
Steels — Determination of total silicon contents — Reduced molybdosilicate spectrophotometric method —

**Part 2:
Silicon contents between 0,01 % and 0,05 %**

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

Partie 2: Teneurs en silicium comprises entre 0,01 % et 0,05 %



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Contents

Page

Foreword	iv
1 Scope	1
2 Normative references	1
3 Principle	1
4 Reagents	1
5 Apparatus	3
6 Sampling	4
7 Procedure	4
7.1 Test portion	4
7.2 Blank test	4
7.3 Determination	4
7.3.1 Dissolution of the test portion	4
7.3.2 Treatment of insoluble residue	4
7.3.3 Preparation of the test solution	4
7.3.4 Development of the colour	5
7.3.5 Spectrophotometric measurements	5
7.4 Establishment of the calibration curve	6
7.4.1 Preparation of the calibration solutions	6
7.4.2 Spectrophotometric measurements	6
7.4.3 Plotting of the calibration curve	6
8 Expression of results	6
8.1 Method of calculation	6
8.2 Precision	7
9 Test report	7
Annex A (informative) Additional information on the interlaboratory test	9
Bibliography	10

Foreword

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

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

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

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

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#).

The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4829-2:1988), which has been technically revised.

ISO 4829 consists of the following parts, under the general title *Steels — Determination of total silicon contents — Reduced molybdosilicate spectrophotometric method*:

- *Part 1: Silicon contents between 0,05 % and 1,0 %*
- *Part 2: Silicon contents between 0,01 % and 0,05 %*

Steels — Determination of total silicon contents — Reduced molybdosilicate spectrophotometric method —

Part 2: Silicon contents between 0,01 % and 0,05 %

1 Scope

This part of ISO 4829 specifies a spectrophotometric method for the determination of total silicon in steels using reduced molybdosilicate.

The method is applicable to silicon contents between 0,01 % and 0,05 % (mass fraction) in steels.

2 Normative references

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

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 Principle

Dissolution of a test portion in a hydrochloric/nitric acids mixture.

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.

4 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, might 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.

4.1 Pure iron, silicon content less than 2 µg/g.

4.2 Sodium peroxide, particle size less than 500 µm.

4.3 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.

4.4 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.

4.5 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.

4.6 Ascorbic acid, 20 g/l solution.

This solution shall be freshly prepared.

4.7 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.

4.8 Hydrogen peroxide, 60 g/l solution.

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

4.9 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.

4.10 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 ([4.4](#)), dilute to 100 ml with water and mix.

4.11 Silicon standard solution, 1 g/l.

Prepare a 1 g/l silicon standard solution by using one of the procedures described in [4.11.1](#) or [4.11.2](#).

4.11.1 Preparation with silica

Weigh to the nearest 0,1 mg, 2,139 3 g of freshly calcined high-purity silica (> 99,9 % SiO_2) 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 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.

4.11.2 Preparation with ammonium hexafluorosilicate

Dry several grams of ammonium hexafluorosilicate $[(\text{NH}_4)_2\text{SiF}_6]$ 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 it 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.

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

4.12 Silicon standard solution, 20 mg/l.

Transfer 10,0 ml of one of the silicon standard solutions (4.11.1 or 4.11.2) into a 500 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 20 µg of silicon.

5 Apparatus

Ordinary laboratory apparatus and the following shall be used.

5.1 Beakers and lids, of polypropylene or polytetrafluoroethylene.

5.2 Zirconium crucibles, of 50 ml capacity.

NOTE As alternative, vitreous carbon crucibles can be used.

5.3 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.

5.4 Spectrophotometer

The spectrophotometer shall be equipped to measure absorbance with a spectral bandwidth 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 a relative deviation, of $\pm 0,3$ % or better.

6 Sampling

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

7 Procedure

7.1 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.

7.2 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 pure iron (4.1) instead of test portion.

It is essential that blank values be controlled at consistently low and reproducible values. It is recommended that duplicate blanks be run with each batch of tests and the mean value be used as the basis for calculation. High or divergent blank values shall be considered unacceptable and steps shall be taken to trace the source of contamination by checking the quality of water and individual reagents before proceeding further. In particular, sodium peroxide and potassium permanganate require careful selection as some grades of these reagents give high blank values. It is recommended that the absorbance blank reading does not exceed 0,050, which is equivalent to 0,008 % (mass fraction) silicon with a 4 cm optical path length.

7.3 Determination

7.3.1 Dissolution of the test portion

Introduce the test portion (7.1) into a 250 ml polypropylene or polytetrafluoroethylene beaker (5.1). Add 85 ml of hydrochloric/nitric acids mixture (4.5), cover with a lid (5.1) 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.

7.3.2 Treatment of insoluble residue

Transfer the paper and residue into a zirconium crucible (5.2) 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 (4.2). 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 (4.4), stir to dissolve any precipitate and add to the filtrate obtained by the procedure given in 7.3.1. Rinse the crucible and lid with water and add the rinsing fractions to the filtrate.

7.3.3 Preparation of the test solution

Dilute the solution from 7.3.2 to approximately 300 ml and cool. Add 5 ml of potassium permanganate solution (4.9), 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 (4.9) to the blank test solution (7.2) 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 (4.8) drop-wise until the precipitate is just dissolved and boil gently for 5 min.

Treat the blank test solution exactly as for 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.

7.3.4 Development of the colour

Pipette two 20,0 ml aliquots of the test solution (7.3.3) and two 20,0 ml aliquots of the blank test solution (7.2) 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:

- 10,0 ml of sodium molybdate solution (4.10) and allow to stand for 20 min;
- 5,0 ml of sulphuric acid solution (4.3);
- 5,0 ml of oxalic acid solution (4.7);
- immediately, 5,0 ml of ascorbic acid solution (4.6).

b) Compensating solution

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

- 5,0 ml of sulphuric acid solution (4.3);
- 5,0 ml of oxalic acid solution (4.7);
- 10,0 ml of sodium molybdate solution (4.10);
- immediately, 5,0 ml of ascorbic acid solution (4.6).

Dilute to the mark with water and mix. Allow each solution (test and blank solutions) and respective compensating solution to stand for 30 min.

7.3.5 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each solution obtained in 7.3.4, at a wavelength of about 810 nm, in a cell of 4 cm optical path length, using water as the reference medium.

Correct the absorbance of each test solution (test portion and blank) by subtracting the absorbance of the respective compensating solution.

Wavelengths other than 810 nm (in the range of 760 nm to 860 nm) may be used, if they give a suitable range of absorbance for the calibration series on the spectrophotometer used. The specific mass absorbance coefficient at 810 nm is $780 \text{ (g Si/l)}^{-1} \text{ cm}^{-1}$.

7.4 Establishment of the calibration curve

7.4.1 Preparation of the calibration solutions

Transfer 0,50 g ± 0,01 g portions of pure iron (4.1) into separate 250 ml polypropylene or polytetrafluoroethylene beakers (5.1) and dissolve in accordance with 7.3.1 and 7.3.2.

Add accurately measured volumes of silicon standard solution (4.12) to give a calibration series for the range of silicon contents indicated in Table 1.

Table 1 — Composition of the calibration solutions

Silicon standard solution (4.12) ml	Corresponding mass of silicon µg	Concentration of silicon in the aliquot after colour development µg/ml
0,0	0	0,000
2,5	50	0,020
5,0	100	0,040
7,5	150	0,060
10,0	200	0,080
12,5	250	0,100

Continue the preparation of the calibration series as described in 7.3.3 but omitting the blank test, and then proceed as described in 7.3.4 but omitting the compensating solutions.

NOTE Blank tests and compensating solutions are not necessary for the calibration solutions as they are corrected by means of the zero member of the series.

7.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each calibration solution prepared in 7.4.1 at a wavelength of about 810 nm (see 7.3.5) in a cell of 4 cm optical path length, using water as the reference medium.

Subtract the absorbance of the zero member solution from the absorbance of each calibration solution.

7.4.3 Plotting of the calibration curve

Establish the calibration curve by plotting the net absorbance values against the silicon concentrations, expressed in micrograms per millilitre, in the measured solutions.

8 Expression of results

8.1 Method of calculation

Convert the corrected absorbance of each test solution (test portion and blank, see 7.3.5) to the corresponding concentration of silicon, in micrograms per millilitre, by using the calibration curve (7.4.3).

The silicon content, c_{Si} , expressed as a percentage (%), is given by Formula (1), Formula (2) and Formula (3):

$$c_{Si} = (c_{Si1} - c_{Si0}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 \quad (1)$$

$$c_{\text{Si}} = (c_{\text{Si1}} - c_{\text{Si0}}) \times \frac{1}{10^6} \times \frac{1\,000}{20} \times \frac{50}{m} \times 100 \quad (2)$$

$$c_{\text{Si}} = (c_{\text{Si1}} - c_{\text{Si0}}) \times \frac{1}{4m} \quad (3)$$

where

V_0 is the volume of the test solution (7.3.3), in millilitres;

V_1 is the volume of the aliquot portion (7.3.4), in millilitres;

V_t is the volume of the colour-developed test solution (7.3.4), in millilitres;

C_{Si0} is the concentration of silicon in the blank test solution (corrected for its compensating solution), expressed in micrograms per millilitre;

C_{Si1} is the concentration of silicon in the test solution (corrected for its compensating solution), expressed in micrograms per millilitre;

m is the mass of the test portion (7.1), in grams.

8.2 Precision

A planned trial of this method was carried out by 15 laboratories at five levels of silicon, each laboratory making three determinations for each level (see Notes 1 and 2).

The results obtained were treated statistically in accordance with ISO 5725:1986^[1] (see Note 3).

The obtained data showed no systematic relationship between silicon content and repeatability, r , or reproducibility, R_w and R . Typical values are 0,004 % (mass fraction) for the repeatability, r , 0,005 % (mass fraction) for the within-laboratory reproducibility, R_w , and 0,006 % (mass fraction) for the reproducibility, R .

The test samples used and the test results obtained on the samples are shown in [Annex A](#).

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725:1986^[1], i.e. one operator, same apparatus, identical operating conditions (same calibration) and a short interval of time.

NOTE 2 The third determination was carried out at a different time (different day) by the same operator as in Note 1, using the same apparatus but with a new calibration.

NOTE 3 From the values obtained on day one, the repeatability, r , and reproducibility, R , were calculated using the procedure specified in ISO 5725:1986^[1]. From the first value obtained on day one and the value obtained on day two, the within-laboratory reproducibility, R_w , was calculated.

9 Test report

The test report shall include the following information:

- all information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;
- method used by reference to this part of ISO 4829, i.e. ISO 4829-2;
- results and unit in which they are expressed;
- any unusual features noted during the determination;

- e) any operation not specified in this part of ISO 4829 or any optional operation which might have influenced the results.

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