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МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

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

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

Aciers et fontes — Dosage du silicium total — Méthode spectrophotométrique au molybdosilicate réduit

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

Reference number
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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4829-2 was prepared by Technical Committee ISO/TC 17, *Steel.*

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

ISO 4829 consists of the following parts, under the general title *Steel and iron — Determination of total silicon content — Reduced molybdosilicate spectrophotometric method:*

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

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

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

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

1 Scope and field of application

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

The method is applicable to silicon contents between 0,01 and 0,05 % (m/m) in steel and iron.

2 References

ISO 377, *Wrought steel — Selection and preparation of samples and test pieces.*

ISO 385-1, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648, *Laboratory glassware — One-mark pipettes.*

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

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

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

Fusion of the acid-insouble 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 sulfuric 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 stated, use only reagents of recognized analytical grade.

Reagents supplied in glass bottles, once opened, may 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.

In addition, only water prepared by distillation shall be used for the preparation of reagent solutions and throughout the procedure. Water demineralized by ion-exchange shall not be used as it may contain significant amounts of colloidal silica.

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 of minus 500 µm.

4.3 Sulfuric acid, diluted 1 + 3.

To 600 ml of water add cautiously, with stirring, 250 ml of sulfuric acid, ϱ about 1,84 g/ml. Cool, dilute to 1 000 ml and mix.

4.4 Sulfuric acid, diluted 1 + 19.

To 800 ml of water add cautiously, with stirring, 50 ml of sulfuric acid, ϱ about 1,84 g/ml. Cool, dilute to 1 000 ml and mix.

4.5 Hydrochloric acid/nitric acid mixture.

Add 180 ml of hydrochloric acid, ϱ about 1,19 g/ml, and 65 ml of nitric acid, ϱ about 1,40 g/ml, to 500 ml of water. Cool, dilute to 1 000 ml and mix.

4.6 Ascorbic acid, 20 g/l solution.

Prepare this solution immediately before use.

4.7 Oxalic acid, solution.

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

4.8 Hydrogen peroxide, solution.

Dilute 200 ml of hydrogen peroxide, 300 g/l, to 1 000 ml and mix.

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

Filter before use.

4.10 Sodium molybdate, solution.

Dissolve 2,5 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in 50 ml of water and filter through a medium-texture filter paper. Immediately before use, add 15 ml of sulfuric acid (4.4), dilute to 100 ml and mix.

4.11 Silicon, standard solution.

4.11.1 Silicon stock solution, containing 1 g of Si per litre.

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

1 ml of this stock solution contains 1 mg of Si.

NOTE — Extraction of the fusion product may require gentle heating.

4.11.2 Silicon standard solution, containing 20 mg of Si per litre.

Transfer 10,0 ml of silicon stock solution (4.11.1) to a 500 ml one-mark volumetric flask. Dilute to the mark and mix. Transfer immediately to a well-stoppered polytetrafluoroethylene bottle for immediate use.

1 ml of this standard solution contains 20 µg of Si.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Beakers and **lids,** of polypropylene or polytetrafluoroethylene.

5.2 Crucibles, of zirconium metal, of 50 ml capacity.

NOTE — Vitreous carbon crucibles may be used as alternatives to zirconium metal crucibles.

5.3 Volumetric glassware.

All volumetric glassware shall be class A, in accordance with ISO 385-1, 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 band width of 10 nm or less at a wavelength of 810 nm. Wavelength measurement shall be accurate to ± 2 nm, as measured by the absorption maximum 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 ± 0,3 % or better.

6 Sampling

Carry out sampling in accordance with ISO 377 or appropriate national standards for iron.

7 Procedure

7.1 Test portion

Weigh, to the nearest 1 mg, 0,50 ± 0,01 g (m) of 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 0,50 ± 0,01 g of pure iron (4.1) instead of the 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 should be considered unacceptable and steps should be taken to trace the source of contamination by checking the quality of the water and of 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 blank reading

does not exceed 0,050 as absorbance, which is equivalent to 0,008 % (*m*/*m*) 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 (see 5.1). Add 85 ml of hydrochloric acid/nitric acid mixture (4.5), cover with a lid (see 5.1) and warm gently to dissolve the test portion, without incurring significant loss of volume.

When solvent action ceases, filter the solution through a hardened close-texture filter paper of known, 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 rinsings through the same filter paper. Wash the filter paper several times with 20 ml quantities of hot water. Keep the filtrate for use in the procedure given in 7.3.2.

7.3.2 Treatment of insoluble residue

Transfer the paper and residue to a zirconium metal crucible (5.2) and ignite at low temperature until carbonaceous matter has been removed, then ignite in a furnace at 600 °C. 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. Cool, add 15 ml of water, cover the crucible with a lid and allow the reaction to subside. Add 15 ml of sulfuric 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 rinsings 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 dropwise 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 (see 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) dropwise 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 to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix. Transfer immediately to a polypropylene or polytetrafluoroethylene container.

7.3.4 Development of the colour

Pipette two 20,0 ml aliquots from the test solution (see 7.3.3) and two 20 ml aliquots of the blank test solution (see 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 liquid through a dry close-texture filter paper into a dry vessel. Discard the first few millilitres.

With the temperature in the range of 15 to 25 °C max., treat each test and compensating solution as stated below, using 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 sulfuric acid (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 sulfuric acid (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 and mix. Allow each test solution (test portion and blank) 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 (see the note), 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.

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

7.4 Establishment of the calibration graph

7.4.1 Preparation of the calibration solutions

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

Add accurately measured volumes of silicon standard solution (4.11.2) to give a calibration series for the range of silicon contents indicated in table 1.

Table 1

Volume of silicon standard solution (4.11.2) 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 treatment 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 tests as both are corrected for via 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 note to 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 graph

Prepare the calibration graph 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) into the corresponding concentration of silicon, in micrograms per millilitre, by using the calibration graph plotted in 7.4.3.

Calculate the silicon (Si) content, expressed as a percentage by mass, from the following formula:

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

$$= (\varrho_{Si1} - \varrho_{Si0}) \times \frac{1}{10^6} \times \frac{1\,000}{20} \times \frac{50}{m} \times 100$$

$$= (\varrho_{Si1} - \varrho_{Si0}) \frac{1}{4m}$$

where

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

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

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

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

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

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

8.2 Precision

A planned trial of this method was carried out by fifteen laboratories at five levels of silicon, each laboratory making three determinations of silicon content at each level.

The results obtained were treated statistically in accordance with ISO 5725 (see notes 1, 2 and 3).

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

The test samples used and the test results obtained on the samples are summarized in the annex.

NOTES

1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725, i.e. one operator, same apparatus, identical operating conditions (same calibration) and a minimum period of time.

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

3 From the values obtained on day 1, the repeatability r and reproducibility R were calculated using the procedure specified in ISO 5725. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility R_w was calculated.

9 Test report

The test report shall include the following particulars:

a) all information necessary for the identification of the sample, the laboratory and the date of the analysis;

b) the method used, by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard or any optional operation which may have influenced the results.

Annex

Additional information on the international co-operative tests

(This annex does not form an integral part of the Standard.)

Table 2 has been derived from the results of the international trials carried out in 1985 on five steel samples in seven countries involving fifteen laboratories. The results of the trials were given in report N 655 issued by ISO/TC 17/SC 1 in March 1986.

Table 2

Sample	Silicon, % (*m*/*m*)			
	Content	r	R_w	R
ECRM 085-1 (0,3 % S free-cutting steel)	0,008	0,002 0	0,002 8	0,005 1
ECRM 285-1 (9 % Co, 5 % Mo, 18 % Ni, 0,7 % Ti steel)	0,015	0,002 2	0,005 7	0,007 2
JSS 023-5 (unalloyed steel)	0,024	0,004 5	0,005 3	0,005 2
BCS 432/1 (unalloyed steel)	0,043	0,006 0	0,007 0	0,009 8
BCS 452/1 (1,3 % Mn steel)	0,055	0,003 8	0,003 2	0,003 8

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