BS EN 10200:2012

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Chemical analysis of ferrous materials — Determination of boron in steels — Spectrophotometric method

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Published by BSI Standards Limited 2012

ISBN 978 0 580 77390 7
ICS 77.040.30

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 October 2012.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 10200

October 2012

ICS 77.040.30

Supersedes EN 10200:1991

English Version

Chemical analysis of ferrous materials - Determination of boron in steels - Spectrophotometric method

Analyse chimique des matériaux ferreux - Détermination du bore dans les aciers - Méthode spectrophotométrique

Chemische Analyse von Eisenwerkstoffen - Bestimmung von Bor in Stahl - Spektrophotometrisches Verfahren

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Ref. No. EN 10200:2012: E

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Foreword

This document (EN 10200:2012) has been prepared by Technical Committee ECISS/TC 102 “Methods of chemical analysis for iron and steel”, the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2013, and conflicting national standards shall be withdrawn at the latest by April 2013.

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This document supersedes EN 10200:1991.

Since the previous edition, no technical changes have been made, but the text has been editorially revised.

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Introduction

The development of the method was carried out by a working group under French convenorship. The results of the inter-laboratory tests have shown that the determination of lower limit application of the method should be 0,000 4 % (m/m) boron, based on a relative deviation not exceeding 10 % within 66 % confidence limits. However, further work has shown that the method may be used for lower boron contents if a higher relative deviation is acceptable.

1 Scope

This European Standard specifies a spectrophotometric method for the determination of boron in steels. The method is applicable to non-alloyed and alloyed steels with boron contents of 0,000 4 to 0,012 0 % (m/m).

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.

EN ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition (ISO 14284)*

3 Principle

Dissolution of a test portion in hydrochloric and nitric acids.

Decomposition of boron compounds (nitrides, etc.) with orthophosphoric and sulphuric acids at 290 °C.

Spectrophotometric measurement at a wavelength of 543 nm of the complex formed between boric acid and curcumin in buffered acetic medium.

4 Reagents

During the analysis, use only reagents of recognised analytical grade and distilled water or water of equivalent purity.

4.1 Pure iron, free of boron or of known low boron content.

4.2. Crystalline sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$).

4.3 Hydrochloric acid, HCl (ρ_{20} = 1,19 g/ml).

4.4 Nitric acid, HNO_3 (ρ_{20} = 1,40 g/ml).

4.5 Sulphuric acid, H_2SO_4 (ρ_{20}= 1,84 g/ml).

4.6 Orthophosphoric acid, H_3PO_4 (ρ_{20}= 1,71g/ml).

4.7 Acetic acid free of aldehyde, CH_3COOH (ρ_{20}= 1,05 g/ml).

Test for absence of aldehyde:

Place 20 ml of the acetic acid (4.7) to be tested and 1 ml of a 1 g/l solution of potassium permanganate ($KMnO_4$) into a 50 ml beaker. In the absence of aldehyde, the initial violet colour of the potassium permanganate will persist; otherwise the solution will become brown, easily identifiable after 15 min.

4.8 Mixture of acetic and sulphuric acids.

Add in small portions whilst cooling under water and swirling, a volume of sulphuric 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 1 000 ml polyethylene one-mark volumetric flask. Dilute to the mark with water and mix.

4.10 Sodium fluoride, 40 g/l solution.

4.11 Boron, 100 mg/l standard solution.

Dissolve 0,285 8 g of boric acid in water in a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Store this solution in a polyethylene flask.

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

4.12 Boron, 2 mg/l standard solution.

Transfer 20 ml of the boron standard solution (4.11) into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Store this solution in a polyethylene flask.

1 ml of this solution contains 2 µg of boron.

4.13 Curcumin, 1,25 g/l acetic solution (prepared immediately before use).

Dissolve 0,125 g of curcumin in 60 ml of acetic acid (4.7) in a polyethylene or quartz vessel. Heat at 40 °C in a water bath and stir with a magnetic stirrer. After dissolution, cool and transfer into a 100 ml polyethylene one-mark volumetric flask. Dilute to the mark with acetic acid (4.7) and mix.

5 Apparatus

Glassware containing boron shall not be used and shall be replaced by polyethylene and quartz vessel rinsed with acetic acid (4.7), then with water and finally dried.

5.1 100 ml quartz beakers, with quartz covers (outside dimensions: 51 mm diameter and 70 mm height).

5.2 Aluminium alloy blocks, allowing a temperature of 290 °C to be achieved and maintained in the test solutions throughout the fuming period.

The block has holes designed to allow the location of the 100 ml quartz beakers and is heated by surface contact with a hotplate.

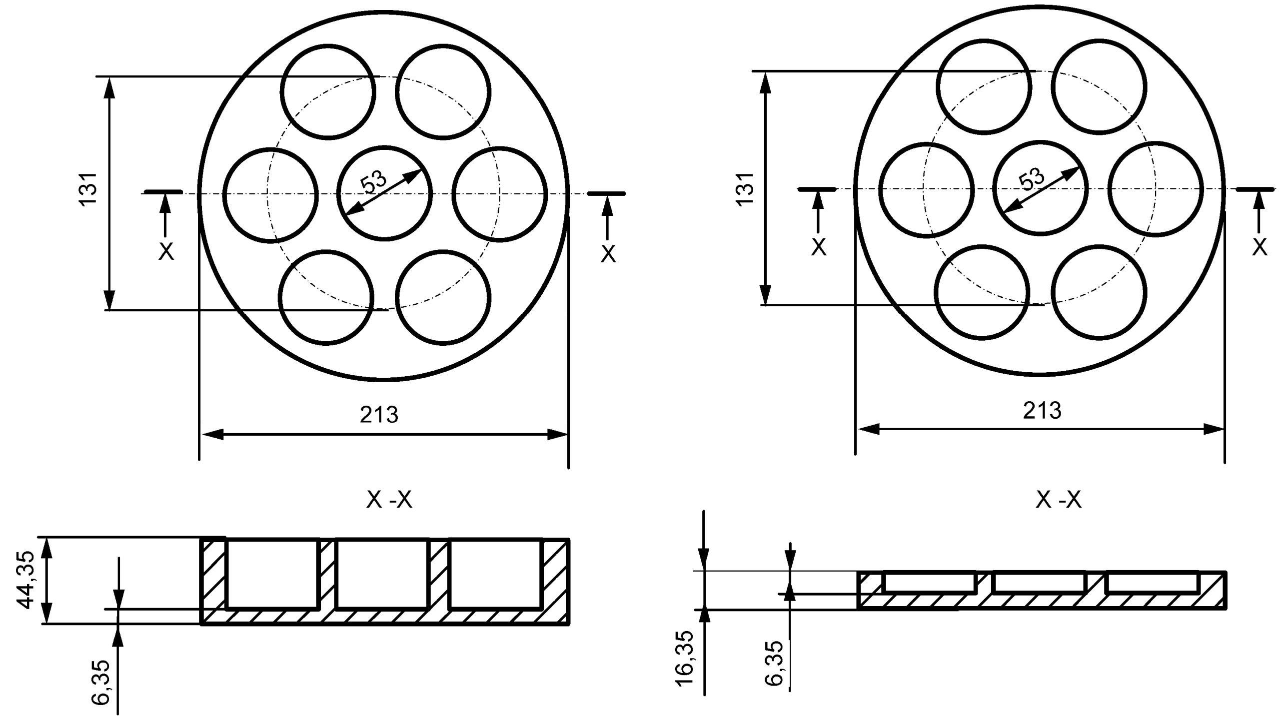
NOTE Diagrams of these blocks are shown in Figures 1 and 2. The dimensions of the holes should be adapted to the dimensions of the quartz beakers available.

5.3 50 ml polyethylene one-mark volumetric flasks.

5.4 100 ml polyethylene flasks.

5.5 Spectrophotometer, suitable for measuring absorbance at a wavelength of 543 nm, with 20 mm cells.

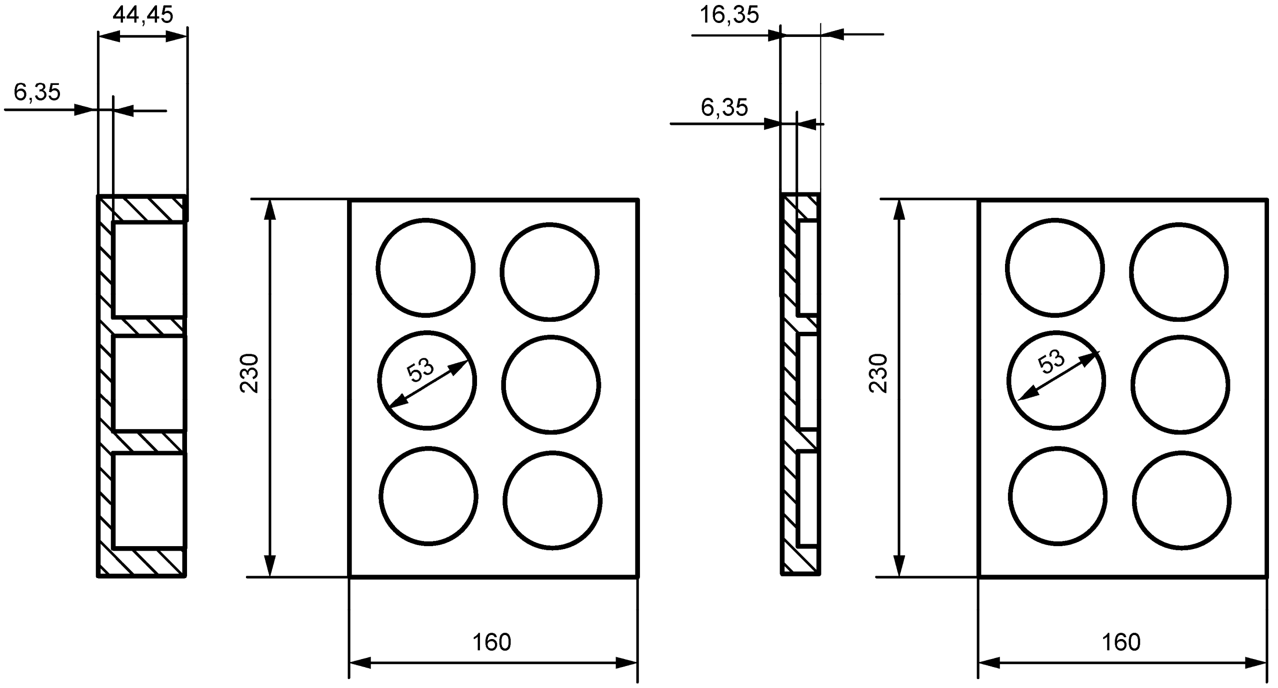
Dimensions in millimetres



NOTE Adapt the dimensions of the holes according to the dimensions of the beakers available.

Figure 1 — Example of circular aluminium alloy heating block

Dimensions in millimetres



NOTE Adapt the dimensions of the holes according to the dimensions of the beakers available.

Figure 2 — Example of a rectangular aluminium alloy heating block

6 Sampling

Sampling shall be carried out in accordance with EN ISO 14284 or an appropriate national standard for steel and iron.

The chips thickness shall be smaller than 1 mm.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,001 g, a test portion (m) as indicated below:

- m = 1 g ± 0,05 g for boron contents less than 0,006 %;
- m = 0,5 g ± 0,03 g for boron contents from 0,006 % to 0,012 %.

NOTE For steel grades with nickel and cobalt total content greater than 30 %, do not take a test portion larger than 0,5 g.

7.2 Blank test

Within each analytical series and in parallel with the analysis of the samples, carry out the analysis of pure iron test portions (4.1), having a mass corresponding to that of the test portions (see 7.1), following the same procedure and using the same quantities of all the reagents.

The absorbance of the blank test solution (A_{b}) and that of the corresponding 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 and add 10 ml hydrochloric acid (4.3) and 5 ml of nitric acid (4.4).

Cover the beaker with a quartz cover and leave it at ambient temperature in order to avoid possible loss of boron at higher temperatures.

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

Heat to copious white sulphuric fumes, swirling from time to time in order to recover any particles attached to the sides of the beaker. Place the beaker in a hole of the aluminium alloy block (5.2) and place the block on a heat source allowing a temperature of 290 °C to be obtained in the solutions. Maintain the heating for 30 min, taking care to replace the quartz cover after the appearance of white fumes.

NOTE The temperature of 290 °C ± 5 °C is obtained by calibration of the heat source by means of a thermometer, graduated from 0 to 350 °C, immersed in a beaker identical to those used for the test and containing the same amounts of the dissolution reagents.

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

Remove from the heat source and allow to cool. Transfer the solution quantitatively into a 50 ml polyethylene one-mark volumetric flask. Dilute to the mark with water and mix.

7.3.2 Formation of the coloured complex

Transfer 1,0 ml of the test solution obtained in accordance with 7.3.1 into a 100 ml polyethylene flask (5.4) previously cleaned and dried.

Add into the flask, whilst swirling in a circular movement to avoid contact with the stopper, the following volumes of reagents:

- 6,0 ml of the mixture of acetic and sulphuric acids (4.8), avoiding contact of the pipette with the neck and sides of the flask; mix;
- 6,0 ml of the curcumin acetic solution (4.13); stopper the flask and mix.

Allow to stand for 2 h 30 min for complete development of the colour. Then add:

- 1,0 ml of orthophosphoric acid (4.6) to stabilise the colour. Shake and allow to stand for 30 min;
- 30,0 ml of the acetic buffer solution (4.9). The solution turns orange. Stopper and shake. Allow to stand for exactly 15 min.

7.3.3 Compensating solution

Transfer 1,0 ml of the test solution obtained in accordance with 7.3.1 into a 100 ml polyethylene flask (5.4) previously 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. Allow to stand for 1 h.

Continue as in 7.3.2. from "Add into the flask, whilst swirling in a circular movement…".

7.3.4 Spectrophotometric measurements

NOTE In order to carry out the spectrophotometric measurements on all the solutions whilst waiting exactly 15 min after the addition of the acetic buffer solution, it is advisable to divide them into a series of 6 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 may be observed and consequently erroneous results obtained.

After adjusting the spectrophotometer to zero absorbance with water, carry out spectrophotometric measurements of the test solution (7.3.2) and the corresponding compensating solution (7.3.3) at a wavelength of 543 nm in cells of 20 mm optical path length. The absorbance of the test solution (A) and that of the compensating solution (A_c) are thus obtained.

7.4 Preparation of the calibration

7.4.1 Preparation of the calibration solutions

Weigh 1,000 g portions of iron (4.1) into a series of six 100 ml quartz beakers and using calibrated pipettes add the volumes of the boron standard solution (4.12) indicated in Table 1.

Table 1 — Composition of the calibration solutions

Volume of boron standard solution (4.12) ml	Corresponding mass of boron mg	Corresponding boron content of test sample % For a test portion of	
		1 g	0,5 g
0	0,000	0	0
1	0,002	0,000 2	0,000 4
5	0,010	0,001 0	0,002 0
10	0,020	0,002 0	0,004 0
20	0,040	0,004 0	0,008 0
30	0,060	0,006 0	0,012 0

Continue as for the test sample (7.3.1, 7.3.2 and 7.3.3).

7.4.2 Spectrophotometric measurements

After adjusting the spectrophotometer to zero absorbance with water, carry out the spectrophotometric measurements of the series of calibration solutions with and without sodium fluoride solution at a wavelength of 543 nm in cells of 20 mm optical path length.

7.4.3 Preparation of the calibration graph

Calculate the difference between the absorbance of each calibration solution with and without sodium fluoride and subtract from these calculated values the value obtained for the zero term of the calibration range.

Establish the calibration graph (which passes through the origin) by plotting the absorbance net values as a function of the boron content, in micrograms.

8 Expression of results

8.1 Calculation of the net absorbance

Calculate the difference in absorbance of each sample solution to be determined and subtract the value of the blank test, obtained under the same conditions. The net absorbance of the boron content to be determined is given by the formula:

$$A_{\mathrm{B}} = \left(A - A_{\mathrm{c}}\right) - \left(A_{\mathrm{b}} - A_{\mathrm{bc}}\right)$$

where

A_{B} is the net absorbance of 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:

$$w_{\mathrm{B}} = \frac{m_{\mathrm{B}}}{10^6} \times \frac{100}{m} = \frac{m_{\mathrm{B}}}{10^4 m}$$

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)

9 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) method used;

c) results;

d) any unusual characteristics noted during the determination;

e) any operation not included in this European Standard or in the document to which reference is made or regarded as optional;

f) date of the test and/or date of preparation or signature of the test report;

g) signature of the responsible person.

Annex A
(informative)

Precision data

The precision data where obtained from samples with boron contents down to 0,000 2 % but on the basis of the results obtained, it was agreed to raise the lower limit of application of the method to 0,000 4 %.

The planned trials of this method were carried out by analysts from 14 laboratories in 7 countries; each analyst made 3 determinations on each of 8 samples (see Notes 1 and 2). The results obtained were treated statistically in accordance with ISO 5725:1986 (see Note 3) and are shown in Table A.1.

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725:1986, i.e. one operator, same apparatus, identical operating conditions (same calibration) and a minimum period of time.

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

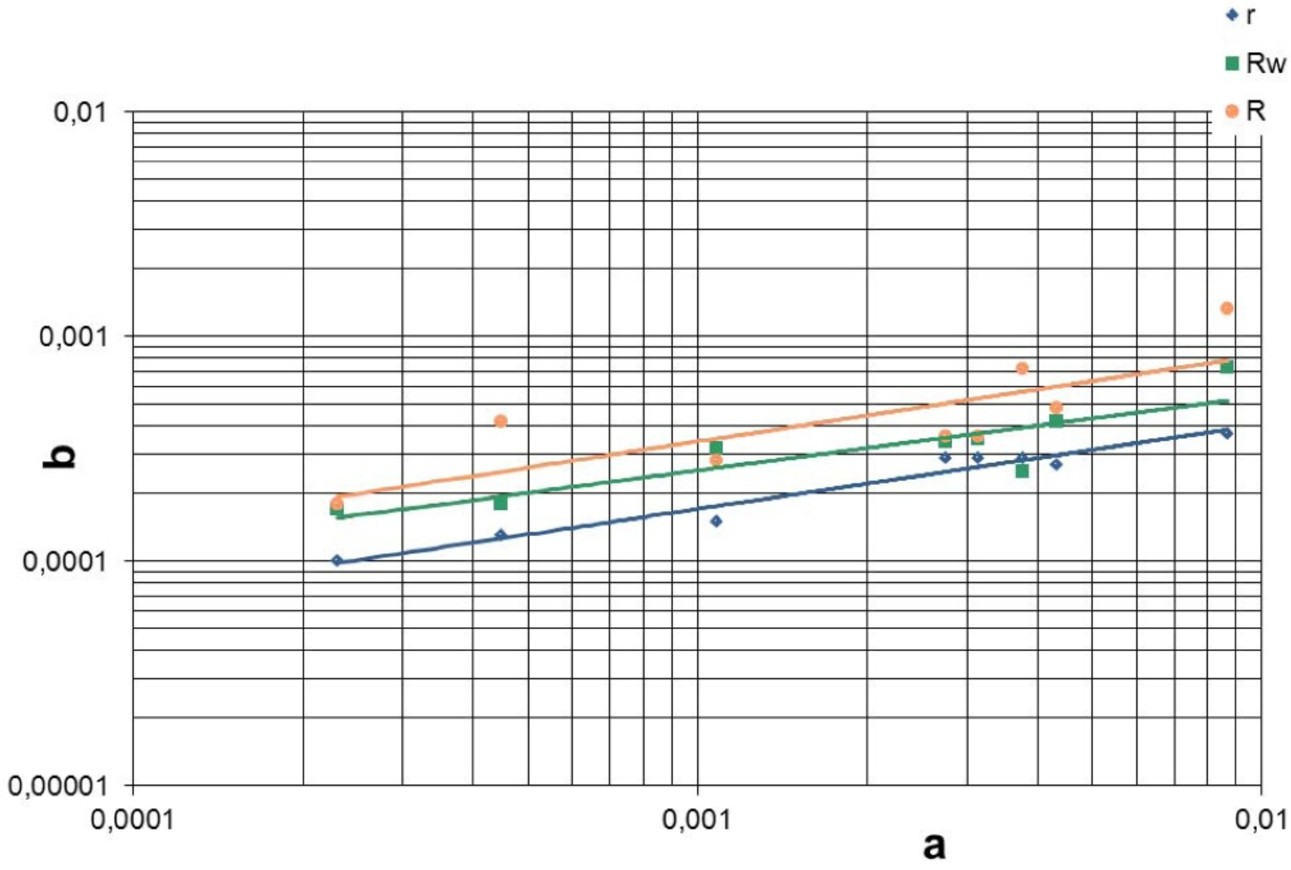
NOTE 3 The repeatability (r) and reproducibility (R) were calculated from the two values obtained on the first day (day 1) using the procedure specified in ISO 5725:1986. The within-laboratory reproducibility (R_w) was calculated from the first value obtained on day 1 and the value obtained on day 2.

Table A.1 — Results of the precision test

Type of test sample	Boron content	Repeatability	Reproducibility	
	m/m %	r %	R_w %	R %
Non-alloyed steel	0,000 23	0,000 10	0,000 17	0,000 18
Non-alloyed steel	0,001 08	0,000 15	0,000 32	0,000 28
Non-alloyed steel	0,002 75	0,000 29	0,000 34	0,000 36
Non-alloyed steel	0,003 15	0,000 29	0,000 35	0,000 36
Non-alloyed steel	0,003 78	0,000 29	0,000 25	0,000 72
Non-alloyed steel	0,008 69	0,000 37	0,000 73	0,001 32
Alloyed steel	0,000 45	0,000 13	0,000 18	0,000 42
Alloyed steel	0,004 32	0,000 27	0,000 42	0,000 48

Figure A1 shows the relationship between boron content (w_B), expressed as a percentage by mass, and repeatability (r), within-laboratory reproducibility (R_w) and reproducibility (R), plotted on a log-log scale.

Logarithmic regression formulae:	Correlation coefficient:	
Log r = 0,376 log w_B – 2,637	0,978	(A.1)
Log R_w = 0,330 log w_B – 2,603	0,867	(A.2)
Log R = 0,384 log w_B – 2,313	0,789	(A.3)



Key

- **a** boron content % (m/m)
- **b** precision (%)

Figure A.1 — Logarithmic relationships between boron content, w_B, repeatability (r) and reproducibility (R_w and R)

Predicted values for r, R_w and R derived from Formulae (A.1) to (A.3) are shown in Table A 2.

Table A.2 — Predicted values for r, R_w and R

Boron content			
w_B %	r %	R_w %	R %
0,000 2	0,000 09	0,000 15	0,000 18
0,000 5	0,000 13	0,000 20	0,000 26
0,001 0	0,000 17	0,000 25	0,000 34
0,002 0	0,000 22	0,000 32	0,000 45
0,005 0	0,000 31	0,000 43	0,000 63
0,010 0	0,000 41	0,000 54	0,000 83

Bibliography

[1] EN ISO 648, *Laboratory glassware —Single-volume pipettes (ISO 648)*

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

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