# International Standard 4829/1

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

# Steel and cast iron — Determination of total silicon content — Reduced molybdosilicate spectrophotometric method —
## Part 1 : Silicon contents between 0,05 and 1,0 %

*Aciers et fontes — Dosage du silicium total — Méthode spectrophotométrique au molybdosilicate réduit — Partie 1 : Teneurs en silicium entre* 0,05 *et* 1,0 %

**First edition — 1986-12-01**

**UDC 669.1 : 669.782 : 543.42** **Ref. No. ISO 4829/1-1986 (E)**

**Descriptors :** steels, cast iron, chemical analysis, determination of content, silicon, spectrophotometric analysis.

Price based on 7 pages

# 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 4829/1 was prepared by Technical Committee ISO/TC 17, *Steel*.

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Printed in Switzerland

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

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

## 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 cast iron.

The method is applicable to silicon contents between 0,05 and 1,0 % (*m/m*) in steel and cast iron soluble in one or the other of the alternative acid mixtures.

## 2 Reference

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

## 3 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) in weak acid solution.

Selective reduction of the molybdosilicate complex to reduced 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 and only distilled water or water of equivalent purity.

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

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

**4.2 Sodium peroxide**, particle size −500 µm.

**4.3 Nitric acid.**

Slowly add 150 ml of nitric acid, $\varrho$ approximately 1,40 g/ml, to 600 ml of water. Cool, dilute to 1 000 ml and mix.

**4.4 Sulfuric acid.**

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

**4.5 Sulfuric acid.**

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

**4.6 Hydrochloric acid/nitric acid mixture.**

Add 180 ml of hydrochloric acid, $\varrho$ about 1,19 g/ml, and 65 ml of nitric acid, $\varrho$ about 1,40 g/ml, to 500 ml of water, cool, dilute to 1 000 ml and mix.

**4.7 Sulfuric acid/nitric acid mixture.**

To 500 ml of water add cautiously, with stirring, 35 ml of sulfuric acid, $\varrho$ about 1,84 g/ml, and 45 ml of nitric acid, $\varrho$ about 1,40 g/ml. Cool, dilute to 1 000 ml and mix.

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

Prepare this solution immediately before use.

**4.9 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.

**4.10 Hydrogen peroxide.**

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

### 4.11 **Potassium permanganate,** 22,5 g/l solution.

Filter before use.

### 4.12 **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 the sulfuric acid (4.5), dilute to 100 ml and mix.

### 4.13 **Silicon,** standard solution.

#### 4.13.1 **Silicon,** stock solution corresponding to 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 % $SiO_2$) (see note 1) and transfer to a platinum crucible. 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 note 2). 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.

#### 4.13.2 **Silicon,** standard solution corresponding to 200 mg of Si per litre.

Transfer 50 ml of the silicon stock solution (4.13.1) to a 250 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 standard solution contains 200 µg of Si.

NOTES

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

2 Extraction of the fusion product may require prolonged digestion in water followed by gentle heating.

## 5 Apparatus

Ordinary laboratory apparatus and

### 5.1 **Beakers,** of polypropylene or polytetrafluoroethylene, of 250 ml capacity.

### 5.2 **Crucibles,** of zirconium metal (see note), of 50 ml capacity.

NOTE — Sintered alumina crucibles may be used as alternatives to zirconium metal crucibles.

### 5.3 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 relative deviation of ± 0,3 % or better.

## 6 Sampling

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

## 7 Procedure

### 7.1 Test portion

Weigh, to the nearest 0,001 g, 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 a blank test using the same quantities of all the reagents but using 0,50 ± 0,01 g of the pure iron (4.1) (see note) instead of the test portion.

NOTE — Pure iron dissolves very slowly in the sulfuric acid/nitric acid mixture (4.7). It may be dissolved in 85 ml of the sulfuric acid (4.5) followed by 35 ml of the nitric acid (4.3).

### 7.3 Determination

#### 7.3.1 Dissolution of the test portion

Transfer the test portion (7.1) into a 250 ml polypropylene or polytetrafluoroethylene beaker (5.1), add 120 ml of the sulfuric acid/nitric acid mixture (4.7) and warm gently to dissolve the test portion (see notes 1 and 2).

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 7.3.3 (see note 3).

NOTES

1 For test portions slow to dissolve, the test portion may be dissolved in 85 ml of the sulfuric acid (4.5) followed by 35 ml of the nitric acid (4.3).

2 For test portions not soluble in the sulfuric acid/nitric acid mixture (4.7), use instead 85 ml of the hydrochloric acid/nitric acid mixture (4.6).

3 If acid-soluble silicon only is required, proceed directly to 7.3.3, but the method for acid-soluble silicon is unsatisfactory as different values could be obtained for some metals depending on the time of dissolution.

### 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 is removed, then ignite in a furnace at 600 °C. Cool and mix the residue with 0,25 g of the sodium peroxide (4.2). Cover with an additional 0,25 g of the sodium peroxide (4.2) 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 the sulfuric acid (4.5), stir to dissolve any precipitate and add to the filtrate from the procedure given in 7.3.1. Rinse the crucible and lid with water and add to the filtrate.

### 7.3.3 Preparation of the test solution

Dilute the solution from 7.3.1 or 7.3.2 to approximately 300 ml and cool. Add 5 ml of the potassium permanganate solution (4.11), followed, if necessary, by further dropwise additions until a definite pink colour is obtained which persists for at least 1 min. Heat to boiling and boil gently for 2 min. If necessary, add the hydrogen peroxide (4.10) dropwise until the precipitated manganese dioxide is just dissolved and boil gently for 5 min. Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

### 7.3.4 Development of the colour

Pipette two 20 ml aliquots from each test solution (7.3.3) (see note) and 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.

With the temperature in the range 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 the sodium molybdate solution (4.12) and allow to stand for 20 min;
- 5,0 ml of the sulfuric acid (4.4);
- 5,0 ml of the oxalic acid solution (4.9);
- immediately, 5,0 ml of the ascorbic acid solution (4.8).

b) Compensating solution — Add, in the following order, shaking after each addition:

- 5,0 ml of the sulfuric acid (4.4);
- 5,0 ml of the oxalic acid solution (4.9);
- 10,0 ml of the sodium molybdate solution (4.12);
- immediately, 5,0 ml of the ascorbic acid solution (4.8).

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

NOTE — 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.

### 7.3.5 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each solution (7.3.4) at a wavelength of about 810 nm (see note), in a cell of adequate optical path length (see table 1), using water as the reference medium.

Correct the absorbance of each test solution (test portion and blank) by subtracting the absorbance of each 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 the 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 (see note to 7.2).

Add accurately measured volumes of the silicon standard solution (4.13.2) to give a calibration series for each range of silicon contents indicated in table 1.

Continue the treatment of the calibration series as described in 7.3.3. to 7.3.4. A single compensating solution suffices for each calibration range.

Allow each calibration solution, together with the compensating solution, to stand 30 min.

### 7.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each solution (7.4.1) at a wavelength of about 810 nm (see note to 7.3.5) in a cell of adequate optical path length (see table 1), using water as the reference medium.

Subtract the absorbance of the compensating solution from the absorbance of each calibration solution. Then obtain the net absorbance value by subtracting the corrected absorbance of the zero member from the corrected absorbance of each calibration solution in the series.

**Table 1**

| Silicon content<br>% (*m*/*m*) | Silicon standard solution (4.13.2)<br>ml | Corresponding mass of silicon<br>µg | Concentration of silicon in the aliquot after colour development<br>µg/ml | Cell optical path length<br>cm |
|---|---|---|---|---|
| 0,05 to 0,10 | 0,00 | 0 | 0,00 | 2 or 4 |
| | 0,50 | 100 | 0,04 | |
| | 1,00 | 200 | 0,08 | |
| | 1,50 | 300 | 0,12 | |
| | 2,00 | 400 | 0,16 | |
| | 2,50 | 500 | 0,20 | |
| 0,10 to 0,50 | 0,00 | 0 | 0,00 | 2 |
| | 2,50 | 500 | 0,20 | |
| | 5,00 | 1 000 | 0,40 | |
| | 7,50 | 1 500 | 0,60 | |
| | 10,00 | 2 000 | 0,80 | |
| | 12,50 | 2 500 | 1,00 | |
| 0,50 to 1,00 | 0,00 | 0 | 0,00 | 1 |
| | 10,00 | 2 000 | 0,80 | |
| | 15,00 | 3 000 | 1,20 | |
| | 20,00 | 4 000 | 1,60 | |
| | 25,00 | 5 000 | 2,00 | |

### 7.4.3 Plotting of the calibration graph and calculation of the angular coefficient $a$

Prepare the calibration graph by plotting the net absorbance values converted to measurement in a 1 cm optical path length cell, against the silicon concentrations, expressed in micrograms per millilitre, in the measured solutions.

Calculate the angular coefficient $a$ from the slope of the calibration graph, if it is a straight line.

## 8 Expression of results

### 8.1 Method of calculation

#### 8.1.1 When the calibration graph is not a straight line

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

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

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

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

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

where

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

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

$d$ is the optical path length, in centimetres, of the cell used for the measurements;

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

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

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

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

#### 8.1.2 When the calibration graph is a straight line

$$\frac{A_1 - A_0}{a} \times \frac{1}{10^6} \times \frac{1}{d} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100$$

$$= \frac{A_1 - A_0}{a} \times \frac{1}{10^6} \times \frac{1}{d} \times \frac{1\,000}{20} \times \frac{50}{m} \times 100$$

$$= \frac{A_1 - A_0}{4adm}$$

where

$A_0$ is the corrected absorbance of the blank solution (7.3.5);

$A_1$ is the corrected absorbance of the test portion solution (7.3.5);

$a$ is the angular coefficient or the absorbance per microgram of silicon per millilitre of solution measured with an optical path length of 1 cm;

$d$ is the optical path length, in centimetres, of the cell used for the measurements;

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

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

$V_t$ is the volume, in millilitres, of the colour-developed test solution (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 eighteen laboratories at ten levels of silicon, each laboratory making four determinations of silicon at each level.

The test samples used are listed in annex A.

The results obtained were treated statistically in accordance with ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by interlaboratory tests.*

The data obtained showed a logarithmic relationship between silicon content and repeatability ($r$) and reproducibility ($R$) of the test results, as summarized in table 2. The graphical presentation of the figures is given in annex B.

**Table 2**

| Level of silicon % $(m/m)$ | Repeatability $r$ | Reproducibility $R$ |
|---|---|---|
| 0,05 | 0,004 | 0,008 |
| 0,1 | 0,006 | 0,012 |
| 0,2 | 0,009 | 0,018 |
| 0,5 | 0,015 | 0,032 |
| 1,0 | 0,023 | 0,049 |

## 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 A

## Additional information on the international co-operative tests

(Not an integral part of this International Standard)

The table 2 in 8.2 has been derived from the results of the international trials carried out in 1983 on one iron and nine steel samples in seven countries involving eighteen laboratories.

The results of the trials were given in a report issued by ISO/TC 17/SC 1 in April 1984. Graphical representation of the precision data is given in annex B.

The test samples used are listed in table 3.

**Table 3**

| Sample | Silicon content<br>% $(m/m)$ |
|---|---|
| ECRM 085 — 1 0,3 % S free-cutting steel | 0,008 |
| JSS 023 — 5 Unalloyed steel | 0,024 |
| BCS 452/1 1,30 % Mn steel | 0,055 |
| ECRM 020 — 1 Unalloyed steel | 0,072 |
| ECRM 081 — 1 Unalloyed steel | 0,105 |
| ECRM 254 — 1 7 % W, 5 % Mo, 2 % V, 5 % Cr steel | 0,19- |
| ECRM 077 — 2 1,25 % Mn steel | 0,293 |
| ECRM 277 — 1 18 % Cr, 10 % Ni steel | 0,417 |
| ECRM 484 — 1 White malleable cast iron | 0,717 |
| ECRM 276 — 1 5 % Cr, 1,5 % Mo, 0,5 % V steel | 0,985 |

NOTES

1 The statistical analysis has been performed in accordance with ISO 5725.

2 Ten samples were used for the co-operative tests. However, as the method is applicable to silicon contents between 0,05 and 1,0 % $(m/m)$, eight points only have been illustrated on the figure in annex B, the data for samples ECRM 085 - 1 and JSS 023 — 5 having been omitted.

# Annex B

## Graphical representation of precision data

(Not an integral part of this International Standard)

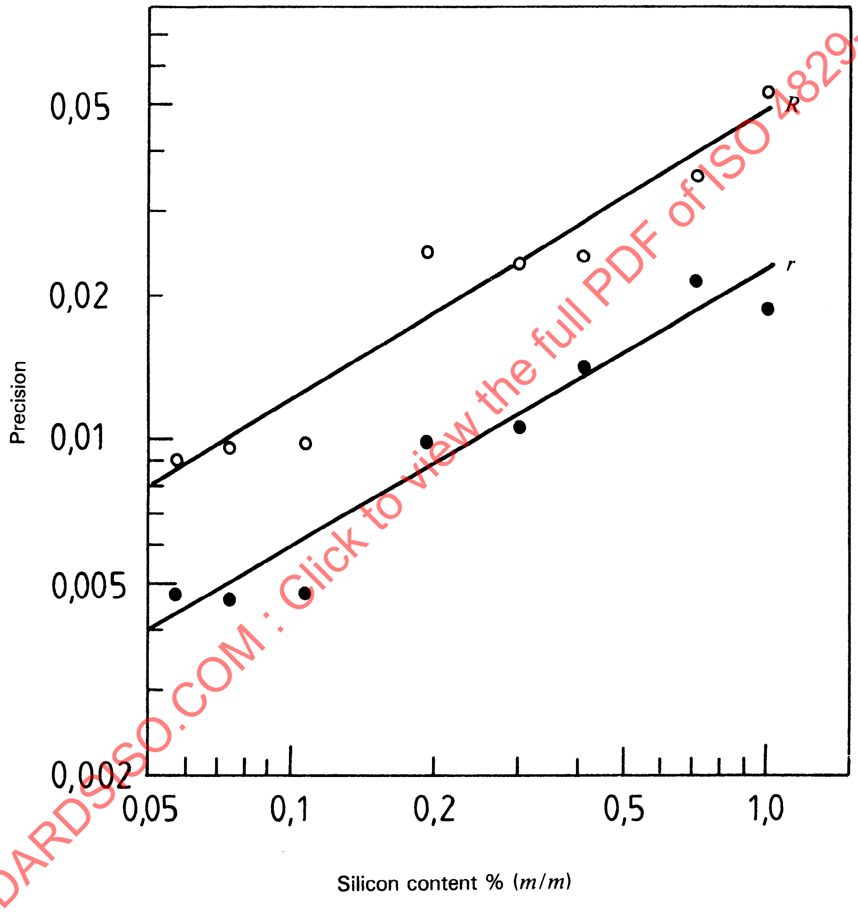

**Figure — Relationship between silicon content and repeatability *r* or reproducibility *R***