INTERNATIONAL STANDARD

ISO 21068-2

First edition
2008-08-01

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

Analyse chimique des matières premières et des produits réfractaires contenant du carbure de silicium —

Partie 2: Détermination de la perte au feu, du carbone total, du carbone libre et du carbure de silicium, de la silice totale et libre, et du silicium total et libre

Reference number
ISO 21068-2:2008(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 21068-2 was prepared by Technical Committee ISO/TC 33, *Refractories.*

ISO 21068 consists of the following parts, under the general title *Chemical analysis of silicon-carbide-containing raw materials and refractory products*:

- *Part 1: General information and sample preparation*
- *Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon*
- *Part 3: Determination of nitrogen, oxygen and metallic and oxidic constituents*

Introduction

ISO 21068, Parts 1 to 3, have been developed from the combination of a Japanese standard JIS 2011 [6] and work items originally developed within CEN. Because there is a wide variety of laboratory equipment in use, the most commonly used methods are described.

This part of ISO 21068 is applicable to the analysis of all refractory products classified in ISO 10081 [2] to [5] (shaped) and ISO 1927 [1] (unshaped) and raw materials containing carbon and/or silicon carbide. Therefore, this part of ISO 21068 covers the full range of analysis from pure silicon carbide to oxidic refractory composition with a low content of silicon carbide and/or nitrides. Primarily, this part of ISO 21068 provides methods to distinguish between different carbon-bound types like total carbon (C_{total}) and free carbon (C_{free}) and derives from these two the silicon carbide content.

If free carbon is present, this part of ISO 21068 includes different types of temperature treatment, in order to determine the mass changes gravimetrically. Frequently, the resulting residue is used for other determinations.

The determination of other groups of analytes described in this part of ISO 21068 are free metals, free silicon (Si_{free}), free aluminum (Al_{free}), free magnesium (Mg_{free}), free iron (Fe_{free}) and the group of oxides from main to trace components.

This part of ISO 21068 also describes the chemical analysis of SiO_2, total Si, oxygen and nitrogen and other oxidic-bound metals which typically occur in the materials.

This part of ISO 21068 represents a listing of analytical methods which is approximately structured according to material composition. However, it is still the user who should prove the applicability of the method, depending on the material and analytical requirements.

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

1 Scope

This part of ISO 21068 specifies analytical techniques for the determination of change in mass by thermal treatment at specified temperatures, and methods for the determination of the total carbon content, free carbon, silicon carbide, silicon, total silica and free silica content of silicon-carbide-containing raw materials and refractory products.

2 Normative references

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

ISO 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*

ISO 9286:1997, *Abrasive grains and crude — Chemical analysis of silicon carbide*

ISO 10060, *Dense, shaped refractory products — Test methods for products containing carbon*

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

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21068-1 apply.

4 Determination of change in mass

4.1 General

The determination of change in mass is defined as a loss or increase in mass caused by heat treatment. Several methods are distinguished based on the sample material, temperature and atmosphere. The determination of change in mass is carried out by a gravimetric method. Heat treatments in air will lead to a loss of volatile matter and carbon and an increase of mass due to oxidation, whereas a heat treatment in argon will only lead to a loss of volatile matter.

Normally, the residue is used for other determinations. Therefore, the change in mass is considered for the calculation of the analytical result. The analytical method which is applied to the residue depends on the matrix and the parameters to be determined. It is up to the user to select the appropriate analytical method.

Table 1 gives an overview of methods of determination of change in mass by heat pretreatments and their different applications.

Table 1 — Methods and application purpose of determination of change in mass

Short title of method	Temperature	Subclause	Application
Loss on drying (LOD_{250})	250 °C	4.2	Attached water and chemically combined water are removed, e.g. in clay containing plastic formulations
Loss on calcination in argon (LOI_{Ar})	750 °C	4.3	All volatile compounds out of pitch- or resin-bonded formulations are removed
Change in mass in air	200 °C	4.4	Volatile compounds are removed from resin-bonded formulations
	400 °C	4.4	Volatile compounds are removed from pitch-bonded formulations
Change in mass (LOI_{750})	750 °C	4.5	Both procedures are suitable to remove carbon (e.g. graphite) from refractory formulations. If fine-grained SiC is present, care should be taken because SiC may be oxidised as well.
Loss on ignition (LOI_{850})	850 °C	4.6	
Loss on ignition ($LOI_{1\,050}$)	1 050 °C	4.7	Loss or gain of mass; attached water, chemically combined water, carbon, organic compounds (e.g. pitch, resin), silicon carbide, and metals are removed

4.2 Determination of the loss on drying at 250 °C (LOD_{250}) gravimetric method

4.2.1 Principle

The test sample is heated at 250 °C ± 10 °C and the loss of mass from attached water is determined.

4.2.2 Apparatus

4.2.2.1 Heat-resistant container, for example with dimensions 200 mm × 150 mm × 30 mm and made from stainless steel.

4.2.3 Procedure

Heat the heat-resistant container at 250 °C ± 10 °C for 30 min. Cool in a desiccator, weigh and record its empty mass , m_0, to the nearest 0,01 g.

Transfer the sample into the container and spread it out flat. Then weigh and record the mass, m_1, of the container and sample to the nearest 0,01 g.

Place the container without a lid in an air bath and heat it at 250 °C ± 10 °C for 16 h. Allow to cool in a desiccator. Weigh and record the mass, m_2, of the container plus the dried sample to the nearest 0,01 g.

4.2.4 Calculation

Calculate the loss on drying at 250 °C, LOD_{250}, as a percentage by mass, using Equation (1).

$$\text{LOD}_{250} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \qquad (1)$$

where

m_0 is the mass of the empty container, in grams;

m_1 is the mass of the container plus the sample before drying, in grams;

m_2 is the mass of the container plus the sample after drying, in grams.

4.3 Determination of the loss on calcination in argon (LOI_{Ar})

4.3.1 Principle

Pretreatment under argon at 750 °C to remove volatile matter. The loss of volatile matter is determined by a gravimetric method.

The residue (R_{Ar}) is normally used for determination of C_{total}, SiC and C_{free} (therefore these parameters will be additionally indexed with $_{\text{Ar}}$), and the change in mass has to be considered for the calculation of the result.

4.3.2 Apparatus

Ordinary laboratory apparatus and the following.

4.3.2.1 **U-tube**, with ground stoppers and filled with magnesium perchlorate.

4.3.2.2 **Resistance furnace**, heatable and adjustable at (750 ± 25) °C, in the centre of the heating zone.

4.3.2.3 **Thermocouple with display**, registering up to 1 200 °C.

4.3.2.4 **Ceramic tube**, with cones or other gastight connector, with an inner diameter $\geqslant$ 16 mm, made from porcelain, sillimanite, quartz or other suitable material.

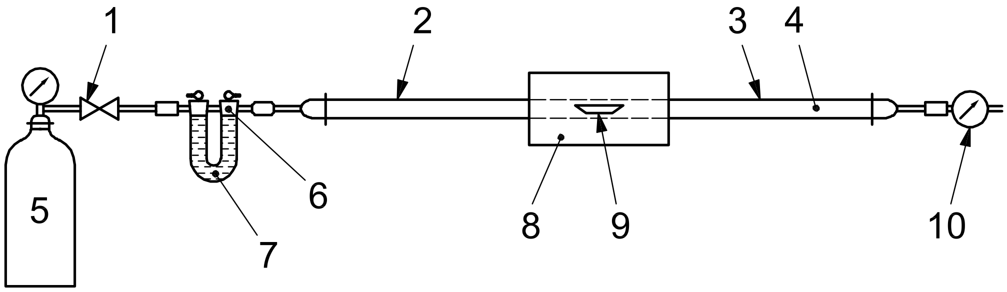
4.3.2.5 **Open combustion boats**, of unglazed ceramic material, the length of which is adapted to the oven's zone of constant temperature. The boats shall be broad enough to accommodate the amount of sample required for the determination.

4.3.2.6 **Gas flowmeter**, with an upper scale reading of around 20 l/h.

The argon-conducting parts, such as tubes and connections, should be made of material proofed against oxygen diffusion. Preferable materials are glass and copper. Silicone is unsuitable.

4.3.2.7 **Test assembly**

The test assembly is set up as shown in Figure 1.



Key

1	valve for pressure control	5	argon cylinder	9	combustion boat
2	cold zone B	6	glass wool	10	gas flowmeter
3	cold zone A	7	magnesium perchlorate		
4	ceramic tube	8	resistance furnace		

Figure 1 — Apparatus set-up for determination of loss on calcination in argon

4.3.3 Reagents

4.3.3.1 Argon, 99,997 %.

4.3.4 Procedure

4.3.4.1 Check of test assembly, blank value determination

To check a newly set up test assembly or to carry out routine checks, a few samples of known volatile-matter content shall be calcined as described in 4.3.4.2 before examining the analytical sample.

The difference between the result found in accordance with 4.3.4.2 and the known volatile-matter content shall be taken into account as the blank value.

4.3.4.2 Determination

Carry out at least two determinations.

Before use, flush the apparatus for at least 15 min with argon.

Weigh the empty combustion boat that has previously been heated at (750 ± 25) °C and record the mass m_0. Weigh 2 g of the sample to the nearest 0,001 g into the combustion boat and record the mass m_1.

Place the combustion boat and sample in cold zone A of the apparatus at $\leqslant$ 200 °C. Pass argon through it at a rate that ensures five changes of gas in the tube within 15 min.

Place the sample in the centre of the heating zone and calcine for 20 min at (750 ± 25) °C, without interruption of the argon stream.

Move the combustion boat into cold zone B and cool in the argon stream at $\leqslant$ 200 °C.

NOTE A period of 20 min is usually required to cool the sample.

Allow the boat to cool to room temperature in a desiccator, weigh to the nearest 0,001 g and record the final mass, m_2.

Repeat the calcination in the argon stream at (750 ± 25) °C until constant mass is obtained, i.e. when two measurements taken at an interval of 30 min do not differ by more than 5 mg.

If the residue is required for the determination of other components, homogenize it and keep it in a closed weighing bottle in a desiccator.

4.3.5 Calculation

Calculate the loss on calcination in argon at 750 °C, $\mathrm{LOI}_{\mathrm{Ar}}$, as a percentage by mass, using Equation (2).

$$\mathrm{LOI}_{\mathrm{Ar}} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{2}$$

where

m_0 is the mass of the empty combustion boat, in grams;

m_1 is the mass of the combustion boat plus sample before ignition, in grams;

m_2 is the mass of the combustion boat plus sample after ignition, in grams.

NOTE The decrease in mass is denoted by a minus sign.

4.4 Determination of the change in mass by heat pretreatment in air

For resin- and pitch-bonded materials, a sample pretreatment shall be performed in accordance with ISO 10060, or the following procedure shall be followed.

Usually before crushing and grinding, subject a sample of approximately 1 kg to heat treatment as follows:

a) resin-bonded materials: 200 °C for 18 h in air;

b) pitch-bonded materials: 400 °C for 18 h in air.

Calculate the change in mass at 200 °C/400 °C, D, as a percentage by mass, using Equation (3).

$$D = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{3}$$

where

m_0 is the mass of the empty container, in grams;

m_1 is the mass of the container plus sample before heat pretreatment, in grams;

m_2 is the mass of the container plus sample after ignition, in grams.

Report the result to the nearest 0,1 %.

When the nature of free carbon is not known, first carry out thermogravimetric analysis to determine the temperature of the heat treatment.

4.5 Determination of the change in mass at 750 °C (LOI_{750})

4.5.1 Principle

Determination of the change in mass as a function of time by ignition at 750 °C in an electric muffle furnace. The loss or increase of mass is determined by a gravimetric method.

4.5.2 Apparatus

4.5.2.1 **Muffle furnace**, with a temperature control from 100 °C to 1 000 °C.

4.5.2.2 **Fused silica dish**, porcelain, or platinum, approximately 60 mm long and 35 mm wide.

4.5.2.3 **Balance**, capable of weighing to 0,1 mg.

4.5.3 Procedure

Weigh the empty dish that has previously been heated at (750 ± 25) °C and record the mass m_0. Weigh 2,5 to 3,5 g of the sample, dried at 110 °C, to the nearest 0,001 g into the combustion boat and record the mass m_1.

Place the dish and the sample in the muffle furnace at 500 °C for 20 min.

Increase the furnace temperature to 750 °C and ignite the sample for a further 1 h 30 min when the furnace has reached the test temperature.

Take the dish out of the furnace and allow it to cool down to room temperature in a desiccator.

Weigh the dish and sample. Record the mass m_2.

Replace the dish and sample in the furnace for a further 30 min and check whether there is a further loss in mass. If so, repeat the whole procedure.

NOTE If a mass increase is observed after the second ignition, do not carry out further ignition because it can indicate possible oxidation of some elements.

4.5.4 Calculation

Calculate the loss on ignition at 750 °C, LOI_{750}, as a percentage by mass, using Equation (4).

$$\mathrm{LOI}_{750} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \qquad (4)$$

where

m_0 is the mass of the empty dish, in grams;

m_1 is the mass of the dish plus sample before ignition, in grams;

m_2 is the mass of the dish plus sample after ignition, in grams.

NOTE The result obtained in this way cannot be considered as the free carbon content.

4.6 Determination of loss on ignition at 850 °C (LOI$_{850}$)

4.6.1 Apparatus

4.6.1.1 Platinum dish, platinum or porcelain (e.g. Type B 20 ml).

4.6.2 Procedure

Heat the platinum dish at 850 °C ± 25 °C for 15 min, cool it in a desiccator, and then weigh the platinum dish. Record the mass of the empty dish m_0.

Weigh 5,0 g of a sample, to the nearest 0,1 g, into the platinum dish and spread it widely and thinly. Record the mass of the dish plus sample m_1.

Put the platinum dish without a cover into an electric furnace and raise the temperature from room temperature to 850 °C ± 25 °C, and keep heating for 3 h. Put the lid on the platinum dish, cool in a desiccator, weigh it and record the mass m_2.

In the case of fusion of the sample containing silicon carbide, silicon nitride and metal silicon, several hours should be spent on a rise of temperature to the 700 °C to 850 °C region. There is a risk of eroding a platinum dish with a rapid rise of temperature to above 850 °C.

4.6.3 Calculation

Calculate the loss on ignition at 850 °C ± 25 °C, R, expressed as a percentage by mass using Equation (5).

$$R = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{5}$$

where

m_0 is the mass of the empty dish, in grams;

m_1 is the mass of the dish plus sample before ignition, in grams;

m_2 is the mass of the dish plus sample after ignition, in grams.

Transfer the residue, after measurement, to an agate mortar, grind and mix lightly to be homogeneously, transfer to a flat weighing bottle (50 mm × 30 mm), and keep in a desiccator. Use it for determination of each component.

4.7 Determination of loss on ignition at 1 050 °C (LOI$_{1\,050}$)

4.7.1 Principle

A sample is heated at 1 050 °C ± 25 °C and loss or gain of mass from loss of attached water, water of crystallization, carbon, organic compounds, silicon carbide, and metals is determined by a gravimetric method.

4.7.2 Apparatus

4.7.2.1 Crucible, platinum or porcelain (e.g. Type B 20 ml).

4.7.3 Procedure

Heat the crucible to 1 050 °C ± 25 °C for a specified time, cool in a desiccator and weigh the empty platinum or porcelain crucible and record the mass m_0.

A platinum crucible should be heated for about 15 min and a porcelain crucible should be heated for about 60 min.

Weigh 1,0 g of the dry sample into the platinum or porcelain crucible to the nearest 0,1 mg, spread thinly and weigh the mass of the crucible and sample and record the mass m_1.

Place the crucible without a lid in an electric muffle furnace and slowly raise the temperature to 1 050 °C ± 25 °C. Maintain this temperature for about 60 min and allow to cool with a lid. Weigh the crucible plus the ignited sample and record the mass m_2.

4.7.4 Calculation

Calculate the loss on ignition, $\mathrm{LOI}_{1\,050}$, as a percentage by mass, using Equation (6).

$$\mathrm{LOI}_{1\,050} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \qquad (6)$$

where:

m_0 is the mass of the empty crucible, in grams;

m_1 is the mass of the crucible plus sample before ignition, in grams;

m_2 is the mass of the crucible plus sample after ignition, in grams.

If a gain on ignition is observed, a minus sign should be added in front of the numerical value.

5 Determination of the total carbon content

NOTE Suitable certified reference materials (CRMs) for the calibration of a carbon analyser are given in Annex A.

5.1 General

The total carbon content, w_{Ctotal}, can be determined using the following methods:

- combustion with oxygen, using either
  - a resistance furnace (RF), with lead borate fusion or tin powder as accelerator/decomposition agent, or
  - an induction furnace (IF), with metal fusion as accelerator;
- detection methods using
  - coulometry,
  - gravimetry,
  - conductometry,
  - infrared absorption,
  - thermal conductivity.

Usual combinations of available equipment are shown in Table 2.

Table 2 — Usual combinations of equipment for carbon determination

Equipment	Coulometry	Conductivity	Gravimetry	IR absorption	Thermal conductivity
Resistance furnace	+	+	+	+	
Induction furnace			+	+	+

The procedures for the determination of total carbon are therefore structured as combustion techniques, detection techniques and detection methods constituting the laboratory procedure.

5.2 Combustion techniques

5.2.1 General

Two different combustion techniques with different decomposing agents/accelerators can be used.

5.2.2 Resistance furnace in oxygen and lead borate as decomposing agent

5.2.2.1 Principle

The sample is heated together with lead borate in a stream of oxygen in a resistance tube furnace to convert the carbon to carbon dioxide by combustion. The sample mass and the details of the combustion depend on the method of determination used. The combustion gases are conducted through a tube containing percarbamide to absorb the oxidation products of the sulfur contained in the sample. The carbon dioxide is absorbed in an alkaline medium and determined either coulometrically, gravimetrically, conductometrically or by infrared absorption.

5.2.2.2 Reagents

Use only reagents of analytical grade.

5.2.2.2.1 Oxygen, 99,99 % or 99,5 %.

NOTE Oxygen 99,99 % is used if the instrument does not have an oxygen-refining capability. Oxygen 99,5 % is used if the instrument has oxygen-refining ability.

5.2.2.2.2 Lead borate, 2 $PbO \cdot B_2O_3$, prepared by melting 45 g of analytical grade lead oxide, PbO, together with 7 g of analytical grade boron trioxide, B_2O_3, for 10 min at (950 °C ± 25) °C, cooling the melt by pouring it onto a clean aluminium plate and then pulverizing it.

5.2.2.3 Apparatus

Ordinary laboratory apparatus and the following.

5.2.2.3.1 Resistance furnace with ceramic tube, capable of being used up to 1 200 °C. The furnace shall be capable of being maintained at a temperature of (1 050 ± 25) °C in the centre of the heating zone. The furnace shall be fitted with a thermocouple connected to a device permitting measurement of the furnace temperature.

Allowance should be made for the fact that, frequently, the temperature indicated on the built-in temperature control display of the furnace deviates from the actual temperature in the ceramic tube. It should be adjusted using an external thermocouple device, measuring the temperature of the heating zone inside the tube.

5.2.2.3.2 Open combustion boats of unglazed ceramic material, the length of which is adapted to the heating zone of the furnace, and which are broad enough to accommodate the amount of sample required for the determination. Before use, the boats shall be heated in a laboratory furnace at 1 000 °C for 1 h and stored in a desiccator after cooling.

5.2.2.4 Setting up of test assembly

Set up the test assembly in accordance with the manufacturer's instructions.

5.2.2.5 Procedure for RF combustion with lead borate

Weigh the required sample mass into the combustion boat and cover it with 1,5 g of lead borate, 2 PbB_2O_3. Preheat the furnace to a temperature of (1 050 ± 25) °C and place the boat in the centre of the heating zone.

Adjust the oxygen flow rate so as to prevent the risk of air being sucked in from the outside.

For the total carbon in the case of coulometric and conductometric methods, the volume of the combustion gas shall generally be reduced to one-tenth.

NOTE Combustion is usually complete after 5 min.

The carbon dioxide gas formed is supplied by carrier gas to the detection unit.

Carry out the determination of the carbon dioxide formed, as described in 5.3.

5.2.3 Resistance furnace in oxygen and tin powder as decomposing agent

5.2.3.1 Principle

The sample is burned with accelerator in an oxygen atmosphere inside a resistance heating furnace and the yielded carbon dioxide (and carbon monoxide) is transferred in the detection unit selected by the user.

5.2.3.2 Reagents

Use only reagents of analytical grade.

5.2.3.2.1 Oxygen, 99,99 % or 99,5 %.

NOTE Oxygen 99,99 % is used if the instrument does not have oxygen-refining capability. Oxygen 99,5 % is used if the instrument has oxygen-refining ability.

5.2.3.2.2 Accelerator, tin powder, with a grain size < 100 µm and with a low blank value.

5.2.3.3 Apparatus

5.2.3.3.1 Combustion boat, porcelain, outer diameter (OD) = 12 mm, inner diameter (ID) = 9 mm, 60 mm long, annealed over 1 050 °C.

5.2.3.3.2 Combustion tube, porcelain, e.g. OD = 25 mm, ID = 20 mm, 600 mm long.

5.2.3.3.3 Furnace, of a carbon determination apparatus. It is composed of oxygen refining, sample burning, combustion-gas refining and carbon-content determining parts.

5.2.3.3.4 Oxygen-refining assembly, composed of an oxidizing tube with electric furnace [copper(II) oxide, CuO, or platinum-silica-wool], a carbon-dioxide-absorbing tube (soda lime) and a dehydration tube [magnesium perchlorate, $Mg(ClO_4)_2$, (for dryness)].

NOTE The oxygen-refining assembly is optional.

5.2.3.3.5 Sample-burning assembly, composed of a tubular electric furnace and porcelain combustion tube. The tubular electric furnace shall be capable of maintaining (1 350 ± 25) °C at the centre of the combustion tube.

5.2.3.3.6 Combustion-gas-refining assembly, composed of a dust chamber filled with glass wool, a desulfurization tube [manganese(IV) oxide, MnO_2], with electric furnace, copper(II) oxide, CuO, oxidizing tube and a dehydration tube [magnesium perchlorate, $Mg(ClO_4)_2$].

NOTE The desulfurization tube and oxidizing tube are optional.

Allowance should be made for the fact that, frequently, the temperature indicated on the built-in temperature control display of the furnace deviates from the actual temperature in the ceramic tube. It should be adjusted using an external thermocouple device, measuring the temperature of the heating zone inside the tube.

5.2.3.4 Setting up of test assembly

Set up the test assembly in accordance with the manufacturer's instructions.

5.2.3.5 Procedure of RF combustion with tin powder

Turn on the power source of the apparatus, raise the combustion tube temperature to 1 350 ± 25 °C, and wait for the carbon determination apparatus to stabilize. Start oxygen flow at the specified pressure and amount and check air-tightness.

NOTE The detailed procedures, for example the test of air tightness, are carried out in accordance with the instruction manual attached to the apparatus.

Measure and spread the sample uniformly on a combustion boat. Cover it with 2 g of accelerator, mix 2 g of accelerator into the sample and spread uniformly, or put the sample between 1 g each of accelerator, like a sandwich, and spread.

Open the valve at the entrance of the combustion tube and put the combustion boat with the sample and accelerator in the centre of the combustion tube. Immediately, close the valve tightly and start oxygen flow.

The carbon dioxide gas formed is supplied by carrier gas to the detection unit.

Carry out the determination of the carbon dioxide formed, as described in 5.3.

5.2.4 Induction furnace (IF) in oxygen and metallic powder as decomposing agent

5.2.4.1 Principle

The sample is heated together with a base metal additive in a stream of oxygen using a high-frequency induction furnace. The carbon dioxide released is transferred by carrier gas to the detection unit.

5.2.4.2 Reagents

5.2.4.2.1 Granulated iron accelerator, e.g. as supplied by the supplier of the furnace.

5.2.4.2.2 Granulated tungsten accelerator, e.g. as supplied by the supplier of the furnace.

5.2.4.2.3 Granulated copper accelerator, e.g. as supplied by the supplier of the furnace.

5.2.4.2.4 Oxygen, 99,99 % or 99,5 %.

NOTE Oxygen 99,99 % is used if the instrument does not have an oxygen-refining capability. Oxygen 99,5 % is used if the instrument has oxygen-refining ability.

5.2.4.3 Apparatus

5.2.4.3.1 Combustion crucibles, of ceramic material with covers and holders. In principle, use the high-frequency combustion crucible and the high-frequency combustion crucible holder as recommended by the apparatus provider.

Use only accelerators with low blank test values.

The empty combustion crucibles should be burned out over 1 000 °C without sample. Combustion crucibles of ceramic material with covers can be supplied by the manufacturer of the furnace.

5.2.4.3.2 High-frequency induction furnace, composed of oxygen-refining, sample-burning and combustion-gas-refining assemblies.

5.2.4.3.3 Oxygen-refining assembly (see 5.2.3.3.4).

5.2.4.3.4 Sample-burning assembly, composed of high-frequency heating furnace and high-frequency oscillator. The high-frequency heating furnace has a copper coil for heating and quartz combustion tube. Put the high-frequency combustion crucible on the holder and keep it at the centre of the coil using the supporting bar.

5.2.4.3.5 Combustion-gas-refining assembly (see 5.2.3.3.6).

5.2.4.4 Set-up of test assembly

Set up the test assembly in accordance with the manufacturer's instructions.

5.2.4.5 Procedure of induction furnace (IF) combustion

Turn on power source of apparatus, adjust each part to stabilize. When each part stabilizes, check for air-tightness.

Transfer the sample to the combustion crucible and add to it 1 g of copper, Cu, and 1 g of iron, Fe, or 1 g of copper and 1 g of tungsten, W, or 1 g of iron and 2 g of tungsten as accelerator. Then the ceramic cover is placed on the crucible. The crucible is placed in the furnace.

This is unit dependent. Put the crucible on its holder and hold it by using a supporting bar at the specified place.

Then, flow oxygen at a specified pressure and amount. Operate the high-frequency heating furnace for the specified time. The combustion gas is transferred in the detection unit at the user's own option.

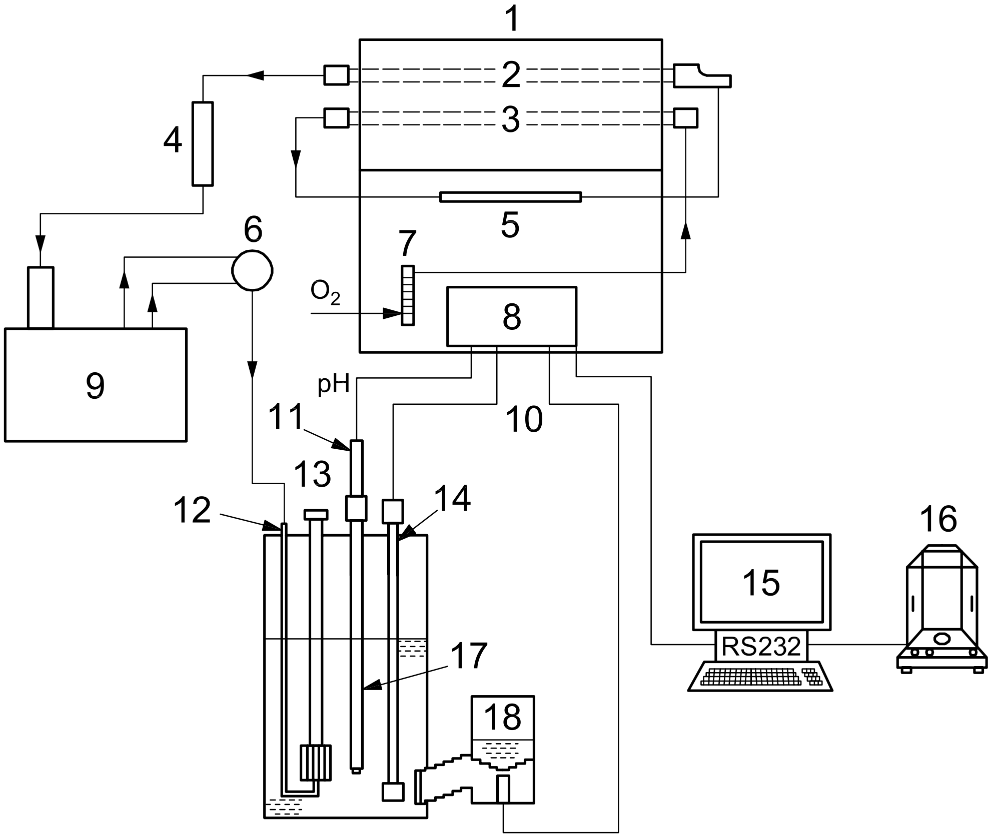
Modern IF combustion units available on the market work automatically. Operate in accordance with the operating instructions.

5.3 Detection techniques

5.3.1 Coulometry

The carbon present in the sample is ignited in a stream of oxygen in a furnace to produce carbon dioxide. Together with the oxygen, the combustion gases are drawn off by a pump through a tube containing percarbamide, which absorbs the oxidation products of the sulfur contained in the sample. The carbon dioxide is transferred to a titration cell filled with alkaline barium perchlorate, $Mg(ClO_4)_2$, solution, where it is absorbed, with a consequent reduction in the alkalinity of the solution. Automatic back titration to the initial pH value of the solution is carried out using electrolytically generated barium hydroxide. According to Faraday's law, the amount of electricity consumed is deemed to be a measure of the absolute carbon content of the sample.

An example of the coulometric determination apparatus is given in Figure 2.



Key

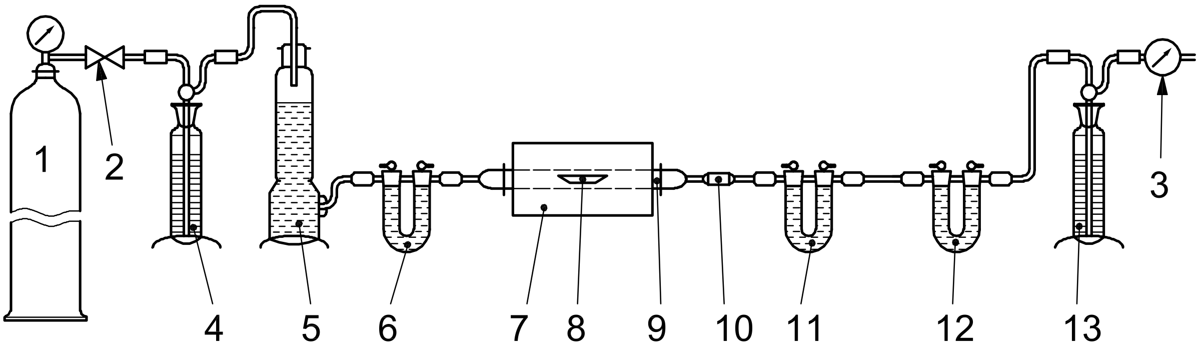
1	furnace	7	flowmeter	13	basket stirrer
2	combustion tube	8	coulometer	14	cathode
3	oxygen-purifying tube	9	gas-splitting pump	15	PC
4	SO_2 absorber	10	electrolysis current	16	balance
5	CO_2 absorber	11	amplifier	17	pH electrode
6	10 % – 100 % gas-splitting valve	12	gas inlet tube	18	anode

Figure 2 — Coulometric determination apparatus

5.3.2 Gravimetry using resistance furnace

The carbon present in the sample is ignited in a stream of oxygen in a resistance furnace to oxidize carbon to carbon dioxide. Together with the oxygen, the combustion gases are passed through tubes containing magnesium perchlorate and percarbamide, which absorbs moisture and oxidation products of the sulfur contained in the sample or which is a product of reaction from sample compounds. The carbon dioxide is transferred to the absorption U-tube containing sodium hydroxide on a carrier, where it is absorbed. The mass increase is directly given by carbon dioxide and calculated via a conversion factor.

An example of the gravimetric determination apparatus is given in Figure 3. The setting up of the test assembly is given in 5.4.2.4.



Key

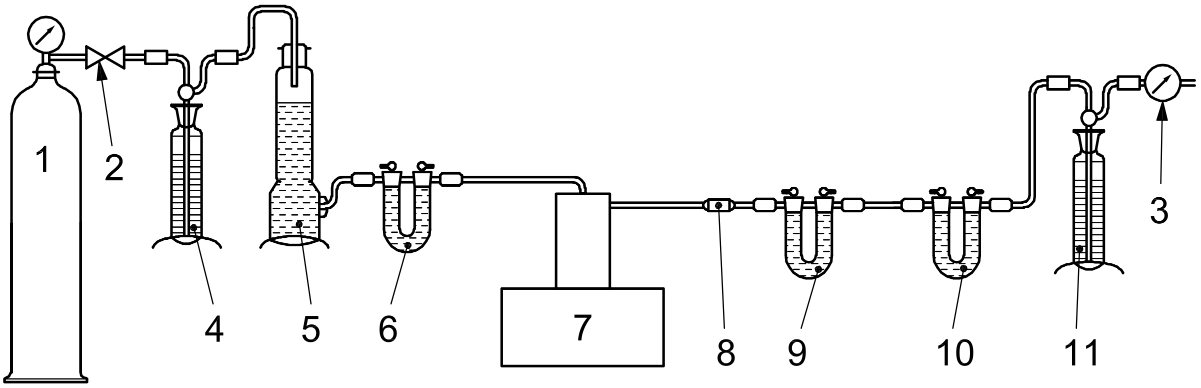
1 oxygen cylinder
2 pressure-controlling valve
3 gas flowmeter
4 gas-washing bottle containing concentrated sulfuric acid
5 drying tower containing sodium hydroxide on a carrier
6 U-tube containing magnesium perchlorate
7 high-frequency induction furnace
8 tube filled with percarbamide
9 U-tube containing magnesium perchlorate
10 absorption U-tube containing sodium hydroxide on a carrier and magnesium perchlorate
11 gas-washing bottle containing 5 % palladium(II) chloride solution
12 absorption U-tube containing sodium hydroxide on a carrier and magnesium perchlorate
13 gas-washing bottle containing 5 % palladium(II) chloride solution

Figure 3 — Apparatus for gravimetric determination using resistance furnace

5.3.3 Gravimetry using high-frequency induction furnace

The carbon present in the sample is ignited in a stream of oxygen in an induction furnace to produce carbon dioxide. Together with the oxygen, the combustion gases are passed through tubes containing magnesium perchlorate and percarbamide, which absorbs moisture and oxidation products of the sulfur contained in or reacted from the sample. The carbon dioxide is transferred to the absorption U-tube containing sodium hydroxide on a carrier, where it is absorbed. The weight increase is directly given by carbon dioxide and calculated by a conversion factor.

An example of the apparatus for gravimetric determination using a high-frequency induction furnace is given in Figure 4. The setting-up of the test assembly is given in 5.4.2.4.



Key

1 oxygen cylinder
2 pressure regulator
3 gas flowmeter
4 gas-washing bottle containing concentrated sulfuric acid
5 drying tower containing sodium hydroxide on a carrier
6 U-tube containing magnesium perchlorate
7 high-frequency induction furnace
8 tube filled with percarbamide
9 U-tube containing magnesium perchlorate
10 absorption U-tube containing sodium hydroxide on a carrier and magnesium perchlorate
11 gas-washing bottle containing 5 % palladium(II) chloride

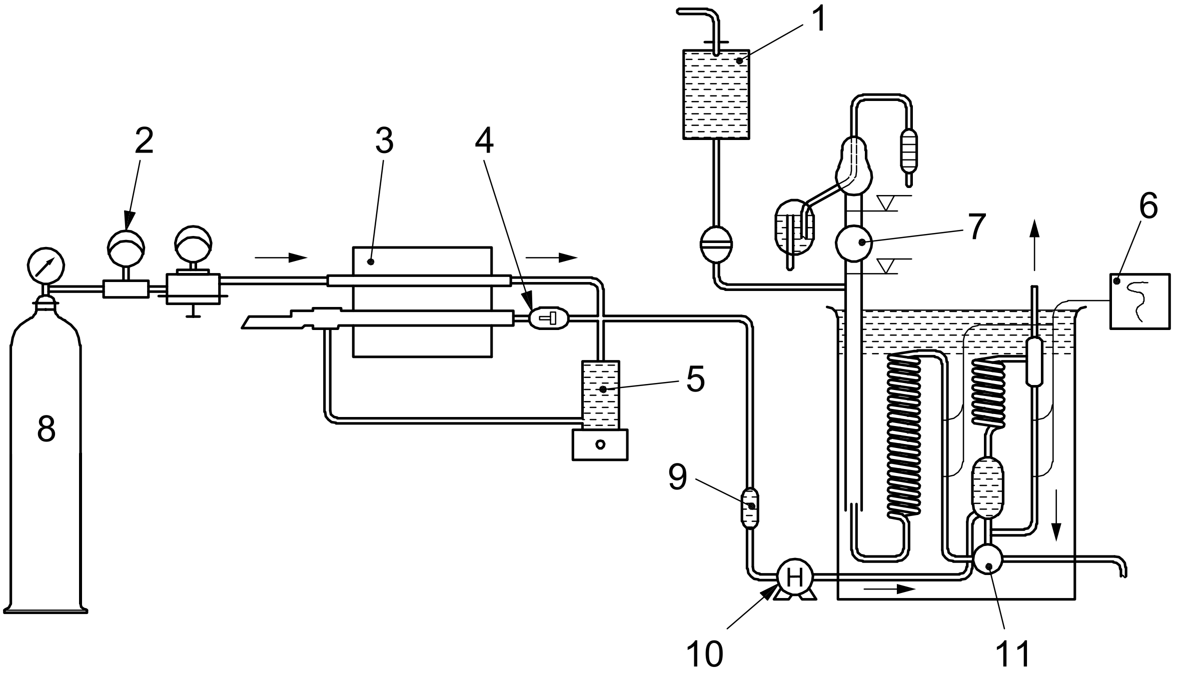
Figure 4 — Apparatus for gravimetric determination using a high-frequency induction furnace

5.3.4 Conductometry

The carbon in the sample is ignited in a stream of oxygen in a furnace to produce carbon dioxide. Together with the oxygen, the combustion gases are drawn off by a pump through a tube containing percarbamide which absorbs the oxidation products of the sulfur contained in the sample.

The carbon dioxide is absorbed in sodium hydroxide solution and its amount calculated from the change in conductivity.

An example of the conductometry apparatus is given in Figure 5.



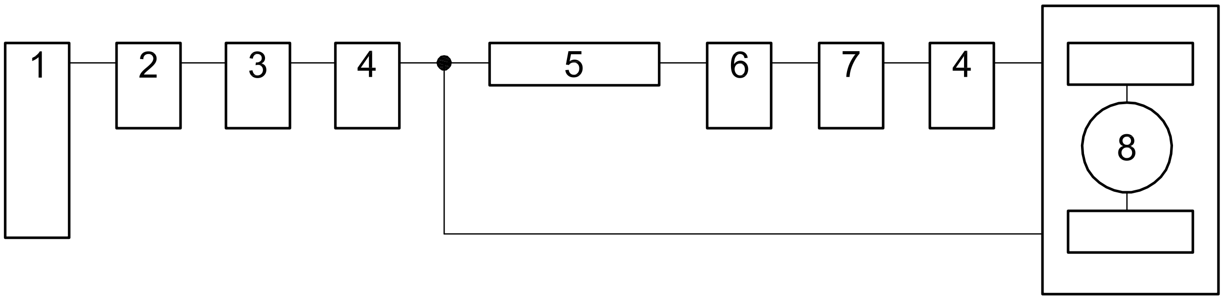
Key

1	stock container	5	container filled with soda lime	9	tube filled with percarbamide
2	double pressure reducing valve	6	self-balancing line recorder	10	measuring pump
3	furnace	7	measuring vessel	11	conductivity measuring cell
4	tube containing quartz wool	8	oxygen cylinder		

Figure 5 — Conductometric determination apparatus

5.3.5 Infrared (IR) method and resistance furnace (RF) combustion

The sample gas is transferred into an infrared analysis apparatus. The infrared absorbance change is measured. An outline of apparatus for determination of total carbon, free carbon, and silicon carbide is given in Figure 6.



Key

1 oxygen cylinder

2 oxidizing tube with electric furnace

3 carbon-dioxide-absorbing tube

4 dehydration tube

5 combustion tube

6 dust tube

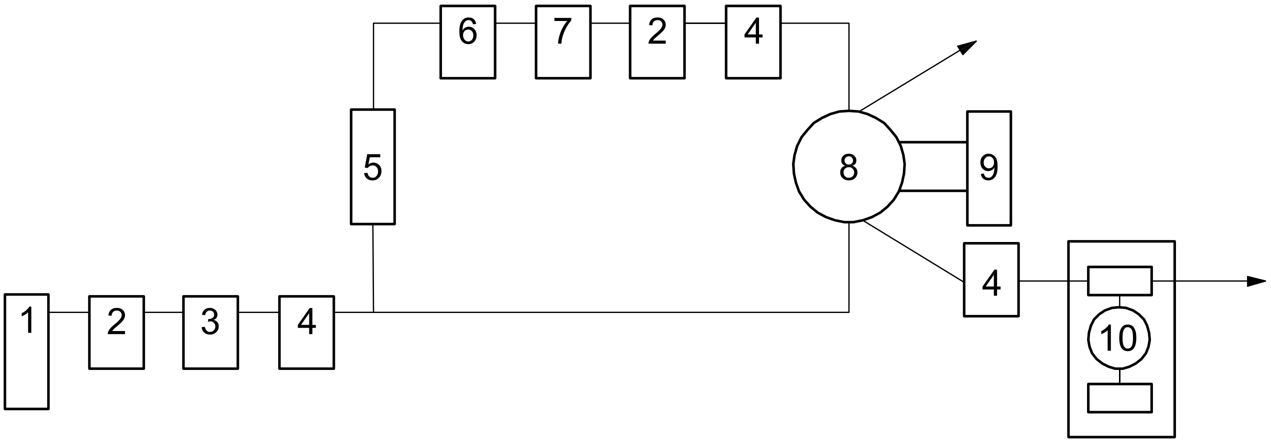
7 desulfurization tube

8 infrared absorption analyser

Figure 6 — Outline of RF combustion apparatus

5.3.6 Thermal conductivity (TC) method and induction furnace (IF) combustion

The sample gas is adsorbed to a collecting tube. Then, the collecting tube is heated and the desorbed carbon dioxide is transferred with oxygen gas to a thermal conductivity analyser in order to measure the change of thermal conductivity. An outline of apparatus for determination of total carbon is given in Figure 7.



Key

1 oxygen cylinder

2 oxidizing tube with electric furnace

3 carbon-dioxide-absorbing tube

4 dehydration tube

5 combustion tube

6 dust tube

7 desulfurization tube

8 flow path converter

9 carbon dioxide capture tube

10 thermal conductivity analyser

Figure 7 — Outline of IF combustion apparatus

5.4 Detection methods

5.4.1 Resistance furnace method with coulometric detection of the released CO_2

5.4.1.1 Combustion and detection

The combustion technique is described in 5.2.2 and the detection technique is described in 5.3.1.

5.4.1.2 Reagents

Use only reagents of analytical grade.

5.4.1.2.1 Barium perchlorate solution: dissolve about 200 g of analytical grade barium perchlorate, $Ba(ClO_4)_2$, in distilled or deionized water and make up to one litre.

5.4.1.2.2 Barium carbonate, $BaCO_3$.

5.4.1.2.3 Hydrogen peroxide adsorbed on urea, $H_2O_2CO(NH_2)_2$, (percarbamide).

5.4.1.2.4 2-propanol, $CH_3CH(OH)CH_3$.

5.4.1.2.5 Buffer solutions, for calibrating the pH meter, as specified by the equipment manufacturer.

5.4.1.3 Apparatus

Ordinary laboratory apparatus and the following.

5.4.1.3.1 Combustion device (see 5.2.2.3).

5.4.1.3.2 Coulometric titration device (see Figure 2).

5.4.1.4 Setting up the test assembly

Set up the test assembly in accordance with the manufacturer's instructions.

5.4.1.5 Check of test assembly, blank value determination

To check a newly set up test assembly or to carry out routine checks, ignite a few reference samples of known carbon content before running the analytical sample. The difference between the carbon content found and the known carbon content of the reference sample shall not exceed the permissible tolerances.

For the blank value, determine the carbon content of lead borate three times using the same amount of lead borate and the same time as is required for the combustion. Subtract the mean of the three determinations as a blank value when calculating the total carbon content.

5.4.1.6 Procedure

Weigh about 40 mg of the sample, to the nearest 0,1 mg, into the combustion boat, ignite and determine as described in 5.2.2 and 5.3.1.

The volume of the combustion gas shall generally be reduced to one-tenth.

Carry out the coulometric determination of the carbon dioxide, CO_2, released as described in the manufacturer's manual.

5.4.1.7 Calculation

Calculate the total mass fraction of carbon, w_{Ctotal}, expressed as a percentage, using Equation (7).

$$w_{\text{Ctotal}} = \frac{(I \times f) - (I^1 \times f^1) \times x}{m_{\text{E}}} \tag{7}$$

where

I is the number of pulses found for the sample;

f is the gas volume reduction factor;

I^1 is the mean number of pulses in the blank value determination as specified in 5.4.1.5.

f^1 is the gas volume reduction factor used for the blank value determination;

m_{E} is the initial sample mass corrected as specified in Clause 5 of ISO 21068-1:2008, in milligrams;

x is a proportionality factor specific to the apparatus for converting the number of pulses to mg of carbon.

NOTE When using older devices, the detected carbon, in coulombs, is indicated in pulses; state of the art devices indicate the mass fraction of carbon as a percentage.

5.4.2 Resistance/induction furnace method with gravimetric detection of the released carbon dioxide

5.4.2.1 Combustion and detection

The combustion technique is described in 5.2.2 to 5.2.4, depending on combustion technique, and the detection technique is described in 5.3.2 and 5.3.3.

5.4.2.2 Reagents

Use only reagents of analytical grade.

5.4.2.2.1 Granulated magnesium perchlorate, $Mg(ClO_4)_2$.

5.4.2.2.2 Sodium hydroxide, NaOH, analytical grade, on a carrier, grain size 2 mm to 3 mm.

5.4.2.2.3 Hydrogen peroxide, adsorbed on urea, H_2O_2 $CO(NH_2)_2$, (percarbamide).

5.4.2.2.4 Palladium(II) chloride solution, $PdCl_2$. Dissolve 0,3 g of (II)(II) chloride, $PdCl_2$, in 10 ml of approximately 36 % hydrochloric acid in a 100 ml volumetric flask, add 5 g of anhydrous sodium acetate, and make up to 100 ml with distilled water; keep the solution in the dark.

5.4.2.2.5 Analytical grade sulfuric acid, H_2SO_4, with a concentration of 96 % to 98 %.

5.4.2.2.6 Glass wool.

5.4.2.3 Apparatus

Ordinary laboratory apparatus and the following.

5.4.2.3.1 Combustion device, depending on combustion technique (see 5.2.2 to 5.2.4).

5.4.2.3.2 Gas-washing bottles.

5.4.2.3.3 Drying tower.

5.4.2.3.4 Absorption vessels, e.g. U-tubes.

5.4.2.3.5 Glass tube for gas-purifying agent.

5.4.2.4 Setting up the test assembly

Glass wool may be placed in the end sections of the U-tube filled with magnesium perchlorate, $Mg(ClO_4)_2$, and the other U-tubes filled with reagents, but under no circumstances shall wool, or any other fibrous organic material, be used.

Fill the absorption U-tube to two-thirds of its capacity with sodium hydroxide on a carrier at the end nearest to the combustion tube and fill the remaining third of the capacity in the opposite limb with magnesium perchlorate.

In setting up the assembly, care shall be taken to ensure that there are no blockages down-stream of the combustion tube and that glass is next to glass in the case of flexible connections.

5.4.2.5 Check of test assembly, blank value determination

To check a newly set up test assembly or to carry out routine checks, ignite a few reference samples of known carbon content before running the analytical sample.

The difference between the result found and the known carbon content of the reference sample shall not exceed the permissible tolerances.

Each time an absorption U-tube is filled with sodium hydroxide on a carrier, a blank determination shall be carried out to check whether the change in mass of the U-tube is within the permissible tolerances.

For blank value determination, determine the carbon content of the accelerator additives three times using the same amount of accelerator and the same time as is required for the combustion. The mean of the three determinations shall be subtracted as a blank value when calculating the total carbon content.

5.4.2.6 Procedure

Weigh 0,1 g to 0,2 g of the sample, to the nearest 0,1 mg, into a combustion crucible/boat, and cover with accelerator. Place the crucible/boat in the furnace. Weigh the absorption U-tube to the nearest 0,1 mg and connect it to the assembly.

After ignition, remove the absorption U-tube from the test assembly. Allow to cool in a desiccator, and then weigh to the nearest 0,1 mg.

If the palladium(II) chloride solution in the washing bottle turns to a dark colour, this is indicative of insufficient oxygen being present during the combustion process. In this case, disregard the results and increase the oxygen flow rate in the next analysis.

5.4.2.7 Calculation

Calculate the total mass fraction of carbon, w_{Ctotal}, expressed as percentage, using Equation (8).

$$w_{\text{Ctotal}} = \left(G - G^1\right) \times \frac{0{,}272\,9}{m_{\text{E}}} \times 100 \qquad (8)$$

where

G is the increase in mass, in grams, of the absorption U-tube;

G^1 is the blank value, in grams, as specified in 5.4.2.5;

m_{E} is the initial sample mass, in grams, corrected as specified in Clause 6;

0,272 9 is the factor for converting carbon dioxide to carbon.

5.4.3 Resistance furnace method with conductometric detection of released carbon dioxide, CO_2

5.4.3.1 Combustion and detection

The combustion technique is described in 5.2.2 and the detection technique is described in 5.3.4.

5.4.3.2 Reagents

Use only reagents of analytical grade.

5.4.3.2.1 Sodium hydroxide solution, c(NaOH) 0,012 5 mol/l.

5.4.3.2.2 Hydrogen peroxide adsorbed on urea, $H_2O_2\ CO(NH_2)_2$, (percarbamide).

5.4.3.2.3 Sodium hydroxide on a carrier, e.g. granulated soda lime, grain size 2 mm to 3 mm.

5.4.3.2.4 Lead borate, $2PbO{\cdot}B_2O_3$, as specified in 5.2.2.2.2.

5.4.3.3 Apparatus

Ordinary laboratory apparatus and the following.

5.4.3.3.1 Combustion device (see 5.2.2.3).

5.4.3.3.2 Conductometric detection system for carbon dioxide (see Figure 5).

5.4.3.4 Setting up the test assembly

Set up the test assembly in accordance with the manufacturer's instructions.

5.4.3.5 Check of test assembly, blank determination

Carry out a check of the test assembly and blank value determination as specified in 5.4.1.5.

5.4.3.6 Procedure

Weigh about 80 mg to 90 mg of the sample, to the nearest 0,1 mg, into the combustion boat, and ignite and detect it as described in 5.2.2 and 5.3.4.

The volume of the combustion gas shall generally be reduced to one-tenth.

Carry out the conductometric determination of the carbon dioxide released as described in the manufacturer's manual.

5.4.3.7 Calculation

Determine the total mass fraction of carbon, w_{Ctotal}, expressed as a percentage, from the plot obtained with a recorder calibrated using reference samples of known carbon content.

5.4.4 Resistance/induction furnace method with detection of the released carbon dioxide, CO_2, by infrared absorption

5.4.4.1 Combustion and detection

The combustion technique is described in 5.2.2 to 5.2.4, depending on combustion technique, and the detection technique is described in 5.3.5.

5.4.4.2 Reagents

Use the reagents specified in the manufacturer's instructions. Use only reagents of analytical grade.

5.4.4.3 Apparatus

Ordinary laboratory apparatus and the following.

5.4.4.3.1 Combustion device, depending on combustion technique (see 5.2.2 to 5.2.4).

5.4.4.3.2 Infrared absorption device (see Figure 6).

5.4.4.4 Setting up the test assembly

Set up and operate the test assembly in accordance with the manufacturer's instructions.

5.4.4.5 Check of test assembly, blank value determination

To check a newly set up test assembly or to carry out routine checks, ignite a few reference samples of known carbon content (see 5.4.4.6) before examining the analytical sample.

The difference between the result found in accordance with 5.4.4.6 and the known carbon content of the reference sample shall not exceed the permissible tolerances.

For blank value determination, determine the carbon content of the accelerator additives three times using the same amount of accelerator (see 5.4.4.6) and the same time as is required for the combustion. The average of the three determinations shall be subtracted as a blank value when calculating the total carbon content.

5.4.4.6 Procedure

Depending on the carbon content, weigh 50 mg to 90 mg of the sample, to the nearest 0,1 mg, into a combustion crucible, and cover with an accelerator. Place the crucible in the furnace and follow the instructions given in 5.2.4 if using an induction furnace, 5.2.2 or 5.2.3 or if using a resistance furnace.

NOTE A ceramic cover upon the crucible can prevent splashing of the sample and accelerator when the reaction is vigorous during combustion.

5.4.4.7 Calculation

Determine the total mass fraction of carbon, w_{Ctotal}, expressed as a percentage, in accordance with the manufacturer's instructions, taking the blank value into account.

5.4.5 Induction furnace combustion — Thermal conductivity method (TC)

5.4.5.1 Combustion and detection

The combustion technique is described in 5.2.4 and the detection technique is described in 5.3.6.

5.4.5.2 Materials and reagents

5.4.5.2.1 Calibration sample: graphite greater than 99,9 % by mass, calcium carbonate greater than 99,9 % by mass, a silicon carbide or carbon sample with known carbon content.

5.4.5.3 Apparatus

Ordinary laboratory apparatus and the following.

5.4.5.3.1 Carbon determination apparatus, with a TC measuring cell, composed of a flow path converter, carbon dioxide collecting tube (synthetic zeolite), and thermal conductivity analyser, and associated equipment. The flow path converter can change the flow path of oxygen whether the carbon dioxide is collected or emitted. The carbon dioxide collecting tube enters the thermostat, which is kept below 50 °C when carbon dioxide is collected or is kept at approximately 300 °C when carbon dioxide is emitted. The thermal conductivity analyser converts the difference between the electric resistances of the sample cell and reference cell to the amount of carbon content through detection, linearization and integrating circuits, and indicates these at an integrating meter. An example is given in Figure 7.

5.4.5.4 Mass of test portion

The mass of the test portion depends on the total carbon content. Weigh the mass given in Table 3 and record it to the nearest 0,1 mg.

Table 3 — Mass of test portion

Total carbon content % by mass	Mass of test portion g
below 10	0,20
10 to 50	0,10
50 to 99	0,05

5.4.5.5 Procedure

Carry out the determination in the following sequence:

a) blank test;

b) calculation of calibration coefficient;

c) measurement of sample.

However, it is not necessary that the start procedure is carried out every time in cases where several samples are continuously measured.

Turn on the power source of the apparatus, adjust each part and allow to stabilize. When each part has stabilized, check that the apparatus is airtight.

Heating for a specified time, transfer the carbon dioxide emitted with oxygen to a thermal conductivity analyser, and read the integrating value.

Open the stopcock at the entrance of the burning tube and put the burning boat with the sample and co-burning agent in the centre of the burning tube. Immediately, turn the stopcock on carefully and let oxygen flow. After a specified time, record the value of the integrating meter (the reading can be called an integrated value).

5.4.5.6 Blank test

Carry out the procedure using the procedure given in 5.4.5.5 without the sample. Calculate the average integrated value obtained from three to five consecutive measurements.

5.4.5.7 Calculation of calibration coefficient

Transfer a specified amount of the sample for calibration, which contains 30 mg to 50 mg of total carbon (for example, 30 mg for graphite, 250 mg for calcium carbonate, or 100 mg for silicon carbide) and carry out the procedure given in 5.4.5.5. Calculate the average integrated value obtained from 3 to 5 consecutive measurements and calculate the calibration coefficient, K, using the following equation.

$$K = \frac{m_\mathrm{c}}{A_0 - A_1} \times \frac{P}{100} \qquad (9)$$

where

m_c is the mass of sample used for calibration, in grams;

P is the percentage of total carbon in the calibration sample, expressed as a percentage by mass;

A_0 is the integrated value of calibration sample;

A_1 is the integrated value of the blank determination obtained in 5.4.5.6.

5.4.5.8 Calculation

Determine the total mass fraction of carbon, w_Ctotal, expressed as a percentage, using Equation (10).

$$w_{\mathrm{Ctota}l} = \frac{(A_2 - A_1) \times K}{m} \qquad (10)$$

where

A_2 is the integrated value obtained in 5.4.5.5;

A_1 is the integrated blank value obtained in 5.4.5.6;

K is the calibration coefficient (g/integrated value) obtained in 5.4.5.7;

m is the mass of test portion, in grams.

A commercially available apparatus can memorize values of blank test and calibration coefficients automatically. The mass of the test samples has to be entered in advance, and after combustion of the sample the apparatus will directly indicate percentage of total carbon in the sample.

6 Determination of free carbon content

6.1 General

For the determination of free carbon, the same detection techniques are used as for total carbon. The detection methods differ between direct and indirect methods after combustion in the resistance furnace.

6.2 Sample decomposition by combustion

6.2.1 General

As a combustion technique, only a resistance furnace without any decomposing agent/accelerator shall be used except in the wet chemical oxidation method described in 6.6.

6.3 Detection techniques

The detection techniques are the same as used for total carbon (see 5.3).

6.4 Direct detection methods

6.4.1 Principle

For direct determination of free carbon, the resistance furnace method is used. The quantification of released carbon dioxide shall be performed by using optionally coulometry, gravimetry, conductimetry, infrared absorption or thermal conductivity. The sample is ignited without any addition of accelerator or decomposing agent. Temperature and ignition time is specified, so that oxidation of silicon carbide can be neglected.

NOTE This direct method for the determination of free carbon is only applicable if oxidation of silicon carbide can be neglected. This is the case, for example, with α-SiC containing not less than 95 % of silicon carbide, SiC, and not more than 2 % of free carbon, C.

6.4.2 Determination of free carbon by coulometric method at 850 °C

6.4.2.1 Reagents

Use the reagents given in 5.4.1.2.

6.4.2.2 Apparatus

Ordinary laboratory apparatus and the test assembly for total carbon determination as described in 5.4.1.3.

NOTE Where the free carbon only is to be determined in accordance with this part of ISO 21068, a furnace capable of being maintained at a temperature of (900 ± 20) °C in the centre of the heating zone is adequate.

6.4.2.3 Set-up of test assembly

Follow the manufacturer's instructions for setting up the test assembly. An example of the test assembly is shown in Figure 2.

6.4.2.4 Check of test assembly, blank value determination

Check a newly set up test assembly or carry out routine checks by igniting a few reference samples of known free carbon content, as described in 6.4.2.5, before running the analytical sample.

The difference between the carbon content found and the known carbon content of the reference sample shall not exceed the permissible tolerances.

Prior to every series of analyses, the blank value shall be determined (with no gas volume reduction) using a precalcined boat, and the mean obtained from three determinations has to be subtracted from the measured values. The blank value is usually between 0,01 % and 0,02 % carbon.

6.4.2.5 Procedure

Weigh to the nearest 0,1 mg about 200 mg of the sample prepared and dried as specified in Clause 5 of ISO 21068-1:2008, into a boat from which any carbon present has previously been removed by calcination, and place the boat in the furnace preheated to a temperature of 850 °C ± 10 °C, as measured in a single point near to the centre of the heating zone. Measure the furnace temperature and adjust it if required. Adjust the oxygen flow rate so that there is no risk of air being sucked in from outside. Unless the free carbon content is particularly low, the volume of the combustion gas shall generally be reduced to one-tenth using a pump as described in 5.3.1.

Carry out the determination of free carbon at the above temperature for exactly 10 min.

6.4.2.6 Calculation

Calculate the mass fraction of free carbon, w_{Cfree}, expressed as a percentage, to the nearest 0,01 %, using Equation (11).

$$w_{\text{Cfree}} = \frac{(I \times f) - (I^{\text{f}} \times f^{\text{f}}) \times x}{m_{\text{E}}} \tag{11}$$

where

I is the number of pulses found for the sample;

f is the gas volume reduction factor;

I^{f} is the mean number of pulses in the blank value determination as specified in 6.4.2.4;

f^{f} is the gas volume reduction factor used for the blank value determination;

m_{E} is the sample mass, in milligrams, corrected as specified in Clause 5 of ISO 21068-1:2008;

x is a proportionality factor specific to the apparatus for converting the number of pulses to carbon content.

6.4.3 Determination of free carbon by gravimetric method at 750°C

6.4.3.1 Reagents

Use the reagents given in 5.4.2.2.

6.4.3.2 Apparatus

Ordinary laboratory apparatus and the test assembly for total carbon determination described in 5.2.2.3 and 5.4.2.3.

NOTE Where free carbon only is to be determined in accordance with this part of ISO 21068, a furnace capable of reaching a temperature of 800 °C in the centre of the heating zone is adequate.

6.4.3.3 Set-up of test assembly

Set up the test assembly as described in 5.4.2.4.

6.4.3.4 Check of test assembly, blank value determination

Check the test assembly as described in 5.4.2.5, using the ignition procedure given in 6.4.3.5.

Maintain the furnace temperature of 750 °C ± 25 °C over the length of the combustion boat (see 4.3.2.5), checking the temperature occasionally using an external thermocouple device (see 4.3.2.3).

Prior to every series of analyses, the blank value shall be determined using a precalcined boat. The mean obtained from three determinations is subtracted from the measured values.

6.4.3.5 Procedure

Before using the test assembly, thoroughly flush the combustion tube with oxygen. After filling, weigh the absorption vessel to the nearest 0,1 mg and connect it to the assembly. Then weigh, to the nearest 0,1 mg, 2 g of the analytical sample, prepared and dried as specified in Clause 5 of ISO 21068-1:2008, into a boat from which any carbon present has been removed by calcination.

Place the boat in the furnace preheated to a temperature of 750 °C ± 25 °C in the centre of the heating zone, and immediately pass oxygen through it, at an adequate flow rate compatible to the volume to be absorbed. Ignite the sample at this temperature in the furnace for 60 min and then remove the absorption tube. Allow to cool in a desiccator, and then weigh to the nearest 0,1 mg.

If the palladium(II) chloride solution in the washing bottle turns to a dark colour, this is indicative of insufficient oxygen being present during the combustion process. In this case, disregard the results and increase the oxygen flow rate in the next analysis.

6.4.3.6 Calculation

Calculate the mass fraction of free carbon, w_{Cfree}, expressed as a percentage, to the nearest 0,01 %, using Equation (12).

$$w_{\mathrm{Cfree}} = \frac{(G - G^{\mathrm{I}}) \times 0{,}272\,9}{m_{\mathrm{E}}} \times 100 \tag{12}$$

where

G	is the increase in mass of the absorption vessel, in grams;
G^{I}	is the blank value determined as described in 6.4.3.4, in grams;
m_{E}	is the sample mass corrected as specified in ISO 21068-1, in grams;
0,272 9	is a factor for converting carbon dioxide to carbon.

6.4.4 Determination of free carbon by conductometric method at 850 °C

6.4.4.1 Reagents

Use the reagents given in 5.4.3.2 except for that given in 5.4.3.2.4.

6.4.4.2 Apparatus

Ordinary laboratory apparatus and the test assembly for total carbon determination as described in 5.4.3.3.

NOTE Where free carbon only is to be determined in accordance with this part of ISO 21068, a furnace capable of reaching a temperature of 900 °C in the centre of the heating zone is adequate.

6.4.4.3 Set-up of test assembly, blank value determination

Set up the test assembly in accordance with the manufacturer's instructions.

Carry out a check of test assembly and blank value determination as described in 6.4.2.4, using the ignition procedure described in 6.4.4.4.

6.4.4.4 Procedure

Weigh, to the nearest 0,1 mg, about 400 mg of the analytical sample, prepared and dried as specified in Clause 5 of ISO 21068-1:2008, into a boat from which any carbon present has previously been removed by calcination, and place the boat in the furnace preheated to a temperature of 850 °C ± 25 °C in the centre of the heating zone. Adjust the oxygen flow rate so that there is no risk of air being sucked in from the outside.

At the above temperature, the determination of free carbon takes 10 min.

6.4.4.5 Calculation

Read the mass fraction of free carbon, C_{free}, expressed as a percentage, from the plot obtained with a recorder calibrated using reference samples of known carbon content. Take the blank value determined in 6.4.4.3 into account.

6.4.5 Determination of free carbon by IR or TC method at 850 °C

6.4.5.1 Principle

The sample is heated in oxygen flow at 850 °C and the content of the carbon dioxide and carbon monoxide yielded is determined using the infrared absorption method or the thermal conductivity method.

6.4.5.2 Reagents

6.4.5.2.1 Oxygen, as described in 5.2.2.2.1.

6.4.5.2.2 Calibration sample, use graphite (above 99,9 % by mass) or a standard substance or carbon-containing sample of which free carbon content is known.

6.4.5.3 Apparatus

6.4.5.3.1 Apparatus as described in 5.2.3.3, except using a quartz glass burning tube instead of a porcelain burning tube.

NOTE The procedure for the determination of the carbon content given in 5.4.4 or 5.4.5 can be used.

6.4.5.3.2 Burning boat. Use a porcelain burning boat 2-type 13,5 mm × 10 mm × 80 mm, a quartz glass burning boat (for example, 14 mm × 10 mm × 80 mm), or platinum burning boat (for example, No. 80).

6.4.5.3.3 Burning tube, quartz glass (for example, 28 mm × 22 mm × 600 mm).

6.4.5.4 Mass of test portion

The mass of test portion depends on the free carbon content as shown in Table 4.

Table 4 — Mass of test portion

Free carbon content % by mass	Mass of test portion g
below 5	0,50
5 to10	0,30
10 to 50	0,10
above 50	0,05

6.4.5.5 Procedure

Carry out the determination in the order of blank test, calculation of calibration coefficient, and measurement of sample, using the following procedure.

Carry out the start procedure as described in 5.2.3.5, with the temperature of the tubular electric furnace at 850 °C ± 25 °C.

Measure and spread the sample uniformly on a burning boat. Open the stopcock on the entrance of the burning tube and put the burning boat with the sample in the centre of the burning tube. Immediately, turn the stopcock on carefully and let oxygen flow. After 10 min, record the value of the integrating meter.

6.4.5.6 Blank test

Carry out the procedure in accordance with 6.4.5.5 without the sample. Recalculate the mean integrated values obtained three to five times.

6.4.5.7 Calculation of calibration coefficient

Carry out the procedure given in 5.4.5.7, using the ignition temperature and ignition time given in 6.4.5.5.

6.4.5.8 Calculation

Calculate the mass fraction of free carbon, w_{Cfree}, expressed as a percentage, to the nearest 0,01 %, using Equation (13).

$$w_{\text{Cfree}} = \frac{(A_2 - A_1) \times K}{m} \times 100 \tag{13}$$

where

A_2 is the integrated value obtained in 6.4.5.5;

A_1 is the integrated value obtained in 6.4.5.6;

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

m is the mass of test portion in grams.

6.5 Indirect detection methods

6.5.1 Principle

The method of indirect determination of the free carbon content takes the oxidation of silicon carbide during the ignition of the free carbon into account, by two alternatives.

For material containing detectable quantities of β-SiC, the method shall be agreed between interested parties. This also applies for material containing more than 2 % free carbon and/or a high proportion of fine particles with a particle size of less than 10 µm, for which only the methods of determination described in 6.5.2 or 6.5.3 yield reliable values.

If there are doubts about using this method, because the substance to be analysed contains volatile constituents, carbonates and/or other reactive additives (Fe, Si, Al), the amounts of these constituents shall be determined and allowed for.

This indirect method of free carbon determination is invalid when the sample contains more than 0,6 % vanadium pentoxide, V_2O_5, or boric acid, H_3BO_3.

Carbon not bound as silicon carbide, SiC, shall not constitute more than 5 %. If the free carbon, C_{free}, content exceeds 5 %, 6.5.4 shall be applied. Alkali oxides or alkali carbonates that act as fluxes interfere with the determination.

The method of indirect determination of free carbon content takes the oxidation of silicon carbide during the ignition of free carbon into account by one of the following methods.

a) Indirect determination of the free carbon by change in mass during calcination in air.

   The following determinations shall be carried out:

   — total mass fraction of carbon, w_{Ctotal}, of the dried starting material, by one of the methods described in 5.4;

   — change in mass on calcination, m_{v}, in air;

   — total mass fraction of carbon of the residue on ignition, w_{CR}, by the method specified in 5.4 chosen for w_{Ctotal}.

b) Indirect determination of the free carbon by weighing back the combustion boat after direct w_{Cfree} determination.

   After determination of the free carbon content as described in 6.4, the combustion boat with the residue is weighed again, and the change in mass is determined. The procedure for w_{Cfree} determination is repeated with the residue until total combustion of free carbon is proved by an increase in mass caused by silicon carbide, SiC, oxidation.

c) Indirect determination of free carbon by calculation

$$w_{\text{Cfree}} = w_{\text{Ctotal}} - w_{\text{CSiC}}$$

where w_{CSiC} is the mass fraction of carbon, calculated from silicon carbide, SiC,

or

$$w_{\text{Cfree}} = w_{\text{Ctotal}} - w_{\text{Cash}}$$

where w_{Cash} is the mass fraction of carbon in the ash after ignition at 750 °C (see 7.4).

6.5.2 Indirect determination by change in mass during calcination in air

6.5.2.1 Reagents

Use the reagents given in 5.4, according to the chosen method.

6.5.2.2 Apparatus

Ordinary laboratory apparatus and the following.

6.5.2.2.1 Laboratory furnace, capable of being maintained at (750 ± 25) °C.

6.5.2.2.2 Agate mortar.

6.5.2.2.3 Apparatus for determining the total carbon content, as described in 5.4, according to the chosen method.

6.5.2.2.4 Crucibles, of ceramic material.

6.5.2.3 Procedure

6.5.2.3.1 Determining the change in mass on calcination in air

Weigh, to the nearest 0,1 mg, about 1 g of the substance prepared and dried as specified in Clause 5 of ISO 21068-1:2008, into a precalcined crucible, calcine in the laboratory furnace for 60 min at (750 ± 25) °C and then cool in a desiccator. Weigh to the nearest 0,1 g. Repeat the calcination at least once for 30 min, and weigh the cooled crucible containing the residue again, to the nearest 0,1 mg.

NOTE A slight increase in mass during the second calcination is acceptable, but a decrease in mass requires the calcination to be continued until the mass is constant or increases.

Use the sample mass determined after the final calcination to calculate the change in mass, m_V.

6.5.2.3.2 Determining the total carbon content of the residue on ignition

After calcination as described in 6.5.2.3.1, place the material in the agate mortar and homogenize without reducing the particle size further. Determine the total carbon content of the residue on ignition, w_{CR}, in accordance with the chosen method as described in 5.4.

6.5.2.3.3 Determining the total carbon content of the starting material

Determine the total carbon content, w_{Ctotal}, of the sample prepared and dried as specified in clause 5 of ISO 21068-1:2008, using the same method as used in 6.5.2.3.2.

6.5.2.4 Calculation

Calculate the change in mass on calcination, m_V, as a percentage by mass, to the nearest 0,01 %, using Equation (14).

$$m_V = \frac{m_A - m_E}{m_E} \times 100 \tag{14}$$

where

m_A is the final sample mass, in grams, corrected as specified in Clause 6 of ISO 21068-1:2008, after calcination at 750 °C;

m_E is the initial sample mass, in grams, corrected as specified in Clause 6 of ISO 21068-1:2008.

A loss in mass shall be written with a negative sign in the formulae below and an increase in mass with a positive sign.

Calculate the residue on ignition, R, expressed as a percentage by mass, to the nearest 0,01 %, using Equation (15).

$$R = 100 + m_x \tag{15}$$

where m_x is the increase in sample mass.

Calculate the mass fraction of free carbon, w_{Cfree}, expressed as a percentage, to the nearest 0,01 %, using either Equations (16) or (17).

$$w_{\text{Cfree}} = \frac{\left[w_{\text{Ctotal}} - \dfrac{R \cdot w_{\text{CR}}}{100} \right]}{1{,}600\,9} - \frac{m_{\text{V}}}{2{,}6641} \tag{16}$$

$$w_{\text{Cfree}} = \frac{w_{\text{Ctotal}} - w_{\text{CR}}}{1{,}600\,9} - \frac{m_{\text{V}} \times w_{\text{CR}}}{160{,}09} - \frac{m_{\text{V}}}{2{,}6641} \tag{17}$$

NOTE The factors used in the equations are calculated using the relative molar masses as follows:

$$1{,}600\,9 = \frac{\text{SiO}_2\text{ - SiC}}{\text{C}} + 1$$

$$\frac{\text{SiO}_2\text{-SiC}}{\text{C}}$$

$$2{,}664\,1 = \frac{\text{SiO}_2\text{ - SiC}}{\text{C}} + 1$$

6.5.2.5 Precision

The repeatability and reproducibility limits and standard deviation, as defined in ISO 5725-2, are given in Table 5.

Table 5 — Precision

Repeatability		Reproductibility	
s_r	r	S_R	R
0,07	0,2	0,21	0,57

6.5.3 Indirect determination by weighing back the combustion boat after direct free carbon determination

6.5.3.1 Reagents

Reagents as specified in 6.4, according to the chosen method.

6.5.3.2 Apparatus

Ordinary laboratory apparatus and the following.

6.5.3.2.1 Apparatus for determining the free carbon content as described in 6.4, according to the chosen method.

6.5.3.3 Procedure

Carry out the direct C_{free} determination as described in 6.4. After the C_{free} determination, allow the boat with the residue of the ignition to cool and store in a desiccator. Weigh the residue.

Repeat this procedure until the mass of the residue is constant or increases. The C_{free} results of the repeated determinations are added to give the “apparent” free carbon content $C_{free\text{-}apparent}$.

6.5.3.4 Calculation

Calculate the change in mass on ignition, m_V, expressed as a percentage by mass, to the nearest 0,01 %, using Equation (18).

$$m_V = \frac{m_A - m_E}{m_E} \times 100 \tag{18}$$

where

m_A is the final sample mass, in grams, corrected as specified in Clause 5 of ISO 21068-1:2008, after the last ignition procedure;

m_E is the initial sample mass, in grams, corrected as specified in Clause 5 of ISO 21068-1:2008.

A loss in mass shall be substituted with a negative sign in the formula below, and an increase in mass with a positive sign.

Calculate the mass fraction of actual free carbon, w_{Cfree}, expressed as a percentage, to the nearest 0,01 %, using Equation (19):

$$w_{Cfree} = \frac{w_{Cfree\text{-}apparent}}{1{,}600\,9} - \frac{m_V}{2{,}6641} \tag{19}$$

where

$w_{Cfree\text{-}apparent}$ is the apparent free carbon content obtained in 6.5.3.3;

m_V is defined in Equation (18);

and the factors are as defined in 6.5.2.4.

6.5.4 Determination of free carbon by calculation

The determination of free carbon is carried out by calculation.

If the mass fraction of silicon carbide is determined as described in 7.5, use Equation (20).

$$w_{Cfree} = w_{Ctotal} - w_{CSiC} \tag{20}$$

where

w_{CSiC} is the carbon content, calculated from SiC determined as described in 7.5.

If the mass fraction of silicon carbide is determined as described in 7.4, use Equation (21) when the oxidation effects on the silicon carbide are negligible.

$$C_{free} = C_{total} - C_{SiC} \tag{21}$$

Use Equation (22) when the oxidation effects on silicon carbide are not negligible.

$$\mathrm{C}_{\mathrm{free}} = \frac{\left[\mathrm{C}_{\mathrm{total}} - \mathrm{C}_{\mathrm{ash}}\left(\frac{100+\Delta P}{100}\right)\right]}{1{,}600\,9} - \frac{\Delta P}{2{,}664\,1} \tag{22}$$

where

ΔP is the loss on ignition at 750 °C, LOI_{750}, as described in 4.5;

$\mathrm{C}_{\mathrm{total}}$ is the total carbon in the sample for loss on ignition at 750 °C, LOI_{750} (see 6.5.2.3.3);

$\mathrm{C}_{\mathrm{ash}}$ is the carbon in the ash after ignition at 750 °C (see 6.5.2.3.2);

and the factors are as defined in 6.5.2.4.

The relationship

$$\mathrm{C}_{\mathrm{free}} \leqslant \mathrm{C}_{\mathrm{total}} - \mathrm{C}_{\mathrm{ash}}\left(\frac{100+\Delta P}{100}\right)$$

shall be observed. If necessary, repeat the determinations.

6.6 Direct determination of free carbon by wet oxidation

6.6.1 Principle

This method uses the strong effect of chromic sulfuric iodic acid. The free carbon content is determined as specified in 10.2.1 of EN 12698-1:2007.

NOTE The free carbon of the sample is oxidized to carbon dioxide by chromic sulfuric iodic acid at a temperature of 130 °C to 140 °C. The inert gas carries the CO_2 to the detection system of choice. SiC does not react under these conditions, or only to a negligible amount even for very fine powders.

7 Determination of silicon carbide content, SiC

7.1 General

The determination of silicon carbide, SiC, is carried out by one of the following methods.

- Indirect quantitative method.

  This method is applied for a sample which has less than half of the ratio of the mass fraction of free carbon, w_{Cfree}, against total carbon, w_{Ctotal}.

- Direct quantitative method.

  This method is applied for a sample that has more than a quarter of the ratio of the content of free carbon against total carbon.

- Direct quantitative method after ignition (ignition method at 750 °C).

- Determination of silicon carbide by chemical method.

7.2 Determination of silicon carbide, SiC, by indirect quantitative method

7.2.1 Principle

The chemically bound carbon is determined by calculation as the difference between the total carbon content determined as described in Clause 5 and the free carbon content determined as described in Clause 6.

7.2.2 Calculation

Calculate the mass fraction of silicon carbide, w_{SiC}, expressed as a percentage, using Equation (23).

$$w_{\text{SiC}} = (w_{\text{Ctotal}} - w_{\text{Cfree}}) \times 3{,}338\ 3 \qquad (23)$$

where

w_{Ctotal} is the total mass fraction of carbon, expressed as a percentage, determined as described in Clause 5;

w_{Cfree} is the mass fraction of free carbon, expressed as a percentage, determined as described in Clause 6;

3,338 3 is a stoichiometric factor used for converting carbon to silicon carbide.

Report the result to the nearest 0,1 %.

7.3 Determination of silicon carbide, SiC, by direct quantitative method

7.3.1 Principle

SiC-bound carbon is directly determined by combustion of a sample already free from C_{free} by preliminary combustion.

A sample for which the content of free carbon has been determined is burned with co-burning agent in an oxygen flow and the yielded carbon dioxide and carbon monoxide are measured by infrared absorption or thermal conductivity or other methods as described in Clause 5.

7.3.2 Reagents

Reagents as described in 5.4.4.2 and/or 5.4.5.2.

7.3.3 Apparatus

7.3.3.1 Apparatus for the quantitative determination of carbon, based on the combustion (resistance/induction heating) infrared absorption method as described in 5.4.4 or the combustion (induction heating) thermal conductivity method as described in 5.4.5.

7.3.4 Test portion

Weigh the sample from the residue after combustion in accordance with 6.4.5.4.

The mass of the test portion after combustion depends on the content of silicon carbide as shown in Table 6.

If necessary, grind slightly by using a mortar.

Table 6 — Mass of test portion

Silicon carbide content % by mass	Mass of test portion to be weighed g
below 30	0,20
above 30	0,10

7.3.5 Procedure

Carry out the quantitative determination using one of the methods described in 5.4, especially 5.4.4 or 5.4.5 .

7.3.6 Blank test

Carry out the procedure given in 7.3.5 without the sample. Determine the mean integrated valued obtained for 3 to 5 consecutive measurements.

7.3.7 Calculation of calibration coefficient

If necessary calculate the calibration coefficient in accordance with the procedure corresponding to the apparatus used.

7.3.8 Calculation

Calculate the mass fraction of silicon carbide, w_{SiC}, expressed as a percentage, using Equation (24).

$$w_{\text{SiC}} = \frac{(A_2 - A_1)\times K\times m_1}{m_2\times m}\times 100\times 3{,}338\ 3 \tag{24}$$

where

A_2 is the integrated value in 7.3.5;

A_1 is the integrated value in 7.3.6;

K is the calibration coefficient in 7.3.7

m is the mass of test portion in 6.4.5.4, in grams;

m_1 is the mass of the sample after combustion in 6.4.5.5, in grams;

m_2 is the mass of test portion in 7.3.4, in grams.

7.4 Determination of silicon carbide, SiC, by ignition method at 750 °C

7.4.1 Principle

The carbon content from silicon carbide is determined by a total carbon method after ignition at 750 °C ± 25 °C (carbon from silicon carbide), then calculation of the corresponding silicon carbide content. Ash thus obtained does not contain free carbon but only contains carbon combined in silicon carbide.

7.4.2 Ash production

Carry out the procedure described in 4.5.3 as follows:

Weigh the test sample in a porcelain dish or in a crucible previously treated at 750 °C overnight and cooled in a desiccator.

Put the dish and the sample into a muffle furnace heated at 500 °C ± 25 °C for 20 min.

Increase the furnace temperature to 750 °C and ignite the sample for 1 h 30 min as soon as the furnace has reached test temperature.

Remove the dish (or crucible) from the furnace and allow it to cool to room temperature in a desiccator.

Weigh the dish and sample.

Place the dish and sample in the furnace again for 30 min and check whether there is a further loss in mass. If so, repeat the whole procedure.

7.4.3 Determination of carbon in ash

The principle and procedure are as described in Clause 5.

7.4.4 Calculation

Calculate the mass fraction of silicon carbide in the ash, w_{SiCash}, expressed as a percentage, using Equation (25).

$$w_{\mathrm{SiC\ ash}} = w_{\mathrm{C}} \times 3{,}338\ 3 \tag{25}$$

where

w_{C} is the mass fraction of carbon in 7.4.3, expressed as a percentage.

Calculate the mass fraction of silicon carbide of the dried sample, w_{SiCdry}, expressed as a percentage, using Equation (26).

$$w_{\mathrm{SiC\ dry}} = w_{\mathrm{C}} \times 3{,}338\ 3 \times \left(\frac{100 - \Delta P}{100} \right) \tag{26}$$

where

ΔP is the change of mass at 750 °C, determined in accordance with 4.5, which is negative for a loss of mass, positive for a gain.

The test sample for the determination of carbon from silicon carbide in the ash may be taken from the ash obtained according to 4.5. However, preferably take out a test sample for ignition. The ash from this sample would provide a test sample for carbon determination. In this case, weigh the dish (or the crucible) previously treated at 750 °C to calculate the mass of ash.

7.5 Determination of silicon carbide, SiC, by chemical method

Determination of silicon carbide by sulfo-hydrofluoric decomposition at room temperature.

7.5.1 Principle

Sulfo-hydrofluoric decomposition at room temperature (for removing SiO_2): the residue containing the silicon of the silicon carbide and the free silicon is subjected to another attack to determine silica by gravimetry after insolubilization by perchloric acid. From this, silica is calculated, then $Si_{SiC+free}$, in order to calculate Si_{SiC} using Si_{free}.

7.5.2 Reagents

Use only reagents of analytical grade.

7.5.2.1 **Hydrofluoric acid**, density 1,14 g/ml.

7.5.2.2 **Sulfuric acid**, density 1,84 g/ml.

7.5.2.3 **Sodium carbonate**.

7.5.2.4 **Sodium peroxide**.

7.5.2.5 **Perchloric acid**, density 1,67 g/ml.

7.5.2.6 **Hydrochloric acid**, density 1,19 g/ml.

7.5.2.7 **Hydrochloric acid solution**, 10 %.

7.5.3 Apparatus

7.5.3.1 **Vitreous carbon crucible**, 25 ml.

7.5.3.2 **Platinum dish**, diameter 60 mm.

7.5.3.3 **Beaker**, PTFE, 250 ml.

7.5.3.4 **Watch glass**, PTFE, diameter 75 mm.

7.5.3.5 **Filters**, slow filtration.

7.5.3.6 **Funnel**, polyvinyl chloride (PVC).

7.5.4 Procedure

Accurately weigh 0,5 g to the nearest 0,000 1 g of sample, previously dried (see Clause 5 of ISO 21068-1:2008), into a PTFE beaker (7.5.3.3).

Dissolve with 10 ml of distilled water, 20 ml of hydrofluoric acid, HF, (7.5.2.1) and few drops of sulfuric acid, H_2SO_4 (7.5.2.2).

Cover the beaker with a PTFE watch glass (7.5.3.4) and allow the dissolution to take place for about 18 h in a fume cupboard.

Dilute with 100 ml water, filter through a filter (7.5.3.5) and put in a PVC funnel (7.5.3.6).

Wash with freshly warmed water until washing water is no longer acidic.

Ignite the filter and residue for 15 min at 750 °C ± 25 °C in a vitreous carbon crucible (7.5.3.1) and allow to cool.

Decompose the residue directly in the crucible with a mix of sodium peroxide (7.5.2.4) and sodium carbonate, Na_2CO_3 (7.5.2.3), prepared as described in 8.4.

Carry out a double insolubilization of silica with perchloric acid, $HClO_4$, (7.5.2.5) and the determination of the silicon content via silica according to 8.4.

7.5.5 Calculation

Calculate the mass fraction of silicon carbide, w_{SiCtotal}, from the silicon content corresponding to silicon of silicon carbide and free silicon, $w_{\text{Si,SiC+free}}$ (obtained in 7.5.4), and free silicon, w_{Sifree}, as described in Clause 9, expressed as percentage by mass, using Equation (27).

$$w_{\text{SiC total}} = \left(w_{\text{Si,SiC+free}} - w_{\text{Sifree}}\right) \times 1{,}428 \tag{27}$$

where

1,428	is the gravimetric factor of Si → SiC;
w_{Sifree}	is the mass fraction of free silicon, expressed as a percentage, determined in accordance with Clause 9.

8 Determination of total silicon content via silica

8.1 Principle

Preliminary ignition of the sample at 750 °C ± 25 °C. Fusion in a vitreous carbon crucible with a mix of sodium peroxide, Na_2O_2, and sodium carbonate, Na_2CO_3. Double dehydration/insolubilization of silica by perchloric acid. Determination of residual silica in the filtrate corrected for the residue left after the hydrofluoric acid treatment.

8.2 Reagents

Use only reagents of analytical grade.

8.2.1 Sodium carbonate, Na_2CO_3.

8.2.2 Sodium peroxide, Na_2O_2.

8.2.3 Hydrochloric acid, HCl, density 1,19 g/ml.

8.2.4 Perchloric acid, $HClO_4$, density 1,67 g/ml.

8.2.5 Hydrofluoric acid, HF, 40 %, density 1,13 g/ml.

8.2.6 Sulfuric acid, H_2SO_4, density 1,84 g/ml.

8.2.7 Hydrochloric acid, HCl, 10 %.

8.3 Apparatus

Ordinary laboratory apparatus and the following.

8.3.1 Vitreous carbon crucible, 25 ml.

8.3.2 Platinum dish, diameter 65 mm.

8.4 Procedure

Weigh 500 mg to the nearest 0,000 1 g of sample, preliminarily dried (see Clause 5 of ISO 21068-1:2008).

Ignite the test sample in a vitreous carbon crucible (8.3.1) in a muffle furnace at 400 °C ± 25 °C, then heat gradually to 750 °C ± 25 °C. Ignite the crucible for 30 min.

Allow to cool to room temperature.

Add 4 g of sodium peroxide (8.2.2) and 2 g of sodium carbonate, Na_2CO_3 (8.2.1). Mix thoroughly.

Heat the crucible on a heating plate at 350 °C ± 10 °C for approximately 4 h.

NOTE The mix darkens.

Heat slowly over a flame until fusion, then heat further until the crucible is red.

Allow to cool, add 2 g of sodium peroxide, Na_2O_2, repeat the fusion and continue to heat the crucible to red heat for 2 min to 3 min.

Allow to cool and treat the fused residue with 150 ml of warm water in a 600 ml high beaker. Withdraw the crucible, wash with water, then hydrochloric acid, HCl (8.2.7).

Add 50 ml hydrochloric acid (8.2.3) to the beaker, concentrate the acid solution, then add 80 ml of perchloric acid, $HClO_4$ (8.2.4) and cover with a watch glass.

Heat until there are white perchloric fumes and continue to heat until fuming ceases.

Cool the beaker, add 25 ml of hydrochloric acid (8.2.3), then 100 ml of warm water.

Boil and allow it to stand.

Filter on a white stripe filter. Wash the beaker with warm hydrochloric acid, HCl (8.2.7).

Wash the filter and silica with hydrochloric acid, HCl (8.2.7) four or five times, then with warm water until no acid trace is detected.

Transfer the filter and the precipitate in a platinum dish and put it in a drying oven.

Concentrate the filtrate on a heating plate, then add 50 ml of perchloric acid, $HClO_4$ (8.2.4).

Heat to white perchloric fumes and continue to heat until fuming ceases. Carry out the procedure as for first dehydration.

Put the two filters together and ignite at 1 000 °C ± 25 °C for 30 min.

Allow to cool down at room temperature in a desiccator, then weigh to constant mass, noting the mass as m_1.

Add 1 ml to 2 ml of water, a few drops of sulphuric acid (8.2.6) and 15 ml of hydrofluoric acid, HF (8.2.5).

Evaporate on a heating plate until white sulphuric fumes disappear, then ignite at 1 000 °C ± 25 °C for 10 min.

Allow to cool down to room temperature and weigh to constant mass, noting the mass as m_2.

8.5 Blank test

In parallel to processing the test samples, carry out blank tests with all reagents in identical conditions.

8.6 Calculation

Calculate the total mass fraction of silicon (as silica), $w_{\text{Si total}}$, expressed as a percentage, using Equation (28).

$$w_{\text{Si total}} = \frac{(m_1 - m_2) \times 100}{m_\text{E} \times 2{,}139} \tag{28}$$

where

m_1 is the mass of the dish before hydrofluoric treatment, in milligrams;

m_2 is the mass of the dish after hydrofluoric treatment, in milligrams;

m_E is the mass of the test sample, in milligrams;

2,139 is the gravimetric factor of Si → SiO_2

NOTE When samples do not contain free carbon as graphite or as bonding agent, analysis can be carried out directly on the dried material (no preliminary ignition). With high silicon contents, it is necessary to determine residual silica in the filtrate after a second insolubilization, either by colorimetry or by any suitable method to control the completeness of insolubilization.

9 Determination of free silicon content

9.1 Principle

The free silicon content, $w_{\text{Si free}}$, is determined by one of the following methods:

- gas volumetric method by determining hydrogen gas produced on boiling a sample of silicon carbide in sodium hydroxide solution;
- silver displacement in a silver fluoride solution and determination of the formed metallic silver. The precipitated silver is dissolved by nitric acid, HNO_3, and titrated by ammonium thiocyanate, NH_4SCN, in the presence of potassium iron(**III**) sulfate, $KFe(SO_4)_2$.

9.2 Pretreatment with hydrochloric acid

When metallic aluminium and/or other interfering metals are present, pretreat the sample with hydrochloric acid prior to the determination of free silicon in accordance with 9.3 or 9.4.

9.3 Silicon determination by hydrogen evolution

9.3.1 Principle

Gas volumetry after developing hydrogen with sodium hydroxide solution. After decomposition of the co-existing metal components by adding hydrochloric acid to the sample, hydrogen gas which is evolved by the addition of sodium hydroxide and by heating is collected by gas burette and the gas volume is measured.

9.3.2 Reagents

9.3.2.1 **Hydrochloric acid**, HCl, (1+1).

9.3.2.2 **Sodium hydroxide solution**, $c(\text{NaOH}) = 250$ g/l.

9.3.2.3 Gas burette indicating liquid.

Add a few drops of sulfuric acid, H_2SO_4, (1+1) and a few drops of methyl orange solution (1 g/l) to 500 ml of water.

9.3.3 Apparatus

9.3.3.1 General

Connect the following equipment as shown in Figure 8. Check that the apparatus is airtight before the measurement.

9.3.3.2 Electric heater, 600 W.

9.3.3.3 Flat-bottomed flask, 100 ml **(alternatively Erlenmeyer flask,** 100 ml**)**

NOTE If a flat-bottomed flask (50 ml) and gas burette (50 ml) are used, use half the mass of test portion and half the added sodium hydroxide solution.

9.3.3.4 Allihn condenser, 400 mm.

9.3.3.5 Connector tube, consisting of a glass tube with outside diameter 8 mm, inside diameter 1 mm, and length 100 mm, bent around the centre part at right angles.

9.3.3.6 Henpel gas burette, 100 ml.

NOTE A water-cooling-style gas burette is preferred.

9.3.3.7 Level bottle, 500 ml, connected to the gas burette with a rubber tube and containing a gas burette with indicating liquid.

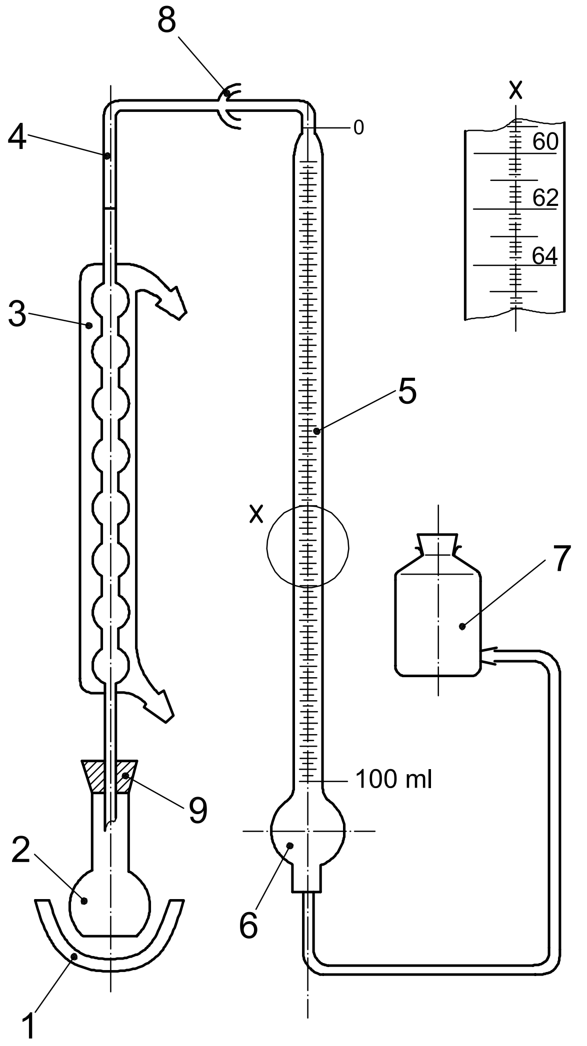
9.3.3.8 Insulation plate, of slate or similar material, placed between the gas burette and the electric heater.

9.3.4 Mass of test portion

The mass of the test portion depends on the free silicon content as shown in Table 7.

Table 7 — Mass of test portion

Free silicon content % by mass	**Mass of test portion** g
below 1	5,0
1 to 2	2,5
2 to 3	1,5
3 to 5	1,0
above 5	0,5



Key

1 electric globe-heater
2 flat-bottomed flask (100 ml)
3 Allihn condenser (400 mm)
4 connecting tube
5 gas burette (100 ml)
6 ball part (180-200 ml)
7 level bottle (500 ml)
8 spherical joint
9 silicon plug with perforation

Figure 8 — Apparatus for determination of free silicon

9.3.5 Procedure

Weigh the sample and transfer to a flat-bottomed flask. Add 10 ml of hydrochloric acid, HCl (1+1), and heat to dryness on a sand bath. After cooling, flow water into the condenser, measure the water temperature at the outlet of the condenser and confirm the temperature change within ± 1 °C after 10 min. Add 40 ml of sodium hydroxide solution, NaOH (250 g/l), to the flat-bottomed flask, connect it to the bottom of the condenser, and put an electric global heater under it.

NOTE It is better to circulate water to the condenser from a thermostat by using a pump.

Promptly balance the liquid surface of the level bottle to the zero line of gas burette and fix the level bottle. Connect the gas burette to the upper part of the condenser by using a connector tube and balance the liquid surface of the level bottle to the liquid surface of the gas burette. Read the scale to the nearest 0,1 ml. Measure the temperature near the gas burette.

Heat the flat-bottomed flask and lower the level bottle until the liquid surface is matched to the level shown in Figure 8 (spherical part of the gas burette). Keep the solution boiling for 90 min, remove the electric heater and dip the flat-bottomed flask with condenser into cold water. When the temperature becomes the same as that before the reaction, balance the liquid surface of the level bottle to the liquid surface of the gas burette. Then read the scale. Measure the temperature and the atmospheric pressure. Do not allow the room temperature to change by more than 3 °C.

9.3.6 Blank test

Carry out the procedure in 9.3.5 without the sample.

9.3.7 Calculation

Calculate the mass fraction of free silicon, $w_{\text{Si free}}$, in the sample, expressed as a percentage, using Equation (29).

$$w_{\text{Si free}} = \frac{(V_1 - V_2) \times f \times 0{,}000\,627}{m} \times 100 \tag{29}$$

where

V_1 is the difference between the scales in 9.3.5, in millilitres;

V_2 is the difference obtained in 9.3.6;

f is the correction coefficient;

m is the mass of test portion, in grams.

The correction coefficient is calculated using Equation (30).

$$f = \frac{273 \cdot (p - p')}{(273 + t) \cdot 101{,}3} \tag{30}$$

where

t is room temperature (or temperature of water in thermostat) in °C;

p is atmospheric pressure in kPa;

p' the water vapour pressure at t °C, in kPa.

9.4 Silicon determination by silver displacement

9.4.1 Principle

Silver displacement in a silver fluoride solution and determination of the formed metallic silver.

9.4.2 Pretreatment

Pretreatment should be carried out if metallic Al, Fe and/or other interfering metals are present.

9.4.2.1 Reagents

9.4.2.1.1 Hydrochloric acid, HCl, 18 % (by mass), density 1,088 g/ml.

9.4.2.2 Apparatus

Ordinary laboratory equipment and the following.

9.4.2.2.1 Device for vacuum filtration.

9.4.2.2.2 Gooch crucible and millipore filter, type BD 0,6 N f 20 cm.

9.4.2.3 Procedure

Weigh 250 mg to the nearest 0,000 1 g of the sample prepared in accordance with Clause 5 of ISO 21068-1:2008 into a 250 ml tall form beaker. Add 25 ml hydrochloric acid, HCl, and cover with a watch glass. Put on a slow heating plate at 100 °C to 150 °C ± 25 °C until the aluminium is dissolved. Allow to cool, wash the watch glass. Filter under vacuum on a Gooch crucible on a millipore filter, type BD 0,6 N, diameter 20 mm. Wash the beaker and crucible until free of any acid. Use the dried residue on the filter for $\mathrm{Si}_{\mathrm{free}}$ determination.

9.4.3 Determination of $w_{\mathrm{Si\ free}}$ by silver displacement

9.4.3.1 Reagents

9.4.3.1.1 Silver fluoride solution, 30 g/l.

Into a 1 000 ml porcelain vessel, pour 80 ml of warm water and 15 g of silver fluoride. Boil for 10 min. Filter and allow to cool. Transfer into a volumetric flask and fill to 500 ml with cold water. Keep protected from light in a brown, glass-stoppered bottle.

9.4.3.1.2 Hydrofluoric acid, HF, density 1,14 g/ml.

9.4.3.1.3 Sodium chloride, NaCl, solution 20 g/l.

9.4.3.1.4 Nitric acid, HNO_3, density 1,33 g/ml and dilute to (1/2).

9.4.3.1.5 Iron ammonium alum, solution 200 g/l.

9.4.3.1.6 Ammonium thiocyanate, NH_4SCN, titrated solution N/10.

9.4.3.2 Apparatus

Ordinary laboratory equipment.

9.4.3.3 Procedure

In a platinum dish, weigh 250 mg ± 0,000 1 g of sample dried at 110 °C ± 10 °C. Decompose with 25 ml silver fluoride solution and 3 ml hydrofluoric acid.

Heat at approximately 70 °C ± 10 °C on a heating plate for 1 h; stir every 5 min with a platinum wire.

NOTE Silver precipitates in grey flakes.

Filter on a flat 125 mm filter for quick filtration, put on a 70 mm funnel. Reserve the filtrate in a polyethylene beaker.

Wash five times with warm water.

Dissolve the precipitate on the filter with 25 ml of warm nitric acid solution (1/2).

Wash five times with warm water. Allow to cool.

Add 2 to 3 drops of iron ammonium alum solution to the dissolved precipitate. Carry out titration with ammonium thiocyanate solution measured by means of a 50 ml Mohr's burette until it changes to pink colour.

9.4.3.4 Blank test

Carry out a blank test as described in 9.4.3.3, omitting the sample.

9.4.3.5 Calculation

Calculate the mass fraction of free silicon, $w_{\text{Si free}}$, expressed as a percentage, using Equation (31).

$$w_{\text{Si free}} = (N - b) \times t \times \cdot \frac{100}{E} \tag{31}$$

where

N is the volume of ammonium thiocyanate solution, in millilitres;

b is the volume obtained in a blank test, in millilitres (b should not exceed 0,1 ml);

t is the theoretical concentration equal to the mass in grams of silicon per 1 ml of N/10 ammonium thiocyanate, NH_4SCN, solution, $t = 0{,}000707$;

E is the mass of the test sample, in grams (0,25).

For a mass fraction of Si up to 5 % and a 250 mg test sample, use an AgF solution with an AgF concentration between 0,7 g/l and 0,8 g/l.

10 Determination of silica content, SiO_2

10.1 General

Two different methods are described:

- calculation of the SiO_2 content from the difference of total SiO_2, SiC and Si_{free};
- a reference method.

10.2 Determination of free and/or combined silica content, SiO_2

The free silica is given by Equation (32).

$$SiO_2 = SiO_{2\text{total}} - SiO_{2\text{freeSi}} - SiO_{2\text{SiC}} \tag{32}$$

where

$SiO_{2\text{total}}$ is the total silica obtained in Clause 8;

$SiO_{2\text{freeSi}}$ is the free Si determined in Clause 9 multiplied by 2,139 29;

$SiO_{2\text{SiC}}$ is the SiC determined in Clause 7 multiplied by 1,498 47.

10.3 Determination of free silica, SiO_2

Determine the free silica content as specified in Clause 9 of EN 12698-1:2007.

This method is used to determine silica in silicon carbide, silicon nitride and other silica-containing materials. It is applicable to materials with a silica content greater than 0,03 %.

The determination involves reaction with hydrofluoric acid, distillation as H_2SiF_6 and subsequent determination of silicon via ICP-OES. This method is not affected by other silicon compounds. Hence, it is possible to analyse the silica content of materials such as silicon carbide and pure silicon.

10.4 Determination of surface silicon dioxide, SiO_2

Determine the surface silica content as described in 3.6 of ISO 9286:1997.

This method is suitable for the determination of the surface SiO_2 content in silicon carbide, SiC, and is based on the reactions:

$$SiO_2 + 2\ KF + 4\ HF \rightarrow K_2SiF_6 + 2\ H_2O$$

The K_2SiF_6 is separated and titrated with a caustic soda (NaOH) solution:

$$K_2SiF_6 + 4\ NaOH \rightarrow 2\ KF + 4\ NaF + SiO_2 + 2\ H_2O$$

The method can be used in the presence of elemental silicon as this does not react under the conditions of this procedure.

If silicates and/or silicides are present there may be a reaction leading to higher surface silicon dioxide ($SiO_{2\ surf}$) results. It should be checked whether this method is applicable in such cases.

11 Expression of results

The test results shall be expressed in accordance with Clause 7 of ISO 21068-1:2008.

12 Test report

The test report shall be presented in accordance with Clause 8 of ISO 21068-1:2008.

Annex A
(informative)

Examples of CRMs for calibration of carbon analyser

Examples of certified reference materials (CRMs) are given in Table A.1.

Table A.1 — Examples of refractory CRMs containing carbon and silicon carbide

CRM No.	Total C g	Free C g	Producer
ECRM 781-1	48,25	37,22	Bureau of Analysed Sample Ltd.
BAM-S003	29,89 ± 0,07	0,049 ± 0,008	Bundesanstalt fur Materialforschung und -prufung
NIST 112b	29,43 ± 0,08	0,26 ± 0,03	National Institute of Standards and Technology
JRRM 1001	29,81 ± 0,04	0,04 ± 0,01	The Technical Association of Refractories, Japan (TARJ)
JRRM 1002	5,03 ± 0,04	4,98 ± 0,04	
JRRM 1003	10,06 ± 0,03	10,01 ± 0,05	
JRRM 1004	20,04 ± 0,06	19,92 ± 0,08	
JRRM 1005	29,93 ± 0,05	29,81 ± 0,09	
JRRM 1006	49,99 ± 0,12	49,97 ± 0,06	
JRRM 1007	36,75 ± 0,05	10,01 ± 0,06	
JRRM 1008	14,12 ± 0,03	5,21 ± 0,05	
JRRM 1009	39,43 ± 0,16	37,67 ± 0,14	

Bibliography

[1] ISO 1927, *Prepared unshaped refractory materials (dense and insulating) — Classification*

[2] ISO 10081-1, *Classification of dense shaped refractory products — Part 1: Alumina-silica*

[3] ISO 10081-2, *Classification of dense shaped refractory products — Part 2: Basic products containing less than 7 % residual carbon*

[4] ISO 10081-3, *Classification of dense shaped refractory products — Part 3: Basic products containing from 7 % to 50 % residual carbon*

[5] ISO 10081-4, *Classification of dense shaped refractory products — Part 4: Special products*

[6] JIS 2011, *Methods for chemical analysis of refractories containing carbon and/or silicon-carbide*

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