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Abrasive grains and crude — Chemical analysis of silicon carbide

Abrasifs en grains ou en roche — Analyse chimique du carbure de silicium

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Contents

Page

Foreword

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 29, *Small tools*, Subcommittee SC 5, *Grinding wheels and abrasives.*

This second edition cancels and replaces the first edition (ISO 9286:1997), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the Scope has been shortened so that it only contains the subject of the document and the aspects covered;

— the structure of document has been revised in its entirety due to several new subclauses;

— new Clause 3 "Terms and definitions" has been added;

— 4.3 (former 3.2) "Preparation of sample" has been revised;

— 4.4 (former 3.4) "Determination of surface carbon ($C_{surf/free}$)" has been revised, consisting of 4.4.2 "Detection by gravimetric method" and 4.4.3 "Detection by infrared absorption (IR)" with direct and indirect method;

— 4.5 (former 3.6) "Determination of surface silicon dioxide (SiO_{2surf})" has been revised, consisting of 4.5.2 "Detection by HF/KF dissolving reactions" and 4.5.3 "Hydrofluoric acid loss"; and 4.5.4 “Molybdenum blue spectrophotometry” has been added;

— 4.6 (former 3.3) "Determination of surface silicon (Si_{surf})" has been revised; and 4.6.3 "Silver displacement method" and 4.6.4 “Molybdenum blue spectrophotometry” have been added;

— former 3.7 "Calculation of the content of residual silicon carbide (SiC_R)" has been moved to 4.10;

— former 3.8 and 3.9 for the determination of surface iron have been revised and moved to 4.9, consisting of the following detection methods: atomic absorption spectrometry (AAS) and induced coupled plasma (ICP);

— former 3.10 and 3.11 for the determination of surface aluminium oxide have been deleted; and determination of surface aluminium has been added to 4.9;

— former 3.12 for the determination of surface calcium oxide and surface magnesium oxide has been deleted; and determination of surface calcium and surface magnesium has been added to 4.9;

— former 4.3 "Determination of total carbon" has been revised by adding the detection by infrared absorption (IR) and has been moved to 4.8;

— former Annexes A and B have been deleted.

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

Abrasive grains and crude — Chemical analysis of silicon carbide

1 Scope

This document specifies the chemical analysis of silicon-carbide-based abrasive grains and crudes. It is applicable for the determination of the surface impurities of abrasives grains and the determination of the SiC content of crushed crude when the silicon carbide content is greater than 95 % (mass fraction).

2 Normative references

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

ISO 9138, *Abrasive grains — Sampling and splitting*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Analysis of surface impurities

4.1 General

This clause applies to the determination of the surface impurities of abrasive grains and crude in their original grain size and state.

All reagents used for the analysis specified in this document shall be of minimum p.a. (pro analysis) quality.

4.2 Sampling

The sample shall be taken from the batch of SiC grains to be analysed according to the method specified in ISO 9138.

4.3 Preparation of sample

4.3.1 Fine grains

This applies to the determination of the surface impurities of abrasive grains in their original grain size and state for grain sizes F500 and finer as well as for grain sizes P1500 and finer. The surface chemical analysis shall be carried out on unprocessed abrasive grains.

The sample shall be dried at (110 ± 5) °C until constant mass is obtained.

4.3.2 Coarse Grains

4.3.2.1 Sample preparation for surface impurity determination

This applies to abrasive grains in their original grain size and state for grain sizes F400 and coarser as well as for grain sizes P1200 and coarser.

The sample shall be dried at (110 ± 5) °C until constant mass is obtained.

4.3.2.2 Sample preparation for total and free carbon determination

This applies to abrasive grains in their original grain size and state for grain sizes F150 to F400 as well as for grain sizes P180 to P1200.

The sample shall be dried at (110 ± 5) °C until constant mass is obtained.

Grain sizes F120 and coarser as well as grain sizes P150 and coarser shall be crushed until all the material passes through a 150 µm sieve.

If a steel mortar is used, the quantity of additional iron contaminant in the sample is generally less than 0,1 % (mass fraction) and therefore insignificant. If the quantity of additional iron contaminant is higher than 0,1 % (mass fraction), it is advisable to make a parallel determination on a sample that is iron free (according to 4.9), taking the added iron due to grinding in the steel mortar into account. The sample shall then be ground using a hard metal or boron carbide mortar.

The mass of the sample for analysis shall be corrected based on Formula (1).

$$m_s = \frac{m_{s1} \cdot (100 - c)}{100} \tag{1}$$

where

m_s is the corrected mass of the sample, in grams (g);

m_{s1} is the mass of the sample containing the metal, dried according to 4.3.2.1, in grams (g);

c is the quantity of iron added due to grinding, mass fraction in per cent (%).

4.3.3 Crude

The crude sample shall be prepared by the following procedure:

Pre-dry an approximate 20 kg sample made up of several pieces in a heating cabinet at (110 ± 5) °C.

Crush the sample in a laboratory jaw crusher to a grain size smaller than 2,5 mm. Sieve the sample through a 2,5 mm sieve, crush the oversize residue and sieve again. Continue in this manner until the whole sample has passed through the sieve. Crush the last coarse grains in a steel mortar as the laboratory jaw crusher is ineffective for small quantities. Mix the whole sample until it is homogenous.

Reduce the sample size to 1 kg by using a sample splitter according to ISO 9138.

Grind the 1 kg sample (< 2,5 mm) in a laboratory roll crusher to a grain size smaller than 1 mm. Sieve the sample through a 1 mm sieve, crush the oversize residue and sieve again. Continue in this manner until the whole sample has passed through the sieve. Crush the last coarse grains in a steel mortar as the laboratory roll crusher is ineffective for small quantities. Mix the whole sample until it is homogenous.

Reduce the sample size to 100 g by using a sample splitter according to ISO 9138.

Grind the 100 g sample (< 1 mm) in a suitable apparatus (e.g. steel mortar) to a grain size smaller than 0,5 mm. Sieve the sample through a 0,5 mm sieve, crush the oversize residue and sieve again. Continue

in this manner until the whole sample has passed through the sieve. Mix the whole sample until it is homogenous.

Reduce the sample size to 25 g by using a sample splitter according to ISO 9138.

Grind the 25 g sample (< 0,5 mm) in the same way as above in order to obtain a grain size distribution smaller than 0,15 mm. Mix the whole sample until it is homogenous.

Dry the finely ground sample until a constant mass is obtained using a heating cabinet at (110 ± 5) °C.

If a steel mortar is used, the quantity of additional iron contaminant in the sample is generally less than 0,1 % (mass fraction) and therefore insignificant. If the quantity of additional iron contaminant is higher than 0,1 % (mass fraction), it is advisable to make a parallel determination on a sample that is iron free (according to 4.9), taking the added iron due to grinding in the steel mortar into account. The sample shall be ground using a hard metal or boron carbide mortar.

The mass of the sample for analysis shall be corrected based on Formula (1).

4.4 Determination of surface carbon ($C_{surf/free}$)

4.4.1 Principle

Depending on the sample preparation, the resulting values are used for the determination of impurity (C_{surf}) or the calculation of silicon carbide content (C_{free}).

For grain sizes finer than F120 and P150: (C_{surf}) = (C_{free}).

Determination of carbon is obtained by heating the sample in a stream of oxygen inside a combustion furnace. The released carbon dioxide shall be detected by one of the following methods: gravimetric method (see 4.4.2) or infrared absorption (IR) (see 4.4.3).

4.4.2 Detection by gravimetric method

4.4.2.1 Apparatus

4.4.2.1.1 Combustion apparatus, according to Figure 1.

4.4.2.2 Procedure

Prior to starting the measurements, purge the combustion furnace using a stream of oxygen for 10 min to 15 min. From the sample prepared according to 4.3 take a test portion (m) of 2 g weighed to within ±1 mg and place it into a previously calcined and weighed combustion boat. Weigh the absorption tube to within ±1 mg and insert it in the combustion furnace. Place the combustion boat containing the test portion into the hot zone of the tube furnace at 900 °C to 915 °C. Pass a stream of oxygen for 30 min at a flow rate of 100 ml/min through the combustion apparatus. Remove the absorption tube and weigh it. The increase in mass corresponds to the mass of carbon dioxide (m_2). Determine the mass of the residue in the combustion boat (m_1) within ±1 mg after cooling it in a desiccator.

4.4.2.3 Expression of results

The content of surface carbon is calculated according to Formula (2).

$$w_{C\_surf} = \frac{(0{,}2729 \cdot m_2) - (0{,}3754 \cdot m_3)}{m} \cdot 100 \quad (2)$$

where

w_{C_surf} is the content of surface carbon (C_{surf}), mass fraction in per cent (%);

m is the mass of the test portion prior to combustion, in grams (g);

m_1 is the mass of the test portion after combustion, in grams (g);

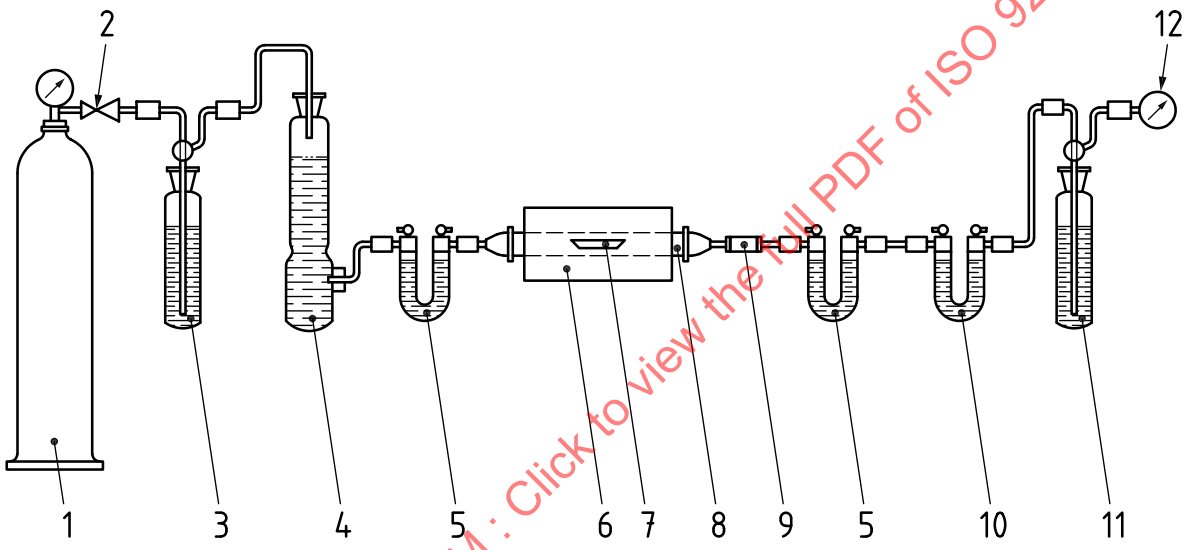
m_2 is the mass of carbon dioxide, in grams (g);

m_3 $= m_1 - m + 0{,}272\ 9\ m_2$

0,272 9 is the quotient of the molecular mass of carbon $M_r(C)$ and carbon dioxide $M_r(CO_2)$;

0,375 4 is the quotient of the molecular mass of carbon $M_r(C)$ and oxygen $M_r(O_2)$.

The method of determination and calculation compensates for possible oxidation of the silicon carbide.



Key

1 oxygen cylinder
2 pressure controlling valve
3 gas washing bottle containing concentrated sulfuric acid
4 drying tower containing sodium hydroxide on a carrier
5 absorption U-tube containing magnesium perchlorate
6 resistance furnace controllable to 1 000 °C
7 combustion boat
8 combustion tube
9 tube filled with percarbamide
10 absorption U-tube containing sodium hydroxide on a carrier and magnesium perchlorate
11 gas washing bottle containing 5 % palladium (II) chloride solution
12 manometer

Figure 1 — Combustion apparatus for gravimetric determination using resistance furnace

4.4.3 Detection by infrared absorption (IR)

4.4.3.1 Direct method

4.4.3.1.1 Principle

The method may be applied if a consideration of silicon carbide oxidation is not necessary.

4.4.3.1.2 Apparatus

Different types of instruments for carbon determination analysis by combustion and IR detection are available. It consists of an oxygen cleaner, a combustion tube, a gas refiner and an IR analyser.

4.4.3.1.3 Procedure and expression of results

From the sample prepared according to 4.3, take a test portion (m). Follow the instructions for the instrument available and report the detected surface or free carbon.

4.4.3.2 Indirect method

4.4.3.2.1 Principle

The method shall be applied if a consideration of silicon carbide oxidation is necessary.

4.4.3.2.2 Apparatus

Use the apparatus as specified in 4.4.3.1.2.

4.4.3.2.3 Procedure

From the sample prepared according to 4.3, take a test portion (m). Follow the instructions for the instrument available. After combustion, cool the test portion in a desiccator and weigh the test portion (m_1) to an accuracy of ±1 mg.

4.4.3.2.4 Expression of results

The content of surface or free carbon is calculated according to Formula (3).

$$w_{\mathrm{C\_surf/free}} = \frac{m_{\mathrm{C}} - 0{,}375\,4 \cdot (m_1 - m + m_{\mathrm{C}})}{m} \cdot 100 \tag{3}$$

where

$w_{\mathrm{C\_surf/free}}$ is the content of surface or free carbon ($C_{surf/free}$), mass fraction in per cent (%);

m_{C} is the mass of carbon detected as CO_2 by the instrument, in grams (g);

m_1 is the mass of the test portion after combustion, in grams (g);

m is the mass of the test portion prior to combustion, in grams (g);

0,375 4 is the quotient of the molecular mass of carbon $M_r(C)$ and oxygen $M_r(O_2)$.

4.5 Determination of surface silicon dioxide (SiO_{2surf})

4.5.1 General

This method is suitable for the determination of the surface SiO_2 content in SiC and is based on the reactions according to 4.5.2 and 4.5.3. If silicates and/or silicides are present, there can be a reaction leading to higher SiO_{2surf} results.

4.5.2 Detection by HF/KF dissolving reactions

4.5.2.1 Principle

This method is based on the following reactions:

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

The K_2SiF_6 is separated and titrated with a sodium hydroxide (NaOH) solution.

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

The method may be applied in the presence of elemental silicon because this does not react under the conditions of this procedure.

4.5.2.2 Reagents

4.5.2.2.1 Potassium fluoride/hydrofluoric acid solution (KF/HF), 125 g KF is dissolved in 800 ml HF, mass fraction of 40 %.

4.5.2.2.2 Hydrochloric acid, solution with a mass fraction of 18 %.

4.5.2.2.3 Wash solution, 100 g KCl is dissolved in 1 l of deionised water (use either a fresh solution or solution cooled down to approximately 10 °C).

4.5.2.2.4 Sodium hydroxide (NaOH), standardized solution, 0,1 mol/l.

4.5.2.2.5 Phenolphthalein indicator, alcohol solution with a mass fraction of 1 %.

4.5.2.2.6 Blue litmus paper.

4.5.2.2.7 Ice cubes.

4.5.2.3 Apparatus

4.5.2.3.1 PTFE (polytetrafluorethylene) or **platinum crucible**.

4.5.2.3.2 Sand bath, adjustable to ±5 °C.

4.5.2.3.3 PE (polyethylene) Büchner funnel, 45 mm diameter, consisting of two parts.

4.5.2.3.4 PE suction bottle.

4.5.2.3.5 Ashless type filter paper, 45 mm diameter, dense against $BaSO_4$.

4.5.2.3.6 Ashless filter paper flake.

4.5.2.3.7 Rubber spatula.

4.5.2.3.8 Conical flask, 300 ml.

4.5.2.3.9 pH-meter, with temperature compensation.

4.5.2.3.10 Burette.

4.5.2.4 Procedure

From the sample prepared according to 4.3 take a test portion (m) of 1 g weighed to within ±1 mg and place it into a PTFE or platinum crucible. Add 15 ml KF/HF solution, then 5 ml HCl (mass fraction of 18 %) and heat on the sand bath for 2,5 h.

During the operation, the volume of liquid shall not be significantly reduced. This is achieved by keeping the temperature of the sand bath at 50 °C ± 5 °C.

Next, place the crucible in a basin of cold water containing ice cubes to speed up cooling. Put a paper filter upon the bottom of the Büchner funnel, and then fill half of the funnel with filter flakes. These are first saturated with wash solution and carefully compacted by pressing slightly. Then filter the cold crucible contents, cleaning the crucible carefully using a rubber spatula and rinsing with the cold wash solution. Wash the residue on the filter with the cold wash solution (approximately 10 °C) and continue to wash until blue litmus no longer shows red coloration. Transfer the residue, together with the filter flakes to a 300 ml conical flask, dilute with hot deionised water, add 10 drops of phenolphthalein solution and titrate to the first persistent red coloration with NaOH (0,1 mol/l).

In the case of coloured solutions a pH-meter with temperature compensation may be used. The end point is at pH 8,2.

A blank determination shall be made and taken into account when evaluating.

4.5.2.5 Expression of results

The content of surface silicon dioxide is calculated according to Formula (4).

$$w_{SiO2\_surf} = \frac{(V - V_0) \cdot 1{,}502}{m \cdot 1\,000} \cdot 100 \quad (4)$$

where

w_{SiO2_surf} is the content of surface silicon dioxide (SiO_{2surf}), mass fraction in per cent (%);

m is the mass of the test portion, according to 4.5.2.4, in grams (g);

V is the volume NaOH (0,1 mol/l) consumption (test portion), in millilitres (ml);

V_0 is the volume NaOH (0,1 mol/l) consumption (blank test), in millilitres (ml);

1,502 is the conversion factor of millilitres of NaOH (0,1 mol/l) to milligrams of SiO_2;

1 000 is the conversion factor of grams (g) to milligrams (mg).

4.5.3 Hydrofluoric acid loss

4.5.3.1 Principle

This method is based on the following reaction:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

4.5.3.2 Fine grains

This method is only suitable for fine grains according to 4.3.1.

4.5.3.2.1 Reagents

4.5.3.2.1.1 Hydrofluoric acid, HF (concentrated).

4.5.3.2.2 Apparatus

4.5.3.2.2.1 PTFE or **platinum crucible**.

4.5.3.2.2.2 Sand bath, controllable to ±5 °C.

4.5.3.2.2.3 Heating cabinet, controllable to 110 °C.

4.5.3.2.3 Procedure

From the sample prepared according to 4.3 take a test portion (m) of 2 g weighed to within ±1 mg and place it into a tared crucible. Add 15 ml of hydrofluoric acid. Place the crucible with test portion on a sand bath at a temperature of 80 °C ± 5 °C and evaporate to dryness. When the test portion appears to be dry, transfer it to a heating cabinet set at 110 °C for 1,5 h to complete the drying, place the crucible in a desiccator, cool and reweigh (m_1).

4.5.3.2.4 Expression of results

The content of surface silicon dioxide is calculated according to Formula (5).

$$w_{SiO2\_surf} = \frac{(m - m_1)}{m} \cdot 100 \quad (5)$$

where

w_{SiO2_surf} is the content of surface silicon dioxide (SiO_{2surf}), mass fraction in per cent (%);

m is the mass of the test portion before HF treatment, in grams (g);

m_1 is the mass of the test portion after HF treatment, in grams (g).

4.5.3.3 Coarse grains and crude

4.5.3.3.1 Principle

This method is only suitable for coarse grains and crude according to 4.3.2 and 4.3.3.

4.5.3.3.2 Reagents

4.5.3.3.2.1 Hydrofluoric acid, HF (concentrated).

4.5.3.3.2.2 Sulfuric acid, H_2SO_4 (concentrated).

4.5.3.3.3 Apparatus

4.5.3.3.3.1 PTFE or **platinum crucible.**

4.5.3.3.3.2 Sand bath, controllable to ±5 °C.

4.5.3.3.3.3 Furnace, capable to operate at 800 °C.

4.5.3.3.4 Procedure

From the sample prepared according to 4.3 take a test portion (m) of 2 g weighed to within ±1 mg and place it into a preheated crucible. Ignite the crucible with the test portion at 750 °C to 800 °C for 30 min. Cool in a desiccator and weigh (m_1), add 10 ml hydrofluoric acid and 1 to 2 drops of sulfuric acid. Evaporate the solution to dryness on a sand bath. When the evolution of sulfur trioxide fumes has stopped, ignite the crucible with the test portion in a furnace at 750 °C to 800 °C for 30 min. Cool the crucible in a desiccator and reweigh (m_2).

4.5.3.3.5 Expression of results

The content of surface silicon dioxide is calculated according to Formula (6).

$$w_{SiO2\_surf} = \frac{(m_1 - m_2)}{m} \cdot 100 \quad (6)$$

where

w_{SiO2_surf} is the content of surface silicon dioxide (SiO_{2surf}), mass fraction in per cent (%);

m_1 is the mass of the test portion after ignition, in grams (g);

m_2 is the mass of the test portion after HF and H_2SO_4 treatment, in grams (g);

m is the mass of the test portion, in grams (g).

4.5.4 Molybdenum blue spectrophotometry

4.5.4.1 Principle

The molybdenum blue spectrophotometry is based on the following chemical reactions:

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

$H_2SiF_6 + 6NH_3 \cdot H_2O \rightarrow 6NH_4F + H_4SiO_4 + 2H_2O$

$7H_4SiO_4 + 12Mo_7O_{24}^{6-} + 72H^+ \rightarrow 7H_8[Si(Mo_2O_7)_6] + 22H_2O$

$H_8[Si(Mo_2O_7)_6] + 4C_{10}H_9NO_4S \rightarrow H_8[Si(Mo_2O_5)(Mo_2O_7)_5] + 4C_{10}H_8NO_4S + 2H_2O$

4.5.4.2 Reagents

4.5.4.2.1 Hydrochloric acid (1+1), take concentrated hydrochloric acid (density 1,19 g/cm^3) and dilute it by volume with water with a ratio of 1:1.

4.5.4.2.2 Hydrochloric acid (1+4), take concentrated hydrochloric acid (density 1,19 g/cm^3) and dilute it by volume with water with a ratio of 1:4.

4.5.4.2.3 Ammonia water (1+4), take concentrated ammonia water (density 0,90 g/cm^3) and dilute it by volume with water with a ratio of 1:4.

4.5.4.2.4 Hydrofluoric acid (1+1), take hydrofluoric acid (volume fraction not less than 40 %) and dilute it by volume with water with a ratio of 1:1.

4.5.4.2.5 Sodium chloride solution (10 %), weigh 10 g of sodium chloride and dissolve it in water, dilute it to 100 ml with deionised water.

4.5.4.2.6 Aluminium chloride solution (45 %), weigh 90 g of aluminium chloride hexahydrate and dissolve it in water, dilute it to 200 ml with deionised water.

4.5.4.2.7 Ammonium molybdate solution (5 %), weigh 5 g of ammonium molybdate and dissolve it in water, dilute it to 100 ml with water, place it for 24 h and filter it for use; if there is precipitation, stop using it.

4.5.4.2.8 Tartaric acid solution (10 %), weigh 10 g tartaric acid and dissolve it in water, and dilute it to 100 ml with water.

4.5.4.2.9 1,2,4-acid solution (0,15 %), weigh 0,30 g of 1,2,4-acid (1-amino-2-naphthol-4-sulfonic acid) and dissolve it in 20 ml of sodium sulfite (Na_2SO_3) solution (7 %), then mix it with 180 ml of sodium bisulfite ($NaHSO_3$) solution (10 %). The service life of this solution is two weeks.

4.5.4.2.10 P-nitrophenol indicator (0,2 % ethanol solution), weigh 0,2 g of p-nitrophenol and dissolve it in ethanol, and dilute it to 100 ml with ethanol.

4.5.4.2.11 Silicon dioxide standard solution (0,05 mg/ml), weigh 0,100 0 g of silicon dioxide (high-purity reagent) burned at 1 000 °C into a platinum crucible. Mix it with 2 g of anhydrous sodium carbonate (reference reagent), cover it with 0,5 g of anhydrous sodium carbonate (reference reagent), send it to a high-temperature furnace for melting at 850 °C to 900 °C for 20 min, take it out, cool it. Clean the outer wall of the crucible, leach it with hot water in a polytetrafluoroethylene beaker. Transfer it to a 1 000 ml volumetric flask after cooling, and dilute it to a volume of 1 000 ml with water, mix well, and immediately transfer it to a clean and dry plastic bottle for storage. 1 ml of this solution contains 0,1 mg silicon dioxide. Use a pipette to transfer 50 ml of the above mentioned 0,1 mg/ml silicon dioxide solution into a 100 ml volumetric flask pre-filled with 10 ml hydrochloric acid (1+4), dilute it to 100 ml with water, and mix it well. This is the silicon dioxide standard solution. 1 ml of this solution contains 0,05 mg of silicon dioxide.

4.5.4.2.12 Blank solution, add 1 ml of sodium chloride solution, 3 ml of hydrochloric acid, 3 ml of hydrofluoric acid and 12 ml of aluminium chloride solution into the polytetrafluoroethylene beaker, mix well, transfer it into a 100 ml plastic volumetric flask, dilute it with water to 100 ml, and mix well.

4.5.4.3 Apparatus

4.5.4.3.1 Visible spectrophotometer, with a wavelength of 700 nm.

4.5.4.4 Procedure

4.5.4.4.1 Determination

From the sample prepared according to 4.3 take a test portion (m) of 0,2 g weighed to within ±1 mg and place it into a polytetrafluoroethylene beaker. Add 1 ml of sodium chloride solution, 3 ml of hydrochloric acid (1+1), 3 ml of hydrofluoric acid, heat it on a water bath at 80 °C to 90 °C for 15 min to 20 min, cool it, and add aluminium chloride solution 12 ml, mix well, transfer it into a 100 ml volumetric flask, dilute it to 100 ml, mix well. After filtering the powder of the test portion with dry filter paper, use a pipette to transfer 10 ml of the filtered solution to a 100 ml volumetric flask, add water to the volume of the solution to 50 ml, add 2 to 3 drops of p-nitrophenol indicator, neutralize with ammonia water until the solution is yellow, and immediately add 5 ml of hydrochloric acid (1+4), then add 5 ml of ammonium molybdate solution, and place it for 15 min. Add 10 ml tartaric acid solution, 5 ml 1,2,4-acid solution, add water to dilute it to 100 ml, mix well, and place it for 30 min. Use a 1 cm cuvette at a wavelength of 700 nm. Measure the absorbance of the cuvette with water as the reference solution. Use the same method for blank test. After subtracting the absorbance of blank test, find out the quality of silicon dioxide on the working curve.

4.5.4.4.2 Drawing of working curve

Take 10 ml of blank solution and put it into eight 100 ml volumetric flasks respectively, and then add 0,00 ml, 0,50 ml, 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 ml and 10,00 ml of silicon dioxide standard solution successively in the volumetric flasks with a micro burette. Operate as per 4.5.4.4.1 to determine its absorbance. After subtracting the absorbance of blank solution, it is relative to the corresponding silicon dioxide mass. The working curve shall be drawn.

4.5.4.5 Expression of results

The content of surface silicon dioxide is calculated according to Formula (7).

$$w_{\mathrm{SiO2\_surf}} = \frac{m_1}{m \cdot \frac{V_1}{V}} \cdot 100 \tag{7}$$

where

$w_{\mathrm{SiO2\_surf}}$ is the content of surface silicon dioxide (SiO_{2_surf}), mass fraction in per cent (%);

m is the mass of the test portion, in grams (g);

m_1 is the mass of silicon dioxide found on the working curve in the sample solution, in grams (g);

V is the total volume of test solution, in millilitres (ml);

V_1 is the volume of the test solution, in millilitres (ml).

4.6 Determination of surface silicon (Si_{surf})

4.6.1 General

Results can be higher than actual due to presence of ferrosilicon type materials which react similarly as silicon metal under the test conditions.

4.6.2 Hydrogen gas volumetric method

4.6.2.1 Principle

Volumetric method based on liberation of hydrogen resulting from the attack on silicon by a boiling sodium hydroxide solution.

$$Si + 2NaOH + H_2O \rightarrow 2H_2 + Na_2SiO_3$$

4.6.2.2 Reagents

4.6.2.2.1 Sodium hydroxide solution, mass fraction of approximately 25 %.

4.6.2.2.2 Deionised water, to be used as a sealing liquid, acidified by several drops of sulfuric acid and slightly coloured with methyl orange.

4.6.2.3 Apparatus

4.6.2.3.1 Apparatus for determination of free silicon, as shown in Figure 2.

4.6.2.3.2 Barometer.

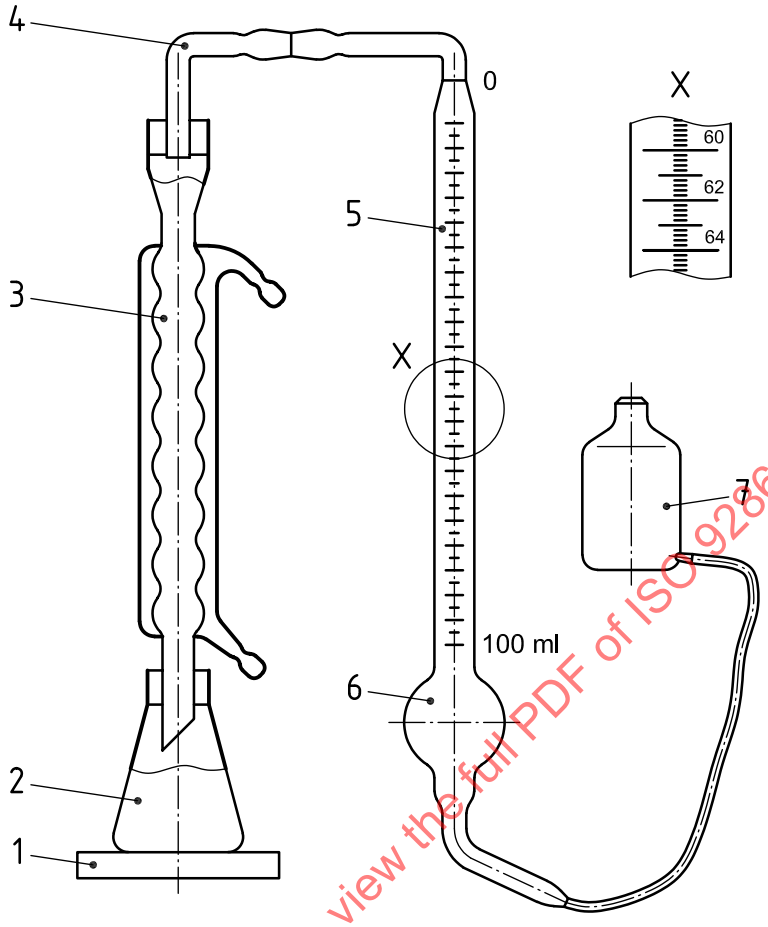
4.6.2.3.3 Thermometer, for measuring ambient temperature.

4.6.2.3.4 Immersion thermometer, for checking the temperature of the cooling liquid.

4.6.2.3.5 Thermostat.

The apparatus shall be assembled as described below and shown in Figure 2.

Place the 100 ml conical flask in an upright position on the electrically heated sand bath. Connect it to the ball condenser by means of the rubber stopper which ensures gas tightness. Place the thermometer in the cooling water using a T-piece. Connect the ball condenser to the upper end of the gas burette by means of a tube passing through the rubber bung. Connect the capillary tube from the lower end of the gas burette to the levelling bottle which contains a sealing liquid.



Key

1	electric heater or sand bath	5	gas burette
2	conical flask (100 ml)	6	additional reservoir
3	ball condenser (0,4 m)	7	levelling bottle
4	angled capillary tube		

Figure 2 — Apparatus for determination of free silicon

4.6.2.4 Procedure

From the sample prepared according to 4.3 take a test portion (m) of 5 g weighed to within ±1 mg and place it into a conical flask. Reduce the test portion (m) to less than 5 g if the volume of hydrogen produced exceeds the capacity of the gas burette due to the high content of surface silicon.

Prior to setting the starting level in the gas burette, allow the cooling water to circulate in the ball condenser for at least 10 min until the temperature is below 15 °C and constant within ±1 °C.

At the time of recording the final level in the gas burette, the temperature of the cooling water shall be identical to that at the start within ±1 °C.

If tap water does not provide the required constant temperature to within ±1 °C, a thermostat shall be inserted into the cooling water circuit.

Record the ambient temperature in the immediate vicinity of the gas burette to an accuracy of ±0,1 °C. If this temperature is not constant, the gas burette shall be fitted with a thermostat.

Add 40 ml of the sodium hydroxide solution, at ambient temperature, to the test portion to be analysed in the conical flask. Connect the flask immediately to the ball condenser, then rapidly adjust the sealing

liquid to the zero point of the gas burette using the levelling bottle. Without changing the position of the levelling bottle connect the capillary tube to the ball condenser and record the initial level of the sealing liquid in the gas burette to an accuracy of ±0,1 ml. Boil the solution for 90 min. During heating and boiling, protect the gas burette against thermal radiation. When the boiling period is over, remove the sand bath and the hot plate.

Cool the conical flask still connected to the ball condenser in a container filled with cold water. Replace the water as often as necessary in order to bring the conical flask and its contents down to the ambient temperature recorded at the beginning of the analysis.

Check that the temperature is identical in both: the conical flask and the ball condenser. Adjust the levels in the levelling bottle and the gas burette and record the liquid level in the gas burette. Record the ambient temperature and the barometric pressure. The difference in the ambient temperature between the beginning and the end of the analysis shall not exceed ±3 °C.

4.6.2.5 Expression of results

The content of surface silicon is calculated according to Formula (8). The result shall be rounded to two decimals.

$$w_{\mathrm{Si\_surf}} = \frac{0{,}000\,627 \cdot V \cdot f}{m} \cdot 100 \tag{8}$$

where

$w_{\mathrm{Si\_surf}}$ is the content of surface silicon ($\mathrm{Si_{surf}}$), mass fraction in per cent (%);

0,000 627 is the conversion factor of the volume of hydrogen gas, in millilitres (ml), to the mass of silicon, in grams (g);

V is the volume of hydrogen collected in the gas burette, in millilitres (ml);

f is the correction factor for reducing the hydrogen gas volume to normal conditions of temperature (0 °C) and pressure (1 013 hPa);

m is the mass of the test portion according to 4.6.2.4, in grams (g).

The correction factor f shall be obtained by reference to correction tables applicable to gases, taking into account the indicated temperature and the steam pressure above the sealing liquid.

4.6.3 Silver displacement method

4.6.3.1 Principle

The silver displacement method is based on the following chemical reactions:

$\mathrm{Ag_2O + 2HF \rightarrow 2AgF + H_2O}$

$\mathrm{Si + 4AgF \rightarrow SiF_4(g) + 4Ag}$

$\mathrm{3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO(g) + 2H_2O}$

$\mathrm{AgNO_3 + NH_4SCN \rightarrow AgSCN + NH_4NO_3}$

4.6.3.2 Reagents

4.6.3.2.1 Hydrochloric acid solution, HCl, mix by volume concentrated HCl with deionised water with a ratio of 1:3.

4.6.3.2.2 Nitric acid solution, HNO_3, mix by volume concentrated HNO_3 with deionised water with a ratio of 1:3.

4.6.3.2.3 Ferric ammonium sulfate indicator solution, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, dissolve 20 g $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$ in deionised water, add 5 ml of HNO_3 and dilute it to 100 ml.

4.6.3.2.4 Ammonium thiocyanate, NH_4SCN (0,1 mol/l).

4.6.3.2.5 Silver fluoride solution, AgF, dissolve 12 g of silver oxide (Ag_2O) in 500 ml concentrated hydrofluoric acid (HF). Allow the solution to stand for at least 24 h and filter (remove excess of Ag_2O) before use.

4.6.3.2.6 Silver nitrate solution, $AgNO_3$ (0,1 mol/l).

4.6.3.3 Apparatus

4.6.3.3.1 Polyethylene funnel, recommended length of stem at least 7 cm.

4.6.3.3.2 Tubing, 10 cm long.

4.6.3.3.3 Pinch clamp.

Fasten the tubing over the stem of a polyethylene funnel.

Equip the tubing with the pinch clamp.

4.6.3.4 Procedure

From the sample prepared according to 4.3 take a test portion (m) of 2 g weighed to within ±1 mg and place it into a 150 ml beaker. Add 60 ml of the hydrochloric acid solution. Boil the solution for 10 min to 15 min. Filter the silicon carbide on a medium paper using the polyethylene funnel. Wash the paper with deionised water until the filtrate is free of chlorides (test with silver nitride solution).

After the funnel has completely drained, attach the pinch clamp to the tube on the funnel. Fill the paper with the silver fluoride solution. Allow the solution to remain in the funnel for at least one hour.

Drain the funnel into a polyethylene beaker. Wash the paper with hot deionised water until the filtrate is free of silver salts (test with dilute hydrochloric acid). Discard the filtrate and washings.

Dissolve the metallic silver in the precipitate by pouring 100 ml of hot nitric acid solution through the paper. Collect the effluent solution in a 400 ml beaker. Wash the paper with deionised water. Dilute the solution to the range of 250 ml to 275 ml. Add 1 ml of the ferric indicator solution. Titrate the solution to first persistent pink colour with ammonium thiocyanate.

4.6.3.5 Expression of results

The content of surface silicon is calculated according to Formula (9).

$$w_{\mathrm{Si\_surf}} = \frac{V \cdot 0{,}702\,2}{m} \tag{9}$$

where

w_{Si_surf} is the content of surface silicon (Si_{surf}), mass fraction in per cent (%);

V is the volume of NH_4SCN (0,1 mol/l) required for titration;

m is the mass of the test portion, in grams (g);

0,702 2 is the conversion factor of the volume NH_4SCN solution, in millilitres (ml), to the mass of silicon, in grams (g).

4.6.4 Molybdenum blue spectrophotometry

4.6.4.1 Principle

The molybdenum blue spectrophotometry is based on the chemical reactions according to 4.5.4.1.

4.6.4.2 Reagents

4.6.4.2.1 Nitric acid (1+1), take concentrated nitric acid (density 1,42 g/cm^3) and dilute it by volume with deionised water with a ratio of 1:1.

4.6.4.2.2 Sodium nitrate solution (10 %), weigh 10 g of sodium nitrate and dissolve it in water, dilute it to 100 ml with water.

4.6.4.3 Apparatus

4.6.4.3.1 Visible spectrophotometer, with a wavelength of 700 nm

4.6.4.4 Procedure

The operation is the same as in 4.5.4.4, but 1 ml of sodium chloride solution is replaced by 1 ml of sodium nitrate solution and 3 ml of hydrochloric acid (1+1) replaced by 3 ml of nitric acid (1+1).

4.6.4.5 Expression of results

The content of surface silicon is calculated according to Formula (10).

$$w_{Si\_surf} = \left[\left(\frac{m_1}{m \cdot \frac{V_1}{V}} \cdot 100 \right) - w_{SiO2} \right] \cdot 0,467\,4 \qquad (10)$$

where

w_{Si_surf} is the content of surface silicon (Si_{surf}), mass fraction in per cent (%);

w_{SiO2} is the content of silicon dioxide (SiO_2), according to Formula (7);

m is the mass of the test portion, in grams (g);

m_1 is the mass of silicon dioxide found on the working curve in the sample solution, in grams (g);

V is the total volume of test solution, in millilitres (ml);