TECHNICAL REPORT

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Steel — Determination of silicon content — Inductively coupled plasma atomic emission spectrometric method

Aciers — Dosage du silicium — Méthode par spectrométrie d'émission atomique avec plasma induit par haute fréquence

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Foreword

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The main task of technical committees is to prepare International Standards. 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.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this Technical Report may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 17055 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Annexes A and B of this Technical Report are for information only.

Steel — Determination of silicon content — Inductively coupled plasma atomic emission spectrometric method

1 Scope

This Technical Report specifies a method for the determination of the content of silicon in steel by means of inductively coupled plasma emission spectrometry.

This method is applicable to silicon contents of mass fraction 0,02 % to 5 %.

The method uses a calibration based on a very close matrix matching of the calibration solutions to the sample and close bracketing of the contents around the approximate concentration of silicon in the sample to be analysed. The concentrations of all elements in the sample has, therefore, to be approximately known. If the concentrations are not known the sample has to be analysed by some semi-quantitative method.

The advantage with this procedure is that all possible interferences from the matrix will be automatically compensated, which will result in high accuracy. This is most important for spectral interferences, which can be severe in very high alloys. However, all possible interferences have to be kept to a minimum. Therefore it is essential that the spectrometer used, meet the performance criteria specified in the method for the selected analytical lines.

2 References

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

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*

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

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3 Principle

The sample is dissolved in a hydrochloric, nitric and hydrofluoric acid mixture. An internal standard element is added and the solution is diluted to known volume. The solution is nebulized into an ICP and the intensity of the emitted light from each element is measured simultaneously with the light emitted from the internal standard element.

4 Reagents

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

4.1 Hydrofluoric acid, HF, 40 % mass fraction, ρ about 1,14 g/ml

4.2 Hydrochloric acid, HCl, ρ about 1,19 g/ml

4.3 Nitric acid, HNO_3, ρ about 1,40 g/ml

4.4 Internal standard solution, 1 000 mg/l

Choose a suitable element to be added as internal standard and prepare a 1 000 mg/l solution.

4.5 Silicon stock standard solution, 1 000 mg/l

Weigh to the nearest 0,001 g, 0,5 g of high purity silicon (minimum 99,95 % mass fraction) and dissolve, without heating, in a mixture of 30 ml hydrofluoric acid (4.1) and 3 ml nitric acid (4.3). Transfer the solution quantitatively to a calibrated 500 ml one-mark plastic volumetric flask. Make up to the mark with water and mix. Ensure that the temperature is the same as that at which the volumetric flask was calibrated.

4.6 Silicon standard solution, 100 mg/l

Using a calibrated pipette, transfer 25 ml of the silicon stock standard solution (4.5) to a calibrated 250 ml one-mark volumetric flask. Add 25 ml of hydrofluoric acid (4.1). Make up to the mark with water and mix. Ensure that the temperature is the same as that at which the volumetric flask was calibrated.

4.7 Standard solutions of interfering elements

Prepare standard solutions for each element over 1 % mass fraction in the test sample. Use pure elements or oxides with silicon contents less than 0,001 % mass fraction.

5 Apparatus

Ordinary laboratory apparatus as well as the following should be used.

5.1 Emission spectrometer

5.1.1 General

The emission spectrometer shall be equipped with an inductively coupled plasma (ICP) and a nebulization system resistant to hydrofluoric acid.

NOTE When a Teflon nebulizer is used, the addition of a surface active agent is recommended in order to avoid liquidation of spray due to poor wetting of fluid in the nebulizer. Alternatively a sapphire nebulizer may be used without surface active agent.

The spectrometer used will be satisfactory if, after optimizing in accordance with 7.2.2 to 7.2.5, it meets the performance criteria given in 5.1.3 to 5.1.6.

The spectrometer can either be of simultaneous or sequential type. A sequential spectrometer can be equipped with an extra arrangement for simultaneous measurement of the internal standard line. In this case the sequential spectrometer can be used with the internal standard technique. If the sequential spectrometer is not equipped with this arrangement an internal standard should not be used.

5.1.2 Analytical lines

This Technical Report does not specify any particular emission line. It is recommended that one of the lines given in Table 1 be used.

Table 1 — Recommended analytical lines together with interfering elements

Element	Wavelength nm	Interferences
Si	251,61	Mo, Mn
Si	288,16	Cr

5.1.3 Minimum practical resolution of the spectrometer

Calculate the bandwidth for the wavelength used including the line for the internal standard. The bandwidth should be less than 0,030 nm.

5.1.4 Minimum short term precision

Calculate the short term precision. The standard deviation should not exceed 0,4 % of the mean absolute or ratioed intensities.

5.1.5 Maximum background equivalent concentration and detection limit

Calculate the background equivalent concentration (BEC) and detection limit (DL) for the analytical line in a solution containing only the analyte element. The values shall be below the values listed in Table 2.

Table 2 — Maximum background equivalent concentration and detection limit

Analytical line	Maximum BEC mg/l	Maximum DL mg/l
Si	0,5	0,015

5.1.6 Graph linearity

The linearity of the calibration curve should be checked.

5.2 Polytetrafluoroethylene – PTFE – beakers

5.3 1 000 and 100 ml polypropylene volumetric flasks

Since hydrofluoric acid is used in this method, replace all volumetric glassware with hydrofluoric acid resistant material such as polypropylene. The volumetric devices should be calibrated in accordance with ISO 648 or ISO 1042 as appropriate.

6 Sampling and samples

Carry out sampling and preparation of the laboratory sample in accordance with ISO 14284 or appropriate national standards for steels.

7 Procedure

7.1 Preparation of test sample solution, T_n

NOTE No blank test solution is prepared in this method. The reason is that the procedure takes into account possible contamination from the reagents used. Since the addition of all reagents is exactly the same in the calibration solutions as in the test sample solution a subtraction of the contents in a blank solution will lead to an erroneous results.

7.1.1 Weigh to the nearest 0,000 5 g, approximately 0,25 g of the test sample and transfer to a PTFE (5.2) or PFA beaker with a graphite base.

7.1.2 Add 10 ml hydrochloric acid (4.2), 2 ml nitric acid (4.3) and 5 ml hydrofluoric acid (4.1). Heat to complete dissolution.

7.1.3 Cool the solution and add 10 ml of water to dissolve the salts.

7.1.4 Cool the solution to room temperature and transfer the solution quantitatively to a 100 ml volumetric polypropylene flask (5.3). If an internal standard is used add 1 ml of the internal standard solution (4.4). It is strongly recommended to use some kind of automatic dispensing system when adding the internal standard, since it is most important that the volume added is exactly the same in the different flasks.

7.1.5 Make up to the mark with water and mix.

7.2 Preparation for spectrometric measurements

7.2.1 Start the ICP and let it run for at least one hour before taking any measurements.

7.2.2 Optimize the instrument according to the manufacturer's instructions.

7.2.3 Prepare the software to measure the intensity, mean value and relative standard deviation of the lines chosen.

7.2.4 If an internal standard is used, prepare the software to calculate the ratio between analyte intensity and internal standard intensity. The intensity of the internal standard shall be measured simultaneously with the analyte intensity.

7.2.5 Check the instrument performance requirements given in 5.1.3 to 5.1.6.

7.3 Pre-analysis of the test sample solution and analysis of blank test solution

7.3.1 Prepare a calibration solution, K_5, corresponding to a silicon concentration of 5 % by mass and matrix matched to the test sample solution. Prepare also a blank calibration solution, K_0, prepared in the same way as the calibration solution but leaving out silicon.

7.3.2 Using a pipette, add 12,5 ml of the silicon stock standard solution (4.5) to a 100 ml volumetric polypropylene flask (5.3) marked K_5.

7.3.3 For all matrix elements, with concentrations above 1 % in the unknown sample, add, using the standard solutions (4.7), the same amount of the matrix elements (to the nearest 1 %) to the calibration sample.

7.3.4 Add all matrix element as in 7.3.3 to a second 100 ml volumetric polypropylene flask (5.3) marked K_0.

7.3.5 Add 10 ml of hydrochloric acid (4.2), 2 ml of nitric acid (4.3) and 5 ml hydrofluoric acid (4.1) to the two flasks, dilute with water and mix.

7.3.6 Measure the absolute or ratioed intensities for the solutions K_0 and K_5 and plot a calibration curve.

7.3.7 Measure the absolute or ratioed intensities for the test sample solution, T_n.

7.3.8 Calculate the approximate concentration in the test sample solution by means of the calibration curve.

7.4 Preparation of calibration solutions for bracketing, K_{Ln} and K_{Hn}

For each sample, n, prepare two matrix matched calibration samples, K_{Ln} and K_{Hn}, with silicon concentrations in K_{Ln} slightly below and in K_{Hn} slightly above the concentration in the unknown sample as follows:

a) From the result in 7.3.8 calculate the approximate amount of Si, m_s in milligrammes, in the dissolved 0,25 g portion of the unknown sample. Using a calibrated pipette, add $m_s \times 0{,}75 < m_{Ln} < m_s \times 0{,}95$ of the silicon standard solution (4.6) or the silicon stock standard solution (4.5), as appropriate, to a 100 ml volumetric polypropylene flask (5.3) marked K_{Ln} and $m_s \times 1{,}05 < m_{Ln} < m_s \times 1{,}25$ to another marked K_{Hn}.

b) For all matrix elements, with concentrations above 1 % in the unknown sample, add, using the standard solutions (4.7), the same amount of the matrix elements to the nearest % to the calibration samples K_{Ln} and K_{Hn}.

c) Proceed as specified in 7.1.2 to 7.1.6

7.5 Analysis of test solutions

7.5.1 Ensure that all solutions, K_{Ln}, K_{Hn} and T_n, are at the same temperature to within 1 °C. Measure the absolute or ratioed intensity of the analytical line beginning with the lowest calibration solution, K_{Ln}. Continue with test sample solution, T_n, and then the highest calibration solution K_{Hn}. Repeat this sequence three times and calculate the mean intensities I_{Ln}, I_{Hn} for the low and high calibration solution and I_T for the test sample solution respectively.

7.5.2 Plot the measured intensities I_{Ln} and I_{Hn} versus the amount of Si, m_{Ln} and m_{Hn}, in the calibration solutions. Determine the amount of Si m_T, in the test sample solution from the calibration curve using the measured intensity I_T.

8 Expression of results

8.1 General

The content of silicon C_{Si}, expressed as a percentage by mass, is then derived as follows:

$$C_{Si} = \frac{m_T 0{,}1}{m}$$

where

m_T is the amount of the element in the test sample solution, expressed in milligrams;

m is the mass of the test portion, in grams.

8.2 Precision

A planned trial of this method was carried out by 14 laboratories in 8 countries, at 9 levels of silicon content, each laboratory making three determinations (see notes 1 and 2) of silicon content on each level. See Table 3.

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, same calibration and 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 with a new calibration.

The test samples used and mean/precision results obtained are listed in Tables A.1 and A.2 respectively.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between silicon content and repeatability limit (r) and reproducibility limits (R_w and R) of the test results (see note 3) as summarized in Table 1. The graphical representation of the data is shown in Figure B.1.

NOTE 3 From the two values obtained on day 1, the repeatability (r) and reproducibility (R) were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility limit (Rw) was calculated using the procedure given in ISO 5725-3.

Table 3 — Precision

Silicon content % mass fraction	r	R_w	R
0,02	0,002 03	0,001 95	0,011 15
0,05	0,003 62	0,003 79	0,019 08
0,10	0,005 61	0,006 26	0,028 65
0,20	0,008 68	0,010 35	0,043 01
0,50	0,015 48	0,020 09	0,073 59
1,00	0,023 97	0,033 20	0,110 48
2,00	0,037 12	0,054 85	0,165 87
5,00	0,066 17	0,106 53	0,283 81

9 Test report

The test report should contain at least 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 Technical Report, i.e ISO/TR 17055;

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

d) the analytical line used;

e) any unusual features noted during the determination;

f) any operation not specified in this Technical Report, or any optional operation which may have influenced the results.

Annex A

(informative)

Additional information on the international cooperative tests

Table A.1 was derived from the results of the international analytical trial carried out in 1996 on 9 steel samples in 8 countries involving 14 laboratories.

Statistical calculation was conducted using selected laboratories which satisfied the requirements of 7.5.1 for a calibration procedure in which the tested sample was sandwiched between at least two CRMs.

The results of the trial were reported in document ISO/TC 17/SC 1 N1269 rev, 2000-09-15. The graphical representation of the precision data is given in annex B.

The test samples used and the results obtained are listed in Tables A.1 and A.2.

Table A.1 — Test samples used in the interlaboratory tests

Sample No.	CRM	Chemical composition % mass fraction								
		Si	C	Mn	Cr	Ni	Mo	Co	Cu	Others
46-1	ECRM 187-1	0,026	0,2	1,3	1,2	0,1	0,04	0,01	0,2	Al: 0,05
46-2	JK 22B	0,255	0,9	1,3	0,5	0,1	0,05	0,01	0,04	W: 0,5, V: 0,1
46-3	JSS 607-8	0,30	0,8	0,4	4	0,05	0,5	4,6	0,03	V: 0,8
46-4	JK 8F	0,424	0,04	1,5	17	11	2,8	0,1	0,05	
46-5	ECRM 281-1	0,929	0,05	0,8	18	9,4		0,02	0,08	Al: 0,01, Ti: 0,2
46-6	JK 5A	1,86	0,03	0,3	0,08	0,1	0,01	0,01	0,1	
46-7	NIST 125 b	2,89	0,03	0,3	0,02	0,04	0,01		0,07	Al: 0,3
46-8	BCS 170/4	2,45	2,1	0,8					0,6	
46-9	SDN 1029	4,90	0,01	0,5	17	19	0,4	0,02	2	