

INTERNATIONAL
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**Steel — Determination of boron content —
Curcumin spectrophotometric method**

*Acier — Dosage du bore — Méthode spectrophotométrique à la
curcumine*

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Reference number
ISO 10153:1991(E)

Foreword

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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 10153 was prepared by Technical Committee ISO/TC 17, *Steel*.

Annex A forms an integral part of this International Standard. Annexes B, C and D are for information only.

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Steel — Determination of boron content — Curcumin spectrophotometric method

1 Scope

This International Standard specifies a curcumin spectrophotometric method for the determination of boron content in steel.

The method is applicable to boron contents between 0,000 5 % (*m/m*) and 0,012 % (*m/m*).

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

Dissolution of a test portion in hydrochloric and nitric acids.

Decomposition of boron compounds (nitrides etc.) with orthophosphoric and sulfuric acids at a temperature of 290 °C.

Formation of a coloured complex between orthoboric acid and curcumin in a buffered acetic medium.

Spectrophotometric measurement at a wavelength of about 543 nm.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and having a very low boron content and only grade 2 water as specified in ISO 3696.

4.1 Pure iron, free of boron or with a known residual amount of boron.

4.2 Sodium hypophosphite monohydrate, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

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

4.4 Nitric acid, ρ about 1,40 g/ml.

4.5 Sulfuric acid, ρ about 1,84 g/ml.

4.6 Orthophosphoric acid, ρ about 1,71 g/ml.

4.7 Acetic acid, free from aldehyde, ρ about 1,05 g/ml.

Pour 20 ml of acetic acid (ρ about 1,05 g/ml) to be checked and 1 ml of potassium permanganate solution (1 g/l) into a 50 ml beaker. In the absence of aldehyde, the initial violet colour of potassium per-

manganate will persist; otherwise the solution will become an easily identifiable brown colour after 15 min.

4.8 Mixture of acetic and sulfuric acids.

Add in small portions, cooling under water and swirling, a volume of sulfuric acid (4.5) to an equal volume of acetic acid (4.7).

4.9 Acetic buffer solution.

Dissolve 225 g of ammonium acetate in 400 ml of water. Add 300 ml of acetic acid (4.7). Filter the solution obtained into a 1000 ml polypropylene volumetric flask. Dilute to the mark with water and mix.

4.10 Sodium fluoride, 40 g/l solution.

Store in a polypropylene bottle.

4.11 Boron, standard solution.

4.11.1 Stock solution, corresponding to 0,10 g of B per litre.

Weigh, to the nearest 0,0001 g, 0,2860 g of orthoboric acid (H_3BO_3). Place in a 250 ml beaker and dissolve in about 200 ml of water. Transfer the solution quantitatively to a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix. Store in a polypropylene bottle.

1 ml of this stock solution contains 0,10 mg of B.

4.11.2 Standard solution, corresponding to 0,002 g of B per litre.

Transfer 20,0 ml of the stock solution (4.11.1) into a 1000 ml one-mark volumetric flask. Dilute to the mark with water and mix. Store in a polypropylene bottle.

Prepare this standard solution immediately before use.

1 ml of this standard solution contains 2 μ g of B.

4.12 Curcumin, acetic acid solution, 1,25 g/l.

Mix 60 ml of acetic acid (4.7) with 0,125 g of curcumin, $[CH_3O(OH)C_6H_3CH:CHCO]_2CH_2$, in a polypropylene or quartz vessel. Heat in a water bath at 40 °C and stir using a magnetic stirrer. After dissolution, cool and transfer to a 100 ml polypropylene volumetric flask. Dilute to the mark with acetic acid and mix.

5 Apparatus

Glassware containing boron shall not be used and shall be replaced by polypropylene or quartz equipment rinsed with acetic acid (4.7) then with water and finally dried. All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus and the following shall be used.

5.1 Quartz beakers with quartz covers, of capacity 100 ml, external dimensions: 51 mm diameter and 70 mm height.

5.2 Polypropylene or polytetrafluoroethylene volumetric flasks, of capacities 50 ml and 100 ml.

5.3 Polypropylene or polytetrafluoroethylene bottle, of capacity 100 ml.

5.4 Aluminium alloy block, with holes designed to allow the positioning of the 100 ml quartz beakers, heated by surface contact with a hot plate. Diagrams of such blocks are shown in annex A. The dimensions of the holes shall be adapted to the dimensions of the quartz beakers available.

5.5 Spectrophotometer, suitable for measuring the absorbance of the solution at a wavelength of 543 nm with 2 cm optical cells.

6 Sampling

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

The size of the chip used shall be smaller than 1 mm.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,0002 g, the masses, m , as a function of the expected boron content as follows:

- content from 0,0005 % (m/m) to 0,006 % (m/m), m is approximately 1,00 g;
- content from 0,006 % (m/m) to 0,012 % (m/m), m is approximately 0,50 g.

For grades of steel with nickel content plus cobalt content greater than 30 % (m/m), use a test portion of approximately 0,50 g.

7.2 Blank test

With each analytical run, carry out an analysis on a portion of pure iron (4.1), corresponding to the mass of test portion used (see 7.1), in parallel with the test portion analysis, using identical reagents, conditions, analytical procedure and dilutions throughout. The absorbance of the blank test solution (A_b) and that of the blank compensating solution (A_{bc}) are thus obtained.

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 100 ml quartz beaker (5.1). Add 10 ml of hydrochloric acid (4.3) and 5 ml of nitric acid (4.4), cover the beaker with a quartz cover (5.1) and leave at the ambient temperature (see note 1).

Wait until dissolution is complete, or until the end of effervescence for samples which are difficult to dissolve. Then, carefully add 10 ml of orthophosphoric acid (4.6) and 5 ml of sulfuric acid (4.5).

Heat to white sulfuric acid fumes, swirling from time to time in order to recover any particles attached to the side of the beaker. Place the reaction beaker in a hole in the aluminium alloy block (5.4) and place this on a heat source permitting a temperature of 290 °C (see note 2) to be obtained in the solution. Maintain heating for 30 min, taking care to replace the quartz cover after the appearance of white fumes.

Remove the beaker from the heat source and allow to cool. Add 30 ml of water to the syrupy solution, warm and stir. Then, carefully add 5 ml of hydrochloric acid (4.3) and bring to the boil. Add 3 g of sodium hypophosphite (4.2) and allow to boil gently for 15 min.

Remove the beaker from the heat source and allow to cool. Transfer the solution quantitatively to a 50 ml polypropylene volumetric flask (5.2), dilute to the mark with water and mix.

NOTES

1 Maintaining the ambient temperature is most important, in order to avoid possible loss of boron at higher temperatures.

2 The temperature of (290 ± 5) °C is obtained by calibrating the heat source with a thermometer, graduated from 0 °C to 350 °C, immersed in a test beaker containing the same amounts of dissolution reagents.

7.3.2 Formation of the coloured complex

Take a 1,0 ml aliquot of the test solution (see 7.3.1) and transfer it to a 100 ml polypropylene volumetric flask (5.2) which has previously been cleaned and dried.

Add to the flask, swirling to avoid contact with the stopper, the following quantities of reagents.

- 6,0 ml of the mixture of acetic and sulfuric acids (4.8), avoiding contact of the pipette with the neck and sides of the flask. Then mix.
- 6,0 ml of curcumin acetic acid solution (4.12). Stopper the flask and mix. Leave to stand for 2 h 30 min for complete development of the colour.
- 1,0 ml of orthophosphoric acid (4.6) to stabilize the colour. Shake and allow to stand for 30 min.
- 30,0 ml of acetic buffer solution (4.9). The solution becomes orange. Stopper, shake and allow to stand for exactly 15 min.

7.3.3 Preparation of the compensating solution

Take a 1,0 ml aliquot of the test solution (see 7.3.1) and transfer it to a 100 ml polypropylene volumetric flask (5.2) which has previously been cleaned and dried. Add 0,2 ml of sodium fluoride solution (4.10) to the bottom of the flask.

Carefully swirl the small volume of solution. Leave to stand for 1 h.

Proceed as specified in 7.3.2 from "Add to the flask, swirling..." to the end.

7.3.4 Spectrophotometric measurements

After adjusting the spectrophotometer to zero absorbance by reference to water, carry out the spectrophotometric measurements (see note 3) of the colour-developed test solution (see 7.3.2) and the corresponding compensating solution (see 7.3.3) at a wavelength of 543 nm with 2 cm cells.

The absorbances of the test solution (A) and the compensating solution (A_c) are thus obtained.

NOTE 3 In order to carry out the spectrophotometric measurements on all the solutions whilst waiting exactly 15 min after the addition of acetic buffer solution (see 7.3.2), it is advisable to divide them into series of six measurements, i.e. 12 flasks. In fact, for long series of measurements where the waiting time cannot be strictly adhered to, the formation of a cloudiness in the solutions can be observed and consequently erroneous results obtained.

7.4 Establishment of the calibration graph

7.4.1 Preparation of calibration solutions

Place $(1,00 \pm 0,01)$ g portions of iron (4.1) in a series of six 100 ml quartz beakers and add the volumes of boron standard solution (4.11.2) as indicated in table 1.

Proceed as specified in 7.3.1, 7.3.2 and 7.3.3.

7.4.2 Spectrophotometric measurements

After adjusting the spectrophotometer to zero absorbance by reference to water, carry out the spectrophotometric measurements on the range of calibration solutions, with and without sodium fluoride solution (4.10), at a wavelength of 543 nm with 2 cm cells.

7.4.3 Plotting the calibration graph

Calculate the difference in absorbance between the solutions with and without sodium fluoride and subtract the value obtained for the zero member from these calculated values.

Prepare the straight line calibration graph, which passes through the origin, by plotting the net absorbance readings against micrograms of boron.

8 Expression of results

8.1 Calculation of the net absorbance

Calculate the difference in absorbance for each solution to be determined and subtract the value for the blank test obtained under the same conditions. The

net absorbance for the boron content to be determined is given by the equation

$$A_B = (A - A_c) - (A_b - A_{bc})$$

where

- A_B is the net absorbance for the boron content to be determined;
- A is the absorbance of the test solution;
- A_b is the absorbance of the blank test solution;
- A_c is the absorbance of the compensating solution for the test solution;
- A_{bc} is the absorbance of the compensating solution for the blank test solution.

8.2 Calculation of the boron content

Convert the net absorbance into the corresponding mass, expressed in micrograms of boron in the test solution, by using the calibration graph (see 7.4.3).

The boron content, w_B , expressed as a percentage by mass, is given by the formula

$$w_B = \frac{m_B}{10^6} \times \frac{100}{m} = \frac{m_B}{10^4 m}$$

where

- m_B is the mass, expressed in micrograms, of boron in the test solution;
- m is the mass, in grams, of the test portion (7.1).

Table 1

Volume of boron standard solution (4.11.2) ml	Corresponding mass of boron µg	Boron content of the test sample, % (m/m)	
		Test portion of 1,00 g	Test portion of 0,50 g
0,0	0	0	0
2,5	5	0,000 5	0,001 0
5,0	10	0,001 0	0,002 0
10,0	20	0,002 0	0,004 0
20,0	40	0,004 0	0,008 0
30,0	60	0,006 0	0,012 0
1) Zero member			

8.3 Precision

A planned trial of this method was carried out by 21 laboratories in eight countries at eight levels of boron, each laboratory making three determinations (see notes 4 and 5) of boron content at each level.

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

The results obtained were treated statistically in accordance with ISO 5725, using the data obtained from the samples containing six levels of boron within the application range.

The data obtained showed a logarithmic relationship between boron content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 6), as summarized in table 2. The graphical representations of the figures are given in annex C.

NOTES

4 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.

5 The third determination was carried out at a different time (on a different day) by the same operator as in note 4 using the same apparatus with a new calibration.

6 From the results obtained on day 1 the repeatability (r) and the reproducibility (R) were calculated using the

procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

The same method was tested by 14 laboratories in seven countries belonging to ECISS/TC 20 using samples containing eight levels of boron. The results of these precision tests are listed in table D.1 for information.

9 Test report

The test report shall include the following information:

- all information necessary for the identification of the sample, the laboratory and the date of analysis;
- the method used by reference to this International Standard;
- the results, and the form in which they are expressed;
- any unusual features noted during the determination;
- any operation not specified in this International Standard, or any optional operation which may have influenced the results.

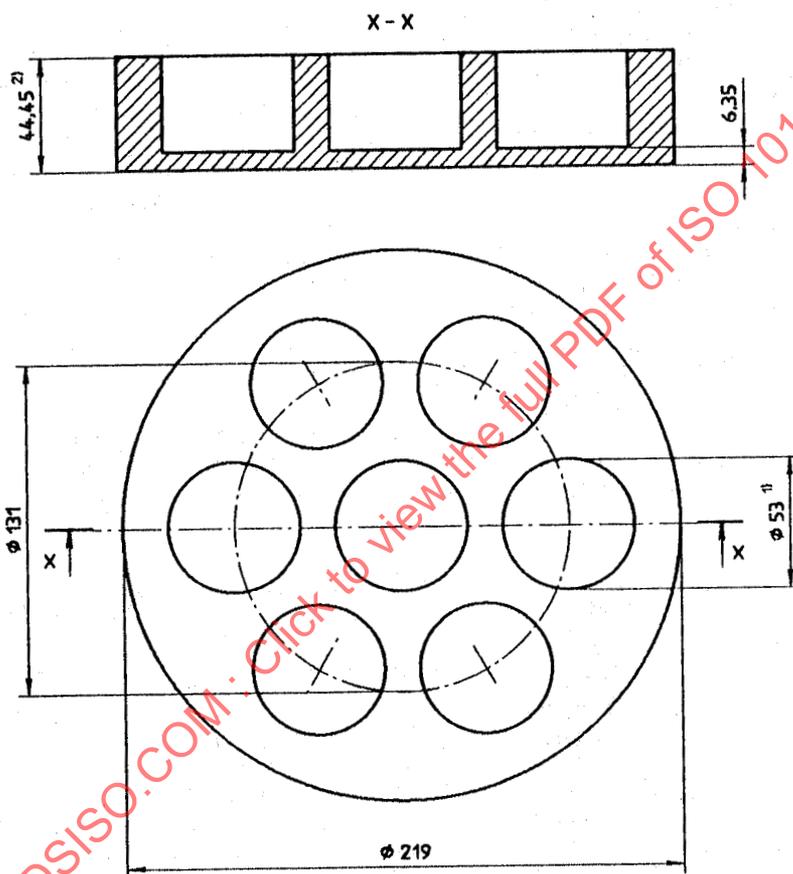
Table 2

Boron content % (m/m)	Repeatability r	Reproducibility	
		R	R_w
0,000 5	0,000 14	0,000 28	0,000 17
0,001 0	0,000 20	0,000 39	0,000 25
0,002 0	0,000 28	0,000 55	0,000 37
0,005 0	0,000 43	0,000 89	0,000 62
0,010 0	0,000 50	0,001 25	0,000 92
0,012 0	0,000 65	0,001 37	0,001 00

Annex A
(normative)

Examples of aluminium alloy blocks

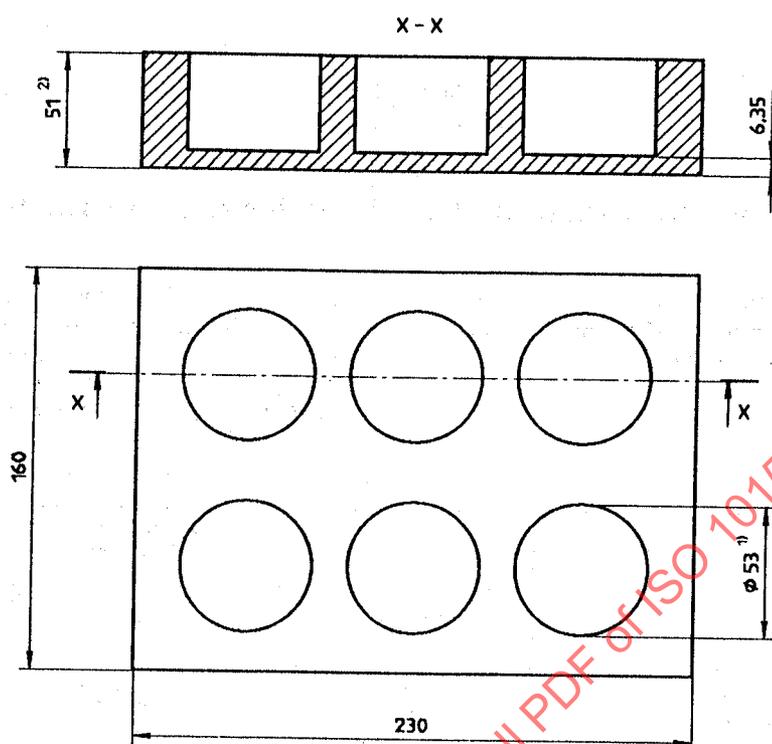
Dimensions in millimetres



- 1) Adapt the diameter of the holes according to the diameter of the beakers used.
- 2) Holes having the same height as the surface of the solution in the beaker can be used if this is preferable.

Figure A.1 — Example of an aluminium alloy block

Dimensions in millimetres



- 1) Adapt the diameter of the holes according to the diameter of the beakers used.
- 2) Holes having the same height as the surface of the solution in the beaker can be used if this is preferable.

Figure A.2 — Example of an aluminium alloy block