BS EN 10211:2013

BSI Standards Publication

Chemical analysis of ferrous materials — Determination of titanium in steels and cast irons — Flame atomic absorption spectrometric method

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National foreword

This British Standard is the UK implementation of EN 10211:2013. It supersedes BS EN 10211:1996 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee ISE/102, Methods of Chemical Analysis for Iron and Steel.

A list of organizations represented on this committee can be obtained on request to its secretary.

ISBN 978 0 580 81798 4

ICS 77.040.30; 77.080.01

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 November 2013.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 10211

November 2013

ICS 77.040.30

Supersedes EN 10211:1995

English Version

Chemical analysis of ferrous materials - Determination of titanium in steels and cast irons - Flame atomic absorption spectrometric method

Analyse chimique des produits ferreux - Détermination du titane dans les aciers et les fontes - Méthode par spectrométrie d'absorption atomique dans la flamme

Chemische Analyse von Eisenwerkstoffen - Bestimmung des Titananteils in Stahl und Eisen - Flammenatomabsorptionsspektrometrisches Verfahren

This European Standard was approved by CEN on 29 September 2013.

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Foreword

This document (EN 10211:2013) 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of an identical text or by endorsement, at the latest by May 2014, and conflicting national standards shall be withdrawn at the latest by May 2014.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 10211:1995.

In comparison with the previous edition of EN 10211, the following technical changes were made:

- Clause 1, “steel and iron” replaced by “non-alloyed and alloyed steels and cast irons”;
- Clause 3, clarification regarding the use of aluminium chloride within both dissolutions described;
- Addition of 5.2.3 (information on the linearity criteria);
- Table 1, addition of terms corresponding to 0,025 % and 0,075 % titanium;
- Subclause 7.6 was merged in Subclause 7.5;
- Clause 8, formula: notation changed;
- Annex A, the notes were included in the text and the correlation coefficients corrected;
- Annex B: added.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies a flame atomic absorption spectrometric method for the determination of titanium in steels and cast irons. The method is applicable to non-alloyed and alloyed steels and cast irons with titanium contents of 0,01 % to 1,0 % (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 648, *Laboratory glassware - Single-volume pipettes (ISO 648)*

EN ISO 1042, *Laboratory glassware - One-mark volumetric flasks (ISO 1042)*

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

3 Principle

Two dissolution procedures are possible and described:

a) The first one is specific to cast irons and is based on dissolution of the test portion with nitric and perchloric acids, followed by evaporation with perchloric acid to dryness. The further steps being a separation of the insolubilised silica by filtration and collection of the filtrate.

b) The second one, which can be used for steels as well as for cast irons is based on dissolution of the test portion with hydrochloric and nitric acid. This dissolution is followed by:

   1) filtration and ignition of the acid insoluble residue and removal of silica with hydrofluoric acid;

   2) fusion of the residue with a mixture of boric acid and sodium carbonate, dissolution of the melt with acid and addition of this solution to the reserved filtrate.

Addition of aluminium chloride as interaction buffer, in both cases.

Nebulisation of the test solution into a slightly fuel rich nitrous oxide/acetylene flame, of an atomic absorption spectrometer.

Spectrometric measurement of the atomic absorption of the 365,3 nm (or 364,3 nm) spectral line emitted by a titanium hollow-cathode lamp.

4 Reagents

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

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

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

4.3 Perchloric acid, $HClO_4$ (ρ_{20} = 1,67 g/ml).

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

4.5 Hydrofluoric acid, HF (ρ_{20} = 1,15 g/ml).

4.6 Nitric acid solution, 1 + 1.

Add 100 ml of nitric acid (4.1) to 100 ml water

4.7 Hydrochloric acid solution, 1 + 1.

Add 100 ml of hydrochloric acid (4.2) to 100 ml water

4.8 Aluminium chloride solution, equivalent to 10 g/l Al.

Dissolve 90 g of hydrated aluminium chloride ($ALCl_3 . 6H_2O$) in a 600 ml beaker with water and transfer the solution into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

4.9 Fusion mixture.

Mix one part by mass of boric acid, H_3BO_3 and one part of sodium carbonate anhydrous, Na_2CO_3.

Store in a stoppered polyethylene container.

4.10 Iron-perchloric matrix solution, 20 g/l Fe.

Weigh, to the nearest 0,01 g, 10,00 g of pure iron free of titanium or of known low titanium content. Transfer into a 600 ml beaker and cover with a watch glass. Add in small portions, 150 ml of nitric acid (4.6). When effervescence ceases, add 200 ml of perchloric acid (4.3). Heat gently, until the iron is completely dissolved.

Continue heating at a temperature at which a steady reflux of white perchloric acid fumes is maintained on the walls of the beaker. Continue heating until there are no perchloric acid fumes visible inside the beaker and the iron perchlorate crystallises.

Allow to cool, add 150 ml of water, swirl and boil gently to dissolve the salts.

Transfer quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

4.11 Iron–chloro nitric matrix solution, 20 g/l Fe.

Weigh, to the nearest 0,01 g, 20,00 g of pure iron free of titanium or of known low titanium content. Transfer into a 600 ml beaker, add 200 ml of water and then 220 ml of hydrochloric acid (4.2), in small portions. Cover with a watch glass and heat gently until effervescence ceases. Add gradually 60 ml of nitric acid (4.1). Heat for about 10 min at about 80 °C, to expel nitrous fumes.

Allow to cool and transfer quantitatively into a 1 000 ml one-mark volumetric flask. Add water until about 600 ml and add 20 g of fusion mixture (4.9). Dissolve, dilute to the mark with water and mix.

4.12 Titanium, 1 g/l standard solution.

Weigh (1 ± 0,001) g of titanium (99,99 % purity), transfer into a 400 ml beaker and cover with a watch glass. Dissolve it in 200 ml of hydrochloric acid solution (4.7) and add two drops of hydrofluoric acid (4.5).

Heat gently until the metal is dissolved. After cooling, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of titanium.

4.13 Titanium, 0,5 g/l standard solution [freshly prepared].

Transfer 50,0 ml of titanium standard solution (4.12) into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this standard solution contains 0,5 mg of titanium.

4.14 Titanium, 0,05 g/l standard solution [freshly prepared].

Transfer 10,0 ml of titanium standard solution (4.12) into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this standard solution contains 0,05 mg of titanium.

5 Apparatus

All volumetric glassware shall be Class A and calibrated, in accordance with EN ISO 648 or EN ISO 1042 as appropriate.

5.1 30 ml platinum crucibles.

5.2 Atomic absorption spectrometer.

This shall be equipped with a titanium hollow-cathode lamp and supplied with nitrous oxide and acetylene sufficiently pure to give a a clear, steady slightly fuel-rich flame, free from water and oil, and free from titanium.

The atomic absorption spectrometer used will be satisfactory if, after optimisation according to 7.5, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the precision criteria given in 5.2.1 to 5.2.3.

It is also recommended that the instrument should conform to the additional performance requirements given in 5.2.4.

5.2.1 Minimum precision.

Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. The standard deviation shall not exceed 1,5 % of the mean absorbance of this solution.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). The standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

5.2.2 Limit of detection.

The limit of detection is a number, expressed in units of concentration (or amount) that describes the lowest concentration level (or amount) of an element that can be determined to be statistically different from an analytical blank.

The limit of detection of titanium in a matrix similar to that of the final test portion solution shall be better than 0,2 µg/ml for the 365,3 nm line and better than 0,1 µg/ml for the 364,3 nm line.

5.2.3 Linearity of calibration.

The value of the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range (expressed as a change in absorbance) determined in the same way.

For instruments with automatic calibration using two or more standard solutions, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

5.2.4 Characteristic concentration.

The characteristic concentration for titanium in a matrix similar to the final test portion solution shall be better than 1,9 µg/ml for the 365,3 nm line and better than 1,4 µg/ml for the 364,3 nm line.

5.3 Ancillary equipment.

A system for acquisition of the measured values, data processing and evaluation is necessary. Usually data processing and evaluation is performed with the appropriate software of the computer, connected to the atomic absorption spectrometer.

Scale expansion can be used until the noise observed is greater than the read-out error and is preferred for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring the absorbances of a suitable solution with and without scale expansion and using the ratio of the signals obtained.

6 Sampling

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

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,001 g, 1 g of the test sample.

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 reagents as used for the determination in accordance with the chosen dissolution method, 7.3.1 or 7.3.2, including iron (solution 4.10 or 4.11 depending on the chosen dissolution).

7.3 Preparation of the test solution

7.3.1 Nitric perchloric dissolution

Transfer the test portion (7.1) into a 250 ml beaker. Cover the beaker with a watch glass and add 15 ml of nitric acid (4.6). When effervescence ceases, add 20 ml of perchloric acid (4.3). Heat gently until the reaction dissolution is achieved.

Continue heating at a temperature at which a steady reflux of white perchloric acid fumes is maintained on the walls of the beaker. Continue heating until there are no perchloric acid fumes visible inside the beaker and the iron perchlorate crystallises.

Allow to cool, add 25 to 30 ml of water, swirl and boil gently for a few minutes. Filter the silica through a medium-texture filter paper and collect the filtrate in a 100 ml volumetric flask. Wash the filter with hot water several times and collect the washings in the same 100 ml volumetric flask.

Allow to cool and add 5 ml of aluminium chloride solution (4.8). Dilute to the mark with water and mix.

7.3.2 Chloro-nitric dissolution with treatment of the residue

Transfer the test portion (7.1) into a 250 ml beaker. Add 20 ml of hydrochloric acid (4.7), cover the beaker with a watch glass and heat gently until effervescence ceases. Add gradually 3 ml of nitric acid (4.1). Heat for about 10 min, at about 80 °C to expel nitrous fumes. Allow to cool.

Filter through a dry filter and collect the filtrate in a 100 ml volumetric flask. Wash the residue on the filter with boiling water (about 40 ml).

Transfer the filter into a platinum crucible (5.1) and cover with a suitable platinum cover.

Place the covered crucible progressively into a muffle furnace set at 900 °C in order to ash the filter and the residue. Allow to stand at 900 °C for about 15 minutes, then remove and allow to cool. Add into the crucible 2 drops of sulphuric acid (4.4) and 2 ml of hydrofluoric acid (4.5). Evaporate to dryness on a hotplate and cool.

Add 1,0 g of the fusion mixture (4.9). Fuse the content of the crucible in a muffle furnace at 1 000 °C for 15 min to 20 min. Allow the crucible to cool and add about 10 ml of water and 1 ml of hydrochloric acid (4.2) to the solidified melt. Heat gently, in order to dissolve the fusion products. Allow the crucible to cool and add this solution quantitatively to the filtrate in the 100 ml volumetric flask. Dilute to the mark with water and mix.

7.4 Preparation of the calibration solutions

Transfer 50 ml of iron solution (4.10) or (4.11) according to the chosen method of dissolution (7.3.1 or 7.3.2) into each of a series of 100 ml volumetric flasks and add 5 ml of aluminium chloride solution (4.8). Using a burette or a pipette, add the volumes of titanium standard solutions (4.13 or 4.14) shown in Table 1. Dilute to the mark with water and mix.

The proposed calibration is given as a guide. It should be adapted in accordance with the sensitivity of the instrument used.

Table 1 — Calibration solutions

Titanium standard solution volume ml	Corresponding titanium mass mg	Iron mass mg	Corresponding content of titanium in the test sample % (*m*/*m*)
0 [a]	0	1 000	0
2,0 (4.14)	0,10	1 000	0,010
5,0 (4.14)	0,25	1 000	0,025
10,0 (4.14)	0,50	1 000	0,050
15,0 (4.14)	0,75	1 000	0,075
20,0 (4.14)	1,00	1 000	0,100
40,0 (4.14)	2,00	1 000	0,200
6,0 (4.13)	3,00	1 000	0,300
10,0 (4.13)	5,00	1 000	0,500
14,0 (4.13)	7,00	1 000	0,700
20,0 (4.13)	10,00	1 000	1,000

[a] Zero member

7.5 Adjustment of atomic absorption spectrometer

Fit the titanium hollow-cathode lamp into the atomic absorption spectrometer (5.2), switch on the current and allow it to stabilise. Adjust the wavelength in the region of 365,3 nm or 364,3 nm to minimum absorbance. Following the manufacturer's instructions, fit the correct burner, light the flame and allow the burner temperature to stabilise.

Adjust the flame to be slightly fuel-rich and the burner height to about 1 cm below the light path.

Aspirate the calibration solution containing the highest content of the analyte and adjust the burner configuration and gas flows to obtain the maximum absorption. It is important to ensure that the flow rate of the acetylene is greater than the minimum flow rate advised by the instrument manufacturer.

Evaluate the criteria of 5.2.1 to 5.2.4 to ensure that the instrument and the chosen wavelength are suitable for the determination by measuring the absorbance of the different solutions required by reference to water.

WARNING —The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points, in particular for solutions containing perchloric acid:

a) Aspirate all solutions for the shortest practical period;

b) Always aspirate distilled water between each solution. Minimise the aspiration of air;

c) Clean the burner frequently. Never allow the burner to clog and wash it thoroughly both inside and out;

d) Ensure that all safety covers are in position and wear approved ear protectors and safety glasses.

7.6 Spectrometric measurements of the calibration solutions

Aspirate the series of calibration solutions (7.4) in succession, into the flame and measure the absorbance for each. Take care to keep the aspiration rate constant throughout the preparation of the calibration curve. Spray water through the burner after each measurement Obtain the net mean absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution.

7.7 Calibration curve

Establish the calibration curve using measured absorbances and corresponding analyte amounts, expressed as µg of titanium per ml. Use appropriate spectrometer software or an off-line computer for regression calculations or prepare a graphical representation.

7.8 Determination

7.8.1 Preliminary spectrometric measurement

Carry out an approximate measurement on the test solution (7.3) following the procedure specified in 7.5 at the same time as the spectrometric measurements are carried out on the calibration solutions (7.6). Estimate the approximate analyte amount by using the calibration curve (7.7).

7.8.2 Spectrometric measurements

Repeat the measurements and obtain the mean absorbance of each test solution and the mean absorbance of the blank solution.

Convert the mean absorbances of the test solution and of the blank solution to µg/ml of titanium by means of the calibration curve.

If pure metals and reagents have been used, the blank test and zero calibration member should give equal and negligibly small absorbances.

8 Expression of results

Calculate the titanium mass fraction, in percent (%), as follows:

$$W_{\mathrm{Ti}} = \frac{(C_1 - C_0) \times V \times 100}{m \times 10^6} = \frac{(C_1 - C_0) \times V}{m \times 10^4} \quad (1)$$

where:

W_{Ti} is the titanium mass fraction in per cent (%);

C_1 is the titanium concentration in the test solution, in micrograms per millilitre (µg/ml);

C_0 is the titanium concentration in the blank test solution, in micrograms per millilitre (µg/ml);

V is the volume of the test solution (7.3). V is equal to 100 ml;

m is the mass of the test portion, in grams (g).

9 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) reference to this European Standard (EN 10211);

c) method used;

d) results;

e) any unusual characteristics noted during the determination;

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

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

h) signature of the responsible person.

Annex A
(informative)

Precision data

A.1 General

Sixteen laboratories in six European countries participated in planned trials of this method. Each laboratory carried out three determinations on each of 12 samples: four cast irons and eight steels.

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

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.

The statistical data obtained are shown in:

— Table A.1 which gives the results obtained on the eight steel samples;

— Tables A.2 and A.3 which give the results obtained on the four cast iron samples.

Table A.1 — Results of precision tests — Dissolution 7.3.2 tested on eight steel samples

Sample label	Certified titanium value	Titanium content found (W_{Ti})	Repeatability	Reproducibility	
	m/m %	m/m %	r %	R_w %	R %
BCS 320	0,021	0,019 2	0,006 1	0,003 9	0,006 7
BCS 452/1	0,031	0,029 0	0,005 2	0,004 1	0,011 1
BCS 453/1	0,073	0,073 2	0,006 3	0,006 0	0,008 6
BCS 451/1	0,105	0,105 6	0,005 9	0,009 3	0,011 8
ECRM 281–1	0,216	0,206 8	0,009 9	0,020 7	0,049 9
IRSID 202–1	0,539	0,531 4	0,015 2	0,022 2	0,059 1
ECRM 128–1	0,890	0,893 8	0,021 4	0,043 3	0,066 7
5RA9OBrK1	1,05	0,994 0	0,015 4	0,093 0	0,186 0

Table A.2 — Results of precision tests — Dissolution 7.3.1 tested on four cast iron samples

Sample label	Certified titanium value	Titanium content found (W_{Ti})	Repeatability	Reproducibility	
	m/m %	m/m %	r %	R_w %	R %
C83C	0,017	0,016 8	0,003 2	0,003 3	0,006 9
A84C (F 06–3)	0,041	0,039 9	0,002 2	0,003 8	0,003 6
A83C	0,060	0,058 4	0,003 5	0,004 5	0,004 4
C82C	0,085	0,084 4	0,001 2	0,003 7	0,006 1

NOTE 1 There were not enough results to allow the calculation of a logarithmic regression. However, an evaluation on the 0,017 % to 0,085 % content range gave mean values of 0,003 for r, 0,004 for R_w and 0,005 for R.

Table A.3 — Results of precision tests — Dissolution 7.3.2 tested on four cast iron samples

Sample label	Certified titanium value	Titanium content found (W_{Ti})	Repeatability	Reproducibility	
	m/m %	m/m %	r %	R_w %	R %
C83C	0,017	0,017 3	0,001 5	0,003 3	0,002 6
A84C (F 06–3)	0,041	0,040 5	0,001 8	0,003 3	0,005 4
A83C	0,060	0,059 4	0,002 3	0,005 2	0,004 6
C82C	0,085	0,086 2	0,002 3	0,003 3	0,005 5

NOTE 2 The results shown in Table A.3 are slightly different from those obtained in accordance with dissolution 7.3.1 (see Table A.2): for the 0,017 to 0,085 % content range, the mean values for r, R_w and R are 0,002, 0,004 and 0,005 respectively.

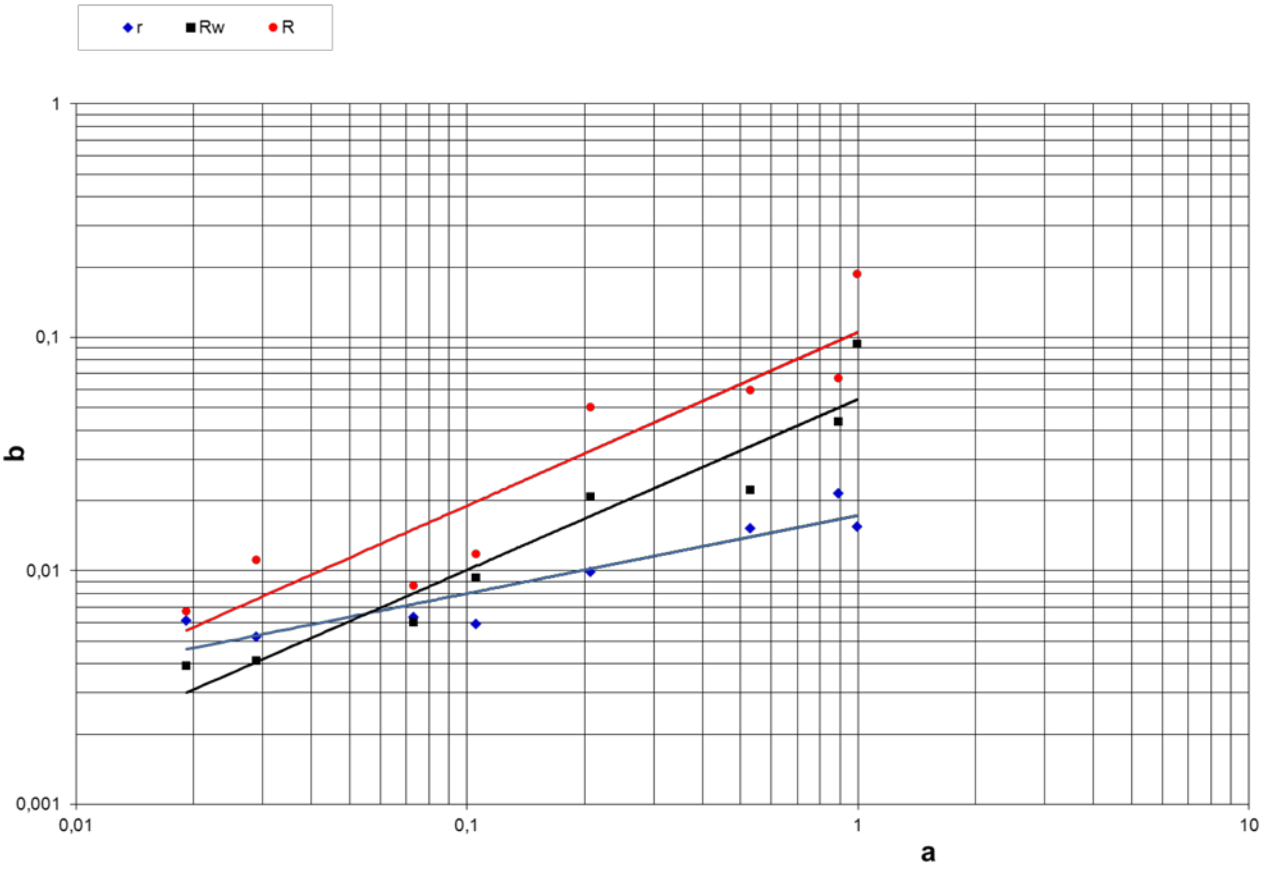
Figure A.1 indicates the logarithmic relationships between the titanium content (W_{Ti}) and the repeatability (r) and reproducibility parameters (R_w and R) for the steel samples, plotted on a log-log scale.

The corresponding logarithmic regression formulae are:

$$\text{Log } r = 0{,}333\,9 \log W_{Ti} - 1{,}763\,0 \qquad \text{Correlation coefficient: 0,862]} \qquad \text{(A.1)}$$

$$\text{Log } R_w = 0{,}731\,0 \log W_{Ti} - 1{,}265\,1 \qquad \text{[Correlation coefficient: 0,924]} \qquad \text{(A.2)}$$

$$\text{Log } R = 0{,}743\,2 \log W_{Ti} - 0{,}977\,5 \qquad \text{[Correlation coefficient: 0,861]} \qquad \text{(A.3)}$$



Key

r	repeatability
R_w	intra laboratory reproducibility
R	reproducibility
a	titanium content % (m/m)
b	precision (%)

Figure A.1 — Logarithmic relationships between titanium content, W_{Ti}, and repeatability (*r*) and reproducibility (R_w and *R*)

The predicted values for *r*, R_w and *R* derived from Formulae (A.1) to (A.3) are shown in Table A.4.

Table A.4 — Predicted values for *r*, R_w and *R*

Titanium content ***(W_{Ti})*** %	**Repeatability** *r* %	**Within-laboratory reproducibility** R_w %	**Reproducibility** *R* %
0,01	0,003 7	0,001 9	0,003 4
0,02	0,004 7	0,003 1	0,005 8
0,05	0,006 3	0,006 1	0,011 4
0,10	0,008 0	0,010 1	0,019 0
0,20	0,010 1	0,016 7	0,031 8
0,50	0,013 7	0,032 7	0,062 9
1,00	0,017 3	0,054 3	0,105 3

A.2 Information on repeatability and reproducibilities

A.2.1 Repeatability, *r*

The difference between two single results found on identical material by one analyst using the same apparatus within a short time interval will exceed the repeatability, *r*, not more than once in 20 cases in the normal and correct operation of the method.

A.2.2 Within-laboratory reproducibility, R_w

The difference between two single and independent results found by the same analyst working in the same laboratory on identical material on different occasions will exceed the within-laboratory reproducibility, R_w, not more than once in 20 cases in the normal and correct operation of the method.

A.2.3 Reproducibility, *R*

The difference between two single and independent results found by two operators working in different laboratories on identical material will exceed the reproducibility, *R*, not more than once in 20 cases in the normal and correct operation of the method.

Annex B
(normative)

Procedures for the determination of instrumental criteria

B.1 Determination of minimum precision

Spray the most concentrated calibration solution 10 times to obtain 10 individual absorbance readings $A_{Ti,max,i}$ and calculate the corresponding mean value $A_{Ti,max}$ and standard deviation $s_{Ti,max}$.

Spray the least concentrated calibration solution (excluding the zero member) 10 times to obtain 10 individual absorbance readings $A_{Ti,min,i}$ and calculate the corresponding mean value $A_{Ti,min}$ and standard deviation $s_{Ti,min}$.

The minimum precisions of the most and least concentrated calibration solutions are obtained from $s_{Ti,max}$ x 100/ $A_{Ti,max}$ and $s_{Ti,min}$ x 100/ $A_{Ti,min}$, respectively.

B.2 Determination of limit of detection

Prepare two solutions each containing the same matrix concentration as the test solution, but with the element of interest at the following known concentrations:

- $C_{Ti,A0,01}$ (µg/ml) to give an absorbance $A_{Ti,A0,01}$ of approximately 0,01;
- the “zero member”, giving an absorbance $A_{Ti,0}$

Alternatively, spray the “zero member” solution and the $C_{Ti,A0,01}$ solution 10 times, recording each reading for 10 s, and using sufficient scale expansion to make the fluctuations in signal clearly visible.

Calculate:

- the mean absorbance ($A_{Ti,0}$) and standard deviation ($s_{Ti,0}$) corresponding to the “zero member” solution readings;
- the mean absorbance ($A_{Ti,A0,01}$) corresponding to the $C_{Ti,A0,01}$ solution readings;
- taking into account the statistical risks α and β each of them at the 95 % level (4,65), calculate the limit of detection (C_{lim}) according to the formula:

$$C_{lim} = \frac{4{,}65 \ x \ s_{Ti,0} \ x \ C_{Ti,A0,01}}{A_{Ti,A0,01} - A_{Ti,0}} \qquad (B.1)$$

B.3 Linearity of calibration

Having established the calibration graph, before the application of any curve straightening device, obtain the net absorbance value A_A corresponding to the top 20 % of the concentration range and the net absorbance A_B corresponding to the bottom 20 % of the concentration range. Calculate A_A/A_B. This shall not be less than 0,7.

B.4 Determination of characteristic concentration, $c_{\mathrm{Ti,cc}}$

Prepare a solution containing the same matrix concentration as the test solution, but with the element of interest at a known concentration $C_{\mathrm{Ti,A0,1}}$ (µg/ml) to give an absorbance $A_{\mathrm{Ti,A0,1}}$ of approximately 0,1.

Spray the $C_{\mathrm{Ti,A0,1}}$ and the “zero member” solutions without scale expansion and measure the absorbances $A_{\mathrm{Ti,A0,1}}$ and $A_{\mathrm{Ti,0}}$.

The characteristic concentration $c_{\mathrm{Ti,cc}}$ is given by the formula:

$$\mathrm{C}_{\mathrm{Ti,cc}} = \frac{\mathrm{C}_{\mathrm{Ti,A0,1}} \times 0{,}0044}{\mathrm{A}_{\mathrm{Ti,A0,1}} \times \mathrm{A}_{\mathrm{Ti,0}}} \qquad \text{(B.2)}$$

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