INTERNATIONAL STANDARD

ISO 439

Second edition
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Steel and iron — Determination of total silicon content — Gravimetric method

Aciers et fontes — Dosage du silicium total — Méthode gravimétrique

Reference number
ISO 439:1994(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 439 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 439:1982), which has been technically revised.

Annexes A and B of this International Standard are for information only.

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

1 Scope

This International Standard specifies a gravimetric method for the determination of the total silicon content in steel and iron.

The method is applicable to silicon contents between 0,10 % (m/m) and 5,0 % (m/m) (see note 1).

NOTE 1 For samples containing molybdenum, niobium, tantalum, titanium, tungsten, zirconium or high levels of chromium, the results are less precise than for unalloyed steels (see annex A).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Attack of a test portion by 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.

4 Reagents

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

4.1 Hydrochloric acid, ρ about 1,19 g/ml.

4.2 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 1.

4.3 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 19.

4.4 Nitric acid, ρ about 1,40 g/ml, diluted 3 + 1.

4.5 Hydrofluoric acid, ρ about 1,14 g/ml.

4.6 Perchloric acid, ρ about 1,67 g/ml (see note 2).

NOTE 2 Perchloric acid (ρ about 1,54 g/ml) may also be used.

4.7 Sulfuric acid, ρ about 1,83 g/ml, diluted 1 + 1.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

Ordinary laboratory apparatus, and

5.1 Platinum crucibles, of capacity approximately 30 ml.

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

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

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general. All evaporations must be carried out in fume cupboards suitable for use with perchloric acid.

7.1 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 % (m/m) and 0,50 % (m/m): $m_0 \approx 5$ g;

b) for silicon contents between 0,50 % (m/m) and 2,5 % (m/m): $m_0 \approx 2,5$ g;

c) for silicon contents between 2,5 % (m/m) and 5,0 % (m/m): $m_0 \approx 1$ g.

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.

7.3 Determination

7.3.1 Acid attack of the test portion and formation of hydrated silicon dioxide

Place the test portion (7.1) in a beaker of acid-resistant glass of suitable capacity.

Add 30 ml of hydrochloric acid (4.1), 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 (4.4). When the fairly violent reaction ceases, rinse the watch glass with a little hot water and collect the washings in the beaker. Add a volume of perchloric acid (4.6) as indicated in table 1.

Table 1

Mass of test portion (7.1) g	Volume of perchloric acid (4.6) ml	
	ρ = 1,67 g/ml	ρ = 1,54 g/ml
5	60	75
2,5	40	50
1	25	35

WARNING — Perchloric acid (4.6) 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. Allow to cool, carefully moisten with 5 ml of hydrochloric acid (4.1) (see note 3), 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).

NOTE 3 For samples containing high chromium contents, more than 5 ml of hydrochloric acid (4.1) should be added to reduce the hexavalent chromium.

7.3.2 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 (5.3) containing a little filter-paper pulp of the same quality.

Wash the beaker and the filter with hot hydrochloric acid (4.3), transferring the hydrated silicon dioxide and acid-insoluble silicon compounds to the filter, and complete the washing, first with hot hydrochloric acid (4.2) and then with cold water until the iron salts are completely eliminated (see note 4).

NOTE 4 The filter should be washed thoroughly in order to avoid popping and loss of residue due to perchloric acid during ignition.

7.3.3 Recovery of silicon compounds in the filtrate

Transfer the filtrate and the washings to the beaker previously used for the attack, 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 and dilute according to the procedure specified in 7.3.1, then filter through a second filter paper (5.3) and wash according to the procedure specified in 7.3.2.

7.3.4 Ignition, volatilization of silicon dioxide and weighing

Put the two filters and their contents together in a platinum crucible (5.1). 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 (5.2) at 1 100 °C for 30 min to 45 min, depending on the quantity of silicon dioxide, for samples containing molybdenum, until a constant mass is obtained.

Allow to cool, add approximately 2 ml of sulfuric acid (4.7) 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 contents (mass in grams: m_1).

Then moisten the ignited silicon dioxide with a few drops of sulfuric acid (4.7) (see note 5), add approximately 5 ml of hydrofluoric acid (4.5), evaporate to dryness and continue heating until the sulfuric acid fumes are completely eliminated.

NOTE 5 If molybdenum, niobium, tantalum, titanium, tungsten or zirconium are present, add 2 ml of sulfuric acid (4.7) 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 contents (mass in grams: m_2).

8 Expression of results

8.1 Method of calculation

The silicon content, w_{Si}, expressed as a percentage by mass, is given by the equation

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

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

where

m_0 is the mass, in grams, of the test portion (7.1);

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

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

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

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

0,467 4 is the Si/SiO_2 coefficient.

Express the results to the second decimal place.

8.2 Precision

A planned trial of this method was carried out by 26 laboratories, using nine levels of total silicon contents, each laboratory making three determinations of total silicon content on each level (see notes 6 and 7).

The test samples used and mean results obtained are listed in table A.1.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between total silicon content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 8) as summarized in table 2. The graphical representation of the data is shown in figure B.1.

Table 2

Total silicon content % (m/m)	Repeatability r	Reproducibility R	R_w
0,10	0,010 5	0,013 9	0,010 5
0,20	0,013 8	0,019 3	0,014 8
0,50	0,019 8	0,030 0	0,023 3
1,00	0,025 9	0,041 9	0,032 9
2,00	0,034 0	0,058 5	0,046 5
5,00	0,048 7	0,090 9	0,073 4

NOTES

6 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.

7 The third determination was carried out at a different time (on a different day) by the same operator as in note 6, using the same apparatus with a new calibration.

8 From the two 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 information:

a) all information necessary for the identification of the sample, the laboratory and the date of 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
(informative)

Additional information on the international cooperative tests

Table 2 was derived from the results of international analytical trials carried out in 1991 on eight steel samples and one iron sample in 11 countries involving 26 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 934, April 1992. The graphical representation of the precision data is given in annex B.

The test samples used are listed in table A.1.

Table A.1

Sample	Total silicon content % (m/m)			Precision data		
	Certified	Found		Repeatability	Reproducibility	
		$\overline{w}_{Si,1}$	$\overline{w}_{Si,2}$	r	R	R_w
BCS 460/1 (low alloy steel) [0,066Nb]	0,098	0,097 3	0,097 2	0,007 6	0,010 3	0,007 8
BCS 220/2 (tool steel) [5Cr, 0,3Co, 5Mo, 2V, 7W]	0,19	0,194	0,192	0,024 9	0,032 4	0,022 6
JSS 030-6 (unalloyed steel)	0,26	0,255	0,255	0,013 4	0,016 3	0,015 7
ECRM 292-1 (stainless steel) [18Cr, 10Ni, 0,6Nb]	0,402	0,404	0,403	0,021 8	0,043 4	0,026 4
BCS 410/2 (low alloy steel) [1,7Cr, 2Ni, 0,4Mo, 0,4V]	1,10	1,090	1,091	0,015 0	0,024 6	0,020 6
ECRM 481-1 (cast iron) [1Ni, 0,05Mg]	2,29	2,284	2,289	0,028 0	0,052 0	0,042 0
BCS 206/3 (high Si, P steel) [3Si, 1,6P]	3,17	3,155	3,152	0,055 9	0,082 9	0,069 5
ECRM F 114-1 (high Si steel)	4,01[1)]	4,012	4,014	0,068 2	0,077 6	0,083 9
CE 034 (silicon steel)	5,18	5,152	5,149	0,037 4	0,115	0,068 7

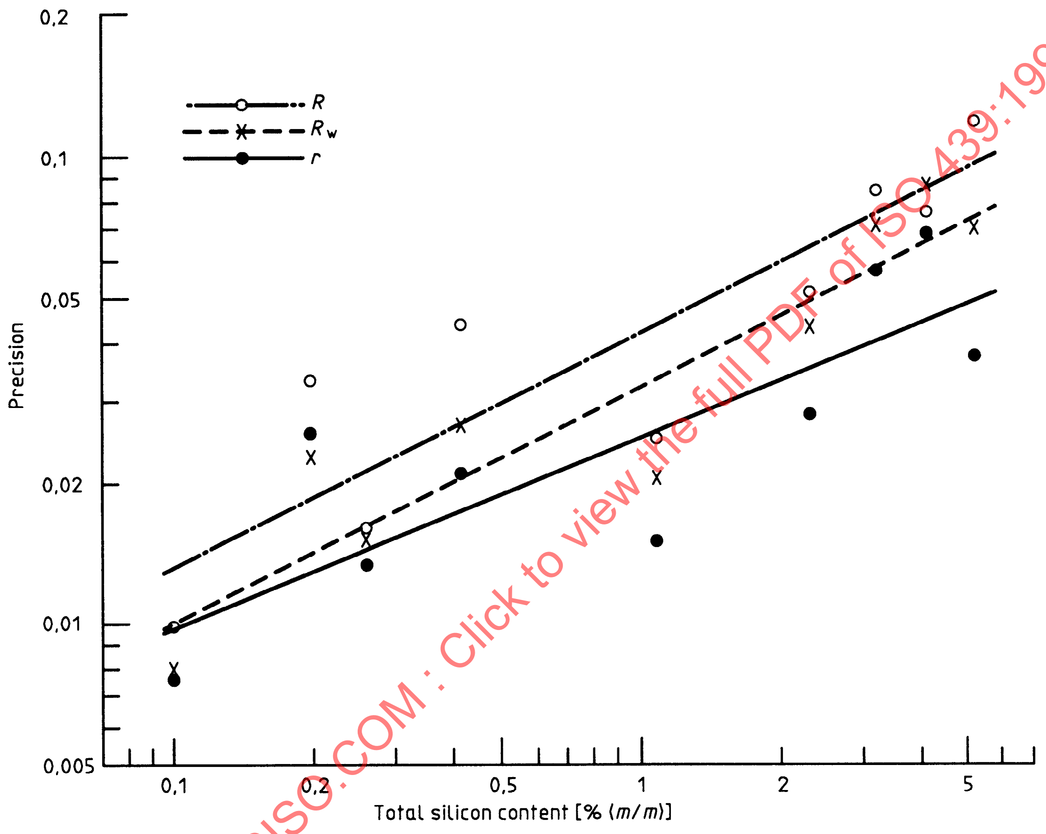
$\overline{w}_{Si,1}$, general mean within a day

$\overline{w}_{Si,2}$, general mean between days

1) Non-certified value.

Annex B
(informative)

Graphical representation of precision data



$\lg r = 0{,}391\ 8\ \lg \overline{w}_{\mathrm{Si},1} - 1{,}586$

$\lg R_{\mathrm{w}} = 0{,}498\ 1\ \lg \overline{w}_{\mathrm{Si},2} - 1{,}482$

$\lg R = 0{,}480\ 5\ \lg \overline{w}_{\mathrm{Si},1} - 1{,}377$

where

$\overline{w}_{\mathrm{Si},1}$ is the average silicon content, expressed as a percentage by mass, obtained within a day;

$\overline{w}_{\mathrm{Si},2}$ is the average silicon content, expressed as a percentage by mass, obtained between days.

Figure B.1 — Logarithmic relationship between total silicon content ($\overline{w}_{\mathrm{Si}}$) and repeatability ($r$) or reproducibility ($R$ and R_{w})

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