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Steel — Determination of boron content — Curcumin spectrophotometric method after distillation

Aciers — Dosage du bore — Méthode spectrophotométrique à la curcumine après distillation

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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 13900 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition.*

Annexes A to C of this International Standard are for information only.

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Steel — Determination of boron content — Curcumin spectrophotometric method after distillation

1 Scope

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

The method is applicable to a boron content of between 0,000 05 % (*m*/*m*) and 0,001 0 % (*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 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

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

ISO 1042:—[1], *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

Dissolution of a test portion in hydrochloric and nitric acids.

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[1] To be published. (Revision of ISO 1042:1983)

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

Distillation of the solution after the addition of methanol and collection of methylborate in a receiver containing sodium hydroxide solution.

Evaporation of the solution to dryness. Formation of a coloured complex between orthoboric acid and curcumin in a methanol medium.

Spectrophotometric measurement at a wavelength of about 550 nm.

4 Reagents

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

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

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

4.3 Nitric acid, ρ about 1,40 g/ml.

4.4 Sulfuric acid, ρ about 1,84 g/ml.

4.5 Orthophosphoric acid, ρ about 1,71 g/ml, boron content less than 0,02 µg/ml.

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

In order to test the acetic acid for the presence of aldehyde, pour 20 ml of acetic acid (ρ about 1,05 g/ml) 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 permanganate will persist ; otherwise the solution will become an easily identifiable brown colour after 15 min.

4.7 Acid mixture A

Add one volume of hydrochloric acid (4.2) to two volumes of acetic acid (4.6).

4.8 Acid mixture B

While cooling under water and swirling, add in small portions a volume of sulfuric acid (4.4) to an equal volume of acetic acid (4.6).

4.9 Sodium hydroxide, 8 g/l solution.

4.10 Methanol, minimum assay 99,6 % (*V*/*V*).

4.11 Boron, standard solution.

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

Weigh, to the nearest 0,000 1 g, 0,286 0 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 (5.2).

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

4.11.2 Standard solution, corresponding to 0,001 g of boron per litre.

Transfer 1,0 ml of the stock solution (4.11.1) to a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix. Store in a polypropylene bottle (5.2).

Prepare this solution immediately before use.

1 ml of this standard solution contains 1 µg of boron.

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

Weigh 0,125 g of curcumin, $[CH_3O(OH)C_6H_3CH{=}CHCO]_2CH_2$, in a polypropylene or quartz vessel, add 60 ml of acetic acid (4.6) and mix. 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.

4.13 Carrier gas, nitrogen, argon or dry air.

5 Apparatus

Glassware, polypropylene or quartz equipment rinsed with acetic acid (4.6) then with water and finally dried. All volumetric glassware shall be grade 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 Volumetric flask, of capacity 100 ml.

5.2 Polypropylene bottles, of capacities 100 ml and 500 ml.

5.3 Distillation apparatus (see annex A), comprising the following equipment.

a) Distillation flask, of capacity 200 ml, made of quartz.

b) Reservoir, made of quartz.

c) Reflux condenser, made of quartz.

d) Receiver, 100 ml quartz beaker marked to indicate a volume of 35 ml.

e) Magnetic stirrer, with rotor covered by polytetrafluoroethene (PTFE).

Suitable forms of apparatus are illustrated in annex A.

5.4 Platinum dish or PTFE beaker, of capacity 100 ml.

5.5 Heater, for methanol evaporation.

6 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,000 1 g, about 0,50 g of the test sample.

7.2 Blank test and determination of boron in the pure iron (4.1)

7.2.1 Determination of boron in the pure iron (4.1)

Prepare two distillation flasks [5.3 a)]. Add 0,250 g of the pure iron (4.1) to one distillation flask and 0,500 g to the other.

Treat both as specified in 7.3.1, 7.3.2, 7.3.3 and 7.3.4.

Convert the absorbance readings obtained into micrograms of boron by means of the calibration graph (7.4).

The mass (m_3), expressed in micrograms, of boron in 0,500 g of the pure iron (4.1) is given by:

$$m_3 = 2 \times (m_6 - m_5)$$

where

m_6 is the mass, expressed in micrograms, of boron in the 0,500 g test;

m_5 is the mass, expressed in micrograms, of boron in the 0,250 g test.

7.2.2 Blank test and blank value

In parallel with the determination of the content and following the same procedure, carry out a blank test using 0,500 g of the pure iron (4.1) and the same quantities of all the reagents.

Obtain the absorbance of the blank test and convert it to micrograms of boron by means of the calibration graph (7.4).

The blank value(m_1) is obtained by subtracting the mass of boron(m_3) in the pure iron used (4.1) from the mass of boron in the blank test(m_4).

Blank value, $m_1 = m_4 - m_3$

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a distillation flask [5.3 a)]. Add 10 ml of hydrochloric acid (4.2) and 5 ml of nitric acid (4.3). Maintain the solution at the ambient temperature (see note 1).

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

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 (4.5) and 5 ml of sulfuric acid (4.4).

Heat until white sulfuric acid fumes are generated, swirling from time to time in order to recover any particles attached to the side of the flask. Place the flask on a heat source permitting a temperature of 290 °C (see note 2) to be obtained in the solution. Maintain heating for 30 min.

NOTE 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 flask containing the same amounts of dissolution reagents.

Remove the flask from the heat source and allow to cool.

7.3.2 Distillation

Place a rotor [5.3 e)] in the distillation flask containing the test solution (see 7.3.1). Assemble the apparatus for distillation (5.3) as shown in figure A.1. Close-fitting ground-glass joints shall be used.

NOTE 3 When the apparatus is used for the first time, or after a long period of disuse, it is essential that blank tests are carried out repetitively until stable low blank values are obtained.

Add 5 ml of sodium hydroxide solution (4.9) to a receiver [5.3 d)]. Place it under the reflux condenser [5.3 c)] and raise until the condenser tip is immersed in sodium hydroxide solution. Maintain the temperature of the reflux condenser at less than 10 °C for distillation. Carefully, while mixing, pour 50 ml of methanol (4.10) through the reservoir [5.3 b)]. Carefully adjust the carrier gas (4.13) flow rate from the gas inlet tube to about 50 ml per min and distil at a rate of 30 ml per 20 min by heating and collect about 30 ml of the distillate. Switch off the heat source to the distillation flask. Rinse down the condenser tip with a small quantity of methanol (4.10).

7.3.3 Formation of the coloured complex

Collect the distillate and washings (see 7.3.2). Transfer the solution to a platinum dish or PTFE beaker (5.4) and wash the receiver with a small quantity of methanol (4.10). Heat gently until methanol in the solution has been evaporated and continue heating to dryness.

Add 1,0 ml of acid mixture A (4.7) to the platinum dish or PTFE beaker containing the residue and mix the residue well using a PTFE bar. Add 6,0 ml of curcumin acetic acid solution (4.12), washing the PTFE bar and mix. Add 4,0 ml of acid mixture B (4.8), mix well and allow to stand for 20 min. Add about 50 ml of methanol (4.10) to dissolve the coloured complex, transfer it to a 100 ml one-mark glass volumetric flask using methanol, dilute to the mark with methanol and mix. Leave to stand for 10 min, then filter by decantation through a dry filter to remove any residue. Collect the filtrate in a dry quartz beaker, discarding the first fractions of the filtrate.

7.3.4 Spectrophotometric measurements

After adjusting the spectrophotometer to zero absorbance by reference to methanol (4.10), carry out the spectrophotometric measurement of the colour-developed test solution (see 7.3.3) at a wavelength of 550 nm with a 1 cm cell.

7.4 Establishment of the calibration graph

7.4.1 Preparation of calibration solutions

Place the same quantities of pure iron (4.1) as the test portion (see 7.1) in a series of seven distillation flasks and add the volumes of boron standard solution (4.11.2) given in table 1.

Proceed as specified in 7.3.1, 7.3.2 and 7.3.3.

Table 1 — Calibration solutions

Volume of boron standard solution (4.11.2) ml	Corresponding mass of boron µg	Boron content of the test sample % (*m*/*m*)
0 [1]	0	0
0,5	0,5	0,000 1
1,0	1,0	0,000 2
2,0	2,0	0,000 4
3,0	3,0	0,000 6
4,0	4,0	0,000 8
5,0	5,0	0,001 0

[1] Zero member

7.4.2 Spectrophotometric measurements

After adjusting the spectrophotometer to zero absorbance by reference to methanol (4.10), carry out the spectrophotometric measurements of the range of calibration solutions, at a wavelength of 550 nm with 1 cm cells.

7.4.3 Plotting the calibration graph

Calculate the difference in absorbance between the solutions and the value obtained for the zero member.

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

8 Expression of results

8.1 Method of calculation

Convert the absorbances of the test solution and of the blank test solution to micrograms of boron by means of the calibration graph (7.4).

The blank value (m_1) is obtained by subtracting the micrograms of boron (m_3) in 0,500 g of the pure iron (4.1) from the micrograms of boron in the blank test (m_4) (see 7.2.2).

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

$$w_B = \frac{(m_0 - m_1)}{m \times 10^6} \times 100$$

$$= \frac{(m_0 - m_1)}{m \times 10^4}$$

where

m_0 is the mass, expressed in micrograms of boron, in the test portion;

m_1 is the mass, expressed in micrograms of boron, of the blank value;

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 nine laboratories in four countries, at five levels of boron of unalloyed steels, each laboratory making three determinations (see notes 4 and 5) of boron content at each level.

NOTES

4 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 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.

The test samples used and mean/precision results obtained are listed in table B.1.

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

The data obtained showed a logarithmic relationship between boron content and repeatability limit (r) and reproducibility limits (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.

Table 2 — Results for repeatability limit and reproducibility limits

Boron content % (m/m)	Repeatability limit r	Reproducibility limits R	 R_W
0,000 05	0,000 001	0,000 068	0,000 039
0,000 1	0,000 003	0,000 075	0,000 050
0,000 2	0,000 008	0,000 082	0,000 063
0,000 5	0,000 031	0,000 093	0,000 086
0,001 0	0,000 085	0,000 101	0,000 109

NOTE 6 From the two values obtained on day 1, the repeatability limit (r) and the reproducibility limit (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 (R_W) was calculated using the procedure specified in ISO 5725-3.