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Fine ceramics (advanced ceramics, advanced technical ceramics) — Methods for chemical analysis of high purity barium titanate powders

Céramiques techniques — Méthodes d'analyse chimique des poudres de titanate de baryum à haute pureté

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Foreword

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

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This document was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Methods for chemical analysis of high purity barium titanate powders

1 Scope

This document specifies methods for the chemical analysis of fine high purity barium titanate powders used as the raw material for fine ceramics.

This document stipulates the determination methods of the barium, titanium, aluminium, cadmium, calcium, cobalt, dysprosium, iron, lead, magnesium, manganese, nickel, niobium, potassium, silicon, sodium, strontium, vanadium, zirconium, carbon, oxygen and nitrogen contents in high purity barium titanate powders. The barium and titanium contents, the major elements, are determined by using an acid decomposition-gravimetric method or an acid decomposition-inductively coupled plasma-optical emission spectrometry (ICP-OES) method. The aluminium, cadmium, calcium, chromium, cobalt, dysprosium, iron, lead, magnesium, manganese, nickel, niobium, potassium, silicon, strontium, vanadium and zirconium contents are simultaneously determined via an acid digestion-ICP-OES method. The nitrogen content is determined by using an inert gas fusion-thermal conductivity method, while that of oxygen is determined via an inert gas fusion-IR absorption spectrometry method. Finally, the carbon content is determined using a combustion-IR absorption spectrometry method or a combustion-conductometry method.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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

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

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Analytes and ranges

a) Barium (Ba), range of 40 % to 60 % (mass fraction).

b) Titanium (Ti), range of 10 % to 30 % (mass fraction).

c) Aluminium (Al), range of 0,001 % to 0,03 % (mass fraction).

d) Cadmium (Cd), range of 0,001 % to 0,03 % (mass fraction).

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

f) Cobalt (Co), range of 0,001 % to 0,03 % (mass fraction).

g) Dysprosium (Dy), range of 0,001 % to 0,03 % (mass fraction).

h) Iron (Fe), range of 0,001 % to 0,03 % (mass fraction).

i) Lead (Pb), range of 0,001 % to 0,03 % (mass fraction).

j) Magnesium (Mg), range of 0,001 % to 0,03 % (mass fraction).

k) Manganese (Mn), range of 0,001 % to 0,03 % (mass fraction).

l) Nickel (Ni), range of 0,001 % to 0,03 % (mass fraction).

m) Niobium (Nb), range of 0,001 % to 0,03 % (mass fraction).

n) Potassium (K), range of 0,001 % to 0,03 % (mass fraction).

o) Silicon (Si), range of 0,001 % to 0,03 % (mass fraction).

p) Sodium (Na), range of 0,001 % to 0,03 % (mass fraction).

q) Strontium (Sr), range of 0,001 % to 0,03 % (mass fraction).

r) Vanadium (V), range of 0,001 % to 0,03 % (mass fraction).

s) Zirconium (Zr), range of 0,001 % to 0,03 % (mass fraction).

t) Total nitrogen (T.N), range of 0,01 % to 5 % (mass fraction).

u) Oxygen (O), range of 10 % to 30 % (mass fraction).

v) Carbon (C), range of 0,01 % to 5 % (mass fraction).

5 Preparation of test sample

5.1 General

The sample preparation method shall be in accordance with ISO 8656-1, unless otherwise mutually agreed upon by the analyser and customer.

5.2 Sampling

The sample shall be collected in accordance with ISO 8656-1.

5.3 Drying

Place a 10 g sample into a flat-type weighing bottle (60 mm × 30 mm) and spread it uniformly over the bottom of the bottle. Place the bottle in an air bath at 110 °C ± 5 °C for 2 h, uncovered, and cool in a desiccator (desiccant: magnesium perchlorate), covered, for 1 h.

5.4 Weighing

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

6 Reporting the 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 the analytical values

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

6.4 Expression of the analytical values

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

a) Barium, titanium, oxygen, and nitrogen: express the results to two decimal places.

b) Others: express the results to three decimal places.

Table 1 — Tolerances for the analytical values

Units: % (mass fraction)

Element	Ba	Ti	Al, Cd, Ca, Co, Dy, Fe, Pb, Mg, Mn, Ni, Nb, K, Si, Na, Sr, V, Zr,	Total N	O	C
Tolerance	0,30[a] 0,40[b]	0,20[a] 0,30 [b]	0,001[c] 0,005[d]	0,01[e] 0,05[f]	0,50	0,005

[a] Acid decomposition-gravimetric method.

[b] Acid decomposition-ICP-OES method.

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

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

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

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

7 Determination of the barium and titanium contents

7.1 Classification of the determination methods

The barium and titanium contents shall be determined by either of the following methods:

— Method A, acid decomposition-gravimetric method;

— Method B, acid decomposition-ICP-OES method.

If analytical results with four significant figures are required, use method A; if two or three significant figures are required, method B can be used.

7.2 Acid decomposition-gravimetric method

7.2.1 Principle

A portion of the sample is decomposed using hydrogen peroxide and hydrochloric acid. The barium present in the test solution is analysed by gravimetric analysis using sulfuric acid. The titanium in the test solution is analysed by gravimetric analysis using ammonia solution.

7.2.2 Reagents

During the analysis, unless otherwise stated, only reagents of recognized analytical grade and only distilled water or water of equivalent purity shall be used.

Reagents shall conform to the requirements of ISO 6353-1, ISO 6353-2 and ISO 6353-3 as appropriate. Specific requirements for the reagents are given in the appropriate clause.

7.2.2.1 Ammonia water (NH_3), (ISO 6353-2, R 3), 25 % (mass fraction).

7.2.2.2 Hydrogen peroxide (H_2O_2), (ISO 6353-2, R 14), 30 % (mass fraction).

7.2.2.3 Hydrochloric acid (HCl), (ISO 6353-2, R 13), 35 % (mass fraction).

7.2.2.4 Sulfuric acid (H_2SO_4), (ISO 6353-2, R 37), 95 % (mass fraction).

7.2.2.5 Hydrogen peroxide (1+10).

7.2.2.6 Hydrochloric acid (1+10).

7.2.2.7 Sulfuric acid (1+1).

7.2.2.8 Water, grade 1 or superior, as specified in ISO 3696.

7.2.3 Apparatus

Ordinary laboratory apparatus together with the following:

7.2.3.1 PTFE beaker, with a range of the appropriate volume (250 ml).

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

7.2.3.3 PTFE pipette, suitable for the transfer of each sample or standard solution.

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

7.2.3.5 Balance, capable of weighing to ± 0,1 mg.

7.2.3.6 Electric furnace, for operation at (1 000 ± 50) °C.

7.2.3.7 Platinum crucible (30 ml).

7.2.3.8 PTFE beaker cover.

7.2.3.9 Volumetric flask (100 ml, 500 ml).

7.2.3.10 Hot plate, with magnetic stirrer.

7.2.4 Procedure

7.2.4.1 Weigh 0,30 g of the test sample and transfer it into a 250 ml PTFE beaker (7.2.3.1). Place the magnetic bar containing the test sample and carefully add 20 ml water, 10 ml hydrogen peroxide (7.2.2.2) and 20 ml hydrochloric acid (7.2.2.3) to the beaker. Cover the beaker with a PTFE beaker cover (7.2.3.8) and heat the contents at (85 ± 5) °C until the test sample is completely dissolved. After cooling, transfer the solution to a 100 ml volumetric flask, dilute with water to the mark and mix well.

The highly pure fine barium titanate powder sample completely decomposes in hydrochloric acid and hydrogen peroxide. However, the presence of impurities or coarse grain in the sample may hinder the decomposition process. If the sample is not completely decomposed by the acid decomposition method, it is recommended that other decomposition methods are applied. These include the acid pressure decomposition, fusion or acid microwave dissolution methods.

7.2.4.2 Transfer a 50 ml aliquot of the test solution (7.2.4.1) to a 250 ml PTFE beaker (7.2.3.1) and add 10 ml sulfuric acid (1+1) (7.2.2.7). After covering the beaker with a PTFE beaker cover (7.2.3.8), heat the contents at 200 °C for 1 h.

7.2.4.3 Filter the solution with ashless filter paper and wash the precipitate several times with hot water. Keep the filtrate and washings in the beaker covered with the watch glass for the determination of the titanium content.

7.2.4.4 Transfer the precipitate and the filter paper to a 30 ml platinum crucible. Heat the crucible in an electric furnace at low temperature until the filter paper has been completely burned to ashes. Heat the crucible and its contents in an electric furnace (1 000 ± 50) °C for 1 h. After cooling in a desiccator, weigh the barium sulfate.

7.2.4.5 Add 50 ml ammonia water (7.2.2.1) to the filtrate (7.2.4.3). Filter the solution with ashless filter paper and wash over the precipitate several times with hot water. Transfer the precipitate with filter paper to a 30 ml platinum crucible. Heat the sample in an electric furnace at low temperature until ashing of the filter paper is complete. Next, heat the crucible and its contents in an electric furnace at (1 000 ± 50) °C for 1 h. After cooling in a desiccator, weigh the titanium oxide.

7.2.5 Blank test

Carry out the procedure described in 7.2.4 without the sample. Designate the final solution as the blank solution.

7.2.6 Calculation

Calculate the barium and titanium contents according to Formula (1).

$$W = \left[\left(W_2 - W_1\right)/m\right] \times V/a \times F_1 \text{ or } F_2 \times 100 \quad (1)$$

where

W is the barium or titanium content, in % (mass fraction);

W_1 is the blank platinum crucible weight, in g;

W_2 is the platinum crucible weight after ignition, in g;

m is the mass of the sample, in g;

V is the test solution volume, in ml;

a is the aliquot solution volume, in ml;

F_1 is the mass ratio of barium in barium sulfate (0,588 4);

F_2 is the mass ratio of titanium in titanium oxide (0,599 3).

7.3 Acid decomposition-ICP-OES method

7.3.1 Principle

Barium and titanium are decomposed in concentrated hydrogen peroxide and hydrochloric acid. The barium and titanium present in the test solution are analysed by ICP-OES at a selected wavelength.

7.3.2 Reagents

Use the reagents described in 7.2.2 together with the following:

7.3.2.1 Barium standard solution (Ba 10 mg/ml).

The SI traceable commercial standard solution is available.

7.3.2.2 Barium standard solution (Ba 1 mg/ml).

Transfer 10 ml barium standard solution (7.3.2.1) to a 100 ml volumetric flask, dilute with water to the mark and mix well.

7.3.2.3 Titanium standard solution (Ti 10 mg/ml).

The SI traceable commercial standard solution is available.

7.3.2.4 Titanium standard solution (Ti 1 mg/ml).

Transfer 10 ml titanium standard solution (7.3.2.3) to a 100 ml volumetric flask, dilute with water to the mark and mix well.

7.3.3 Apparatus

Use the apparatus described in 7.2.3 together with the following:

7.3.3.1 ICP-OES.

7.3.4 Procedure

7.3.4.1 Carry out the procedures described in 7.2.4.1.

7.3.4.2 After cooling, transfer a 10 ml aliquot of the solution into a 500 ml volumetric flask, dilute with water to the mark and mix well. This solution is used as the test solution.

7.3.4.3 Spray a portion of the test solution into the argon plasma flame of the ICP-OES, then measure the emission intensity for barium at 455,40 nm, 493,40 nm and 233,52 nm, and that for titanium at 334,94 nm, 336,12 nm and 337,27 nm.

7.3.5 Blank test

Perform the operation described in 7.3.4 without using a sample to obtain the blank test value.

7.3.6 Drawing of the calibration curve

Transfer 0 ml, 1 ml, 2 ml, 3 ml, 4 ml and 5 ml aliquots of the barium and titanium standard solutions (7.3.2.2 and 7.3.2.4, respectively) to separate 100 ml volumetric flasks. To each flask, add 5 ml hydrochloric acid (1+10) and 5 ml hydrogen peroxide (1+10). Dilute with water to the mark and mix well.

7.3.7 Calculation

Determine the barium and titanium concentrations in the test solution and blank from the calibration curve. Calculate the barium and titanium contents, *W*, expressed in the percentage mass fraction, from Formula (2).

$$W = \left[\left(m_s - m_b\right)/m\right] \times 500/10 \times 100 \quad (2)$$

where

W is the barium and titanium content, in % (mass fraction);

m_s is the mass of barium and titanium in the test solution, in g;

m_b is the mass of barium and titanium in the blank solution, in g;

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

8 Determination of the trace element contents

8.1 Principle

To prepare the test solution, the sample is decomposed in hydrochloric acid and hydrogen peroxide. Aluminium, cadmium, calcium, chromium, cobalt, dysprosium, iron, lead, magnesium, manganese, nickel, niobium, potassium, silicon, strontium, vanadium and zirconium are determined by ICP-OES at the selected wavelength.

8.2 Reagents

Use the reagents described in 7.2.2 together with the following:

8.2.1 Element standard solutions.

The SI traceable commercial standard solution is available for each of the following elements.

— aluminium standard solution (Al, 1 mg/ml);

— cadmium standard solution (Cd, 1 mg/ml);

— calcium standard solution (Ca, 1 mg/ml);

— cobalt standard solution (Co, 1 mg/ml);
— dysprosium standard solution (Dy,1 mg/ml);
— iron standard solution (Fe, 1 mg /ml);
— lead standard solution (Pb, 1 mg/ml);
— magnesium standard solution (Mg, 1 mg/ml);
— manganese standard solution (Mn, 1 mg /ml);
— nickel standard solution (Ni, 1 mg/ml);
— potassium standard solution (K, 1 mg/ml);
— silicon standard solution (Si, 1 mg/ml);
— sodium standard solution (Na, 1 mg/ml);
— strontium standard solution (Sr, 1 mg/ml);
— vanadium standard solution (V, 1 mg/ml);
— zirconium standard solution (Zr, 1 mg/ml).

8.2.2 Mixed standard solution (each element 50 mg/l), place 5 ml each of the element standard solutions (8.2.1) in a 100 ml volumetric flask. Dilute with water to the mark and mix well. Attention shall be paid to ensure that no precipitation occurs during the mixing. Prepare a fresh solution before use.

8.3 Apparatus

Use the apparatus described in 7.2.3.

8.4 Procedure

8.4.1 Carry out the procedures described in 7.2.4.1. This solution is designated as the test solution.

8.4.2 Spray a portion of the test solution into the argon plasma flame of an ICP-OES and measure the emission intensity at the appropriate wavelength (Table 2). Interferences may be encountered. Carefully choose the optimum wavelength that is free from concomitants.

Table 2 — Examples of an analytical wavelength for each element

Element	Wavelength 1 nm	Wavelength 2 nm
Al	396,15	308,21
Cd	228,80	214,44
Ca	317,93	315,88
Co	228,61	238,89
Dy	353,17	394,46
Fe	238,20	239,56
Pb	220,35	217,00
Mg	285,21	279,07
Mn	257,61	259,37
Considering the spectral interferences and the sensitivities, choose the higher-order spectral lines, if available.		

Table 2 *(continued)*

Element	Wavelength 1 nm	Wavelength 2 nm
Ni	231,60	221,64
Nb	309,41	313,07
K	766,49	—
Si	251,61	212,41
Na	589,59	—
Sr	407,77	421,55
V	290,88	292,46
Zr	343,82	339,19
Considering the spectral interferences and the sensitivities, choose the higher-order spectral lines, if available.		

8.5 Blank test

Perform the operation described in 8.4 without taking a sample to obtain the blank test value.

8.6 Drawing of the calibration curve

Pour 16 ml barium solution (7.3.2.1) and 8 ml titanium solution (7.3.2.3) separately into five 100 ml volumetric flasks. Add 0 ml, 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of the mix standard solution (8.2.2) stepwise and precisely. Add 20 ml hydrochloric acid (7.2.2.3) and 10 ml hydrogen peroxide (7.2.2.2), dilute with water to the mark and mix well. Spray a portion of each solution into the argon plasma flame of the ICP-OES and measure the emission intensity at the appropriate wavelength.

8.7 Calculation

Determine the concentration of each element in the test solution and in the blank from the calibration curve. Calculate the element content, W_i, expressed as the percent mass fraction, from Formula (3).

$$W_i = \left[\left(m_i - m_b\right)/m\right] \times 100 \tag{3}$$

where

W_i is the content of each element, in % (mass fraction);

m_i is the mass of each element in test solution, in g;

m_b is the mass of each element in blank solution, in g;

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

NOTE The analytical results obtained from the round-robin test are listed in Annex A.

9 Determination of the total nitrogen content

9.1 Principle

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

9.2 Reagents

The reagents can vary substantially for different instruments. However, in all cases the reagents specified by the instrument manufacturer shall be used.

The reagents used shall be as follows:

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

9.2.2 Flux, in shot or basket form made of tin or nickel. Use a combination of metals that are different from that of the capsule.

9.2.3 Boron nitride certified reference materials (CRM), shall be heated at 1 000 °C for 2 h, and then cooled in a desiccator before use.

NOTE Silicon nitride CRM can also be used.

9.3 Apparatus

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

9.3.2 Graphite crucible, suitable for use in an impulse furnace (Figure 1).

Dimensions in mm

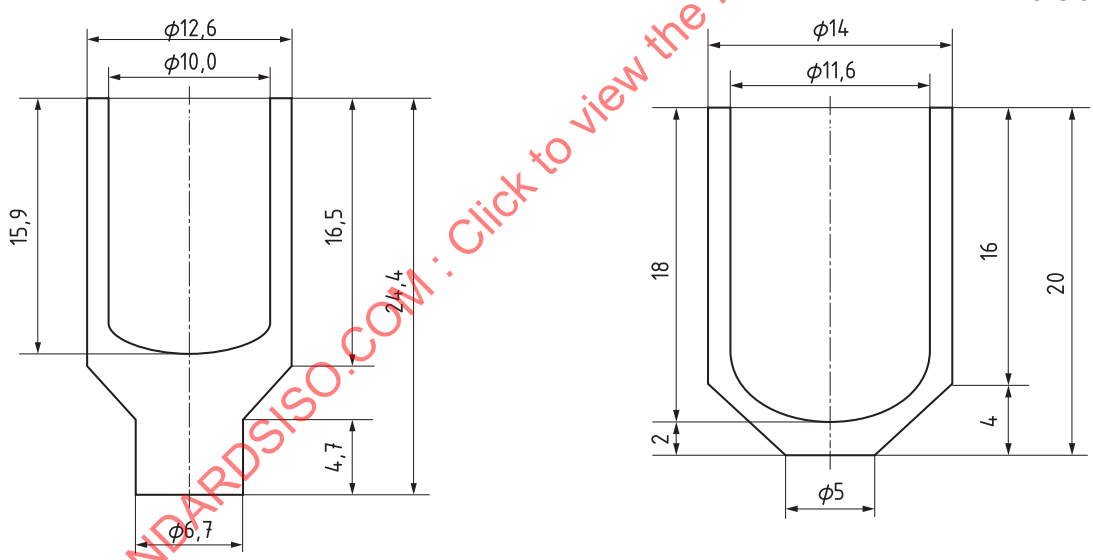
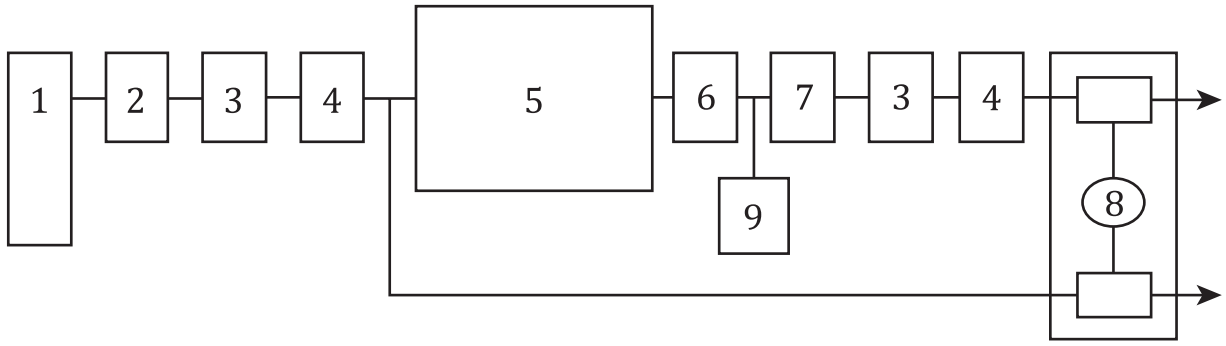


Figure 1 — Examples of a graphite crucible

9.4 Instrument

A commercial nitrogen analyser may be used to determine the nitrogen content. It usually comprises an inert gas refiner, furnace, extracted gas refiner, gas extractor and nitrogen detector. Figure 2 is a block diagram of such an instrument.



Key

1 helium supplier
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
9 IR spectrometer for oxygen determination (optional)

NOTE Each instrument has its own unique design characteristics and operational requirements.

Figure 2 — Block diagram of the inert gas fusion-thermal conductivity method

9.4.1 Inert gas refiner, comprising, for example, a deoxidation tube (reduced copper) with an electric furnace, carbon dioxide absorption tube (sodium hydroxide and so on shots) and dehydration tube (magnesium perchlorate). A denitrification tube (sponge titanium) is attached in some instruments.

9.4.2 Gas extractor, comprising, for example, a sample feeder and impulse furnace. The sample feeder can place the sample-embedded capsule into the graphite crucible in the impulse furnace under an inert gas flow. The impulse furnace shall be capable of attaining a temperature of 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.

9.4.3 Extracted gas refiner, comprising, for example, a dust-collecting tube (glass wool), carbon dioxide absorption tube (sodium hydroxide shots), oxidation tube with an electric furnace and a dehydration tube (magnesium perchlorate).

9.4.4 Gas detector, comprising a thermal conductivity detector and integration meter.

NOTE Other commercial instruments for nitrogen analysis are available. Each has its own unique design characteristics and operational requirements. Operation details can be found in the instrument manufacturer instruction manual.

9.5 Procedure

9.5.1 Starting up of the instrument

Switch on the instrument and set the controls to the specified values in accordance with the manufacturer operation instructions. Wait until it becomes stable.

9.5.2 Preliminary heating

Set a new graphite crucible to the specified position in the impulse furnace. Allow the inert gas to flow and then turn on the furnace. Heat the graphite crucible at the degassing temperature for the specified period and, subsequently, to the gas extraction temperature. The temperature adjustment of the graphite crucible is achieved by adjusting the electrical current, voltage or power. The relationship between the temperature and the current/voltage must be achieved before the equipment is used.

Read the integration meter (hereafter referred to as "integral value"). Repeat the degassing and the extraction steps until a stable integral value is obtained.

9.5.3 Degassing of the graphite crucible

Measure the specified amount of bath metal in a new graphite crucible and place it at the specified position of the impulse furnace. Weigh a 0,02 g to 0,04 g sample in a capsule and enclose it using a jig. If complete extraction of nitrogen can be achieved, collect 0,1 g of the sample.

Place the capsule at the specified position of the sample blower. Feed the inert gas and energize the graphite crucible. Heat it at the degassing temperature for the specified period and subsequently degas the graphite crucible and bath metal. The degassing temperature shall be 100 °C higher than the gas extraction temperature.

9.5.4 Measuring

Place the sample-embedded capsule into the graphite crucible. Energize the crucible and heat the sample at the gas extraction temperature for the specified period. Read the integral value. The optimum gas extraction temperature shall be determined beforehand by using a CRM of known nitrogen content (9.2.3).

NOTE Because the commercial instruments for analysing nitrogen might be fully automated, many of the steps described above are carried out without the need for any operator intervention.

9.6 Blank test

Perform the process described in 9.5 without taking a sample to obtain the blank test value. Repeat this operation three to five times and calculate the average value.

9.7 Calculation of the calibration coefficient

Use the nitrogen CRM of known total nitrogen content. Some boron nitride powder (or silicon nitride powder) reference materials are available. Perform the process described in 9.5 using the sample for calibration. Average the values obtained by repeating the measurements three to five times and calculate the calibration coefficient according to Formula (4).

$$K = \left(m \times N_T / 100\right) / \left(A_1 - A_0\right) \tag{4}$$

where

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

m is the mass of the sample for calibration, in g;

N_T is the total nitrogen content in the sample for calibration, in % (mass fraction);

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test.

9.8 Calculation

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

$$N_T = (A_2 - A_0) \times K / m \times 100 \quad (5)$$

where

N_T is the total nitrogen content in the sample, in % (mass fraction);

A_2 is the integral value of the sample;

A_0 is the integral value of the blank test;

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

m is the mass of the sample, in g.

NOTE Some commercial instruments can calculate the blank test value. In these cases, the calibration coefficient and the nitrogen content can be calculated automatically.

10 Determination of the oxygen content

10.1 Principle

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

10.2 Reagents

Use the reagents described in 9.2 as well as the following:

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

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

10.2.3 Magnesium perchlorate, reagent grade, with the particle size range 0,7 mm to 1,2 mm, for moisture absorption. Use the purity specified by the instrument manufacturer.

10.3 Apparatus

Use the apparatus described in 9.3.

10.4 Instrument

Use the instruments described in 9.4, except for the components of the gas separator and the detector. The extracted gas refiner does not include a carbon dioxide absorption tube (sodium hydroxide shots) and a dehydration tube (magnesium perchlorate). An IR spectrometer is used instead of a thermal conductivity detector. A commercial oxygen analyser is available.

10.5 Procedure

Weigh a 0,02 g to 0,04 g sample and perform the operation in accordance with 9.5.

10.6 Blank test

Perform the procedure described in 10.5 without taking a sample to obtain the blank test value. Repeat these operations three to five times and calculate the average.

10.7 Calculation of the calibration coefficient

Use 0,010 g yttrium oxide or 0,030 g nitride of known oxygen content for the calibration. Some silicon nitride powder (or boron nitride powder) reference materials are also available. Average the values from three to five measurements and calculate the calibration coefficient according to Formula (6).

$$K = \left(m \times O / 100\right) / \left(A_1 - A_0\right) \tag{6}$$

where

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

m is the mass of the sample for calibration, in g;

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

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test.

10.8 Calculation

Calculate the oxygen content in the sample according to Formula (7).

$$O = \left[\left(A_2 - A_0\right) \times K / m\right] \times 100 \tag{7}$$

where

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

A_2 is the integral value of the sample;

A_0 is the integral value of the blank test;

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

m is the mass of the sample, in g.

NOTE Because some commercial instruments can calculate the blank test value, the calibration coefficient and the oxygen content can be determined automatically.

11 Determination of the carbon content

11.1 Classification of the determination methods

Method A, combustion (resistance furnace)-IR absorption spectrometry.

Method B, combustion (radio frequency heating furnace)-thermal conductometry.

Method C, combustion (radio frequency heating furnace)-IR absorption spectrometry.

11.2 Combustion (resistance furnace)-IR absorption spectrometry

11.2.1 Principle

A sample is combusted under an oxygen flow with combustion accelerators in a resistance furnace. The generated carbon oxides are determined using an IR spectrometer and the integrated values are converted to a value corresponding to the carbon content.

11.2.2 Reagents

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

11.2.2.2 Combustion accelerators, tin, in sandy form.

Combustion accelerators (other than tin) or a combination of metals (such as tin and iron) may be used, provided that they satisfy the criteria required for combustion accelerators.

11.2.2.3 Calcium carbonate, of more than 99,9 % purity (mass fraction), heated at 500 °C to 550 °C for 2 h and cooled in a desiccator (desiccant: magnesium perchlorate).

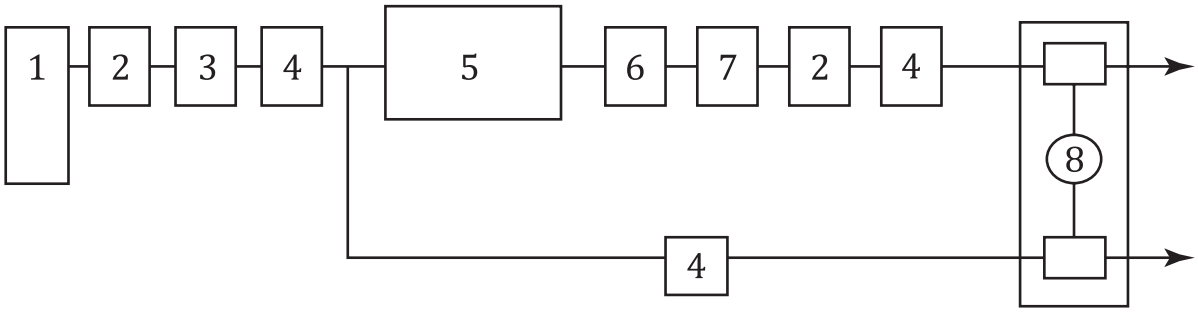
11.2.3 Apparatus

11.2.3.1 Combustion tube, use the tube specified by the apparatus manufacturer.

11.2.3.2 Combustion boat, use the boat specified by the apparatus manufacturer. Perform preliminary combustion at 1 350 °C before use.

11.2.4 Instrument

A commercial carbon analyser may be used for the determination of the carbon content. It usually comprises an oxygen refiner, furnace, combustion gas refiner and carbon detector. Figure 3 is a block diagram of such an instrument.



Key

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

NOTE Each instrument has its own unique design characteristics and operational requirements.

Figure 3 — Block diagram of a carbon analyser for combustion (resistance furnace)-IR absorption spectrometry

11.2.4.1 Oxygen refiner, comprising, for example, an oxidation tube (copper oxide) with an electric furnace, carbon dioxide absorption tube (sodium hydroxide shots) and dehydration tube (magnesium perchlorate).

11.2.4.2 Furnace for combusting the sample, comprising, for example, a tubular electric resistance furnace and combustion tube. The tubular electric resistance furnace shall be able to regulate the temperature of the central section (100 mm or longer) of the combustion tube to 1 350 °C.

11.2.4.3 Combustion gas refiner, comprising, for example, a dust-collecting tube (glass wool), sulfur dioxide trap (manganese dioxide), oxidation tube (copper oxide or platinum-based catalyst) with an electric furnace and dehydration tube (magnesium perchlorate).

11.2.4.4 Carbon detector, comprising an IR spectrometer to detect the carbon dioxide and other components. For carbon dioxide, the IR spectrometer detects the differential between the intensities of the IR absorption of a sample and those of the reference cells as electric signals using a detector. It converts the value to the carbon content via a linearization and integration circuits. The result is displayed on an integration meter. Another type of instrument measures the IR absorption of carbon dioxide and carbon monoxide separately and displays the sum of both measurements as the carbon content.

NOTE Some commercial IR spectrometers measure carbon dioxide without a reference cell.

11.2.5 Procedure

11.2.5.1 Stabilization of the instrument

Switch on the instrument and set each of the components to the designated conditions. Wait for the components to stabilize.

11.2.5.2 Mixture of the sample and combustion accelerators

Weigh a 0,3 g to 0,5 g sample in a combustion boat and spread it evenly. Next, evenly cover the sample with 2 g combustion accelerators. Alternatively, mix the sample with tin and spread evenly or spread the sample so that it is sandwiched between 1 g of combustion accelerator on each side.

11.2.5.3 Sample combustion

Remove the plug of the combustion tube, insert the boat loaded with the sample and combustion accelerators into the centre of the combustion tube and immediately attach the plug. Switch on the oxygen flow and operate the furnace for the designated duration.

11.2.5.4 Measurement

Propel the generated carbon dioxides, along with the oxygen, through the combustion gas refiner and into the IR spectrometer. After the designated time has elapsed, measure the integrated values.

11.2.6 Blank test

Perform the procedure described in 11.2.5 without taking a sample to obtain the blank test value.

11.2.7 Calculation of the calibration coefficient

Use 0,250 g calcium carbonate or 0,500 g nitride of known carbon content (calibration sample) to perform the operation described in 11.2.5. Calculate the calibration coefficient according to Formula (8) or Formula (9), respectively.

a) When calcium carbonate is used, refer to Formula (8).

$$K = \left(m \times 0{,}120\,0\right) / \left(A_1 - A_0\right) \tag{8}$$

where

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

m is the mass of calcium carbonate, in g;

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test.

b) When the nitride sample is used, refer to Formula (9).

$$K = \left(m \times C / 100\right) / \left(A_1 - A_0\right) \tag{9}$$

where

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

m is the mass of the sample for calibration, in g;

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

A_1 is the integral value of the sample for calibration;

A_0 is the integral value of the blank test.

11.2.8 Calculation

Calculate the carbon content in the sample according to Formula (10).

$$C = \left[\left(A_2 - A_0 \right) \times K / m \right] \times 100 \quad (10)$$

where

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

A_2 is the integral value of the sample;

A_0 is the integral value of the blank test;

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

m is the mass of the sample, in g.

11.3 Combustion (radio frequency heating furnace)-thermal conductometry

11.3.1 Principle

A sample is combusted under an oxygen flow with combustion accelerators in a radio frequency heating furnace. The generated carbon dioxide is determined using a thermal conductometer and the integrated value is converted to a value corresponding to the carbon content.

11.3.2 Reagents

Use the reagents described in 11.2.2 except for the combustion accelerator. For the combustion accelerators, use granular copper, tungsten, chipped iron or any other substances recommended by the instrument manufacturer.

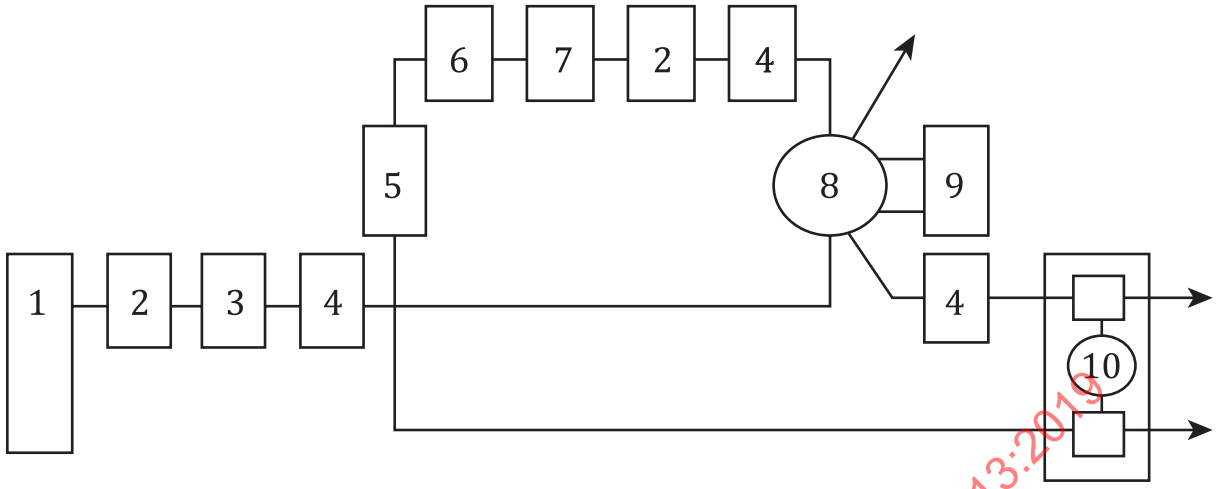
11.3.3 Apparatus

11.3.3.1 Combustion crucible, of the type specified by the apparatus manufacturer.

11.3.3.2 Receptacle, of the type specified by the apparatus manufacturer.

11.3.4 Instrument

A commercial carbon analyser may be used for the determination of the carbon content. It usually comprises an oxygen refiner, furnace, combustion gas refiner and carbon detector. Figure 4 is a block diagram of such an instrument.



Key

1 oxygen supplier
2 oxidation tube with electric furnace
3 carbon dioxide trap
4 dehydration tube
5 combustion tube
6 dust collector
7 sulfur dioxide trap
8 duct converter
9 carbon dioxide collector
10 thermal conductometer

NOTE Each instrument has its own unique design characteristics and operational requirements.

Figure 4 — Block diagram of a carbon analyser for combustion (radio frequency heating furnace)-thermal conductometry

11.3.4.1 Oxygen refiner, as described in 11.2.4.1.

11.3.4.2 Furnace for combusting the sample, comprising, for example, a radio frequency heating furnace and oscillator.

11.3.4.3 Combustion gas refiner, as described in 11.2.4.3.

11.3.4.4 Carbon detector, comprising, for example, a flow converter, carbon dioxide collection tube (synthetic zeolite) and thermal conductometer.

11.3.5 Procedure

11.3.5.1 Stabilization of the instrument

Switch on the instrument and set each of the components to the designated conditions. Wait for the components to stabilize.

11.3.5.2 Mixture of the sample and combustion accelerators

Weigh a sample in the combustion crucible and add 1 g each of copper and iron or copper and tungsten over it.