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Steel and cast iron — Determination of silicon content — Gravimetric method

Aciers et fontes — Détermination des teneurs en silicium — Méthode gravimétrique

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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).

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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 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 third edition cancels and replaces the second edition (ISO 439:1994), which has been technically revised. The main change compared to the previous edition is:

- a complete reevaluation of the precision data.

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.

Steel and cast iron — Determination of silicon content — Gravimetric method

1 Scope

This document specifies a gravimetric method for the determination of the silicon content in steel and cast iron.

The method is applicable to silicon contents between 0,10 % (mass fraction) and 5,0 % (mass fraction).

NOTE For samples containing molybdenum, niobium, tantalum, titanium, tungsten, zirconium or high levels of chromium, the results are less accurate than for unalloyed matrixes.

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 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:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Dissolution of a test portion with hydrochloric and nitric acids.

Conversion of acid-soluble silicon compounds to hydrated silicon dioxide by evaporation with perchloric acid until white fumes appear. Filtration of the hydrated silicon dioxide and acid-insoluble silicon compounds, ignition to form impure silicon dioxide and then weighing.

Treatment of the ignited residue with hydrofluoric and sulfuric acids, followed by ignition and weighing.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and grade 2 water as specified in ISO 3696.

5.1 Hydrochloric acid, ρ approximately 1,19 g/ml.

5.2 Hydrochloric acid solution, 1 + 1.

Add 500 ml of hydrochloric acid (5.1) to 500 ml of water and mix.

5.3 Hydrochloric acid solution, 1 + 19.

Add 10 ml of hydrochloric acid (5.1) to 190 ml of water and mix.

5.4 Nitric acid solution, 3 + 1.

Add 150 ml of nitric acid, ρ approximately 1,40 g/ml, to 50 ml of water and mix.

5.5 Hydrofluoric acid, ρ approximately 1,14 g/ml.

5.6 Perchloric acid, ρ approximately 1,67 g/ml.

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

NOTE Perchloric acid (ρ approximately 1,54 g/ml) can also be used.

5.7 Sulphuric acid solution, 1 + 1.

Cautiously add 50 ml of sulphuric acid, ρ approximately 1,84 g/ml, to 50 ml of water, allow to cool and mix.

6 Apparatus

Ordinary laboratory equipment and the following shall be used:

6.1 Platinum crucibles, of capacity approximately 30 ml.

6.2 Muffle furnace, adjustable from 800 °C up to 1 100 °C.

6.3 Filter paper, medium-texture, of known low ash content.

7 Sampling

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

8 Procedure

8.1 Test portion

Use millings or drillings of a maximum thickness of 0,2 mm.

According to the presumed silicon content, weigh, to the nearest 1 mg, the following mass (m_0) of the test portion:

a) for silicon contents between 0,10 % (mass fraction) and 0,50 % (mass fraction): m_0 approximately 5 g;

b) for silicon contents between 0,50 % (mass fraction) and 2,5 % (mass fraction): m_0 approximately 2,5 g;

c) for silicon contents between 2,5 % (mass fraction) and 5,0 % (mass fraction): m_0 approximately 1 g.

8.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all reagents as used for the determination.

8.3 Determination

8.3.1 Acid dissolution of the test portion and formation of hydrated silicon dioxide

Place the test portion (8.1) in a beaker of suitable capacity.

Add 30 ml of hydrochloric acid (5.1), and then gently heat the beaker covered with a watch glass until the reaction ceases. Oxidize by careful addition of 15 ml of nitric acid (5.4). When the violent reaction ceases, rinse the watch glass with a little portion of hot water and collect the washings in the beaker. Add the volume of perchloric acid (5.6) indicated in Table 1.

Table 1 — Volume of perchloric acid (5.6)

Mass of test portion (8.1) g	**Volume of perchloric acid (5.6)** ml	
	ρ = 1,67 g/ml	ρ = 1,54 g/ml
5	60	75
2,5	40	50
1	25	35

WARNING — Perchloric acid (5.6) must be added cautiously in small portions, especially when a 5 g test portion has been taken, in order to avoid boiling over, due to a very violent reaction.

Heat the uncovered beaker slightly until the attack is complete and then, increase the rate of heating. As soon as the first white perchloric acid fumes appear, cover the beaker with the watch glass and continue fuming for about 20 min.

If the alloy contains chromium at contents greater than 1 %, it is recommended to wait for the appearance of the characteristic red colour of the chromic acid. At this stage, chromium can be removed as chromyl chloride: slowly pour down along the sides of the beaker 1 ml to 2 ml of hydrochloric acid (5.1). Continue heating, until abundant perchloric fumes appear and chromium re-oxidises. Repeat as many times as necessary until the perchloric fumes are no longer orange-coloured, when hydrochloric acid is added again.

Allow to cool, carefully moisten with 5 ml of hydrochloric acid (5.1), heat slightly, dilute with 100 ml of water at 70 °C to 80 °C and heat again until the salts are dissolved (taking care not to allow the solution to boil).

8.3.2 Filtration and washing

With a rubber-tipped glass rod, detach any hydrated silicon dioxide or acid-insoluble silicon compounds that may be adhering to the beaker and filter immediately through a filter paper (6.3) containing a little filter-paper pulp of the same quality.

Wash the beaker and the filter with hot hydrochloric acid (5.3), transferring the hydrated silicon dioxide and acid-insoluble silicon compounds to the filter, and complete the washing, first with hot hydrochloric acid (5.2) and then with cold water until the iron salts are completely eliminated.

NOTE The filter is washed thoroughly in order to avoid popping and loss of residue due to perchloric acid during ignition.

8.3.3 Recovery of silicon compounds in the filtrate

Transfer the filtrate and the washings to the beaker previously used for the dissolution, evaporate them by heating until dense white fumes of perchloric acid are evolved, and maintain a steady refluxing of acid on the walls of the beaker for about 20 min. Moisten with water and dilute according to the procedure specified in 8.3.1, then filter through a second filter paper (6.3) and wash according to the procedure specified in 8.3.2.

8.3.4 Ignition, volatilization of silicon dioxide and weighing

Put the two filters and their contents together in a platinum crucible (6.1). Heat at between 500 °C and 600 °C until the filters are completely incinerated, then cover the crucible partially with a platinum cover and ignite in the muffle furnace (6.2) at 1 100 °C for 30 min to 45 min, depending on the quantity of silicon dioxide and, for samples containing molybdenum, until a constant mass is obtained.

Allow to cool, add approximately 2 ml of sulfuric acid (5.7) to the crucible, heat carefully and continue heating until the sulfuric acid fumes are completely eliminated. Then ignite in the muffle furnace at 800 °C to constant mass.

Allow to cool in a desiccator and weigh the crucible and its content (mass in grams: m_1).

Then moisten the ignited silicon dioxide with a few drops of sulfuric acid (5.7), add approximately 5 ml of hydrofluoric acid (5.5), evaporate to dryness and continue heating until the sulfuric acid fumes are completely eliminated.

NOTE If molybdenum, niobium, tantalum, titanium, tungsten or zirconium are present, add 2 ml of sulfuric acid (5.7) in order to avoid any partial volatilization of the fluorides of these elements.

Complete the ignition in the muffle furnace at 800 °C for 10 min.

Allow to cool in a desiccator, then weigh the crucible and its content (mass in grams: m_2).

9 Expression of results

9.1 Method of calculation

The silicon content, w_{Si}, expressed as a percentage by mass, is given by Formula (1):

$$w_{\mathrm{Si}} = 0{,}467\,4 \times \frac{(m_1 - m_2) - (m_3 - m_4)}{m_0} \times 100 \qquad (1)$$

$$w_{\mathrm{Si}} = 46{,}74 \times \frac{(m_1 - m_2) - (m_3 - m_4)}{m_0}$$

where

m_0 is the mass of the test portion, expressed in grams;

m_1 is the mass of the crucible and the impure silicon dioxide, expressed in grams;

m_2 is the mass of the crucible and residue after volatilization of the silicon dioxide, expressed in grams;

m_3 is the mass of the crucible and the impure silicon dioxide in the blank test, expressed in grams;

m_4 is the mass of the crucible and residue after volatilization of the silicon dioxide in the blank test, expressed in grams;

0,467 4 is the Si/SiO_2 coefficient.

9.2 Precision

A planned test of this method was carried out by 26 laboratories, at nine levels of silicon, each laboratory making three determinations of the silicon content at each level.

The test samples used are listed in Table A.1, and the experimental precision data obtained are shown in Table A.2.

The results obtained were treated statistically in accordance with ISO 5725-2:1994 and ISO 5725-3:1994.

A graphical representation of the experimental precision data is given in Annex B.

The smoothed precision data, expressed as a percentage (mass fraction), shown in Table 2 were calculated from the relationships between the silicon content mean values and repeatability and reproducibility experimental data (see Annex A and Annex B).

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

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in NOTE 1 using the same apparatus.

NOTE 3 When revising the present document, the precision data were revaluated: this new statistical treatment has led to the removal of the whole data of one laboratory.

Table 2 — Precision data (smoothed values)

Silicon content	**Repeatability limit** % (mass fraction)	**Reproducibility limit** % (mass fraction)	
% (mass fraction)	r	R_w	R
0,1	0,009	0,010	0,013
0,2	0,013	0,014	0,018
0,5	0,020	0,022	0,028
1,0	0,028	0,031	0,039
2,0	0,039	0,045	0,054
5,0	0,061	0,072	0,083

10 Test report

The test report shall include the following information:

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

b) method used by reference to this document, i.e. ISO 439:2020;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(informative)

Additional information on the international interlaboratory test

Table 2 was derived from the results of an international interlaboratory test carried out in 1991 on seven steel samples and two cast iron samples in 11 countries and involving 26 laboratories.

The results of the test were reported in document ISO/TC 17/SC 1 N 934, April 1992.

Table A.1 — Test samples used for the precision test

Sample	Chemical composition, %																						
	Si	C	Mn	P	S	Cr	Ni	Al	As	B	Ca	Co	Cu	Mo	Mg	N	Nb	Pb	Sb	Sn	Ti	V	W	Zr
BCS 460/1 (Carbon steel)	0,098	0,452	0,67	0,043	0,012	—	—	0,012	—	0,002 8	—	0,014	—	—	—	—	0,066	0,001 3	0,003 8	—	—	0,060	—	0,006
BCS 220/2 (High speed tool steel)	0,19	0,88	0,30	0,023	0,029	5,12	0,12	—	—	—	—	0,32	0,09	4,92	—	—	—	—	—	0,019	—	1,94	6,97	—
ECRM 292-1 (Stainless steel)	0,402	0,036 7	1,744	0,017 5	0,005 5	18,00	10,09	—	—	—	0,000 6	0,025 5	0,039 1	0,046 4	—	0,064 0	0,571	—	—	—	—	—	—	—
BCS 410/2 (Low alloy steel)	1,10	0,428	0,419	0,074	0,041	1,68	2,07	0,046	0,005 3	—	—	0,0248	0,436	0,432	—	0,015 5	—	—	—	—	—	0,44	—	—
ECRM 481-1 (Ductile (nodular) cast iron)	2,29	3,91	0,448	0,019	0,004	0,063	1,19	0,023	0,010	—	—	—	0,150	—	0,051	—	—	—	—	—	—	—	—	—
BCS 206/3 (High Si and P cast iron)	3,17	—	0,72	1,63	0,049	0,053	0,068	—	0,019	—	—	—	0,10	—	—	—	—	—	—	—	—	0,050	—	—
ECRM 114-1 (Low alloy steel)	4,0	0,044	0,065	0,030 5	0,004	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
JSS 030-6 (Low alloy steel)	0,26	0,185	0,72	0,017	0,014 6	—	—	0,029	—	—	—	—	0,016	—	—	0,004	—	—	—	—	—	—	—	—
CE 034 (Silicon steel)	5,18	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—