc.

The sample feeder can throw the sample-embedded capsule into the graphite crucible in the impulse furnace under inert gas flow. The impulse furnace shall be capable of attaining about 3 000 °C. The upper water-cooled copper electrode is fixed; whereas the lower electrode moves vertically. The graphite crucible is sandwiched between both electrodes.

8.3.4.3 Combustion gas purifier, consisting of a dust collecting tube filled with glass wool, a carbon dioxide absorption tube with sodium hydroxide shots for gas analysis, a dehydration tube with magnesium perchlorate for drying, etc.

8.3.4.4 Gas detector, consisting of a thermal conductivity detector and an integration meter.



Key

1 helium bomb
2 oxygen trap with electric heater
3 carbon dioxide trap
4 dehydration tube
5 impulse furnace
6 dust collector
7 oxidation tube with electric heater
8 thermal conductivity detector

Figure 4 — Block diagram of inert gas fusion–thermal conductivity method

8.3.5 Procedure

a) **Amount of sample.** Take 0,02 g to 0,04 g of the sample. If complete extraction of nitrogen can be achieved, take up to 0,1 g of the sample.

b) **Starting up of the instrument.** Switch on the instrument and set the controls to the specified values in accordance with the manufacturer's instruction for operation. Wait until it becomes stable.

c) **Preliminary heating.** Set a new graphite crucible to the specified position of the impulse furnace. Flow the inert gas, and then turn on the furnace. Heat the graphite crucible at the degassing temperature for the specified period, and then heat it at the gas extraction temperature. Read the integration meter (thereafter referred to as "integral value"). Repeat the steps of the degassing and the gas extraction until a stable integral value is obtained.

d) **Degassing of the graphite crucible.** Put the specified amount of bath metal into a new graphite crucible and place it at the specified position of the impulse furnace. Weigh the sample in a capsule and enclose by using a jig. Place the capsule at the specified position of sample blower. Feed the inert gas and energize the graphite crucible. Heat it at the degassing temperature for the specified period and degas the graphite crucible and the bath metal.

e) **Measuring.** Throw the sample-embedded capsule into the graphite crucible. Energize the crucible, and heat the sample at the gas extraction temperature for the specified period and read the integral value.

8.3.6 Blank test

Run blank determinations according to the operations of 8.3.5 without taking a sample. Repeat these operations three to five times and obtain an average value.

8.3.7 Calculation of calibration coefficient

Use the nitride whose nitrogen content is known and oxygen content is not greatly different from the sample for calibration. Some of reference materials of silicon nitride powder can be available. If

the nitride whose oxygen content is greatly different from that of the sample is used for calibration, errors may arise. Perform the operations of 8.3.5 with using the sample for calibration. Average the values obtained by repeating three to five times measurements and calculate the calibration coefficient according to Formula (6). Some of commercial instruments can calculate the blank test value, the calibration coefficient and the content of nitrogen automatically.

$$K = (m \times N/100) / (A_1 - A_0) \quad (6)$$

where

K is the calibration coefficient, g/integral value;

m is the weighed amount of the sample for calibration, g;

N is the content of nitrogen in the sample for calibration, % (mass fraction);

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test in 8.3.6.

8.3.8 Calculation

Calculate the content of total nitrogen in the sample according to Formula (7).

$$T.N = [\{(A_2 - A_0) \times K\} / m] \times 100 \quad (7)$$

where

$T.N$ is the content of total nitrogen in the sample, % (mass fraction);

A_2 is the integral value of the sample in 8.3.5;

A_0 is the integral value of the blank test in 8.3.6;

K is the calibration coefficient, g/integral value, in 8.3.7;

m is the weighed amount of the sample, g.

8.4 Fusion-ammonia separation-acidimetric titration method

The procedure shall be in accordance with EN 12698-1, 7.3.

9 Determination of aluminium, iron, and calcium

9.1 Principle

A sample is decomposed in a pressure decomposition vessel with a mixture of nitric acid and hydrofluoric acid to bring solution. After removing silicon by a mixture of hydrofluoric and sulfuric acid treatment, evaporate the product to dryness and dissolve in hydrochloric acid. Aluminium, iron, and calcium in the solution are determined using ICP-OES.

9.2 Reagents

Reagents of analytical grade shall be used. Reagent solutions shall be preserved in plastic bottles.

9.2.1 Water, of grade 1 or superior specified in ISO 3696.

9.2.2 Nitric acid.

9.2.3 Hydrofluoric acid.

9.2.4 Sulfuric acid (1+1), of prepared with sulfuric acid and water by equivolumetric proportion.

9.2.5 Hydrochloric acid (1+1), of prepared with hydrochloric acid and water by equivolumetric proportion.

9.2.6 Standard aluminium solution (Al 1 mg/ml).

9.2.7 Standard iron solution (Fe 1 mg/ml).

9.2.8 Standard calcium solution (Ca 1 mg/ml).

NOTE Commercial standard solutions being SI traceable are available.

9.3 Apparatus and instrument

Use ordinary laboratory apparatus for chemical analysis and the following.

9.3.1 Platinum crucible (20 ml).

9.3.2 Pressure decomposition vessel, as per 8.2.3.2.

9.3.3 Platinum dish.

9.3.4 Air bath, capable of heating at 160 °C ± 5 °C.

9.3.5 Balance, readable to 0,1 mg.

9.3.6 Hot plate.

9.3.7 Inductively coupled plasma optical emission spectrometer (ICP-OES).

9.4 Procedure

a) **Sample decomposition**

Weigh 0,50 g of the sample in a platinum crucible (20 ml) and add 1 ml of nitric acid and 10 ml of hydrofluoric acid. Position the crucible into a pressure decomposition vessel and close according to the manufacturer's instructions. If an antistatic device is available during weighing, the sample can be directly weighed into the vessel. Place the vessel into an air bath and heat at 160 °C ± 5 °C for 16 h. Acid pressure decomposition under microwave irradiation can also be performed, if available.

After cooling, disassemble the vessel. Transfer the solution into a platinum dish by washing the crucible with water. Add 2 ml of sulfuric acid (1+1) and evaporate to dryness. Add 4 ml of hydrochloric acid (1+1) and 20 ml of water and heat to dissolve the salt on a hot plate. Dilute the solution with water to make constant volume of 100 ml for the test solution.

b) **ICP-OES measurement**

Adjust the operating conditions of the ICP-OES in accordance with the manufacturer's instructions and chose appropriate wavelength of each element considering spectral interferences and analytical sensitivities.

Aspirate an aliquot of the test solution into an Ar plasma of ICP-OES to obtain an emission intensity value.

9.5 Blank test

Run blank determinations according to the operations of 9.4 without taking a sample.

9.6 Drawing calibration curve

Prepare calibration solutions to span the range of concentrations of aluminium, iron, and calcium in the test solution. Each calibration solution shall have a similar matrix to the test solution.

With those calibration solutions, draw calibration curves for aluminium, iron, and calcium to establish the relation between the emission intensity and the amount of each element. Then, aspirate the test solutions and blank solutions to obtain the amount of each element in the test solutions

9.7 Calculation

With the amount of aluminium, iron and calcium obtained with the calibration curves in 9.6 and blanks in 9.5, calculate the contents of aluminium, iron, and calcium according to Formulae (8), (9), and (10).

$$Al = \{ (A_1 - A_2) / m \} \times 100 \quad (8)$$

$$Fe = \{ (A_3 - A_4) / m \} \times 100 \quad (9)$$

$$Ca = \{ (A_5 - A_6) / m \} \times 100 \quad (10)$$

where

Al is the content of aluminium in the sample, % (mass fraction);

Fe is the content of iron in the sample, % (mass fraction);

Ca is the content of calcium in the sample, % (mass fraction);

A_1 is the amount of aluminium in the test solution, g;

A_2 is the amount of aluminium in the blank test, g;

A_3 is the amount of iron in the test solution, g;

A_4 is the amount of iron in the blank test, g;

A_5 is the amount of calcium in the test solution, g;

A_6 is the amount of calcium in the blank test, g;

m is the weighed amount of the sample, g.

10 Determination of oxygen

10.1 Principle

A sample is fused together with flux in a graphite crucible under inert gas flow. The oxygen generated from the sample reacts with carbon of the graphite crucible to form carbon monoxide. After removing concomitants such as moisture and dust, carbon monoxide is determined after converted into carbon dioxide or directly determined using IR spectrometry.

10.2 Reagents

The same as 8.3.2.

10.3 Apparatus

The same as 8.3.3.

10.4 Instrument

The same as 8.3.4 except for the components of the gas separator and the detector. The combustion gas purifier does not include a carbon dioxide absorption tube with sodium hydroxide shots for gas analysis, a dehydration tube with magnesium perchlorate for drying, etc. The detector is an IR spectrometer instead of a thermal conductivity detector. A commercial oxygen analyser is available.

10.5 Procedure

Take 0,02 g to 0,04 g of the sample. Perform the operations in accordance with 8.3.5.

10.6 Blank test

Run blank determinations according to the operations of 10.5 without taking a sample. Repeat these operations three to five times and obtain an average value.

10.7 Calculation of calibration coefficient

Use 0,010 g of yttrium oxide [more than 99,99 % (mass fraction) of purity, ignited at 1,000 °C for 2 h] or 0,030 g of the nitride whose oxygen content is known for calibration. Some of reference materials of silicon nitride powder can be available. Average the values obtained by repeating three to five times measurements and calculate the calibration coefficient according to Formulae (11) and (12). Some of commercial instruments can calculate the blank test value, the calibration coefficient, and the carbon content automatically.

a) When yttrium oxide is used

$$K = (G \times 0{,}2126) / (A_1 - A_0) \tag{11}$$

where

K is the calibration coefficient, g/integral value;

G is the weighed amount of yttrium oxide, g;

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test in 10.6.

b) When the nitride sample is used

$$K = (G \times O/100) / (A_1 - A_0) \quad (12)$$

where

K is the calibration coefficient, g/integral value;

G is the weighed amount of the sample for calibration, g;

O is the oxygen content of the sample for calibration, % (mass fraction);

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test in 10.6.

10.8 Calculation

Calculate the content of oxygen in the sample according to Formula (13).

$$O = [\{(A_2 - A_0) \times K\} / m] \times 100 \quad (13)$$

where

O is the content of oxygen, % (mass fraction);

A_2 is the integral value of the sample in 10.5;

A_0 is the integral value of the blank test in 10.6;

K is the calibration coefficient, g/integral value;

m is the weighed amount of the sample, g.

11 Determination of carbon

11.1 Classification of determination methods

Carbon shall be determined by any of the following methods:

— Method A: Combustion (RF furnace)–IR absorption spectrometry;

— Method B: Combustion (resistance furnace)–coulometry;

— Method C: Combustion (resistance furnace)–gravimetry;

— Method D: Combustion (resistance furnace)–conductometry.

11.2 Combustion (RF furnace)-IR absorption spectrometry

11.2.1 Principle

A sample is combusted in an oxygen flow with an accelerator. The generated carbon oxides are determined using an IR spectrometer after converting them completely into carbon dioxide.

11.2.2 Reagents

Reagents shall be as follows.

11.2.2.1 Oxygen, more than 99,99 % (volume fraction) of purity.

11.2.2.2 Accelerator, made of copper, iron, or tungsten.

Use an appropriate combination of these metals referred to the manufacturer's instruction of the instrument used.

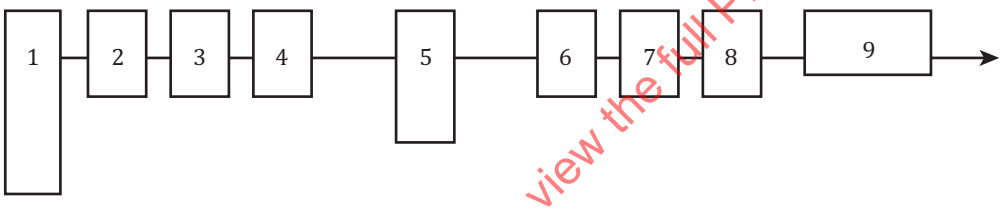
11.2.3 Apparatus

11.2.3.1 Combustion crucible, suitable for the instrument.

11.2.3.2 Pedestal, suitable for the instrument.

11.2.4 Instrument

It consists of the following components such as an oxygen refiner, a furnace, a combustion gas refiner, a gas detector, etc. A commercial carbon analyser is available. The block diagram is shown in Figure 5.



Key

1 oxygen bomb
2 oxidation tube with electric heater
3 carbon dioxide trap
4 dehydration tube
5 RF furnace
6 dust collector
7 oxidation tube with electric heater
8 sulfur trioxide trap
9 IR spectrometer

Figure 5 — Block diagram of carbon analyser for combustion-IR spectrometry

11.2.4.1 Oxygen refiner, consisting of an oxidation tube with an electric furnace (copper oxide), a carbon dioxide absorption tube (sodium hydroxide shots for gas analysis), a dehydration tube (magnesium perchlorate for drying), etc.

11.2.4.2 Furnace, consisting of a combustion tube and electric parts for high-frequency heating.

11.2.4.3 Combustion gas purifier, consisting of a dehydration tube (magnesium perchlorate for drying), a dust collecting tube (glass wool), a desulfurization tube (manganese dioxide), an oxidation tube (copper oxide) with an electric furnace, etc.

11.2.4.4 Gas detector, consisting of an IR spectrometer and an integration meter.

11.2.5 Procedure

a) Switch on the instrument and set the controls to the specified values according to the manufacturer's instruction. Wait until the instrument becomes stable.

b) Take 0,50 g of the sample in the combustion crucible and spread it over uniformly. Cover the sample uniformly with the accelerator, 1 g of copper and 1 g of iron, or 1 g of copper and 1 g of tungsten.

c) Place the crucible on pedestal in the furnace and activate the instrument for measurement.

11.2.6 Blank test

Run blank determinations according to the operations of 11.2.5 without taking a sample.

11.2.7 Calculation of calibration coefficient

Use 0,250 g of calcium carbonate (more than 99,9 % (mass fraction) of purity, ignited at 500 °C to 550 °C for 2 h) or 0,500 g of the nitride with known carbon content for calibration. Some of reference materials of silicon nitride powder with known carbon content can be available. Average the values obtained by repeating three to five times measurements and calculate the calibration coefficient according to Formulae (14) and (15). Some of commercial instruments can calculate the blank test value, the calibration coefficient, and the content of carbon automatically.

a) When calcium carbonate is used,

$$K = (G \times 0{,}1200) / (A_1 - A_0) \tag{14}$$

where

K is the calibration coefficient, g/integral value;

G is the weighed amount of calcium carbonate, g;

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test in 11.2.6.

b) When the nitride sample is used,

$$K = (G \times C/100) / (A_1 - A_0) \tag{15}$$

where

K is the calibration coefficient, g/integral value;

G is the weighed amount of the sample for calibration, g;

C is the content of carbon in the sample for calibration, % (mass fraction);

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test in 11.2.6.

11.2.8 Calculation

Calculate the content of carbon in the sample according to Formula (16).

$$C = [\{(A_2 - A_0) \times K\} / m] \times 100 \quad (16)$$

where

C is the content of carbon, % (mass fraction);

A_2 is the integral value of the sample in 11.2.5;

A_0 is the integral value of the blank test in 11.2.6;

K is the calibration coefficient, g/integral value;

m is the weighed amount of the sample, g.

11.3 Combustion (resistance furnace)-coulometry

The procedure shall be in accordance with ISO 21068-2, 5.3.1 and 5.4.1.

11.4 Combustion (resistance furnace)-gravimetry

The procedure shall be in accordance with ISO 21068-2, 5.3.2 and 5.4.2.

11.5 Combustion (resistance furnace)-conductometry

The procedure shall be in accordance with ISO 21068-2, 5.3.4 and 5.4.3.

12 Determination of fluorine and chlorine

12.1 Principle

A sample is pyrohydrolysed under steam and oxygen flow to extract fluorine and chlorine as its hydride from the sample. Fluorine and chlorine collected into alkaline aqueous absorbent are determined using ion chromatography or spectrophotometry.

12.2 Reagents

Reagents of analytical grade shall be used.

12.2.1 Water, of grade 1 or superior specified in ISO 3696.

12.2.2 Sodium hydroxide solution (0,1 g/l), of prepared with sodium hydroxide and water.

12.2.3 Standard fluoride solution (F 1 mg/ml).

12.2.4 Standard chloride solution (Cl 1 mg/ml).

12.2.5 Oxygen gas, more than 99,5 % (volume fraction) of purity.

12.2.6 Sodium hydroxide solution (0,02 g/l), of prepared with sodium hydroxide and water.

12.2.7 Lanthanum-alizarin complexone, of commercially available.

12.2.8 Acetone.

12.2.9 Mercury (II) thiocyanate solution [0,3 g in 100 ml of 95 % (volume fraction) ethanol].

12.2.10 Ammonium iron (II) sulfate solution [6 g in 100 ml of nitric acid (4+9)].

NOTE A commercial standard solution being SI traceable is available.

12.3 Apparatus and instruments

12.3.1 Pyrohydrolysis apparatus, consisting of the following components.

12.3.1.1 Furnace, capable of heating at 1 000 °C to 1 200 °C.

12.3.1.2 Reaction tube, made of heat-resistant materials such as mullite, alumina, quartz, etc.

12.3.1.3 Combustion boat, made of heat-resistant materials such as mullite, alumina, platinum, etc. fitted to the reaction tube.

12.3.1.4 Steam generator, consisting of a flask and a mantle heater and capable of controlling at 90 °C to 100 °C.

12.3.1.5 Flow controller, capable of controlling oxygen flow rate up to 300 ml/min.

12.3.1.6 Delivery tube, connected to a condenser, if necessary.

12.3.1.7 Receiver, made of glass filled in 10 ml of sodium hydroxide solution (0,1 g/l) as an absorbent.

12.3.2 Ion chromatograph, with the separation column suitable for the determination of fluoride and chloride.

12.3.3 Spectrophotometer, with an 1 cm length cell for visible range.

12.4 Procedure

12.4.1 Extraction of fluorine and chlorine from the sample

Take 0,5 g of the sample in the combustion boat. Just as it is placed in the centre of the reaction tube, close the system with the delivery tube immediately. Start to feed a steam and oxygen to begin to pyrohydrolyse the sample at 1 000 °C to 1 200 °C for 20 min under an adequate rate of oxygen flow.

Wash down the delivery tube and the tip of the condenser, and then transfer the distillate and washings in the receiver into a volumetric flask. Add water to the mark to prepare the test sample solution.

12.4.2 Determination of fluorine and chlorine

Fluorine and chlorine can be simultaneously determined using ion chromatography. Specific spectrophotometry can be also available for fluorine and chlorine, independently.

12.4.2.1 Determination of fluorine and chlorine using ion chromatography

Inject an aliquot of the test sample solution into an ion chromatograph to determine fluorine and chlorine. Refer to ISO 21438-3 for fluorine and ISO 21438-2 for chlorine, respectively. It will be found that fluorine and chlorine could be simultaneously determined in the same condition at one run. Determine the content of fluorine and chlorine in the test solutions using calibration solutions containing the identical quantities of reagents as in the determination.

12.4.2.2 Determination of fluorine using spectrophotometry

Spectrophotometric determination method of fluorine alternative to ion chromatography can be available. According to ISO 2828, react fluorine in the test sample solution with lanthanum-alizarin complexone to yield a blue coloured complex. Determine the fluorine by spectrophotometric method using calibration solutions containing the identical quantities of reagents as in the determination.

12.4.2.3 Determination of chlorine using spectrophotometry

Spectrophotometric determination method of chlorine alternative to ion chromatography can be available. React chlorine in the test sample solution with mercury (II) thiocyanate and ammonium iron (II) sulfate to yield a yellow coloured complex. Measure the absorbance of the yellow product at 460 nm by using a spectrophotometer according to the following.

To an aliquot of the test sample solution prepared in 12.4.1 in a 50 ml volumetric flask, add 5.0 ml of mercury (II) thiocyanate solution. Then, add 2,0 ml of ammonium iron (II) sulfate solution to yield yellow coloured complex and dilute with water to the mark. Stand for 30 min to develop coloration and measure the absorbance at 460 nm.

12.5 Blank test

Run blank determinations according to the operations of 12.4 without taking a sample.

12.6 Drawing calibration curve

Prepare calibration solutions to span the range of concentrations of fluorine and chlorine in the test solution. Each calibration solution shall have a similar matrix to the test solution.

With those calibration solutions, draw calibration curves for fluorine and chlorine to establish the relation between the signal intensity and the amount of fluorine and chlorine.

12.7 Calculation

Obtain the amount of fluorine and chlorine by 12.4.2 and 12.5 referring to the calibration curve drawn in 12.6 and calculate the content of fluorine and chlorine in the sample according to Formulae (17) and (18).

$$F = \{(A_1 - A_0) / m\} \times 100 \quad (17)$$

where

F is the content of fluorine in the sample, % (mass fraction);

A_1 is the amount of fluorine in the test solution, g;

A_0 is the amount of fluorine in the blank test, g;

m is the weighed amount of the sample, g.

$$Cl = \{(A_2 - A_0) / m\} \times 100 \quad (18)$$

where

Cl is the content of chlorine in the sample, % (mass fraction);

A_2 is the amount of chlorine in the test solution, g;

A_0 is the amount of chlorine in the blank test, g;

m is the weighed amount of the sample, g.

13 Reporting analytical values

13.1 Number of analyses

Analyse the sample twice on different days.

13.2 Evaluation of analytical values

a) When the difference between two analytical values does not exceed the tolerance shown in Table 1, the average value shall be reported.

b) When the difference between two analytical values exceeds the tolerance shown in Table 1, perform additional two analyses. When the difference does not exceed the tolerance, the average value thereof shall be reported. If the difference also exceeds the tolerance, the median of four analytical values shall be reported.

13.3 Expression of analytical values

The analytical values shall be given in % (mass fraction) in dryness.

a) Total silicon and total nitrogen

Express the results with four figures with second decimal place.

b) Others

Express the results with third decimal place.

Table 1 — Tolerances on analytical values

Unit: % (mass fraction)

Total Si	Total N	Al	Fe	Ca	O	C	F	Cl
0,15	0,15[a] 0,35[b]	0,001[c] 0,005[d]	0,001[c] 0,003[d]	0,001[c] 0,012[d]	0,090	0,020	0,010	0,005

[a] Acid pressure decomposition–distillation separation–acidimetric titration method.

[b] Inert gas fusion–thermal conductivity method.

[c] Applicable to the content of less than 0,01 % (mass fraction).

[d] Applicable to the content of not less than 0,01 % (mass fraction).

14 Test report

The test report shall contain, as a minimum, the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of test;

b) a reference to this International Standard (i.e. ISO 17947);

c) the method used, by reference to this International Standard;

d) the results, and the form in which they are expressed;

e) any unusual features noted during the test;

f) any operation not specified in this International Standard, or any optional operation which might have influenced the results.

Annex A
(informative)

List of commercial certified reference materials

[1] ERM-ED 101 “silicon nitride powder” from BAM

Annex B
(informative)

Analytical results obtained from a round robin test

A round robin test was carried out to validate "JIS R 1603. Three certified reference materials of Si_3N_4 (JCRM R 003, 004 and 005 supplied by The Ceramic Society of Japan) were analysed by expert laboratories in Japan. Analytical results obtained from the test are given in Tables B.1 to B.4.

Table B.1 — Analytical results of JCRM R 003 for major and minor elements in % (mass fraction)

No.	Lab.		T.Si	T.N	Al	Fe	Ca	O	C
1	A	1	59,48	39,04	0,000 3	0,003 9	0,000 1	1,22	0,093
		2	59,46	39,05	0,000 1	0,004 0	<0,000 1	1,27	0,104
		mean	59,47	39,05	0,000 2	0,004 0	0,000 1	1,27	0,099
		R	0,02	0,01	0,000 2	0,000 1		0,05	0,011
2	B	1	59,54	39,10	<0,002	0,004 3	<0,000 5	1,26	
		2	59,59	39,09	<0,002	0,004 4	<0,000 5	1,27	
		mean	59,57	39,10		0,004 4		1,27	
		R	0,05	0,01		0,000 1		0,01	
3	C	1	59,33	38,88	<0,003	0,004 6	<0,000 1		0,103
		2	59,34	38,83	<0,003	0,004 1	<0,000 1		0,096
		mean	59,34	38,86		0,004 4			0,100
		R	0,01	0,05		0,000 5			0,007
4	D	1	59,70	39,26		0,004 6			
		2	59,71	39,18		0,004 4			
		mean	59,71	39,22		0,004 5			
		R	0,01	0,08		0,000 2			
5	E	1	59,37	39,04	<0,001	0,005 4	0,001 0		
		2	59,30	39,04	<0,001	0,003 2	0,001 5		
		mean	59,34	39,04		0,004 3	0,001 3		
		R	0,07	0,00		0,002 2	0,000 5		
6	F	1	59,64	38,95	<0,001	0,004 1	0,000 2	1,31	0,087
		2	59,74	38,90	<0,001	0,003 8	0,000 2	1,29	0,083
		mean	59,69	38,93		0,004 0	0,000 2	1,30	0,085
		R	0,10	0,05		0,000 3	0,000 0	0,02	0,004
7	G	1	59,62	38,75	<0,000 1	0,004 6	<0,000 5		0,084
		2	59,46	38,68	0,000 1	0,004 8	<0,000 5		0,092
		mean	59,54	38,72		0,004 7			0,088
		R	0,16	0,07		0,000 2			0,008
8	H	1	59,53	39,13	<0,000 5	0,003 7	0,000 8	1,18	0,087
		2	59,54	39,10	<0,000 5	0,004 0	0,001 2	1,26	0,099
		mean	59,54	39,12		0,003 9	0,001 0	1,22	0,093
		R	0,01	0,03		0,000 3	0,000 4	0,08	0,012