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Second edition
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Steel and cast iron — Determination of total silicon contents — Reduced molybdosilicate spectrophotometric method —

Part 1:
Silicon contents between 0,05 % and 1,0 %

Aciers et fontes — Détermination du silicium total — Méthode spectrophotométrique au silicomolybdate réduit —

Partie 1: Teneurs en silicium comprises entre 0,05 % et 1,0 %

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Contents

Foreword

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

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

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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4829-1:1986), which has been technically revised.

A list of all the parts in the ISO 4829 series can be found on the ISO website.

Steel and cast iron — Determination of total silicon contents — Reduced molybdosilicate spectrophotometric method —

Part 1:
Silicon contents between 0,05 % and 1,0 %

1 Scope

This document specifies a spectrophotometric method for the determination of total silicon in steel and cast iron using reduced molybdosilicate.

The method is applicable to the determination of silicon mass fraction between 0,05 % and 1,0 %.

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 648, *Laboratory glassware — Single-volume pipettes*

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

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

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

Dissolution of a test portion in an acid mixture appropriate to the alloy composition.

Fusion of the acid-insoluble residue with sodium peroxide. Formation of the oxidized molybdosilicate (yellow) complex in weak acid solution.

Selective reduction of the molybdosilicate complex to a blue complex with ascorbic acid, after increasing the sulphuric acid concentration and adding oxalic acid to prevent the interference of phosphorus, arsenic and vanadium.

Spectrophotometric measurement of the reduced blue complex at a wavelength of about 810 nm.

5 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696. Water demineralized by ion-exchange shall not be used as it may contain significant amounts of colloidal silica.

Reagents supplied in glass bottles, once opened, can absorb moisture and become reactive to glassware. Alkaline reagents, e.g. sodium carbonate and sodium peroxide, are particularly susceptible.

To avoid the risk of significant contamination arising from this source, it is recommended that only freshly opened bottles of all reagents be used for the preparation of reagent solutions.

To avoid adventitious contamination, the water shall be prepared, as required, for the specific purpose and collected in polypropylene containers for immediate use.

All solutions shall be freshly prepared and stored in polypropylene or polytetrafluoroethylene containers.

5.1 **Pure iron**, silicon content less than 5 µg/g.

5.2 **Sodium peroxide**, particle size less than 500 µm.

5.3 **Nitric acid**, ρ, approximately 1,40 g/ml, diluted 3 + 17.

Slowly add 150 ml of nitric acid, ρ, approximately 1,40 g/ml, to 600 ml of water. Cool, dilute to 1 l with water and mix.

5.4 **Sulphuric acid**, ρ, approximately 1,84 g/ml, diluted 1 + 3.

Add cautiously, while stirring, 250 ml of sulphuric acid, ρ, approximately 1,84 g/ml to 600 ml of water. Cool, dilute to 1 l with water and mix.

5.5 **Sulphuric acid**, ρ, approximately 1,84 g/ml, diluted 1 + 19.

Add cautiously, while stirring, 50 ml of sulphuric acid, ρ approximately 1,84 g/ml to 800 ml of water. Cool, dilute to 1 l with water and mix.

5.6 **Hydrochloric/nitric acids mixture**.

Add 180 ml of hydrochloric acid, ρ, approximately 1,19 g/ml, and 65 ml of nitric acid, ρ, approximately 1,40 g/ml, to 500 ml of water. Cool, dilute to 1 l with water and mix.

5.7 **Sulphuric/nitric acids mixture**.

Add cautiously, while stirring, 35 ml of sulphuric acid, ρ approximately 1,84 g/ml, and 45 ml of nitric acid, ρ, about 1,40 g/ml to 500 ml of water. Cool, dilute to 1 l with water and mix.

5.8 **Ascorbic acid**, 20 g/l solution.

This solution shall be freshly prepared.

5.9 **Oxalic acid**, 50 g/l solution.

Dissolve 5 g of oxalic acid di-hydrate ($C_2H_2O_4 \cdot 2H_2O$) in water, dilute to 100 ml with water and mix.

5.10 **Hydrogen peroxide**, 60 g/l solution.

Dilute 200 ml of hydrogen peroxide, 300 g/l, to 1 l with water and mix.

5.11 Potassium permanganate, 22,5 g/l solution.

This solution shall be filtered before use in order to remove the fine particles of MnO_2 that may be present in the solution, as they will interfere with the measurement.

5.12 Sodium molybdate, 25 g/l solution.

Dissolve 2,5 g of sodium molybdate di-hydrate ($Na_2MoO_4{\cdot}2H_2O$) in 50 ml of water and filter through a medium-texture filter paper.

Immediately before use, add 15 ml of sulphuric acid (5.5), dilute to 100 ml with water and mix.

5.13 Silicon standard solution, 1 g/l.

Prepare a 1 g/l silicon standard solution by using one of the procedures described in a) or b).

a) Preparation with silica.

Weigh to the nearest 0,1 mg, 2,139 3 g of freshly calcined high-purity silica (SiO_2 mass fraction > 99,9 %) and transfer to a platinum crucible.

The high-purity silica shall be calcined for 1 h at 1 100 °C and cooled in a desiccator immediately before use.

Mix thoroughly with 16 g of anhydrous sodium carbonate (Na_2CO_3) and fuse at 1 050 °C for 30 min. Extract the fusion product with 100 ml of water in a polypropylene or polytetrafluoroethylene beaker.

NOTE Extraction of the fusion product might require gentle heating.

Transfer the extract, which should contain no trace of residue, into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix. Transfer immediately into a well-stoppered polytetrafluoroethylene bottle for storage.

1 ml of this standard solution contains 1 mg of silicon.

b) Preparation with ammonium hexafluorosilicate.

Dry several grams of ammonium hexafluorosilicate [$(NH_4)_2SiF_6$] for about 1 h at 105 °C to 110 °C in an oven and cool to room temperature in a desiccator.

Weigh to the nearest 0,1 mg, 3,171 0 g of the dried product. Transfer into a suitable plastic beaker and dissolve it in hot water (approximately 80 °C).

Allow to cool and transfer the solution quantitatively into a 500 ml polyethylene one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this standard solution contains 1 mg of silicon.

5.14 Silicon standard solution, 200 mg/l.

Transfer 50,0 ml of one of the silicon stock solutions [5.13 a) or b)] into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix. Transfer immediately to a well-stoppered polytetrafluoroethylene bottle for immediate use.

1 ml of this standard solution contains 200 µg of silicon.

6 Apparatus

Ordinary laboratory apparatus and the following shall be used.

6.1 Beakers and lids, of polypropylene or polytetrafluoroethylene.

6.2 Zirconium crucibles, of 50 ml capacity.

NOTE As alternative, sintered alumina crucibles can be used.

6.3 Volumetric glassware.

All volumetric glassware shall be Class A, in accordance with ISO 648 or ISO 1042, as appropriate.

The use of glassware shall be restricted to a minimum of contact time and borosilicate glass shall be used as far as possible.

6.4 Spectrophotometer.

The spectrophotometer shall be equipped to measure absorbance with a spectral band width of 10 nm or less, at a wavelength of 810 nm, with suitable optical path length cells. Wavelength adjustment shall be accurate to ±2 nm, as measured by the maximum absorption of a didymium filter at 803 nm, or other suitable calibration method. The absorption measurement for the solution of maximum absorbance shall have a repeatability, expressed as relative deviation, of ±0,3 % or better.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel and cast iron.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,001 g, approximately 0,5 g of the test sample in the form of fine chips, turnings, millings or filings.

8.2 Blank test

In parallel with the determination and following the same procedure, carry out two blank tests using the same quantities of all the reagents but using, to the nearest 0,001 g, approximately 0,5 g of high-purity iron (5.1) instead of test portion.

NOTE High-purity iron dissolves very slowly in the sulfuric/nitric acids mixture (5.7). It can be dissolved in 85 ml of the sulfuric acid (5.5) followed by 35 ml of the nitric acid (5.3).

8.3 Determination

8.3.1 Dissolution of the test portion

Introduce the test portion (8.1) into a 250 ml polypropylene or polytetrafluoroethylene beaker (6.1). Add 120 ml of the sulfuric/nitric acids mixture (5.7).

For test portions slow to dissolve, the test portion may be dissolved in 85 ml of the sulfuric acid (5.5) followed by 35 ml of the nitric acid (5.3).

For test portions not soluble in the sulfuric/nitric acids mixture (5.7), use instead 85 ml of the hydrochloric acid/nitric acid mixture (5.6).

Cover with a lid (6.1) and heat gently to dissolve the test portion, without incurring significant loss of volume.

When effervescence has ceased, filter the solution through a hardened close-texture filter paper of specified low ash content and collect the filtrate in a 500 ml beaker. Rinse the beaker with 20 ml of hot water, remove adherent particles with a rubber tipped rod and filter the rinsing fractions through the same filter paper. Wash the filter paper several times with 20 ml portions of hot water. Keep the filtrate.

8.3.2 Treatment of insoluble residue

Transfer the paper and residue into a zirconium crucible (6.2) and ignite at low temperature until carbonaceous matter has been removed, and then ignite in a furnace at 600 °C. Allow to cool and mix the residue with 0,25 g of sodium peroxide (5.2). Cover with an additional 0,25 g of sodium peroxide and heat in the furnace at 600 °C for 10 min. Allow to cool, add 15 ml of water, cover the crucible with a lid and allow the reaction to subside. Add 15 ml of sulphuric acid (5.5), stir to dissolve any precipitate and add to the filtrate obtained by the procedure given in 8.3.1. Rinse the crucible and lid with water and add the rinsing fractions to the filtrate.

8.3.3 Preparation of the test solution

Dilute the solution from 8.3.2 to approximately 300 ml and cool. Add 5 ml of potassium permanganate solution (5.11), followed, if necessary, by further drop-wise additions until a definite pink colour is obtained which persists for at least 1 min.

Add the same amount of potassium permanganate solution (5.11) to the blank test solution (8.2) as is required to produce the pink colour in the test solution.

Heat to boiling and boil gently for 2 min. If precipitation of manganese dioxide occurs, add hydrogen peroxide (5.10) drop-wise until the precipitate is just dissolved and boil gently for 5 min.

Treat the blank test solution exactly as the test solution, even though no precipitation of manganese dioxide occurs.

Cool, transfer into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

Transfer immediately into a polypropylene or polytetrafluoroethylene container.

8.3.4 Development of the colour

Pipette two 20,0 ml aliquots of the test solution (8.3.3) and two 20,0 ml aliquots of the blank test solution (8.2) into separate 50 ml borosilicate one-mark volumetric flasks. In each case, one aliquot is for the test and the other is for the compensating solution.

Solutions of test samples containing niobium or tantalum will give finely divided precipitates on dilution. Allow the precipitate to settle and immediately prior to taking aliquots, pour the supernatant solution through a dry close-texture filter paper into a dry vessel. Discard the first few millilitres.

At a temperature range between 15 °C and 25 °C, treat each test and compensating solution as stated below, using calibrated pipettes for all reagent solution additions.

a) Test solution.

   Add, in the following order, shaking after each addition:

   1) 10,0 ml of sodium molybdate solution (5.12) and allow to stand for 20 min;

   2) 5,0 ml of sulphuric acid solution (5.4);

   3) 5,0 ml of oxalic acid solution (5.9);

   4) immediately, 5,0 ml of ascorbic acid solution (5.8).

b) Compensating solution.

   Add, in the following order, shaking after each addition:

   1) 5,0 ml of sulfuric acid solution (5.4);