BS ISO 17942:2014

BSI Standards Publication

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

…making excellence a habit.™

National foreword

This British Standard is the UK implementation of ISO 17942:2014.

The UK participation in its preparation was entrusted to Technical Committee RPI/13, Advanced technical ceramics.

A list of organizations represented on this committee can be obtained on request to its secretary.

ISBN 978 0 580 78551 1

ICS 81.060.30

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 August 2014.

Amendments issued since publication

Date	Text affected

INTERNATIONAL
STANDARD

ISO
17942

First edition
2014-08-15

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

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

Reference number
ISO 17942:2014(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 describes the chemical analysis of boron nitride powders for use in fine ceramics applications. Determination methods of both main and trace constituents of interest are fully covered.

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

1 Scope

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

This International Standard stipulates the analysis methods of total boron, free boron, total nitrogen, aluminium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, silicon, sodium, titanium, vanadium, zinc, carbon, and oxygen in boron nitride powders for fine ceramics. Total boron is determined by using either a fusion–titration method or a fusion–inductively coupled plasma-optical emission spectrometry (ICP-OES). Free boron is determined by using either an acid digestion–ICP-OES or a methanol extraction–ICP-OES. If necessary, the boron amount which arises from the hydrolysis of boron nitride during sample treatment is corrected using spectrophotometry. Total nitrogen is determined by using either an acid pressure decomposition–distillation separation–titration method or an inert gas fusion–thermal conductivity method. Silicon is determined by using a fusion–ICP-OES. Aluminium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, titanium, vanadium, zinc are determined by using an acid pressure decomposition–ICP-OES or a fusion–ICP-OES. Sodium and potassium are determined by using atomic absorption spectrometry (AAS), flame emission spectrometry (FES), or ICP-OES following acid pressure decomposition. Carbon is determined by using a combustion–IR absorption spectrometry or a combustion–thermal conductivity method. Oxygen is determined by using an inert gas fusion–IR absorption spectrometry.

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.

EN 12698-1:2007, *Chemical analysis of nitride bonded silicon carbide refractories - Part 1: Chemical methods*

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

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

ISO 9138, *Abrasive grains — Sampling and splitting*

ISO 21068-2:2008, *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*

3 General rules in chemical analysis

Chemical analysis shall be performed in accordance with general rules regulated as standards, if available.

4 Analysis items

Analysis items specified in this International Standard shall be as follows:

a) Total boron (T.B)

b) Free boron (F.B)

c) Total nitrogen (T.N)

d) Silicon (Si)

e) Aluminium (Al)

f) Cadmium (Cd)

g) Calcium (Ca)

h) Chromium (Cr)

i) Cobalt (Co)

j) Copper (Cu)

k) Iron (Fe)

l) Lead (Pb)

m) Magnesium (Mg)

n) Manganese (Mn)

o) Nickel (Ni)

p) Titanium (Ti)

q) Vanadium (V)

r) Zinc (Zn)

s) Sodium (Na)

t) Potassium (K)

u) Carbon (C)

v) Oxygen (O)

5 Sampling, weighing, and drying of sample

The method of preparing samples shall be in accordance with ISO 9138 unless otherwise mutually agreed upon between the analyser and customer.

5.1 Sampling

Take the sample in accordance with ISO 9138.

5.2 Weighing

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

5.3 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 (120 ± 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.

6 Reporting analytical values

6.1 Number of analyses

Analyse the sample twice on different days.

6.2 Blank test

Upon analysis, perform a blank test to correct the measured values.

6.3 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.

6.4 Expression of analytical values

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

a) **Total boron and total nitrogen** — express the results with two to four figures according to the method used.

b) **Free boron** — express the results with two to four figures according to the method used.

c) **Others** — express the results to the third decimal place.

Table 1 — Tolerance on analytical values

Unit: % (mass fraction)

Component	total-B	free-B	total-N	Si, Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Ti, V, Zn, K, Na	C	O
Tolerance	0,30		0,30[a] 0,40[b]	0,001[c] 0,005[d]	0.005	0,01[e] 0,05[f]

[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).

[e] Applicable to the content of less than 1,0 % (mass fraction).

[f] Applicable to the content of not less than 1,0 % (mass fraction).

7 Determination methods of total boron

7.1 Classification of determination methods

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

— Method A, fusion–acidimetric titration method

— Method B, fusion–ICP-OES

7.2 Fusion-acidimetric titration method

7.2.1 Principle

Fuse the sample with sodium carbonate and dissolve the melt in hydrochloric acid. Adjust the solution to pH 6,4 after removal of carbon dioxide. Add mannitol, and then titrate with sodium hydroxide solution to pH 6,4.

This method shall be used to obtain the results of three or four figures.

7.2.2 Reagents

Reagents of analytical grade shall be used. Reagent solutions shall be preserved in plastic bottles (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available.). The standard solutions being SI traceable shall be used.

7.2.2.1 Water, Grade 1 or superior as specified in ISO 3696.

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

7.2.2.3 Hydrochloric acid (1+1), (1+50), prepare from hydrochloric acid, respectively.

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

7.2.2.5 Sodium hydroxide solution (200 g/l), (40 g/l), (20 g/l), prepare from sodium hydroxide, respectively.

7.2.2.6 Ethanol (95).

7.2.2.7 Ethanol–Sodium hydroxide (1+1) mixed solution, prepare by mixing the same volume of ethanol (95) and a sodium hydroxide solution (200 g/l).

7.2.2.8 Mannitol.

7.2.2.9 Boric acid, more than 99,5 % (mass fraction) of purity.

7.2.2.10 Standard boron solution, weigh 1 g of boric acid (7.2.2.9) in a platinum crucible (for example, 30 ml) and heat it initially at a low temperature and finally at about 1 100 °C. After cooling in a desiccator, weigh the mass of boric oxide as B_2O_3. Take the product into a 200 ml beaker together with the crucible and add 100 ml of hot water. Heat and dissolve it. After cooling, transfer the solution into a 200 ml volumetric flask and dilute with water to the mark.

7.2.2.11 Methyl-red indicator solution, prepare by dissolving 0,10 g of methyl-red with 50 ml of ethanol (95) (7.2.2.6) to make up to 100 ml by adding water.

7.2.2.12 0.2 mol/ l Sodium hydroxide solution, weigh 50 g of sodium hydroxide in a polyethylene bottle and dissolve in 50 ml of water under cooling. Stand for a few days with a cap to precipitate sodium carbonate. Take 20 ml of the supernatant and dilute with water to 2 000 ml. Preserve it into a polyethylene bottle equipped with an absorption tube of carbon dioxide. The volume of equivalent to the boron shall be obtained according to the following. Take exactly 50 ml of the standard boron solution (7.2.2.10) into a 200 ml beaker and add 12 ml of hydrochloric acid (1+1) (7.2.2.3) and a few drops of methyl-red indicator solution (7.2.2.11). After neutralization with the sodium hydroxide solution (40 g/l) (7.2.2.5), operate in accordance with 7.2.5 g). Calculate the factor of this solution according to the following formula:

$$F = \left(G \times \frac{0{,}174\,8}{V_0} \right) \times \frac{50}{200} \qquad (1)$$

where

F is the factor of boron content of 0,2 mol/l sodium hydroxide solution per 1 ml (g/ml);

G is the weighed amount of boric acid in 7.2.2.9 (g);

V_0 is the consumed volume of 0,2 mol/l sodium hydroxide solution after addition of mannitol in 7.2.2.12 (ml).

7.2.3 Apparatus

Apparatus shall be as follows:

7.2.3.1 Platinum crucible (30 ml), with a platinum lid.

7.2.3.2 Electric furnace, adjustable to the temperature of (1 100 ± 25) °C.

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

7.2.4 Amount of sample

The weighed amount of the sample shall be 0,10 g.

7.2.5 Operation

The operation shall be as follows.

a) Take the sample aliquot into a platinum crucible (30 ml) and 2 ml of the ethanol–sodium hydroxide mixed solution (7.2.2.7).

b) Heat on a hot plate, and then evaporate until dry.

c) Add 2,0 g of sodium carbonate and heat initially at a low temperature. Elevate the temperature gradually to start fusing (heat carefully to prevent the contents from scattering) by using an electric furnace or a Bunsen burner and keep the temperature for 15 min ~ 30 min during fusion. Fuse the sample at 950 °C ~ 1 000 °C. Keep the temperature as low as possible.

d) Stand the crucible for cooling with a lid and place the crucible into a 300 ml beaker. Add 50 ml of water and 10 ml of hydrochloric acid (1+1) (7.2.2.3) and heat it on a hot plate with a watch glass to dissolve the melt.

e) After dissolving, wash the crucible with small amount of water and add a few drops of the methyl-red indicator solution (7.2.2.11). Neutralize the solution with a sodium hydroxide solution until its colour turns yellow, and then add hydrochloric acid (1+50) (7.2.2.3) to return to red again.

f) Remove carbon dioxide in the solution by boiling or by purging nitrogen gas for 5 min with the watch glass. Cool down to room temperature and wash the watch glass with small amount of water before removing. Keep the total water volume not more than 150 ml while washing.

g) Stirring with a magnetic stirrer, titrate with 0,2 mol/l sodium hydroxide solution (7.2.2.12), depict a titration curve around pH 6,4 using a pH meter, and determine the inflection point of the curve. After removing the electrode, add 25 g of mannitol (7.2.2.8). Titrate again with the sodium hydroxide solution (7.2.2.12), depict a titration curve around pH 8,5, and determine the inflection point of the curve. Calculate the total volume of titrant between two inflection points.

7.2.6 Blank test

Perform operations of 7.2.5 a) to 7.2.5 g) without taking a sample to obtain the blank test value of boron.

7.2.7 Calculation

Calculate the content of total boron in the sample according to the following formula:

$$T.B=\frac{(V_1-V_0)\times F}{m}\times 100 \qquad (2)$$

where

$T.B$ is the content of total boron in the sample [% (mass fraction)];

V_1 is the total volume of the 0,2 mol/l sodium hydroxide solution after the first addition of mannitol in 7.2.5 g) (ml);

V_0 is the total volume of the 0,2 mol/l sodium hydroxide solution of the blank test after the first addition of mannitol in 7.2.6 (ml);

F is the factor of the 0,2 mol/l sodium hydroxide solution in 7.2.2.12 (g);

m is the weighed amount of the sample in 7.2.5 a) (g).

7.3 Fusion-ICP-OES

7.3.1 Principle

To prepare a test solution, decompose the sample using base, spray into the argon plasma flame of ICP-OES, and measure the emission intensity at a selected wavelength.

This method can be used to obtain the results of two figures.

7.3.2 Reagents

Use only reagents of analytical grade unless stated to the contrary and prepare all solutions using distilled or deionized water and store in polyethylene bottles.

WARNING — Hydrochloric acid causes burns and has an irritating vapour. Prevent inhalation and contact with skin and eyes. Proceed as for sulfuric acid, carrying out the dilution in a fume cupboard.

7.3.2.1 Hydrochloric acid, concentrated, density 1,095 g/ml.

7.3.2.2 Hydrochloric acid (1+1 solution), carefully add 50 ml of acid to 50 ml of water to a beaker cooled in a water bath. Stir the mixture continuously. Allow to cool and store.

7.3.2.3 Nitric acid, ρ 1,42 g/ml.

7.3.2.4 Sodium peroxide (Na_2O_2).

7.3.2.5 Sodium carbonate, anhydrous.

7.3.2.6 Ethanol.

7.3.2.7 Boron standard solution, containing 1,000 g of boron (*B*) per litre. Do not dry. Dissolve 5,716 g of anhydrous H_3BO_3 (B fraction = 0,174 9), accurately weighed to at least four significant figures, in reagent water and dilute in a 1 l volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass container. The use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware. A 1 ml of this standard solution contains 1,0 mg of boron.

7.3.3 Apparatus

Apparatus are ordinary laboratory apparatus and the following:

7.3.3.1 Glass beaker, with a range of appropriate volumes (100 ml, 250 ml).

7.3.3.2 Volumetric flask, with a range of appropriate volumes (100 ml, 250 ml, 500 ml, and 1 000 ml).

7.3.3.3 Burette, with a 0,1 ml scale and a maximum volume of 50 ml.

7.3.3.4 One-mark pipette, suitable for the transfer of each sample solution or standard solution.

7.3.3.5 Nickel crucibles.

7.3.3.6 Burner, such as a Mecker burner or a Bunsen burner.

7.3.3.7 Desiccator, containing dried silica gel as the drying agent.

7.3.3.8 Inductively coupled plasma emission spectrometer.

NOTE Refer to the manufacturer’s instructions for operation.

7.3.4 Procedure

7.3.4.1 Preparation of test solution

a) Weigh, to the nearest 0,001 g, approximately 1,0 g of the test sample, and transfer the test sample in a nickel crucible.

b) Add 2,0 g of anhydrous sodium carbonate and 2,0 g of sodium peroxide and mix intimately. Heat over a burner slowly at first and gradually raise the temperature to the full heat until complete fusion.

CAUTION — When heating the sample in the burner, carbon dioxide is produced. So be careful when heating the sample.

c) Cool to ambient temperature and place in a 250 ml beaker. Extract with approximately 150 ml of water containing 2 ml to 3 ml ethanol, heat to boiling until the melt from the walls of the crucible has been separated. Remove the crucible and wash it with a small amount of water.

d) Add 10 ml of hydrochloric acid (7.3.2.1) and heat to 100 °C until the melt is completely dissolved. Pour the dissolved sample into a 250 ml volumetric flask, make up to the mark, and mix.

e) Pipette 25 ml of the solution from the 250 ml volumetric flask into a new 250 ml volumetric flask, make up to the mark, and mix. This solution is used as the test solution.

7.3.4.2 Blank test

Carry out the procedure given in 7.3.4.1 without the sample, but omit the fusion of the flux. Designate the resulting solution as blank solution.

7.3.4.3 Preparation of the calibration curve

a) To a series of six 100 ml volumetric flasks, add respectively 0 ml, 1 ml, 5 ml, 10 ml, 20 ml, and 50 ml boron standard solution (7.3.2.7). Add to each flask 5 ml hydrochloric acid 1+1, dilute to mark, and mix.

b) Spray a portion of each solution into the argon plasma flame of the inductively coupled plasma atomic emission spectrometer, and measure the emission intensity for boron at 249,677 nm, 249,772 nm, or 208,809 nm. Interferences may be encountered. Carefully choose the optimum wavelength free from concomitants.

7.3.5 Calculation

Determine the concentration of boron in the test solution and in the blank from the calibration curve. Calculate the boron content, B, as total boron, expressed in percent mass fraction, from Formula (3):

$$T.B = \frac{(C_1 - C_2) \times V}{m} \times 10^4 \tag{3}$$

where

$T.B$ is the total boron content in mass fraction (%);

C_1 is the concentration, expressed in milligrams per litre, of boron in test solution;

C_2 is the concentration expressed in milligrams per litre, of boron in blank test;

V is the volume, in millilitres, of the test solution described in 7.3.4.1 d);

m is the mass, in grams, of the test portion.

8 Determination methods of free boron

8.1 Classification of determination methods

Boron nitride may somewhat tend to receive hydrolysis and yield equivalent of boron oxide and ammonia; only the latter evaporates. The determination of boron oxide in boron nitride may be critical when the equivalence between total boron and total nitrogen is evaluated. There are two approaches to extract boron oxide in boron nitride with acid or methanol, but either of them is accompanied by the slight dissolution of boron nitride. Extraction of only boron oxide without dissolving boron nitride is difficult. However, the contribution of boron generated from boron nitride can be evaluated by the determination of ammonia whose amount is equivalent to the boron.

Boron oxide shall be determined by any of the following methods. Both method A and method B include the correction procedure for the boron amount which arises from the hydrolysis of boron nitride during sample treatment stages. If analytical results with three or four figures are required for the total boron, method A or C shall be used; whereas if two figures, either method A or C, without the correction procedure or method B, can be used.

— Method A, Sulfuric acid digestion–ICP-OES and spectrophotometry

— Method B, Nitric acid digestion–ICP-OES

— Method C, Methanol extraction–borate separation–ICP-OES and spectrophotometry

8.2 Sulfuric acid digestion-ICP-OES and spectrophotometry

8.2.1 Principle

Dissolve the sample in sulfuric acid and filtrate the insoluble. Determine boron by using ICP-OES. If analytical results of three or four figures for the total boron are determined, the correction procedure including ammonia determination of 8.2.5 a) and 8.2.5 c) to 8.2.5 f) shall be necessary.

8.2.2 Reagents

Reagents shall be as follows.

8.2.2.1 Water, as specified in 7.2.2.1**.**

8.2.2.2 Sulfuric acid, 0,5 mol/l, prepare with sulfuric acid.

8.2.2.3 EDTA solution (5 g/100 ml), prepare with EDTA.

8.2.2.4 Sodium hydroxide solution (20 g/100 ml), prepare with sodium hydroxide.

8.2.2.5 Phenol.

8.2.2.6 Acetone.

8.2.2.7 Sodium phenoxide solution, take 55 ml of a sodium hydroxide solution (20 g/100 ml) (8.2.2.4) in a beaker and gradually add 25 g of phenol (8.2.2.5) to the solution cooling in cold water. After cooling, add 6 ml of acetone (8.2.2.6) and dilute with water to 200 ml. Store in a dark room below 10 °C.

8.2.2.8 Sodium hypochlorite solution, [1 % (mass fraction) of available chlorine]. Prepare by diluting a commercial sodium hypochlorite solution, 5 % ~ 12 % (mass fraction) of available chlorine content, with water. Prepare fresh immediately before use.

8.2.2.9 Ammonium ion standard solution (NH_4^+ 1 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

8.2.2.10 Ammonium ion standard solution (NH_4^+ 0.1 mg/ml), take 10 ml of an ammonium ion standard solution (NH_4^+ 1 mg/ml) (8.2.2.9) into a 100 ml plastic volumetric flask and dilute with water to the mark.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flask.

8.2.2.11 Boron standard solution (B 1 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

8.2.2.12 Boron standard solution (B 0,1 mg/ml), take 10 ml of a boron standard solution (1 mg/ml) (8.2.2.11) into a 100 ml plastic volumetric flask, and dilute with water to the mark. Prepare fresh immediately before use.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flask.

8.2.3 Instruments

Instruments shall be as follows.

8.2.3.1 ICP optical emission spectrometer.

8.2.3.2 Spectrophotometer.

8.2.4 Amount of sample

The weighed amount of sample shall be 0,5 g.

8.2.5 Operation

The operation shall be as follows.

a) Take the sample into a 200 ml plastic beaker (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available), and add 15ml of 0,5 mol/l sulfuric acid (8.2.2.2) and 35 ml of water. While stirring it occasionally at room temperature, let it stand for 2 h. Wash out the solution into a 100 ml volumetric flask and dilute with water to the mark. After shaking well, filter the solution with a dried filter paper. This filtrate shall be used as the sample solution.

b) Spray a portion of the solution of 8.2.5 a) into an Ar plasma of ICP-OES and measure the emission intensity of boron at optimum wavelength, for example, 249,77 nm.

NOTE The optimum wavelengths used for the measurement depend on the performance of each ICP spectrometer. Select the wavelength at which the measurement is not affected by concomitants. For equipment which can be used to measure with higher order spectrum lines, higher wavelength shall be used considering spectral interference and sensitivity.

c) Take an aliquot of the sample solution 8.2.5 a) (NH_4^+ 5 µg ~ 100 µg) in a 100 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and add water to make about 30 ml.

d) Add 1 ml of the EDTA solution 8.2.2.3 and 10 ml of the sodium phenoxide solution (8.2.2.7) and mix well.

e) Add 5ml of the sodium hypochlorite solution (8.2.2.8) and dilute with water to the mark and shake well. Keep the temperature of the solution at 20 °C ~ 25 °C and let it stand for 30 min.

f) Take an aliquot of the solution in an absorption cell and measure the absorbance in the vicinity of 630 nm.

8.2.6 Blank test

Perform operations of 8.2.5 a) and 8.2.5 b) without taking a sample to obtain the blank test value of boron and perform operations of 8.2.5 a) and 8.2.5 c) to 8.2.5 f) to obtain the blank value of ammonia.

8.2.7 Drawing calibration curves

a) Take 15 ml of 0.5 mol/l sulfuric acid (8.2.2.2) and 35 ml of water into several 100 ml plastic flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available), then add exactly 0 ml ~ 10 ml of the boron standard solution (8.2.2.12) stepwise. Dilute with water to the mark and mix well. These solutions for the calibration curve shall contain 0 µg ~ 1 000 µg of boron. Operate the step of 8.2.5 b) and establish the relation between the emission intensity and the amount of boron to draw a calibration curve.

b) Take exactly 0 ml to 20 ml of the ammonium ion standard solution (8.2.2.10) stepwise (NH_4^+ 0 µg ~ 200 µg) into several 100 ml plastic flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and add water to make about 30ml. Operate the steps of 8.2.5 c) to 8.2.5 f) and establish the relation between the emission intensity and the amount of ammonium to draw a calibration curve.

8.2.8 Calculation

Obtain the amount of boron by 8.2.5 a) to 8.2.5 b) and 8.2.6 referring to the calibration curve drawn in 8.2.7 a); whereas obtain the amount of ammonia by 8.2.5 c) to 8.2.5 f) and 8.2.6 according to the calibration curve drawn in 8.2.7 b). Calculate the content of free boron (boron oxide) in the sample according to the following formula:

$$F.B = \frac{\left[\left(A_1 - A_0\right)\times 3{,}220\right] - \left[\left(A_2 - A_{00}\right)\times 1{,}930\right]}{m}\times 100 \qquad (4)$$

where

$F.B$	is the content of free boron as boron oxide in the sample [% (mass fraction)];
A_1	is the amount of boron in the sample solution obtained by 8.2.5 b) and 8.2.7 a) (g);
A_0	is the amount of boron in the blank test solution obtained by 8.2.6 and 8.2.7 a) (g);
A_2	is the amount of ammonim ions in the sample solution obtained by 8.2.5 f) and 8.2.7 b) (g);
A_{00}	is the amount of ammonium ions in the blank test solution obtained by 8.2.6 and 8.2.7 b) (g);
m	is the weighed amount of the sample in 8.2.5 a) (g);
3,220	is the conversion factor of boron (B) into boron oxide (B_2O_3);
1,930	is the conversion factor of ammonium ion into the equivalent boron oxide (B_2O_3).

8.3 Nitric acid digestion-ICP-OES

8.3.1 Principle

Nitric acid digestion–ICP-OES is a method in which the soluble compounds in the boron nitride powder are obtained by treatment with diluted nitric acid. After filtration, the free boron in filtrate is determined by inductively coupled plasma–atomic emission spectroscopy.

8.3.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of equivalent purity.

8.3.2.1 Water, use water purified in accordance with ISO 3696.

8.3.2.2 Nitric acid, ρ 1,42 g/ml.

8.3.2.3 Nitric acid, (1+9), Nitric acid (8.3.2.2) diluted 1+9.

8.3.2.4 Boron standard solution, containing 100 mg of boron (B) per litre. Transfer 10 ml of the boron standard solution (7.3.2.7) to 100 ml volumetric flask up to mark with water and mix.

8.3.3 Apparatus

Apparatus are ordinary laboratory apparatus and the following.

8.3.3.1 **Glass beaker**, with a range of appropriate volumes (250 ml).

8.3.3.2 **Volumetric flask**, with a range of appropriate volumes (100 ml, 250 ml).

8.3.4 Procedure

8.3.4.1 Preparation of test solution

Weigh, to the nearest 0,001 g, approximately 3,0 g of the test sample, and transfer to a 250 ml glass beaker. Add 100 ml of the nitric acid (1+9) and heat to boiling for approximately 3 h. Cool the solution and then filter through a 15 cm paper of medium porosity. Rinse the beaker and wash the residue with water. Transfer the filtrate to 250 ml volumetric flask make up to mark with water and mix. This solution is used as the test solution.

8.3.4.2 Blank test

Carry out the procedure given in 8.3.4.1 without the sample, but omit the fusion of the flux. Designate the resulting solution as blank solution.

8.3.4.3 Preparation of the calibration solution and calibration curve

To a series of four 100 ml volumetric flasks, add respectively 0 ml, 1 ml, 5 ml, and 10 ml boron standard solution (7.3.2.7). Add to each flask 5 ml nitric acid (1+9), dilute to mark, and mix. Aspirate the calibration solutions into the inductively coupled plasma-atomic emission spectrometer (7.3.3.8). Measure the emission intensities for boron at 249,677 nm, 249,772 nm, or 208,809 nm.

8.3.5 Calculation

Determine the concentration of boron in the test solution and in the blank from the calibration curve. Calculate the boron content, *F.B*, as free boron, expressed in milligrams per kilogram, from Formula (5):

$$F.B = \frac{(C_1 - C_2) \times V}{m} \tag{5}$$

where

$F.B$ is the content of free boron as boron oxide in mg/kg (mass fraction);

C_1 is the concentration, expressed in milligrams per litre, of boron in test solution;

C_2 is the concentration expressed in milligrams per litre, of boron in blank test;

V is the volume, in millilitres, of the test solution;

m is the mass, in grams, of the test portion.

8.4 Methanol extraction-borate separation-ICP-OES and spectrophotometry

8.4.1 Principle

Convert boron oxide in the sample into a volatile borate by heating with methanol, trap into a calcium hydroxide solution and determine the boron in the solution using ICP-OES. If analytical results of three or four figures for the total boron are determined, the correction procedure including ammonia determination of 8.4.5 b) shall be necessary.

8.4.2 Reagents

Reagents shall be as follows.

8.4.2.1 Water, as specified in 7.2.2.1.

8.4.2.2 Methanol.

8.4.2.3 Calcium hydroxide saturated solution, add 500 ml of water to 5 g of calcium hydroxide and seal with an airtight stopper. After shaking vigorously, use the supernatant. Prepare fresh immediately before use.

8.4.2.4 Hydrochloric acid (1+1), prepare from hydrochloric acid by diluting with the same volume of water.

8.4.2.5 Nitrogen gas, more than 99,99 % (volume fraction) of purity.

8.4.2.6 Sulfuric acid (25 mmol/l), prepare from sulfuric acid.

8.4.2.7 EDTA solution (5 g/100 ml), as specified in 8.2.2.3.

8.4.2.8 Sodium hydroxide solution (20 g/100 ml), as specified in 8.2.2.4.

8.4.2.9 Phenol, as specified in 8.2.2.5.

8.4.2.10 Acetone, as specified in 8.2.2.6.

8.4.2.11 Sodium phenoxide solution, as specified in 8.2.2.7.

8.4.2.12 Sodium hypochlorite solution (1 % (mass fraction) of effective chlorine), as specified in 8.2.2.8.

8.4.2.13 Ammonium ion standard solution (NH_4^+ 1 mg /ml), as specified in 8.2.2.9.

8.4.2.14 Ammonium ion standard solution (NH_4^+ 0.1 mg/ml), as specified in 8.2.2.10.

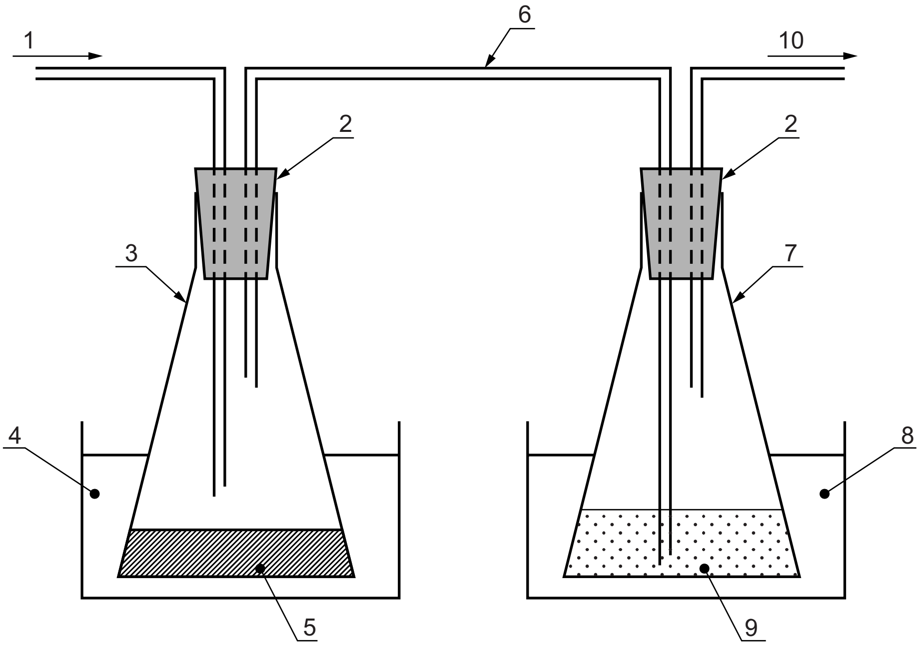
8.4.2.15 Boron standard solution (B 1 mg/ml), as specified in 8.2.2.11.

8.4.2.16 Boron standard solution (B 0.1 mg/ml), as specified in 8.2.2.12.

8.4.3 Apparatus and instruments

Apparatus and instruments shall be as follows.

8.4.3.1 Separator of boron, Figure 1 shows an example of a separator consisting of two parts, a reactor and a receiver. Connect two 200 ml Erlenmeyer flasks (one for a reactor and another for a receiver) by a quarts tube with a nitrogen gas inlet and an exhaust outlet. The flask for a reactor should be dried prior to use.



Key

1	N_2 gas
2	silicone rubber cap
3	reactor for borate generation
4	water bath at the temperature of 70 °C
5	sample with methanol
6	quartz tube
7	receiver for borate collection
8	iced water cooling reservoir
9	absorber of calcium oxide solution
10	exhaust

Figure 1 — Example of a separator for boron

8.4.3.2 Water bath, adjustable to 70 °C.

8.4.3.3 Iced water cooling reservoir, capable to cool the receiver.

8.4.3.4 ICP optical emission spectrometer.

8.4.3.5 Spectrophotometer.

8.4.4 Amount of sample

The weighed amount of sample shall be 0,5 g.

8.4.5 Operation

The operation shall be as follows.

a) ICP-OES for the determination of boron

   1) Take a sample into a 200 ml Erlenmeyer flask (8.4.3.1) as a reactor and add 20 ml of methanol (8.4.2.2). Add 50 ml of the calcium hydroxide saturated solution (8.4.2.3) into another 200 ml Erlenmeyer flask (8.4.3.1) as a receiver and assemble a separator.

   2) Place the Erlenmeyer flask (8.4.3.1) as a reactor in a water bath at 70 °C and flow nitrogen gas (8.4.2.5) into the flask at 400 ml/min for 30 min. Receive the generated borate in the receiver which is placed in an iced water cooling reservoir (8.4.3.3).

   3) Wash out the solution in the receiver into a 200 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and add 5 ml of hydrochloric acid (1+1) (8.4.2.4). Dilute with water to the mark and shake well to prepare the sample solution for boron determination.

   4) Spray a portion of the solution 8.4.5 a) 3) into an Ar plasma of ICP-OES and measure the emission intensity of boron at the wavelength, at which the measurement is not affected by concomitants, for example, 249,77 nm.

b) Spectrophotometry for the determination of ammonia

   If analytical results of three or four figures for the total boron are required, this procedure shall be necessary.

   1) Take a sample in a 200 ml Erlenmeyer flask (8.4.3.1) as a reactor and add 20 ml of methanol (8.4.2.2). Add 20 ml of 25 mmol/l sulfuric acid (8.4.2.6) into another 200 ml Erlenmeyer flask (8.4.3.1) as a receiver and assemble a separator.

   2) Place the Erlenmeyer flask (8.4.3.1) as a reactor in a water bath at 70 °C and flow nitrogen gas (8.4.2.5) into the flask at 400 ml/min for 30 min. Receive the generated ammonia in the receiver which is placed in an iced water cooling reservoir (8.4.3.3).

   3) Wash out the solution in the receiver into a 100 ml plastic volumetric flask. Dilute with water to the mark and shake well to prepare the sample solution for ammonia determination.

   4) Take an aliquot of the sample solution (NH_4^+ 5 µg ~ 100 µg) into a 100 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and add water to make about 30 ml.

   5) Add 1 ml of the EDTA solution (8.4.2.7) and 10ml of the sodium phenoxide solution (8.4.2.11) and mix well.

   6) Add 5ml of the sodium hypochlorite solution (8.4.2.12) and dilute with water to the mark and shake well. Keep the solution at 20 °C to 25 °C for 30 min.

   7) Take an aliquot of the solution 8.4.5 b) 6) in an absorption cell and measure the absorbance in the vicinity of 630 nm. Correct the boron amount resulting from the hydrolysis of boron nitride.

8.4.6 Blank test

a) **ICP-OES for boron** — perform operations of 8.4.5 a) 1) to 8.4.5 a) 4) without taking a sample to obtain the blank test value of boron.

b) **Spectrophotometry for ammonia** — perform operations of 8.4.5 b) 1) to 8.4.5 b) 7) without taking a sample to obtain the blank value of ammonia.

8.4.7 Drawing calibration curves

a) **ICP-OES for boron** — Take 10 ml of methanol (8.4.2.2), 25 ml of the calcium hydroxide saturated solution 8.4.2.3) and 2,5 ml of hydrochloric acid (1+1) (8.4.2.4) into several 100 ml plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available), then add exactly 0 ml to 10 ml of the boron standard solution 8.4.2.16 stepwise. Dilute with water to the mark and mix well. These solutions for calibration curve shall contain 0 µg to 1 000 µg of boron. Operate as 8.4.5 a) 4) and establish the relation between the emission intensity and the amount of boron to draw the calibration curve.

b) **Spectrophotometry for ammonia** — Take 10 ml of methanol (8.4.2.2) and 10 ml of sulfuric acid 25 mmol/l (8.4.2.6) into several 100 ml plastic volumetric flasks, then add exactly 0 ml ~ 20 ml of the ammonium ion standard solution (8.4.2.13) stepwise (NH_4^+ 0 µg ~ 200 µg). Dilute with water to make about 30ml and perform 8.4.5 b) 5) to 8.4.5 b) 7). Establish the relation between the emission intensity and the amount of ammonia to draw the calibration curve.

8.4.8 Calculation

Obtain the amount of boron by 8.4.5 a) and 8.4.6 a) referring to the calibration curve drawn in 8.4.7 a); whereas obtain the amount of ammonia by 8.4.5 b) and 8.4.6 b) referring to the calibration curve drawn in 8.4.7 b). Calculate the content of free boron (boron oxide) in the sample according to the following formula:

$$F.B = \left\{ \frac{\left[(A_3 - A_0) \times 3{,}220 \right]}{m_1} - \frac{\left[(A_4 - A_{00}) \times 1{,}930 \right]}{m_2} \right\} \times 100 \qquad (6)$$

where

$F.B$	is the content of free boron as boron oxide in the sample [% (mass fraction)];
A_3	is the amount of boron in the sample solution obtained by 8.4.5 a) and 8.4.7 a) (g);
A_0	is the amount of boron in the blank test solution obtained by 8.4.6 a) and 8.4.7 a) (g);
A_4	is the amount of ammonium ions in the sample solution obtained by 8.4.5 b) and 8.4.7 b) (g);
A_{00}	is the amount of ammonim ions in the blank test solution obtained by 8.4.6 b) and 8.4.7 b) (g);
m_1	is the weighed amount of the sample in 8.4.5 a) 1) (g);
m_2	is the weighed amount of the sample in 8.4.5 b) 1) (g);
3,220	is the conversion factor of boron (B) into boron oxide (B_2O_3);
1,930	is the conversion factor of ammonia into the equivalent boron oxide (B_2O_3).

9 Determination methods of total nitrogen

9.1 Classification of determination methods

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

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

- Method B, Fusion–distillation separation–acidimetric titration method
- Method C, Inert gas fusion–thermal conductivity method

9.2 Acid pressure decomposition-distillation separation-acidimetric titration method

9.2.1 Principle

Decompose the sample in a pressure decomposition vessel with a mixture of hydrofluoric acid and sulfuric acid to convert nitrogen into ammonium salt. Add boric acid and transfer the solution into a distillation flask. Add sodium hydroxide and perform steam distillation. Let the distilled ammonia react with a known amount of amidosulfuric acid and titrate the excess amidosulfuric acid with a standardized sodium hydroxide solution.

9.2.2 Reagents

9.2.2.1 Water, as specified in 7.2.2.1.

9.2.2.2 Hydrofluoric acid.

9.2.2.3 Sulfuric acid.

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

9.2.2.5 Sodium hydroxide solution (500 g/l), dissolve 500 g of sodium hydroxide (9.2.2.4) in 1 000 ml of water.

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

9.2.2.7 0.1mol/l amidosulfuric acid solution, weigh 10,0 g of amidosulfuric acid to the nearest to 0,1 mg and dissolve in water. Dilute exactly with water to 1 000 ml. Calculate the factor of this solution according to the following formula:

$$F_1 = G \times \frac{P}{(9{,}7093 \times 100)} \qquad (7)$$

where

F_1 is the factor of the 0,1 mol/l amidosulfuric acid solution;

G is the weighed amount of the amidosulfuric acid (g);

P is the purity of the amidosulfuric acid in 9.2.2.6 [% (mass fraction)].

9.2.2.8 0.1 mol/l sodium hydroxide solution, dissolve 4,0 g of sodium hydroxide (9.2.2.4) in 1 000 ml of water. Take exactly 50 ml of the 0,1 mol/l amidosulfuric acid solution (9.2.2.7) in a beaker (200 ml) and dilute with water to about 100 ml. Titrate this solution with 0,1 mol/l sodium hydroxide solution using a pH meter. Take the end point as pH 5,5 and obtain the volume of the 0,1 mol/l sodium hydroxide solution consumed. Calculate the factor of this solution according to the following formula:

$$F_2 = F_1 \times \frac{50,00}{V} \tag{8}$$

where

F_2 is the factor of the 0,1 mol/l sodium hydroxide solution;

F_1 is the factor of the 0,1 mol/l amidosulfuric acid solution in 9.2.2.7;

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

9.2.2.9 Boric acid, as specified in 7.2.2.9.

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

9.2.3 Apparatus

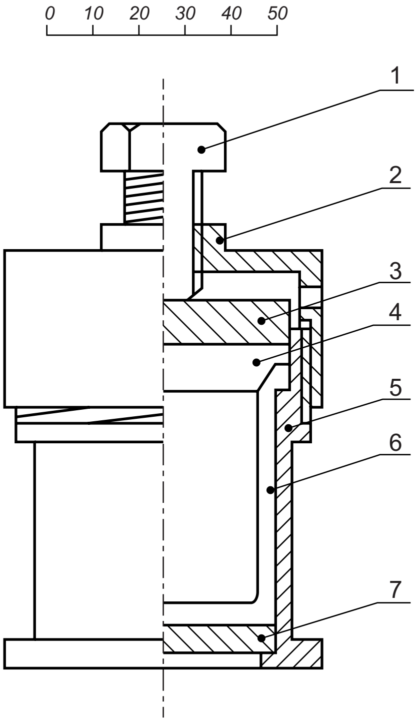
Apparatus shall be as follows.

9.2.3.1 Platinum crucible (20 ml).

9.2.3.2 Pressure decomposition vessel, in general, a commercial pressure decomposition vessel may be used. An example is shown in Figure 2.

NOTE When using a PTFE inner vessel which had contact with nitric acid, the lower values of nitrogen may be obtained. Therefore, use the vessels for the exclusive use in this analysis.

Dimensions in mm



Key

1 centre screw

2 screw cap

3 top plate

4 PTFE cap

5 cylinder

6 PTFE bottle

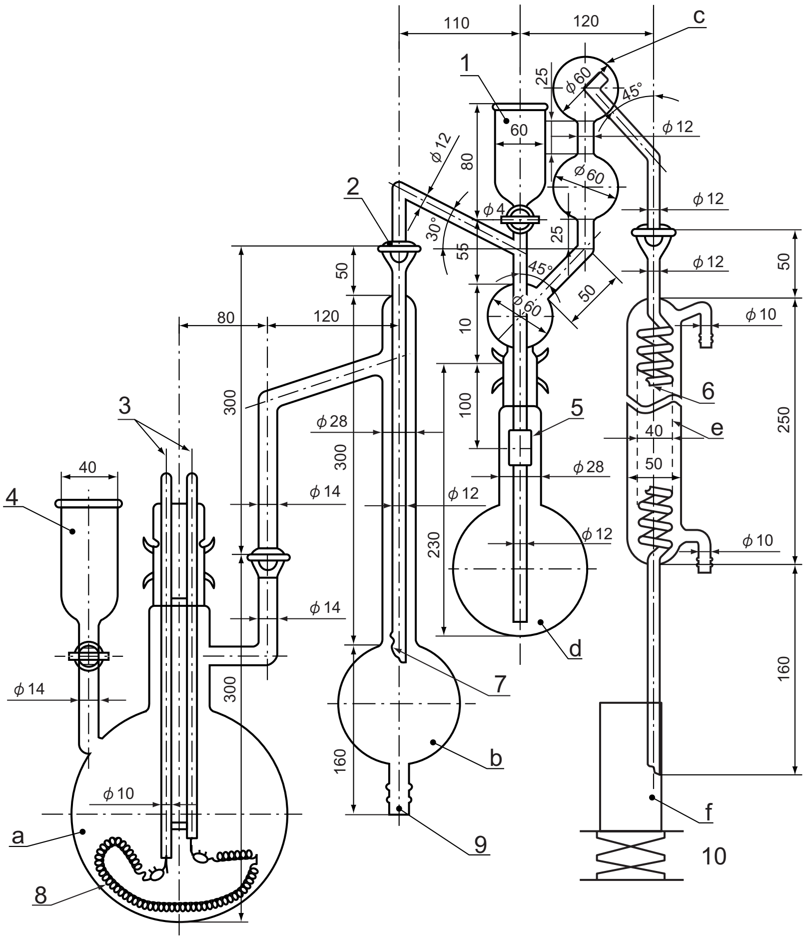
7 bottom plate

Figure 2 — Example of pressure decomposition vessel

9.2.3.3 Air bath, adjustable temperature to (180 ± 5) °C.

9.2.3.4 Steam distillation apparatus, in general, the following instruments shall be coupled as shown in Figure 3. Each component shall be made of hard glass coupled by common ground joints and fixed by springs or clamps.

Dimensions in mm



Key

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

Figure 3 — Example of steam distillation apparatus

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

b) **Trap**, the bottom of a bulb shall be connected to a rubber tube with a pinchcock for a drain. The tip of steam leading-out tube shall have several small holes.

c) **Bulb**, equipped with a steam leading-in tube, a funnel with a stopcock, 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.

d) **Distillation flask (750 ml).**

e) **Coiled condenser.**

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

9.2.3.5 pH meter, as specified in 7.2.3.3.

9.2.4 Amount of sample

The weighed amount of sample shall be 0,1 g.

9.2.5 Operation

The operation shall be as follows.

a) **Acid pressure decomposition of sample.** Weigh 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 PTFE inner vessel and close the pressure vessel according to the manufacturer's instructions. Place the vessel into an air bath and heat at (180 ± 5) °C for 16 h.

   NOTE Acid pressure decomposition under micro wave irradiation can be performed if available.

b) **Preparation of sample solution.** After cooling, disassemble the pressure vessel. Transfer the solution in the PTFE inner vessel into a 100 ml plastic beaker. Add 5 g of boric acid (9.2.2.9) and mix well.

   NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic beaker.

c) **Preparation of steam distillation apparatus.** After transferring the sample solution 9.2.5 b) into a distillation flask, assemble a distillation apparatus and add exactly 50 ml of the 0,1 mol/l amidosulfuric acid solution (9.2.2.7) 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) (9.2.2.5) 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**. Water in the steam generation flask shall be kept boiling by opening the pinchcock at the bottom of the trap. When sending steam, close the pinchcock. Control the heater to produce steam at the flow rate of 4,5 ml to 5,0 ml per min. Perform the steam distillation. 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.

   NOTE When using a new distillation apparatus or an 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 (9.2.2.8) using a pH meter. Take the end point as pH 5,5 and obtain the volume of the 0,1 mol/l sodium hydroxide solution consumed.

9.2.6 Recovery measurement

Weigh 0,280 g of ammonium sulfate (9.2.2.10) to the nearest 0,1 mg in the platinum crucible (20 ml), perform operations of 9.2.5 and calculate the recovery according to the following formula:

$$R=\left\{\left[\left(50{,}00\times F_1\right)-\left(V\times F_2\right)\right]\times\left[\frac{0{,}0014007}{\left(G\times 0{,}2120\right)}\right]\right\}\times 100 \qquad (9)$$

where

R is the recovery (%);

F_1 is the factor of the 0,1 mol/l amidosulfuric acid solution in 9.2.2.7;

V is the consumed volume of the 0,1 mol/l sodium hydroxide solution in 9.2.5 h) (ml);

F_2 is the factor of the 0,1 mol/l sodium hydroxide solution in 9.2.2.8;

G is the weighed amount of the ammonium sulfate (g).

9.2.7 Calculation

Calculate the content of total nitrogen in the sample according to the following formula:

$$T.N=\left\{\frac{\left[\left(50{,}00\times F_1\right)-\left(V\times F_2\right)\right]\times\left[0{,}0014007\times\left(100/R\right)\right]}{m}\right\}\times 100 \qquad (10)$$

where

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

F_1 is the factor of the 0,1 mol/l amidosulfuric acid solution in 9.2.2.7;

V is the consumed volume of the 0,1 mol/l sodium hydroxide solution in 9.2.5 h) (ml);

F_2 is the factor of the 0,1 mol/l sodium hydroxide solution in 9.2.2.8;

R is the recovery in 9.2.6 (%);

m is the weighed amount of the sample in 9.2.5 a) (g).

9.3 Fusion-ammonia separation-acidimetric titration method

The procedure shall be in accordance with EN 12698-1, 7.2.

9.4 Inert gas fusion-thermal conductivity method

9.4.1 Principle

Fuse the sample 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.

9.4.2 Reagents

Reagents shall be as follows.

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

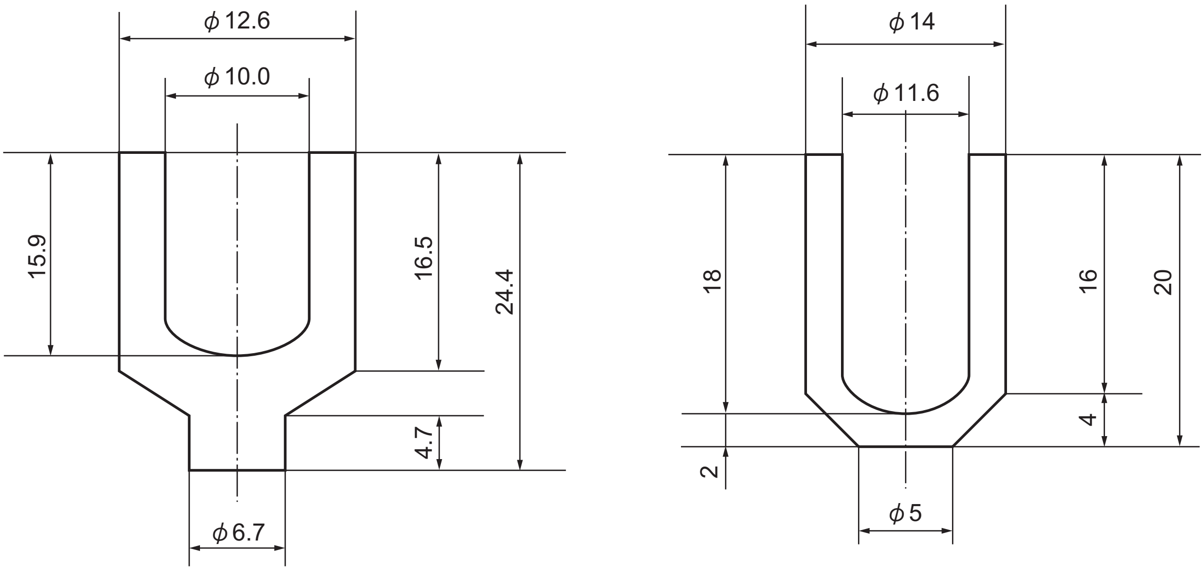
9.4.2.2 Flux, shot or basket form made of tin or nickel. For bath metal, use a combination of metals which is different from a capsule.

9.4.3 Apparatus

9.4.3.1 Capsule, made of nickel or tin. It is used for taking a sample.

9.4.3.2 Graphite crucible, suitable for impulse furnace. An example is shown in Figure 4 a) and Figure 4 b).

Dimensions in mm

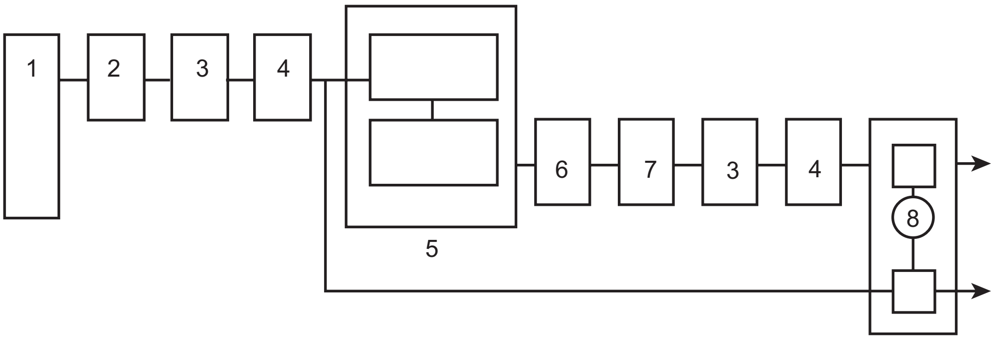


a) b)

Figure 4 — Example of graphite crucible

9.4.4 Instrument

A commercial nitrogen analyser is available. It consists of an inert gas refiner, a gas extractor, a gas separator, a gas detector, etc. The block diagram is shown in Figure 5.



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 5 — Block diagram of inert gas fusion–thermal conductivity method

9.4.4.1 Inert gas refiner, consisting of a deoxidation tube (filled with reduced copper) with an electric furnace, a carbon dioxide absorption tube (filled with sodium hydroxide shots for gas analysis), a dehydration tube (filled with magnesium perchlorate for drying), etc. A denitrification tube (filled with sponge titanium) is attached in some instruments.

9.4.4.2 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.

9.4.4.3 Gas separator, 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.

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

9.4.5 Amount of sample

The weighed amount of sample shall be 0,02 g to 0,04 g. If complete extraction of nitrogen can be achieved, take a sample up to 0,1 g.

9.4.6 Operation

The operation shall be as follows.

a) **Starting up of the instrument.** Switch on the instrument and set the controls to the specified values. Wait until it becomes stable.

NOTE Refer to the manufacturer’s instruction for operation.

b) **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.

c) **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 put electricity through the graphite crucible. Heat it at the degassing temperature for the specified period and degas the graphite crucible and the bath metal.

NOTE 1 The optimum volume of charging the bath metal and the sample depends on the instrument used. So it is intended to be preliminarily acquired using a sample whose nitrogen content is known.

NOTE 2 The temperature of graphite crucible depends on the current or power supplied to itself. The correlation is intended to be predetermined. If an apparatus has a bath metal thrower, it is preferable to throw the bath metal after degassing the graphite crucible, and then degas it. The degassing temperature is intended to be set higher than the gas extraction temperature.

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

NOTE Since the optimum gas extraction temperature depends on the instrument used, predetermine it using a sample whose nitrogen content is known.

9.4.7 Blank test

Perform the operations of 9.4.6 without taking a sample to obtain the blank test value. Repeat these operations two to five times and obtain an average value.

9.4.8 Calculation of calibration coefficient

Use the nitride sample whose nitrogen content is known for calibration (the silicon nitride whose amount of nitrogen is obtained according to the measurement in 9.2 may be used.). However, the nitride sample whose oxygen content is greatly different from the sample for measurement shall not be taken as the sample for calibration, because errors may arise. Perform the operations of 9.4.6 c) and 9.4.6 d) with taking the sample for calibration. Average the values by repeating these operations several times and calculate the calibration coefficient according to the following formula:

$$K = \frac{\left(G \times \frac{P}{100}\right)}{(A_1 - A_0)} \tag{11}$$

where

K is the calibration coefficient (g/integral value);

G is the weighed amount of the sample for calibration (g);

P is the nitrogen content in the sample for calibration [% (mass fraction)];

A_1 is the integral value of the sample for calibration in 9.4.6 d);

A_0 is the integral value of the blank test in 9.4.7.

NOTE Some of commercial instruments can calculate the blank test value, the calibration coefficient, and the nitrogen content automatically.

9.4.9 Calculation

Calculate the content of total nitrogen in the sample according to the following formula:

$$T.N=\left[\frac{\left(A_2-A_0\right)\times K}{m}\right]\times 100 \tag{12}$$

where

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

A_2 is the integral value of the sample in 9.4.6 d)**;**

A_0 is the integral value of the blank test in 9.4.7**;**

K is the calibration coefficient in 9.4.8 (g/integral value);

m is the weighed amount of the sample in 9.4.5 (g).

10 Determination method of silicon

10.1 Determination method

The silicon shall be determined by using fusion–ICP-OES.

10.2 Principle

Fuse the sample with sodium carbonate, dissolve the melt in hydrochloric acid, and dilute with water to a constant volume. Spray a portion of the solution into an Ar plasma of ICP-OES and measure the emission intensity.

10.3 Reagents

Reagents shall be as follows.

10.3.1 Water, as specified in 7.2.2.1, shall be preserved in a plastic bottle.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic bottle.

10.3.2 Hydrochloric acid (1+100), prepare from hydrochloric acid.

10.3.3 Sodium hydroxide solution (200g/l), as specified in 7.2.2.5.

10.3.4 Ethanol (95), as specified in 7.2.2.6.

10.3.5 Ethanol– Sodium hydroxide (1+1) mixed solution, as specified in 7.2.2.7.

10.3.6 Sodium carbonate, anhydrous, as specified in 7.2.2.2.

10.3.7 Standard silicon solution (Si 1 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

10.3.8 Standard silicon solution (Si 50 µg/ml).

10.3.9 Sodium chloride solution (NaCl 25 g/100 ml).

10.4 Apparatus and instrument

Apparatus and instrument shall be as follows.

10.4.1 Platinum crucible, as specified in 7.2.3.1.

10.4.2 Electric furnace.

10.4.3 ICP optical emission spectrometer.

10.5 Amount of sample

The weighed amount of sample shall be 0,50 g.

10.6 Operation

The operation shall be as follows.

a) Weigh the sample into a platinum crucible (30 ml) and add 2 ml of an ethanol–sodium hydroxide (1+1) mixed solution (10.3.5).

b) Heat it on a hot plate, and then evaporate it until dry.

c) Add 2,0 g of sodium carbonate and heat initially at a low temperature. Then, elevate the temperature gradually to fuse and keep that temperature for 15 min ~ 30 min during fusion. Fuse the sample at 950 °C to 1 000 °C. Keep the temperature as low as possible.

d) Stand the crucible for cooling with a lid and place the crucible into a 200 ml beaker. Add 50 ml of water and 10 ml of hydrochloric acid (1+1) (7.2.2.3) and heat it with a watch glass on the hot plate to dissolve the melt.

e) Transfer the solution into a 100 ml plastic volumetric flask.

   NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flask.

f) Dilute with water up to the mark and mix well.

g) Spray a portion of the solution into an Ar plasma of ICP-OES and measure the emission intensity at the wavelength of 251,612 nm, for example.

10.7 Blank test

Perform the operations of 10.6 a) to 10.6 g) without taking a sample to obtain the blank test value of silicon.

10.8 Drawing calibration curves

Take 10 ml of the sodium chloride solution (10.3.9) in several 100 ml plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and add exactly 0 ml ~ 8 ml (0 mg ~ 0,4 mg) of a standard silicon solution stepwise. Add 3 ml of hydrochloric acid (1+1) (7.3.2.2) and dilute with water up to the mark. Perform the operation of 10.6 g) using these solutions and construct the relation between the emission intensity and the amount of silicon.

10.9 Calculation

Obtain the amount of silicon by 10.6 and 10.7 referring to the calibration curve drawn in 10.8 and calculate the content of silicon in the sample according to the following formula:

$$S_i = \left[\frac{(A_1 - A_0)}{m} \right] \times 100 \qquad (13)$$

where

Si is the content of silicon in the sample [% (mass fraction)];

A_1 is the amount of silicon in the sample obtained by 10.6 and 10.8 (g);

A_0 is the amount of silicon in the blank test obtained by 10.7 and 10.8 (g);

m is the weighed amount of the sample in 10.6 a) (g).

11 Determination methods of aluminium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, titanium, vanadium, and zinc

11.1 Classification of determination methods

Aluminium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, titanium, vanadium, and zinc shall be determined by using either of the following methods. Method A will give better determination sensitivities for most elements because of fewer salt concomitants.

- Method A, acid pressure decomposition–ICP-OES
- Method B, fusion–ICP-OES

11.2 Acid pressure decomposition-ICP-OES

11.2.1 Principle

Decompose the sample in a pressure decomposition vessel with an acid mixture. Evaporate the product until dry and dissolve the salt in hydrochloric acid. Dilute with water to a constant volume. Spray this solution into an Ar plasma of ICP-OES and measure the emission intensity of each element. Boron nitride can be decomposed with a variety of mixture of acids (hydrofluoric acid, sulfuric acid, nitric acid, and hydrochloric acid), however, hydrofluoric acid is indispensable. A mixture of nitric acid and hydrofluoric acid, that of hydrochloric acid and hydrofluoric acid and that of hydrofluoric acid, sulfuric acid, and nitric acid can be used. Select a suitable mixture of acids to achieve complete decomposition. For example, either a mixture of 7 ml of nitric acid (1+1) and 3 ml of hydrofluoric acid or a mixture of 10 ml of hydrofluoric acid, 5 ml of sulfuric acid (1+1), and 1 ml of nitric acid (1+1) is often used.

11.2.2 Reagents

Reagents shall be as follows. Solutions shall be preserved in plastic bottles (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). The standard solutions being SI traceable shall be used.

11.2.2.1 Water, as specified in 7.2.2.1.

11.2.2.2 Hydrofluoric acid.

11.2.2.3 Sulfuric acid (1+1).

11.2.2.4 Nitric acid (1+1).

11.2.2.5 Hydrochloric acid (1+1).

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

11.2.2.7 Ammonium sulfate solution [$(NH_4)_2SO_4$ 250 g/l], dissolve 250 g of ammonium sulfate (11.2.2.6) in 1 000 ml of water.

11.2.2.8 Standard aluminium solution (Al 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.9 Standard cadmium solution (Cd 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.10 Standard calcium solution (Ca 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.11 Standard chromium solution (Cr 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.12 Standard cobalt solution (Co 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.13 Standard copper solution (Cu 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.14 Standard iron solution (Fe 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.15 Standard lead solution (Pb 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.16 Standard magnesium solution (Mg 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.17 Standard manganese solution (Mn 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.18 Standard nickel solution (Ni 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.19 Standard titanium solution (Ti 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.20 Standard vanadium solution (V 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.21 Standard zinc solution (Zn 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.2.2.22 Mixed standard solution (each element 50 mg/l), Take and mix 5 ml each of 11.2.2.8 to 11.2.2.21 in a 100 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). Dilute with water to the mark and mix well. Attention shall be paid to whether any precipitation is not formed by the mixing. Prepare fresh immediately before use.

11.2.3 Apparatus and instrument

Apparatus and instrument shall be as follows.

11.2.3.1 Platinum crucible, as specified in 7.2.3.1.

11.2.3.2 Platinum dish, for example, 75 ml.

11.2.3.3 Pressure decomposition vessel, as specified in 9.2.3.2.

11.2.3.4 Air bath, adjustable temperature to (180 ± 5) °C.

11.2.3.5 ICP optical emission spectrometer.

11.2.4 Amount of sample

The weighed amount of sample shall be 0,2 g ~ 1,0 g.

11.2.5 Operation

The operation shall be as follows.

a) Weigh the sample in a platinum crucible (30 ml) and add up to 16 ml of a suitable mixture of acids. Put the crucible into a PTFE inner vessel and close the pressure vessel according to the manufacturer's instructions. Place the vessel in an air bath and heat at (180 ± 5) °C for 16 h.

NOTE Acid pressure decomposition under micro wave irradiation can be performed if available.

b) After cooling, disassemble the pressure vessel. Transfer the solution in the PTFE inner vessel into a platinum dish (11.2.3.2) when washing the crucible and the vessel, and then heat on a hot plate until dry. Subsequently heat the dish on a hot plate at 330 °C ~ 340 °C to remove the acids.

c) Continue heating to reach dryness. After cooling, add 5 ml of hydrochloric acid (1+1) (11.2.2.5) and 5 ml of water to dissolve the salt on a hot plate. Transfer the solution into a 50 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and dilute with water to the mark.

d) Spray a portion of the solution 11.2.5 c) into an Ar plasma of ICP-OES and measure the emission intensity at the wavelengths shown in Table 2, for example.

Table 2 — Example of analytical wavelength of each element in nm

Al: 394,401	Cd: 228,802	Ca: 317,933	Cr: 267,716
Co: 228,616	Cu: 327,396	Fe: 238,204	Pb: 220,353

Table 2 *(continued)*

Mg: 285,213	Mn: 257,610	Ni: 231,604	Ti: 334,941
V: 309,311	Zn: 206,200		

NOTE Carefully choose the optimum analytical wavelengths free from concomitants because they depend on the performance of an ICP-OES instrument. Considering spectral interference and sensitivity, choose higher order spectral lines if available.

11.2.6 Blank test

Perform the operations of 11.2.5 a) to 11.2.5 d) without taking a sample to obtain the blank test value of each element.

11.2.7 Drawing calibration curves

Take 10 ml of the ammonium sulfate solution (11.2.2.7) and 5 ml of hydrochloric acid (1+1) (11.2.2.5) in several 50 ml of plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). Add exactly 0 ml ~ 10 ml of the mixed standard solution (11.2.2.22) stepwise to each flask and dilute with water to the mark. Perform the operation of 11.2.5 d) using these solutions and establish the relation between the emission intensity and the amount of each element.

11.2.8 Calculation

Obtain the amount of each element by (11.2.5) and (11.2.6) referring to the calibration curves drawn in (11.2.7) and calculate the content of each element in the sample according to the following formula:

$$E_i = \left[\frac{(A_i - A_0)}{m} \right] \times 100 \tag{14}$$

where

E_i is the content of each element in the sample [% (mass fraction)];

A_i is the amount of each element in the sample obtained by 11.2.5 and 11.2.7 (g);

A_0 is the amount of each element in the blank test obtained by 11.2.6 and 11.2.7 (g);

m is the weighed amount of the sample in 11.2.5 a) (g).

11.3 Fusion-ICP-OES

11.3.1 Principle

Fuse the sample with sodium carbonate, dissolve the melt in hydrochloric acid and dilute to a constant volume. Spray a portion of the solution into an Ar plasma of ICP-OES and measure the emission intensity.

11.3.2 Reagents

Reagents of analytical grade shall be used. Reagent solutions shall be preserved in plastic bottles (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). The standard solutions being SI traceable shall be used.

11.3.2.1 Water, Grade 1 or superior specified in ISO 3696.

11.3.2.2 Sodium carbonate, **anhydrous**, as specified in 7.2.2.2.

11.3.2.3 Hydrochloric acid (1+1), prepare from hydrochloric acid.

11.3.2.4 Sodium hydroxide solution (200 g/l), prepare from sodium hydroxide.

11.3.2.5 Ethanol (95).

11.3.2.6 Ethanol–Sodium hydroxide (1+1) mixed solution, prepare by mixing the same volume of ethanol (95) and a sodium hydroxide solution (200 g/l).

11.3.2.7 Boric acid, as specified in 7.2.2.9

11.3.2.8 Boron solution for matrix (H_3BO_3 12,5 g/100 ml), dissolve 12,5 g of boric acid **11.3.2 g)** in 100 ml of water.

11.3.2.9 Sodium chloride, more than 99,5 % (mass fraction) of purity.

11.3.2.10 Sodium solution for matrix (NaCl 25 g/100 ml), dissolve 25 g of sodium chloride **11.3.2 i)** in 100 ml of water.

11.3.2.11 Standard aluminium solution (Al 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.12 Standard cadmium solution (Cd 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.13 Standard calcium solution (Ca 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.14 Standard chromium solution (Cr 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.15 Standard cobalt solution (Co 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.16 Standard copper solution (Cu 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.17 Standard iron solution (Fe 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.18 Standard lead solution (Pb 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.19 Standard magnesium solution (Mg 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.20 Standard manganese solution (Mn 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.21 Standard nickel solution (Ni 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.22 Standard titanium solution (Ti 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.23 Standard vanadium solution (V 1,0 mg/ml)

NOTE A commercial standard solution being SI traceable is available.

11.3.2.24 Standard zinc solution (Zn 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

11.3.2.25 Mixed standard solution (each element 50 mg/l), take 5 ml each of 11.3.2.11 to 11.3.2.24 in a 100 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and mix. Dilute with water to the mark and mix well. Attention shall be paid to whether any precipitation is not formed by the mixing. Prepare fresh immediately before use.

11.3.3 Apparatus and instrument

11.3.3.1 Platinum crucible, as specified in 7.2.3.1

11.3.3.2 Electric furnace.

11.3.3.3 ICP optical emission spectrometer.

11.3.4 Amount of sample

The weighed amount of sample shall be 0,50 g.

11.3.5 Operation

The determination operation shall be according to the following procedure.

a) Weigh the sample into a platinum crucible (30 ml) and add 2 ml of an ethanol–sodium hydroxide (1+1) mixed solution (11.3.2.6.)

b) Heat it on a hot plate, and then evaporate it until dry.

c) Add 2,0 g of sodium carbonate and heat initially at a low temperature. Then, elevate the temperature gradually to fuse by using an electric furnace or a Bunsen burner and keep that temperature for 15 min ~ 30 min during fusion.

   NOTE Fuse the sample at 950 °C to 1 000°C. Keep the temperature as low as possible.

d) Stand the crucible for cooling with a lid and place the crucible into a 200 ml beaker. Add 50 ml of water and 10 ml of hydrochloric acid (1+1) (11.3.2.3) and heat it with a watch glass on a hot plate to dissolve the melt.

e) Remove carbon dioxide in the solution by boiling or by purging nitrogen gas for 5 min with the watch glass. Cool down to room temperature and wash the watch glass with small amount of water before removing.

f) Transfer the solution into a 100 ml plastic volumetric flask and dilute with water to the mark.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available.

g) Spray a portion of the solution into an Ar plasma of ICP-OES and measure the emission intensity of each element

11.3.6 Blank test

Perform the operations of 11.3.5 a) to 11.3.5 g) without taking a sample to obtain the blank test value of each element.

11.3.7 Drawing calibration curves

Take each of 10 ml of the boron solution for matrix (11.3.2.8), 10 ml of the sodium solution for matrix (11.3.2.10) and 10 ml of hydrochloric acid (1+1) in several 100 ml plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and add exactly 0 ml ~ 8 ml (0 mg ~ 0,4 mg) of the mixed standard solution (11.3.2.25) stepwise. Perform the operation of 11.3.5 g) using these solutions and construct the relation between the emission intensity and the amount of each element.

11.3.8 Calculation

Obtain the amount of each element by 11.3.5 and 11.3.6 referring to the calibration curves drawn in 11.3.7 and calculate the content of each element in the sample according to the following formula:

$$E_i = \left[\frac{\left(A_i - A_0\right)}{m} \right] \times 100 \qquad (15)$$

where

E_i is the content of each element in the sample [% (mass fraction)];

A_i is the amount of each element in the sample obtained by 11.3.5 and 11.3.7 (g);

A_0 is the amount of each element in the blank test obtained by 11.3.6 and 11.3.7 (g);

m is the weighed amount of the sample in 11.3.5 a) (g).

12 Determination methods of sodium and potassium

12.1 Classification of determination methods

Sodium and potassium shall be determined by using any of the following methods:

- Method A, Acid pressure decomposition–AAS;
- Method B, Acid pressure decomposition–FES;
- Method C, Acid pressure decomposition–ICP-OES.

12.2 Acid pressure decomposition-AAS

12.2.1 Principle

Decompose the sample in a pressure decomposition vessel with a mixture of hydrofluoric acid, sulfuric acid, and nitric acid. Evaporate the product until dry and dissolve the salt in hydrochloric acid. Dilute with water to a constant volume. Spray the solution into an air-acetylene flame of AAS and record the absorbance of sodium or potassium.

12.2.2 Reagents

Reagents shall be as follows. Solutions shall be preserved in plastic bottles (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). The standard solutions being SI traceable shall be used.

12.2.2.1 Water, as specified in 7.2.2.1.

12.2.2.2 Hydrofluoric acid.

12.2.2.3 Sulfuric acid (1+1).

12.2.2.4 Nitric acid (1+1).

12.2.2.5 Hydrochloric acid (1+1).

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

12.2.2.7 Ammonium sulfate solution [$(NH_4)_2SO_4$ 250 g/l], dissolve 250 g of ammonium sulfate (12.2.2.6) in 1 000 ml of water.

12.2.2.8 Standard sodium solution (Na 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

12.2.2.9 Standard potassium solution (K 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

12.2.2.10 Mixed standard solution (Na and K each 50 µg/l), take and mix 5 ml each of 12.2.2.8 and 12.2.2.9 in a 100 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). Dilute with water to the mark and mix well. Prepare fresh immediately before use.

12.2.3 Apparatus and instrument

Apparatus and instrument shall be as follows.

12.2.3.1 Platinum crucible, as specified in 7.2.3.1.

12.2.3.2 Platinum dish, for example, 75 ml.

12.2.3.3 Atomic absorption spectrometer.

12.2.4 Amount of sample

The weighed amount of sample shall be 0,2 g ~ 1,0 g.

12.2.5 Operation

The operation shall be as follows.

a) Weigh the sample in a platinum crucible (30 ml) and add up to 16 ml of a suitable mixture of acids. Put the crucible into a PTFE inner vessel and close the pressure vessel according to the manufacturer's instructions. Place the vessel in an air bath and heat at (180 ± 5) °C for 16 h.

NOTE Acid pressure decomposition under micro wave irradiation can be performed if available.

b) After cooling, disassemble the pressure vessel. Transfer the solution in the PTFE inner vessel into a platinum dish (11.2.3.2) when washing the crucible and the vessel, and then heat on a hot plate until dry. Subsequently, heat the dish on a hot plate at 330 °C ~ 340 °C to remove the acids.

c) Continue heating to reach dryness. After cooling, add 5 ml of hydrochloric acid (1+1) (11.2.2.5) and 5 ml of water to dissolve the salt on a hot plate. Transfer the solution into a 50 ml plastic volumetric flask (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available) and dilute with water to the mark.

d) Spray a portion of the solution of 12.2.5 c) into an air-acetylene flame of atomic absorption spectrometer and measure the absorbance of sodium or potassium at the wavelengths of 589,0 nm or 766,5 nm, respectively.

12.2.6 Blank test

Perform the operations of 12.2.5 a) to 12.2.5 d) without taking a sample to obtain the blank test value of sodium or potassium.

12.2.7 Drawing calibration curves

Take 10 ml of the ammonium sulfate solution (12.2.2.7) and 5 ml of hydrochloric acid (1+1) (12.2.2.5) in several 50 ml of plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). Add exactly 0 ml ~ 10 ml of the mixed standard solution (12.2.2.10) stepwise to each flask and dilute with water to the mark. Perform the operation of 12.2.5 d) using these solutions and establish the relation between the absorbance and the amount of sodium or potassium.

12.2.8 Calculation

Obtain the amount of sodium or potassium by 12.2.5 and 12.2.6 referring to the calibration curves drawn in 12.2.7 and calculate the content of sodium or potassium in the sample according to the following formula:

$$E_i = \left[\frac{\left(A_i - A_0 \right)}{m} \right] \times 100 \tag{16}$$

where

E_i is the content of sodium or potassium in the sample [% (mass fraction)];

A_i is the amount of sodium or potassium in the sample obtained by 12.2.5 and 12.2.7 (g);

A_0 is the amount of sodium or potassium in the blank test obtained by 12.2.6 and 12.2.7 (g);

m is the weighed amount of the sample in 12.2.5 a) (g).

12.3 Acid pressure decomposition-FES

12.3.1 Principle

Decompose the sample in a pressure decomposition vessel with a mixture of hydrofluoric acid, sulfuric acid and nitric acid. Evaporate the product until dry and dissolve the salt in hydrochloric acid. Dilute with water to a constant volume. Spray the solution into an air-acetylene flame of FES and record the emission intensity of sodium or potassium.

12.3.2 Reagents

Reagents shall be as follows. Solutions shall be preserved in plastic bottles (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). The standard solutions being SI traceable shall be used.

12.3.2.1 Water, as specified in 7.2.2.1.

12.3.2.2 Hydrofluoric acid.

12.3.2.3 Sulfuric acid (1+1).

12.3.2.4 Nitric acid (1+1).

12.3.2.5 Hydrochloric acid (1+1).

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

12.3.2.7 Ammonium sulfate solution [$(NH_4)_2SO_4$ 250 g/l], dissolve 250 g of ammonium sulfate (12.3.2.6) in 1 000 ml of water.

12.3.2.8 Standard sodium solution (Na 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

12.3.2.9 Standard potassium solution (K 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

12.3.2.10 Mixed standard solution (Na and K each 50 µg/l), take and mix 5 ml each of 12.3.2.8 and 12.3.2.9 in a 100 ml plastic volumetric flask. Dilute with water to the mark and mix well. Prepare fresh immediately before use.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flask.

12.3.2.11 Mixed solution for adjusting wavelength (Na 5 µg/ml, K 5 µg/ml), prepare by diluting the mixed standard solution of sodium and potassium (12.3.2.10) with water by a factor of 10.

12.3.3 Apparatus and instrument

Apparatus and instrument shall be as follows.

12.3.3.1 Platinum crucible, as specified in 7.2.3.1.

12.3.3.2 Platinum dish, as 11.2.3.2.

12.3.3.3 Flame emission spectrometer

12.3.4 Amount of sample

The weighed amount of sample shall be 0,2 g ~ 1,0 g.

12.3.5 Operation

The operation shall be as follows.

a) Weigh the sample in a platinum crucible (30 ml) and add up to 16 ml of a suitable mixture of acids. Put the crucible into a PTFE inner vessel and close the pressure vessel according to the manufacturer's instructions. Place the vessel in an air bath and heat at (180 ± 5) °C for 16 h.

NOTE Acid pressure decomposition under micro wave irradiation can be performed if available.

b) After cooling, disassemble the pressure vessel. Transfer the solution in the PTFE inner vessel into a platinum dish when washing the crucible and the vessel, and then heat on a hot plate until dry. Subsequently, heat the dish on a hot plate at 330 °C ~ 340 °C to remove the acids.

c) Continue heating to reach dryness. After cooling, add 5 ml of hydrochloric acid (1+1) (12.3.2.5) and 5 ml of water to dissolve the salt on a hot plate. Transfer the solution into a 50 ml plastic volumetric flask and dilute with water to the mark.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flask.

d) Spray a portion of the mixed solution for adjusting wavelength (12.3.2.11) into an air-acetylene flame of FES. Adjust the spectrometer to give the maximum emission intensity of sodium or potassium in the vicinity of 589,0 nm or 766,5 nm, respectively. Finally, adjust the spectrometer reading to zero while spraying water.

e) Spray a portion of the solution of 12.3.5 c) into an air-acetylene flame of flame emission spectrometer and measure the absorbance of sodium or potassium at the wavelengths of 589,0 nm or 766,5 nm, respectively.

12.3.6 Blank test

Perform the operations of 12.3.5 a) to 12.3.5 e) without taking a sample to obtain the blank test value of sodium or potassium.

12.3.7 Drawing calibration curves

Take 10 ml of the ammonium sulfate solution (12.3.2.7) and 5 ml of hydrochloric acid (1+1) (12.3.2.5) in several 50 ml of plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). Add exactly 0 ml ~ 10 ml of the mixed standard solution (12.3.2.10) stepwise to each flask and dilute with water to the mark. Perform the operation of 12.3.5 e) using these solutions and establish the relation between the emission intensity and the amount of sodium or potassium.

12.3.8 Calculation

Obtain the amount of sodium or potassium by 12.3.5 and 12.3.6 referring to the calibration curves drawn in 12.3.7 and calculate the content of sodium or potassium in the sample according to the following formula:

$$E_j = \left[\frac{\left(A_j - A_0 \right)}{m} \right] \times 100 \tag{17}$$

where

E_j is the content of sodium or potassium in the sample [% (mass fraction)];

A_j is the amount of sodium or potassium in the sample obtained by 12.3.5 and 12.3.7 (g);

A_0 is the amount of sodium or potassium in the blank test obtained by 12.3.6 and 12.3.7 (g);

m is the weighed amount of the sample in 12.3.5 a) (g).

12.4 Acid pressure decomposition-ICP-OES

12.4.1 Principle

Decompose the sample in a pressure decomposition vessel with a mixture of hydrofluoric acid, sulfuric acid, and nitric acid. Evaporate the product until dry and dissolve the salt in hydrochloric acid. Dilute with water to a constant volume. Spray the solution into an Ar plasma of ICP-OES and record the emission intensity of sodium or potassium.

12.4.2 Reagents

Reagents shall be as follows. Solutions shall be preserved in plastic bottles (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). The standard solutions being SI traceable shall be used.

12.4.2.1 Water, as specified in 7.2.2.1.

12.4.2.2 Hydrofluoric acid.

12.4.2.3 Sulfuric acid (1+1).

12.4.2.4 Nitric acid (1+1).

12.4.2.5 Hydrochloric acid (1+1).

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

12.4.2.7 Ammonium sulfate solution [$(NH_4)_2SO_4$ 250 g/l], dissolve 250 g of ammonium sulfate (12.4.2.6) in 1 000 ml of water.

12.4.2.8 Standard sodium solution (Na 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

12.4.2.9 Standard potassium solution (K 1,0 mg/ml).

NOTE A commercial standard solution being SI traceable is available.

12.4.2.10 Mixed standard solution (Na and K each 50 µg/l). Take and mix 5 ml each of 12.3.2.8 and 12.3.2.9 in a 100 ml plastic volumetric flask. Dilute with water to the mark and mix well. Prepare fresh immediately before use.

NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flasks.

12.4.3 Apparatus and instrument

Apparatus and instrument shall be as follows.

12.4.3.1 Platinum crucible, as specified in 7.2.3.1.

12.4.3.2 Platinum dish, for example, 75 ml.

12.4.3.3 ICP optical emission spectrometer, as 7.3.3.8.

12.4.4 Amount of sample

The weighed amount of sample shall be 0,2 g ~ 1,0 g.

12.4.5 Operation

The operation shall be as follows.

a) Weigh the sample in a platinum crucible (30 ml) and add up to 16 ml of a suitable mixture of acids. Put the crucible into a PTFE inner vessel and close the pressure vessel according to the manufacturer's instructions. Place the vessel in an air bath and heat at (180 ± 5) °C for 16 h.

   NOTE Acid pressure decomposition under micro wave irradiation can be performed if available.

b) After cooling, disassemble the pressure vessel. Transfer the solution in the PTFE inner vessel into a platinum dish (12.4.3.2) with washing the crucible and the vessel, and then heat on a hot plate until dry. Subsequently heat the dish on a hot plate at 330 °C ~ 340 °C to remove the acids.

c) Continue heating to reach dryness. After cooling, add 5 ml of hydrochloric acid (1+1) (12.3.2.5) and 5 ml of water to dissolve the salt on a hot plate. Transfer the solution into a 50 ml plastic volumetric flask and dilute with water to the mark.

   NOTE Products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available for the plastic volumetric flask.

d) Spray a portion of the solution of 12.3.5 c) into an air-acetylene flame of flame emission spectrometer and measure the absorbance of sodium or potassium at the wavelengths of 589,0 nm or 766,5 nm, respectively.

12.4.6 Blank test

Perform the operations of 12.4.5 a) to 12.4.5 d) without taking a sample to obtain the blank test value of sodium or potassium.

12.4.7 Drawing calibration curves

Take 10 ml of the ammonium sulfate solution (12.4.2.7) and 5 ml of hydrochloric acid (1+1) (12.4.2.5) in several 50 ml of plastic volumetric flasks (products made of polyethylene, polypropylene, and tetrafluoroethylene resin are available). Add exactly 0 ml ~ 10 ml of the mixed standard solution (12.4.2.10) stepwise to each flask and dilute with water to the mark. Perform the operation of 12.4.5 d) using these solutions and establish the relation between the emission intensity and the amount of sodium or potassium.

12.4.8 Calculation

Obtain the amount of sodium or potassium by 12.4.5 and 12.4.6 referring to the calibration curves drawn in 12.4.7 and calculate the content of sodium or potassium in the sample according to the following formula:

$$E_k = \left[\frac{\left(A_k - A_0 \right)}{m} \right] \times 100 \tag{18}$$

where

E_k is the content of sodium or potassium in the sample [% (mass fraction)];

A_k is the amount of sodium or potassium in the sample obtained by 12.4.5 and 12.4.7 (g);

A_0 is the amount of sodium or potassium in the blank test obtained by 12.4.6 and 12.4.7 (g);

m is the weighed amount of the sample in 12.4.5 a) (g).

13 Determination methods of carbon

13.1 Classification of determination methods

Carbon shall be determined by any of the following methods:

- Method A, Combustion (resistance furnace)–IR absorption spectrometry;
- Method B, Combustion (RF furnace)–conductometry;
- Method C, Combustion (RF furnace)–IR absorption spectrometry;
- Method D, Combustion (resistance furnace)–coulometry;
- Method E, Combustion (resistance furnace)–gravimetry;
- Method F, Combustion (resistance furnace)–conductometry.

13.2 Combustion (resistance furnace)-IR absorption spectrometry

13.2.1 Principle

Burn the sample under oxygen flow by a resistance furnace with an accelerator. The generated carbon dioxide and carbon monoxide are analysed by an IR spectrometer.

13.2.2 Reagents

Reagents shall be as follows.

13.2.2.1 Oxygen, more than 99,9 % (volume fraction) of purity.

13.2.2.2 Accelerator, tin of powder form. Any other materials, other than tin, may be used if they are confirmed as suitable accelerators.

13.2.2.3 Calcium carbonate, more than 99,9 % (mass fraction) of purity. It shall be heated at 500 °C to 550 °C for 2 h and cooled in a desiccator.

13.2.3 Apparatus

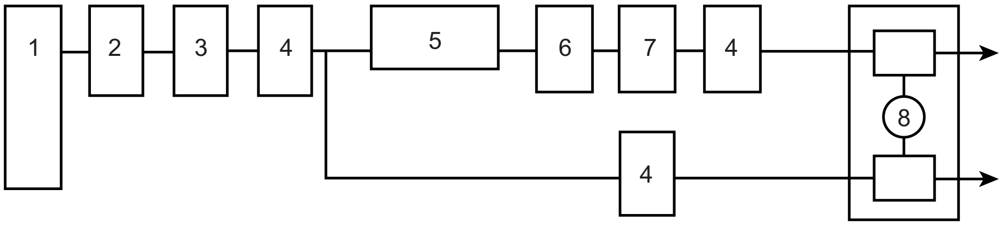
In general, apparatus shall be as follows.

13.2.3.1 Combustion tube, for example, o.d. 25 mm × i.d. 20 mm × 700 mm long.

13.2.3.2 Combustion boat, for example, o.d. 13,5 mm × i.d. 10 mm × 80 mm long.

13.2.4 Instrument

A commercial carbon analyser is available. It consists of an oxygen refiner, a furnace, a combustion gas purifier, a gas detector, etc. The block diagram is shown in Figure 6.



Key

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

Figure 6 — Block diagram of carbon analyser for combustion (resistance furnace)–IR absorption spectrometry

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

13.2.4.2 Furnace, consisting of a tubular resistance furnace, a porcelain combustion tube, etc. The tubular resistance furnace shall be capable of keeping the middle part of the combustion tube, 150 mm or longer, at 1 350°C.

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

13.2.4.4 Gas detector, consisting of an IR spectrometer for carbon dioxide and other components. The infrared spectrometer measures the difference of IR absorption between a sample cell and a reference one and converts it into the carbon content in the sample. Some instruments measure IR absorption of carbon dioxide and carbon monoxide separately and convert the sum into the carbon content.

13.2.5 Amount of sample

The weighed amount of sample shall be 0,3 g to 0,5 g.

13.2.6 Operation

The operation shall be as follows.

a) **Starting up of the instrument**. Switch on the instrument and set the controls to the specified values according to the manufacturer's instruction. Raise the temperature of combustion tube to 1 350 °C and wait until the instrument becomes stable.

NOTE The temperature of graphite crucible depends on the current or power supplied to itself. The correlation is intended be predetermined. If an apparatus has a bath metal thrower, it is preferable to throw the bath metal after degassing the graphite crucible, and then degas it. The degassing temperature is intended to be set higher than the gas extraction temperature.

b) **Mixing of the sample and accelerator**. Take the sample on the combustion boat and spread it over uniformly. Cover the sample uniformly with 2 g of tin, or sandwich the sample by 1 g each of tin.

c) **Combustion of the sample**. Open the cock at the entrance of combustion tube. Insert the boat loaded with both the sample and the accelerator to the middle of combustion tube. Close the cock immediately and flow oxygen. Read the integration meter after the specified time.

13.2.7 Blank test

Perform the operations of 13.2.6 a) to 13.2.6 c) without taking a sample to obtain the blank test value.

13.2.8 Calculation of calibration coefficient

Use 0,250 g of calcium carbonate (13.2.2.3) or 0,500 g of sample whose total carbon content is known (sample for calibration). Perform the operations of 13.2.6 b) and 13.2.6 c) and calculate the calibration coefficient by the following formulae:

a) When calcium carbonate is used,

$$K = \frac{G \times 0{,}1200}{\left(A_1 - A_0\right)} \tag{19}$$

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 calcium carbonate in 13.2.6 c);

A_0 is the integral value of the blank test in 13.2.7.

b) When sample for calibration is used,

$$K = \frac{\left[\left(G \times P\right)/100\right]}{\left(A_2 - A_0\right)} \tag{20}$$

where

K is the calibration coefficient (g/integral value);

G is the weighed amount of the sample for calibration (g);

P is the total carbon content in the sample for calibration [% (mass fraction)];

A_2 is the integral value of the sample for calibration in 13.2.6 c);

A_0 is the integral value of the blank test in 13.2.7;

13.2.9 Calculation

Calculate the content of carbon in the sample according to the following formula:

$$C = \left[\left(A_3 - A_0\right) \times \frac{K}{m}\right] \times 100 \tag{21}$$

where

C is the content of carbon in the sample [% (mass fraction)];

A_3 is the integral value of the sample in 13.2.6 c);

A_0 is the integral value of the blank test in 13.2.7;

K is the calibration coefficient in 13.2.8 (g/integral value);

m is the weighed amount of the sample in 13.2.6 b) (g);

13.3 Combustion (RF furnace)-conductometry

13.3.1 Principle

Burn the sample under oxygen flow by an RF furnace with an accelerator. The generated carbon dioxide is analysed by using a conductometric detector.

13.3.2 Reagent

Reagent shall be in accordance with 13.2.2. Copper of shot form, tungsten of shot form, or iron of chip form shall be used as an accelerator referred to the manufacturer's instruction of the instrument used.

13.3.3 Apparatus

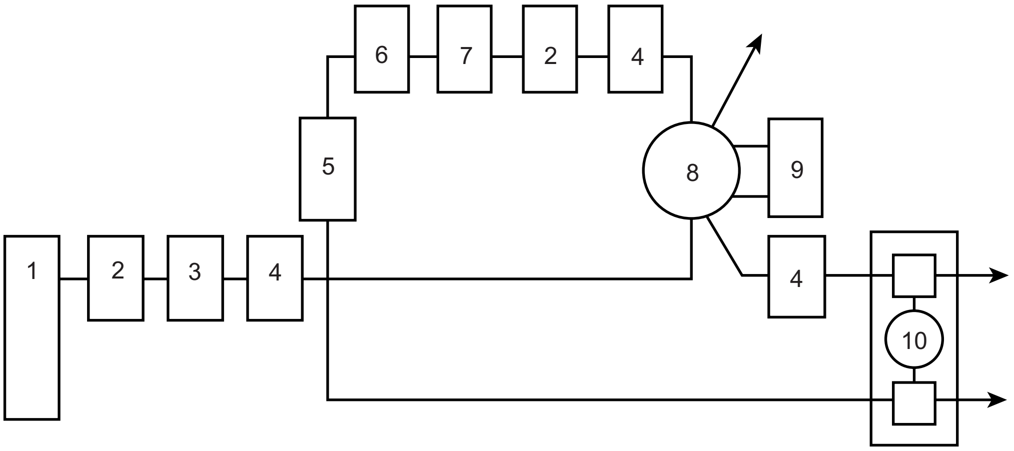
Apparatus fitting to the instrument shall be used according to the manufacturer's instruction.

13.3.3.1 RF combustion crucible, suitable for the instrument used.

13.3.3.2 Pedestal, recommended in the instruction of the instrument used.

13.3.4 Instrument

A commercial carbon analyser is available. It consists of an oxygen refiner, a furnace, a combustion gas refiner, a gas detector, etc. The block diagram is shown in Figure 7.



Key

1	oxygen bomb
2	oxidation tube with electric heater
3	carbon dioxide trap
4	dehydration tube
5	furnace
6	dust collector
7	sulfur dioxide trap
8	flow path selector
9	carbon dioxide trap
10	conductometric detector

Figure 7 — Block diagram of carbon analyser for combustion (RF furnace)–conductometry

13.3.4.1 Oxygen refiner, as specified in 13.2.4.1.

13.3.4.2 Furnace, consisting of an RF furnace, an RF transmitter, etc.

13.3.4.3 Combustion gas purifier, as specified in 13.2.4.3.

13.3.4.4 Gas detector, consisting of a flow path converter, a carbon dioxide trap (synthetic zeolite), a conductometric detector, etc.

13.3.5 Amount of sample

The weighed amount of sample shall be 0,3 g to 0,5 g.

13.3.6 Operation

The operation shall be as follows. Some instruments automatically perform the steps of c) and d) below.

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

NOTE Refer to the manufacturer's instructions for operation.

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

c) **Combustion and adsorption.** Set the crucible into the furnace and activate the instrument. The carbon dioxide generated is trapped in an absorption tube.

d) **Release and measurement.** Heat the absorption tube to release the absorbed carbon dioxide and introduce it to the detector. Read the integration meter.

13.3.7 Blank test

Perform the operations of 13.3.6 a) to 13.3.6 d) without taking a sample to obtain the blank test value.

13.3.8 Calculation of calibration coefficient

Calculation shall be in accordance with 13.2.8.

13.3.9 Calculation

Calculation shall be in accordance with 13.2.9.

13.4 Combustion (RF furnace)-IR absorption spectrometry

13.4.1 Principle

Burn the sample under oxygen flow by an RF furnace with an accelerator. The generated carbon dioxide and carbon monoxide are detected by an IR spectrometer.

13.4.2 Reagents

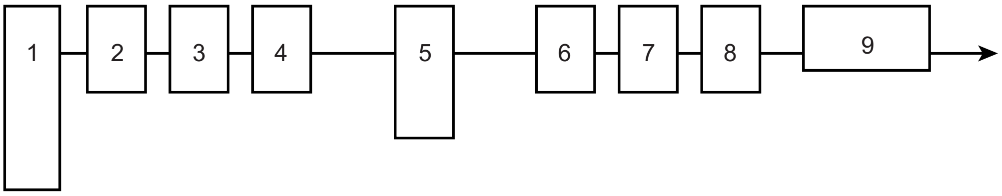
Reagent shall be in accordance with 13.2.2. Copper of shot form, tungsten of shot form or iron of chip form shall be used as an accelerator as referred to in the manufacturer's instruction of the instrument used.

13.4.3 Apparatus

Apparatus shall be in accordance with 13.3.3.

13.4.4 Instruments

Instruments shall be in accordance with 13.3.4. The block diagram is shown in Figure 8.



Key

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

Figure 8 — Block diagram of carbon analyser for combustion (RF furnace)–IR absorption spectrometry

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

13.4.4.2 Furnace, as 13.3.4.2.

13.4.4.3 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.

13.4.4.4 Gas detector, as 13.3.4.4.

13.4.5 Amount of sample

The weighed amount of sample shall be 0,3 g to 0,5 g.

13.4.6 Operation

The operation shall be as follows.

a) **Starting up of the instrument**. Switch on the instrument and set the controls to the specified values according to the manufacturer’s instruction. Wait until the instrument becomes stable.

NOTE Refer to the manufacturer’s instructions for operation.

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

c) **Measuring.** Set the crucible into the furnace and activate the instrument.

13.4.7 Blank test

Perform the operations of 13.4.6 a) to 13.4.6 c) without taking a sample to obtain the blank test value.

13.4.8 Calculation of calibration coefficient

Calculation shall be in accordance with 13.2.8.

13.4.9 Calculation

Calculation shall be in accordance with 13.2.9.

13.5 Combustion (resistance furnace)-coulometry

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

13.6 Combustion (resistance furnace)-gravimetry

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

13.7 Combustion (resistance furnace)-conductometry

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

14 Determination method of Oxygen

14.1 Determination method

Oxygen shall be determined by using inert gas fusion–IR absorption spectrometry.

14.2 Inert gas fusion-IR absorption spectrometry

14.2.1 Principle

Fuse the sample together with a flux in a graphite crucible under inert gas flow to extract oxygen from the sample. The elemental oxygen is determined using an IR spectrometer after converted into carbon monoxide or carbon dioxide.

14.2.2 Reagents

14.2.2.1 Helium, more than 99,99 % (volume fraction) of purity. Some instruments require nitrogen (more than 99,99 % (volume fraction) of purity) or argon (more than 99,99 % (volume fraction) of purity) in place of helium.

14.2.2.2 Flux, as 9.4.2.2.

14.2.2.3 Yttrium oxide, more than 99,99 % (mass fraction) of purity. It shall be heated at 1 000 °C for 2 h, and cooled in a desiccator before use.

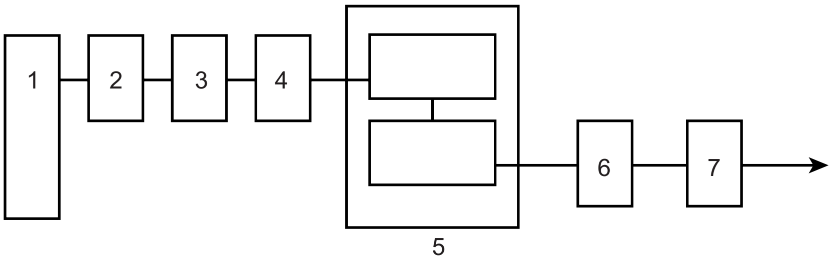
14.2.3 Apparatus

Apparatus shall be in accordance with 9.4.3.

14.2.4 Instrument

A commercial oxygen analyser is available. It consists of an inert gas refiner, a gas extractor, a gas purifier or a gas converter, a gas detector, etc. The block diagrams are shown in Figure 9 and Figure 10.

14.2.4.1 Instrument with an IR spectrometer for carbon monoxide (Figure 9)



Key

1	helium bomb
2	oxygen trap with electric heater
3	carbon dioxide trap
4	dehydration tube
5	impulse furnace
6	dust collector
7	IR spectrometer for carbon monoxide

Figure 9 — Block diagram of oxygen analyser for Inert gas fusion–IR absorption spectrometry of carbon monoxide

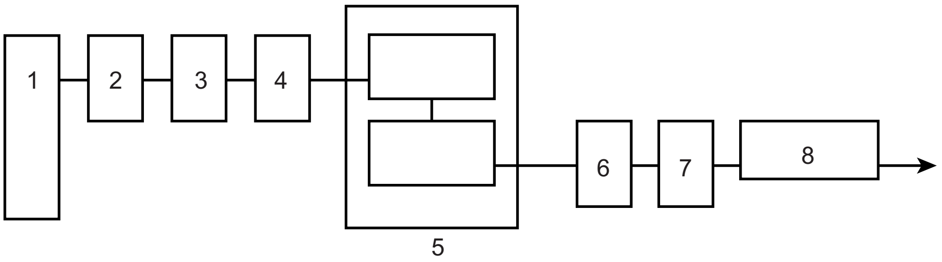
a) **Inert gas refiner**, as specified in 9.4.4.1.

b) **Gas extractor**, as specified in 9.4.4.2.

c) **Gas purifier**, consisting of a dust collecting tube (glass wool) and other components.

d) **Gas detector**, consisting of an IR spectrometer for carbon monoxide.

14.2.4.2 Instrument with an IR spectrometer for carbon dioxide (Figure 10)



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	IR spectrometer for carbon dioxide

Figure 10 — Block diagram of oxygen analyser for Inert gas fusion–IR absorption spectrometry of carbon dioxide

a) **Inert gas refiner**, as specified in 14.2.4.1 a).

b) **Gas extractor**, as specified in 14.2.4.1 b).

c) **Gas convertor**, as 14.2.4.1 c) but an oxidation tube (copper oxide) for converting carbon monoxide into carbon dioxide is added.

d) **Gas detector**, consisting of an IR spectrometer for carbon dioxide.

14.2.5 Amount of sample

The weighed amount of sample shall be 0,02 to 0,04 g.

14.2.6 Operation

Perform the operation in accordance with 9.4.6.

14.2.7 Blank test

Perform the operations of 14.2.6 without taking a sample to obtain the blank test value.

14.2.8 Calculation of calibration coefficient

Perform the operations of 14.2.6, taking 0,010 g of yttrium oxide for a calibrator. Repeat these operations 3 to 5 times and obtain an average value. Calculate the calibration coefficient by the following formula:

$$K = \frac{G \times 0{,}2126}{\left(A_1 - A_0\right)} \tag{22}$$

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 yttrium oxide;

A_0 is the integral value of the blank test in 14.2.7.

14.2.9 Calculation

Calculate the content of oxygen in the sample according to the following formula:

$$O = \left[\left(A_1 - A_0\right) \times \frac{K}{m}\right] \times 100 \tag{23}$$

where

O is the content of oxygen in the sample [% (mass fraction)];

A_1 is the integral value of the sample in 14.2.6;

A_0 is the integral value of the blank test in 14.2.7;

K is the calibration coefficient in 14.2.8 (g/integral value);

m is the weighed amount of the sample in 14.2.5 (g);

15 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 analysis;

b) the method used, by reference to this standard;

c) the results and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard or any optional operation which may have influenced the results.

Annex A
(informative)

List of commercial certified reference materials

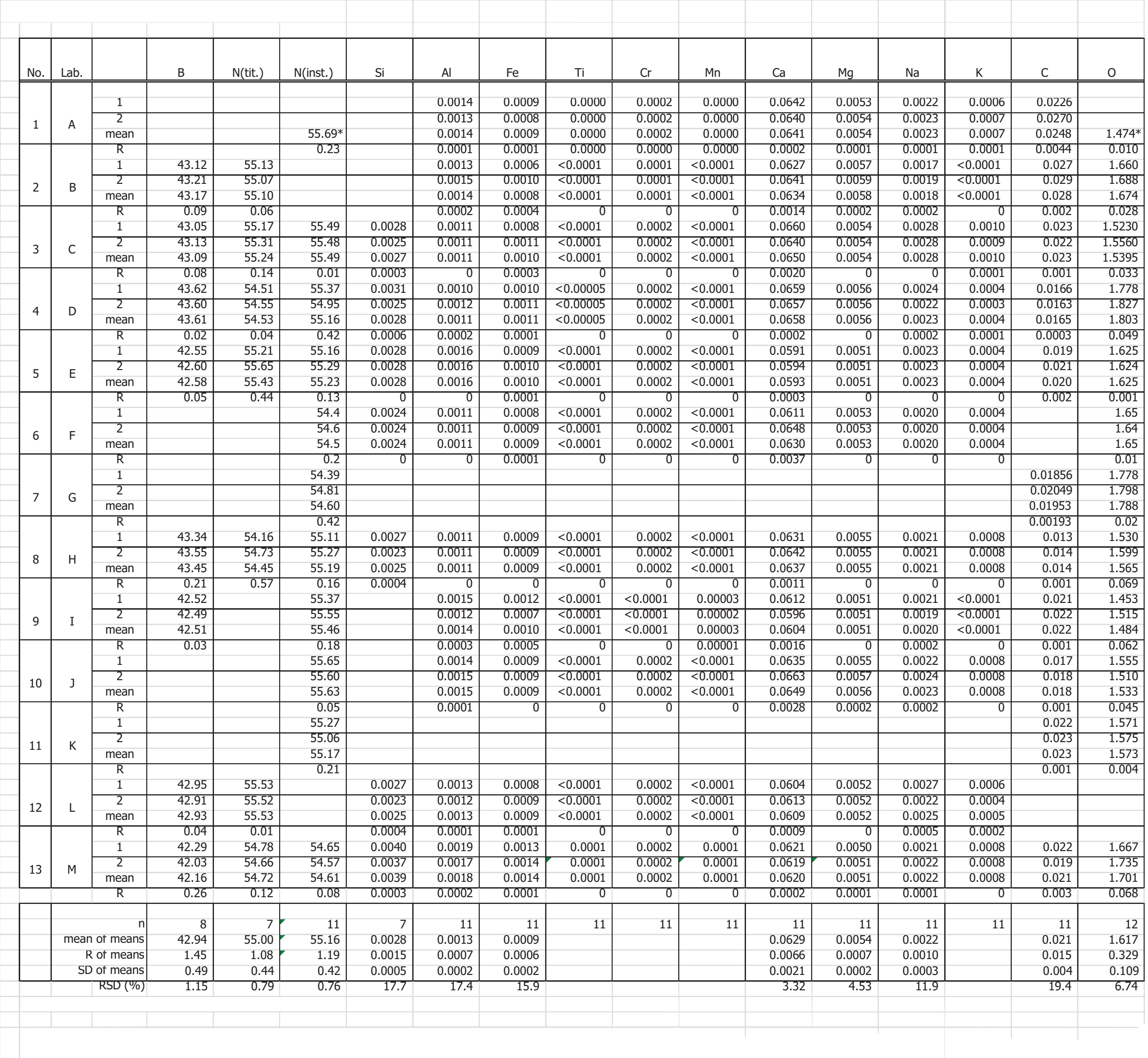
[1] ERM-ED 103 “boron nitride powder” from BAM

Annex B
(informative)

Analytical results obtained from a round robin test

A round robin test was carried out to establish “JCRS 108: Methods for chemical analysis of boron nitride powders for fine ceramics” from The Ceramic Society of Japan. Thirteen laboratories participated in the test and three BN samples (referred to BN1, BN2, and BN3) were analysed. Analytical results obtained from the test are given in Table B.1 to Table B.4.

Table B.1 — Analytical results of BN3-1 sample for major and minor elements in mass fraction (%)



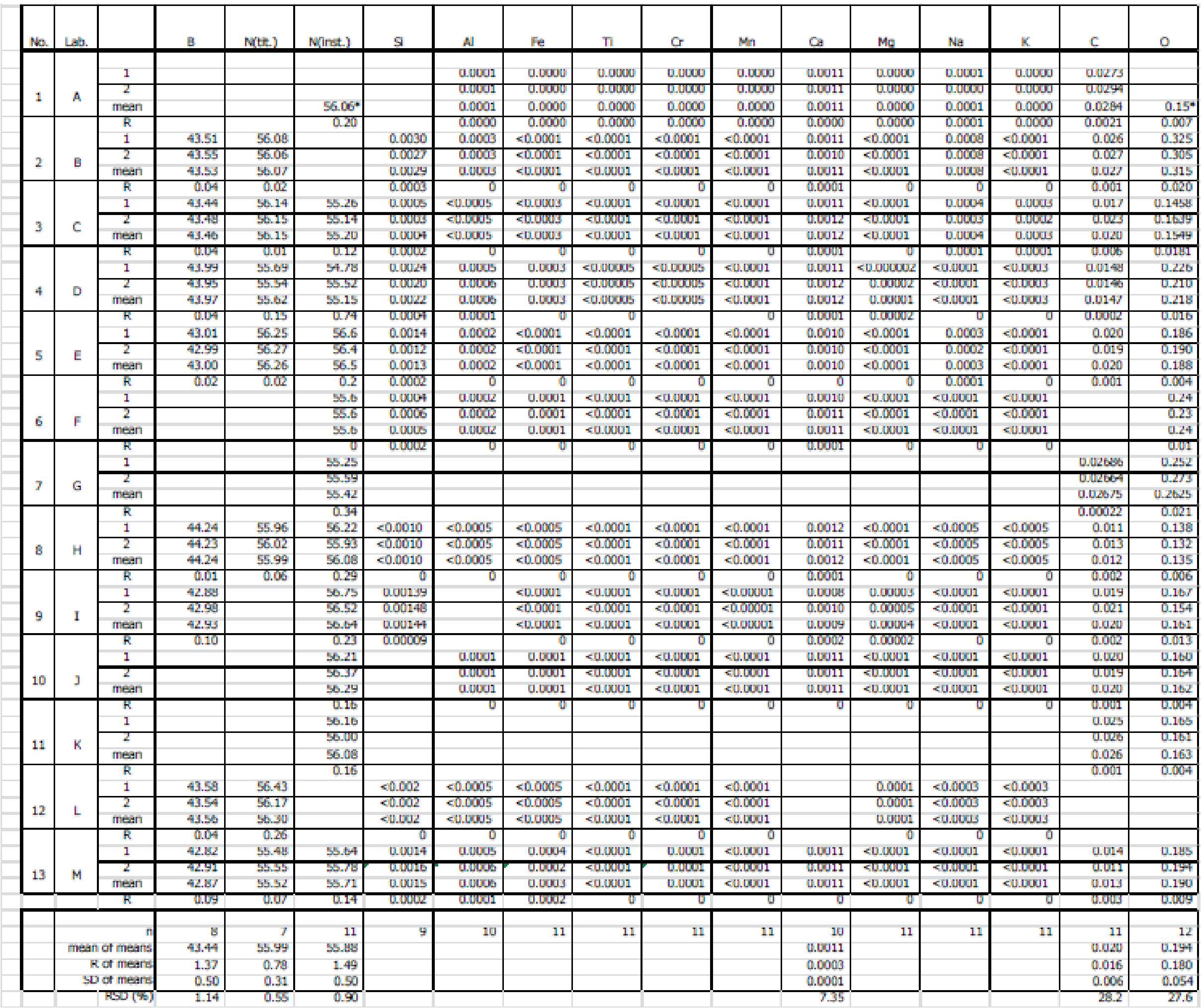
No.	Lab.		B	N(tit.)	N(inst.)	Si	Al	Fe	Ti	Cr	Mn	Ca	Mg	Na	K	C	O
1	A	1					0.0014	0.0009	0.0000	0.0002	0.0000	0.0642	0.0053	0.0022	0.0006	0.0226	
		2					0.0013	0.0008	0.0000	0.0002	0.0000	0.0640	0.0054	0.0023	0.0007	0.0270	
		mean			55.69*		0.0014	0.0009	0.0000	0.0002	0.0000	0.0641	0.0054	0.0023	0.0007	0.0248	1.474*
		R			0.23		0.0001	0.0001	0.0000	0.0000	0.0000	0.0002	0.0001	0.0001	0.0001	0.0044	0.010
2	B	1	43.12	55.13			0.0013	0.0006	<0.0001	0.0001	<0.0001	0.0627	0.0057	0.0017	<0.0001	0.027	1.660
		2	43.21	55.07			0.0015	0.0010	<0.0001	0.0001	<0.0001	0.0641	0.0059	0.0019	<0.0001	0.029	1.688
		mean	43.17	55.10			0.0014	0.0008	<0.0001	0.0001	<0.0001	0.0634	0.0058	0.0018	<0.0001	0.028	1.674
		R	0.09	0.06			0.0002	0.0004	0	0	0	0.0014	0.0002	0.0002	0	0.002	0.028
3	C	1	43.05	55.17	55.49	0.0028	0.0011	0.0008	<0.0001	0.0002	<0.0001	0.0660	0.0054	0.0028	0.0010	0.023	1.5230
		2	43.13	55.31	55.48	0.0025	0.0011	0.0011	<0.0001	0.0002	<0.0001	0.0640	0.0054	0.0028	0.0009	0.022	1.5560
		mean	43.09	55.24	55.49	0.0027	0.0011	0.0010	<0.0001	0.0002	<0.0001	0.0650	0.0054	0.0028	0.0010	0.023	1.5395
		R	0.08	0.14	0.01	0.0003	0	0.0003	0	0	0	0.0020	0	0	0.0001	0.001	0.033
4	D	1	43.62	54.51	55.37	0.0031	0.0010	0.0010	<0.00005	0.0002	<0.0001	0.0659	0.0056	0.0024	0.0004	0.0166	1.778
		2	43.60	54.55	54.95	0.0025	0.0012	0.0011	<0.00005	0.0002	<0.0001	0.0657	0.0056	0.0022	0.0003	0.0163	1.827
		mean	43.61	54.53	55.16	0.0028	0.0011	0.0011	<0.00005	0.0002	<0.0001	0.0658	0.0056	0.0023	0.0004	0.0165	1.803
		R	0.02	0.04	0.42	0.0006	0.0002	0.0001	0	0	0	0.0002	0	0.0002	0.0001	0.0003	0.049
5	E	1	42.55	55.21	55.16	0.0028	0.0016	0.0009	<0.0001	0.0002	<0.0001	0.0591	0.0051	0.0023	0.0004	0.019	1.625
		2	42.60	55.65	55.29	0.0028	0.0016	0.0010	<0.0001	0.0002	<0.0001	0.0594	0.0051	0.0023	0.0004	0.021	1.624
		mean	42.58	55.43	55.23	0.0028	0.0016	0.0010	<0.0001	0.0002	<0.0001	0.0593	0.0051	0.0023	0.0004	0.020	1.625
		R	0.05	0.44	0.13	0	0	0.0001	0	0	0	0.0003	0	0	0	0.002	0.001
6	F	1			54.4	0.0024	0.0011	0.0008	<0.0001	0.0002	<0.0001	0.0611	0.0053	0.0020	0.0004		1.65
		2			54.6	0.0024	0.0011	0.0009	<0.0001	0.0002	<0.0001	0.0648	0.0053	0.0020	0.0004		1.64
		mean			54.5	0.0024	0.0011	0.0009	<0.0001	0.0002	<0.0001	0.0630	0.0053	0.0020	0.0004		1.65
		R			0.2	0	0	0.0001	0	0	0	0.0037	0	0	0		0.01
7	G	1			54.39											0.01856	1.778
		2			54.81											0.02049	1.798
		mean			54.60											0.01953	1.788
		R			0.42											0.00193	0.02
8	H	1	43.34	54.16	55.11	0.0027	0.0011	0.0009	<0.0001	0.0002	<0.0001	0.0631	0.0055	0.0021	0.0008	0.013	1.530
		2	43.55	54.73	55.27	0.0023	0.0011	0.0009	<0.0001	0.0002	<0.0001	0.0642	0.0055	0.0021	0.0008	0.014	1.599
		mean	43.45	54.45	55.19	0.0025	0.0011	0.0009	<0.0001	0.0002	<0.0001	0.0637	0.0055	0.0021	0.0008	0.014	1.565
		R	0.21	0.57	0.16	0.0004	0	0	0	0	0	0.0011	0	0	0	0.001	0.069
9	I	1	42.52		55.37		0.0015	0.0012	<0.0001	<0.0001	0.00003	0.0612	0.0051	0.0021	<0.0001	0.021	1.453
		2	42.49		55.55		0.0012	0.0007	<0.0001	<0.0001	0.00002	0.0596	0.0051	0.0019	<0.0001	0.022	1.515
		mean	42.51		55.46		0.0014	0.0010	<0.0001	<0.0001	0.00003	0.0604	0.0051	0.0020	<0.0001	0.022	1.484
		R	0.03		0.18		0.0003	0.0005	0	0	0.00001	0.0016	0	0.0002	0	0.001	0.062
10	J	1			55.65		0.0014	0.0009	<0.0001	0.0002	<0.0001	0.0635	0.0055	0.0022	0.0008	0.017	1.555
		2			55.60		0.0015	0.0009	<0.0001	0.0002	<0.0001	0.0663	0.0057	0.0024	0.0008	0.018	1.510
		mean			55.63		0.0015	0.0009	<0.0001	0.0002	<0.0001	0.0649	0.0056	0.0023	0.0008	0.018	1.533
		R			0.05		0.0001	0	0	0	0	0.0028	0.0002	0.0002	0	0.001	0.045
11	K	1			55.27											0.022	1.571
		2			55.06											0.023	1.575
		mean			55.17											0.023	1.573
		R			0.21											0.001	0.004
12	L	1	42.95	55.53		0.0027	0.0013	0.0008	<0.0001	0.0002	<0.0001	0.0604	0.0052	0.0027	0.0006		
		2	42.91	55.52		0.0023	0.0012	0.0009	<0.0001	0.0002	<0.0001	0.0613	0.0052	0.0022	0.0004		
		mean	42.93	55.53		0.0025	0.0013	0.0009	<0.0001	0.0002	<0.0001	0.0609	0.0052	0.0025	0.0005		
		R	0.04	0.01		0.0004	0.0001	0.0001	0	0	0	0.0009	0	0.0005	0.0002		
13	M	1	42.29	54.78	54.65	0.0040	0.0019	0.0013	0.0001	0.0002	0.0001	0.0621	0.0050	0.0021	0.0008	0.022	1.667
		2	42.03	54.66	54.57	0.0037	0.0017	0.0014	0.0001	0.0002	0.0001	0.0619	0.0051	0.0022	0.0008	0.019	1.735
		mean	42.16	54.72	54.61	0.0039	0.0018	0.0014	0.0001	0.0002	0.0001	0.0620	0.0051	0.0022	0.0008	0.021	1.701
		R	0.26	0.12	0.08	0.0003	0.0002	0.0001	0	0	0	0.0002	0.0001	0.0001	0	0.003	0.068
		n	8	7	11	7	11	11	11	11	11	11	11	11	11	11	12
		mean of means	42.94	55.00	55.16	0.0028	0.0013	0.0009				0.0629	0.0054	0.0022		0.021	1.617
		R of means	1.45	1.08	1.19	0.0015	0.0007	0.0006				0.0066	0.0007	0.0010		0.015	0.329
		SD of means	0.49	0.44	0.42	0.0005	0.0002	0.0002				0.0021	0.0002	0.0003		0.004	0.109
		RSD (%)	1.15	0.79	0.76	17.7	17.4	15.9				3.32	4.53	11.9		19.4	6.74

NOTE 1 Values with * were calculated from five determinations.

NOTE 2 N(tit.): Acid pressure decomposition — distillation separation — acidimetric method for nitrogen

NOTE 3 N(inst.): Inert gas fusion — thermal conductivity method for total nitrogen (instrumental)

Table B.2 — Analytical results of BN3-2 sample for major and minor elements in mass fraction (%)



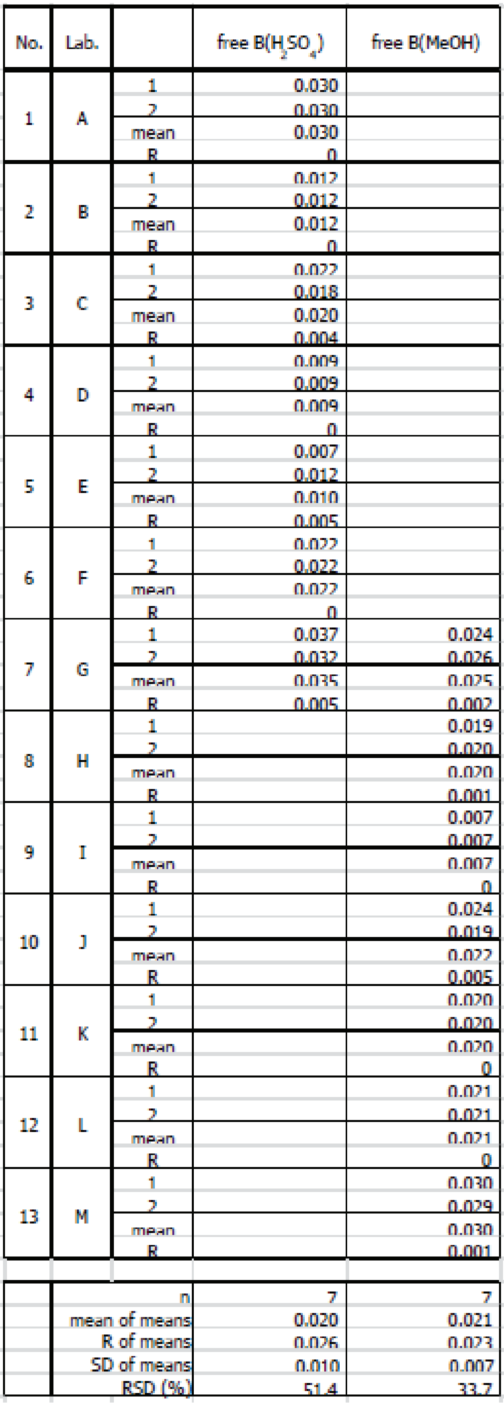
No.	Lab.		B	N(tit.)	N(inst.)	Si	Al	Fe	Ti	Cr	Mn	Ca	Mg	Na	K	C	O
1	A	1					0.0001	0.0000	0.0000	0.0000	0.0000	0.0011	0.0000	0.0001	0.0000	0.0273	
		2					0.0001	0.0000	0.0000	0.0000	0.0000	0.0011	0.0000	0.0000	0.0000	0.0294	
		mean			56.06*		0.0001	0.0000	0.0000	0.0000	0.0000	0.0011	0.0000	0.0001	0.0000	0.0284	0.15*
		R			0.20		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0021	0.007
2	B	1	43.51	56.08		0.0030	0.0003	<0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	0.0008	<0.0001	0.026	0.325
		2	43.55	56.06		0.0027	0.0003	<0.0001	<0.0001	<0.0001	<0.0001	0.0010	<0.0001	0.0008	<0.0001	0.027	0.305
		mean	43.53	56.07		0.0029	0.0003	<0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	0.0008	<0.0001	0.027	0.315
		R	0.04	0.02		0.0003	0	0	0	0	0	0.0001	0	0	0	0.001	0.020
3	C	1	43.44	56.14	55.26	0.0005	<0.0005	<0.0003	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	0.0004	0.0003	0.017	0.1458
		2	43.48	56.15	55.14	0.0003	<0.0005	<0.0003	<0.0001	<0.0001	<0.0001	0.0012	<0.0001	0.0003	0.0002	0.023	0.1639
		mean	43.46	56.15	55.20	0.0004	<0.0005	<0.0003	<0.0001	<0.0001	<0.0001	0.0012	<0.0001	0.0004	0.0003	0.020	0.1549
		R	0.04	0.01	0.12	0.0002	0	0	0	0	0	0.0001	0	0.0001	0.0001	0.006	0.0181
4	D	1	43.99	55.69	54.78	0.0024	0.0005	0.0003	<0.00005	<0.00005	<0.0001	0.0011	<0.000002	<0.0001	<0.0003	0.0148	0.226
		2	43.95	55.54	55.52	0.0020	0.0006	0.0003	<0.00005	<0.00005	<0.0001	0.0012	0.00002	<0.0001	<0.0003	0.0146	0.210
		mean	43.97	55.62	55.15	0.0022	0.0006	0.0003	<0.00005	<0.00005	<0.0001	0.0012	0.00001	<0.0001	<0.0003	0.0147	0.218
		R	0.04	0.15	0.74	0.0004	0.0001	0	0		0	0.0001	0.00002	0	0	0.0002	0.016
5	E	1	43.01	56.25	56.6	0.0014	0.0002	<0.0001	<0.0001	<0.0001	<0.0001	0.0010	<0.0001	0.0003	<0.0001	0.020	0.186
		2	42.99	56.27	56.4	0.0012	0.0002	<0.0001	<0.0001	<0.0001	<0.0001	0.0010	<0.0001	0.0002	<0.0001	0.019	0.190
		mean	43.00	56.26	56.5	0.0013	0.0002	<0.0001	<0.0001	<0.0001	<0.0001	0.0010	<0.0001	0.0003	<0.0001	0.020	0.188
		R	0.02	0.02	0.2	0.0002	0	0	0	0	0	0	0	0.0001	0	0.001	0.004
6	F	1			55.6	0.0004	0.0002	0.0001	<0.0001	<0.0001	<0.0001	0.0010	<0.0001	<0.0001	<0.0001		0.24
		2			55.6	0.0006	0.0002	0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001		0.23
		mean			55.6	0.0005	0.0002	0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001		0.24
		R			0	0.0002	0	0	0	0	0	0.0001	0	0	0		0.01
7	G	1			55.25											0.02686	0.252
		2			55.59											0.02664	0.273
		mean			55.42											0.02675	0.2625
		R			0.34											0.00022	0.021
8	H	1	44.24	55.96	56.22	<0.0010	<0.0005	<0.0005	<0.0001	<0.0001	<0.0001	0.0012	<0.0001	<0.0005	<0.0005	0.011	0.138
		2	44.23	56.02	55.93	<0.0010	<0.0005	<0.0005	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0005	<0.0005	0.013	0.132
		mean	44.24	55.99	56.08	<0.0010	<0.0005	<0.0005	<0.0001	<0.0001	<0.0001	0.0012	<0.0001	<0.0005	<0.0005	0.012	0.135
		R	0.01	0.06	0.29	0	0	0	0	0	0	0.0001	0	0	0	0.002	0.006
9	I	1	42.88		56.75	0.00139		<0.0001	<0.0001	<0.0001	<0.00001	0.0008	0.00003	<0.0001	<0.0001	0.019	0.167
		2	42.98		56.52	0.00148		<0.0001	<0.0001	<0.0001	<0.00001	0.0010	0.00005	<0.0001	<0.0001	0.021	0.154
		mean	42.93		56.64	0.00144		<0.0001	<0.0001	<0.0001	<0.00001	0.0009	0.00004	<0.0001	<0.0001	0.020	0.161
		R	0.10		0.23	0.00009		0	0	0	0	0.0002	0.00002	0	0	0.002	0.013
10	J	1			56.21		0.0001	0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	0.020	0.160
		2			56.37		0.0001	0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	0.019	0.164
		mean			56.29		0.0001	0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	0.020	0.162
		R			0.16		0	0	0	0	0	0	0	0	0	0.001	0.004
11	K	1			56.16											0.025	0.165
		2			56.00											0.026	0.161
		mean			56.08											0.026	0.163
		R			0.16											0.001	0.004
12	L	1	43.58	56.43		<0.002	<0.0005	<0.0005	<0.0001	<0.0001	<0.0001		0.0001	<0.0003	<0.0003		
		2	43.54	56.17		<0.002	<0.0005	<0.0005	<0.0001	<0.0001	<0.0001		0.0001	<0.0003	<0.0003		
		mean	43.56	56.30		<0.002	<0.0005	<0.0005	<0.0001	<0.0001	<0.0001		0.0001	<0.0003	<0.0003		
		R	0.04	0.26		0	0	0	0	0	0		0	0	0		
13	M	1	42.82	55.48	55.64	0.0014	0.0005	0.0004	<0.0001	0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	0.014	0.185
		2	42.91	55.55	55.78	0.0016	0.0006	0.0002	<0.0001	0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	0.011	0.194
		mean	42.87	55.52	55.71	0.0015	0.0006	0.0003	<0.0001	0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	0.013	0.190
		R	0.09	0.07	0.14	0.0002	0.0001	0.0002	0	0	0	0	0	0	0	0.003	0.009
		n	8	7	11	9	10	11	11	11	11	10	11	11	11	11	12
		mean of means	43.44	55.99	55.88							0.0011				0.020	0.194
		R of means	1.37	0.78	1.49							0.0003				0.016	0.180
		SD of means	0.50	0.31	0.50							0.0001				0.006	0.054
		RSD (%)	1.14	0.55	0.90							7.35				28.2	27.6

NOTE 1 Values with * were calculated from five determinations.

NOTE 2 N(tit.): Acid pressure decomposition — distillation separation — acidimetric method for nitrogen

NOTE 3 N(inst.): Inert gas fusion — thermal conductivity method for total nitrogen (instrumental)

Table B.3 — Analytical results of BN1 sample for free B (B_2O_3) of two different methods in mass fraction (%)

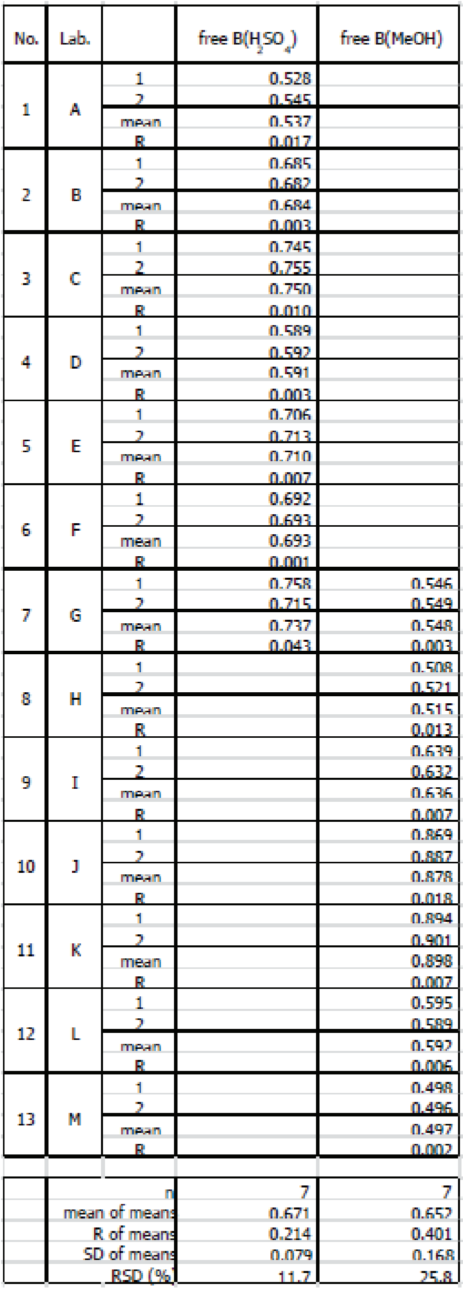


No.	Lab.		free B(H_2SO_4)	free B(MeOH)
1	A	1	0.030	
		2	0.030	
		mean	0.030	
		R	0	
2	B	1	0.012	
		2	0.012	
		mean	0.012	
		R	0	
3	C	1	0.022	
		2	0.018	
		mean	0.020	
		R	0.004	
4	D	1	0.009	
		2	0.009	
		mean	0.009	
		R	0	
5	E	1	0.007	
		2	0.012	
		mean	0.010	
		R	0.005	
6	F	1	0.022	
		2	0.022	
		mean	0.022	
		R	0	
7	G	1	0.037	0.024
		2	0.032	0.026
		mean	0.035	0.025
		R	0.005	0.002
8	H	1		0.019
		2		0.020
		mean		0.020
		R		0.001
9	I	1		0.007
		2		0.007
		mean		0.007
		R		0
10	J	1		0.024
		2		0.019
		mean		0.022
		R		0.005
11	K	1		0.020
		2		0.020
		mean		0.020
		R		0
12	L	1		0.021
		2		0.021
		mean		0.021
		R		0
13	M	1		0.030
		2		0.029
		mean		0.030
		R		0.001
		n	7	7
		mean of means	0.020	0.021
		R of means	0.026	0.023
		SD of means	0.010	0.007
		RSD (%)	51.4	33.7

NOTE 1 Free $B(H_2SO_4)$: Sulfuric acid digestion — ICP-OES and spectrophotometry

NOTE 2 Free B(MeOH): Methanol extraction — boratE separation — ICP-OES and spectrophotometry

Table B.4 — Analytical results of BN2 sample for free B (B_2O_3) of two different methods in mass fraction (%)



No.	Lab.		free B(H_2SO_4)	free B(MeOH)
1	A	1	0.528	
		2	0.545	
		mean	0.537	
		R	0.017	
2	B	1	0.685	
		2	0.682	
		mean	0.684	
		R	0.003	
3	C	1	0.745	
		2	0.755	
		mean	0.750	
		R	0.010	
4	D	1	0.589	
		2	0.592	
		mean	0.591	
		R	0.003	
5	E	1	0.706	
		2	0.713	
		mean	0.710	
		R	0.007	
6	F	1	0.692	
		2	0.693	
		mean	0.693	
		R	0.001	
7	G	1	0.758	0.546
		2	0.715	0.549
		mean	0.737	0.548
		R	0.043	0.003
8	H	1		0.508
		2		0.521
		mean		0.515
		R		0.013
9	I	1		0.639
		2		0.632
		mean		0.636
		R		0.007
10	J	1		0.869
		2		0.887
		mean		0.878
		R		0.018
11	K	1		0.894
		2		0.901
		mean		0.898
		R		0.007
12	L	1		0.595
		2		0.589
		mean		0.592
		R		0.006
13	M	1		0.498
		2		0.496
		mean		0.497
		R		0.002
	n		7	7
	mean of means		0.671	0.652
	R of means		0.214	0.401
	SD of means		0.079	0.168
	RSD (%)		11.7	25.8

NOTE 1 Free $B(H_2SO_4)$: Sulfuric acid digestion — ICP-OES and spectrophotometry

NOTE 2 Free B(MeOH): Methanol extraction — boratE separation — ICP-OES and spectrophotometry

Annex C
(informative)

Spectral lines for ICP-OES

Adjust the optics and operating conditions of the ICP-OES in accordance with the manufacturer's instructions and choose appropriate wavelength of each element considering spectral interferences and analytical sensitivities. The examples are listed below.

Al; I 394,401 nm

Cd; I 228,802 nm

Ca; II 317,933 nm

Cr; II 267,716 nm*

Co; II 228,616 nm

Cu; I 327,396 nm

Fe; II 238,204 nm*

K; I 766,490 nm

Pb; II 220,353 nm

Mg; II 285,213 nm

Mn; II 257,610 nm

Na; I 589,592 nm

Ni; II 231,604 nm

Si; I 251,612 nm

Ti; II 334,941 nm

V; II 309,311 nm

Zn; II 260,200 nm

*Fe II 238,204 nm and Cr II 267,716 nm will be interfered by platinum. Use another line such as Fe II 259,940 nm and Cr II 283,563 nm if samples were decomposed by fusion method in a platinum crucible or a platinum dish.

Bibliography

[1] ISO 31-0, *Quantities and units — Part 0: General principles*

[2] ISO 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

[3] ISO 836, *Terminology for refractories*

[4] ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

[5] ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

[6] ISO 3819, *Laboratory glassware — Beakers*

[7] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[8] ISO 5725-6, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

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

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

[11] ISO 6955, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary*

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

[13] ISO 10058-1:2008, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and determination of gravimetric silica*

[14] ISO 10058-3, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 3: Flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES)*

[15] ISO 21068-1:2008, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 1: General information and sample preparation*

[16] 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*

[17] ISO 21079-3, *Chemical analysis of refractories containing alumina, zirconia and silica - Refractories containing 5 % to 45 % of ZrO2 (alternative to the X-ray fluorescence method) - Part 3: Flame atomic absorption spectrometry (FAAS) and inductively coupled plasma emission spectrometry (ICP-AES)*

[18] ISO 21587-1, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and gravimetric silica*

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

[20] 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*

[21] 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*

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

[23] JCRS 108, *Methods for chemical analysis of boron nitrides powders for fine ceramics (The Ceramic Society of Japan, 2005)*

[24] Herman Blumenthal. *Determination of boron in metal borides*. *Anal. Chem.* 1951, **23** pp. 992–994

[25] Hisashi Morikawa, Yoshinori Uwamino, Yasuo Iida, Akira Tsuge, Toshio Ishizuka, Bunseki Kagaku. *Determination of impurities in boron nitride by ICP-AES*. 1988, **37** pp. T218–T221

[26] G.F. Telegin, G.Ya. Chapyshev, N.N. Shilkina, Russ. *Analysis of boron nitride by flame spectrometry*. *J. Anal. Chem.* 1989, **44** pp. 1510–1513

[27] Bennett H., & Reed R.A. *Chemical Methods of Silicate Analysis*. Chapter 20. Academic Press, London, New York, 1971

ICS 81.060.30

Price based on 60 pages

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards-based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

...making excellence a habit.™