BS EN 10178:2024

BSI Standards Publication

Steels — Determination of niobium — Spectrophotometric method

bsi.

National foreword

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The UK participation in its preparation was entrusted to Technical Committee ISE/1, Iron and steel standards co-ordinating committee.

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Published by BSI Standards Limited 2024

ISBN 978 0 539 26725 9

ICS 77.040.30; 77.080.20

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 June 2024.

Amendments/corrigenda issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 10178

June 2024

ICS 77.040.30

Supersedes EN 10178:1989

English Version

Steels - Determination of niobium - Spectrophotometric method

Aciers - Détermination du niobium - Méthode spectrophotométrique

Stähle - Bestimmung von Niob - Photometrisches Verfahren

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Ref. No. EN 10178:2024 E

Contents

European foreword

This document (EN 10178:2024) has been prepared by Technical Committee CEN/TC 459/SC 2 “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of an identical text or by endorsement, at the latest by December 2024, and conflicting national standards shall be withdrawn at the latest by December 2024.

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

This document supersedes EN 10178:1999.

In comparison with the previous edition, the following technical modifications have been made:

— normative references: updated;

— Clause 3 Terms and definitions: added;

— reference 5.13: added;

— reference 5.18: title simplified;

— Clause 6: developed and subclauses 6.1 and 6.2, added;

— Clause 7: updated;

— former subclause 7.3.3: included in 8.3.2;

— Clause 10: updated;

— Bibliography: added.

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1 Scope

This document specifies a spectrophotometric method for the determination of niobium in steels.

The method is applicable to all grades of steels with niobium contents up to 1,3 % (by mass), with a lower limit of detection of 0,002 % (by mass).

The precision data of the present method are given in Annex A.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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)*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Dissolution of a test portion with hydrochloric acid followed by oxidation with hydrogen peroxide. Precipitation of niobium and tantalum with phenylarsonic acid using zirconium as a carrier.

Formation of a complex of niobium with 4-(2-pyridylazo)-resorcinol (PAR) in a buffered sodium tartrate medium.

Spectrophotometric measurement of the coloured compound at a wavelength of 550 nm.

5 Reagents

5.1 General

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

5.2 Iron, of high purity, free from niobium

5.3 Potassium hydrogen sulphate ($KHSO_4$)

5.4 Hydrochloric acid, ρ_{20} 1,19 g/ml approximately

5.5 Hydrochloric acid, solution 1 + 4

Carefully add 40 ml of hydrochloric acid (5.4) to 160 ml of water and mix.

5.6 Hydrochloric acid, solution 1 + 9

Carefully add 20 ml of hydrochloric acid (5.4) to 180 ml of water and mix.

5.7 Sulphuric acid, solution 1 + 1

Carefully add 100 ml of sulphuric acid (ρ_{20} 1,84 g/ml approximately) to 100 ml of water.

Allow to cool and mix.

5.8 Sulphuric acid, solution 1 + 4

Carefully add 20 ml of sulphuric acid (ρ_{20} 1,84 g/ml approximately) to 80 ml of water.

Allow to cool and mix.

5.9 Ethylenediaminetetraacetic acid di-sodium salt, (EDTA Na_2), 15 g/l

Store in polyethylene bottle.

5.10 Hydrogen peroxide, 30 % w/v (100 vol.)

5.11 Phenylarsonic acid, 40 g/l

5.12 Phenylarsonic acid, 0,5 g/l

5.13 4-(2-pyridylazo)-resorcinol mono-sodium salt, (PAR), 0,6 g/l

The di-sodium salt can also be used but the identical salt shall be used for both calibration and tests.

5.14 Glacial acetic acid, ρ_{20} 1,05 g/ml, approximately

5.15 Sodium acetate buffer, 350 g/l

Dissolve 350 g of sodium acetate trihydrate in 700 ml of water, add 5,5 ml of glacial acetic acid (5.14), dilute to 1 000 ml with water and mix.

Adjust the pH value to 6,3 with small additions of acetic acid (5.14) or sodium hydroxide (5.16) using a pH meter (6.2) for the measurement.

5.16 Sodium hydroxide, 120 g/l

Store in a polyethylene bottle.

5.17 Tartaric acid, 100 g/l

5.18 Zirconium nitrate, 3 g/l solution in hydrochloric acid medium

Dissolve 0,3 g of zirconium nitrate in 50 ml of hydrochloric acid solution (5.5). Filter through a fine texture filter paper, dilute to 100 ml with water and mix.

5.19 Niobium standard solution, 0,2 g/l

Weigh 0,143 1 g of niobium pentoxide and transfer into a platinum dish. Fuse with 3,5 g of potassium hydrogen sulphate (5.3). Cool and dissolve in 40 ml of tartaric acid (5.17). Add 160 ml of tartaric acid (5.17).

Transfer quantitatively into a 500 ml volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,2 mg of niobium.

6 Apparatus

6.1 Ordinary laboratory equipment

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

6.2 pH meter

6.3 Spectrophotometer, equipped to measure absorbance at a wavelength of 550 nm, with cells of 4 cm or 1 cm optical path length.

7 Sampling

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

8 Procedure

8.1 Test portion

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

8.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test on a 1 g test portion of pure iron (5.2), using the same quantities of all reagents as used for the determination.

8.3 Determination

8.3.1 Preparation of the test solution

Transfer the test portion (8.1) into a 400 ml squat beaker, add 40 ml of hydrochloric acid solution (5.4), cover with a watch glass and heat until the acid action ceases. Cool slightly and carefully add 5 ml of hydrogen peroxide (5.10). Boil the solution for 1 min, dilute to approximately 200 ml with hot water and add 5 ml of zirconium nitrate (5.18).

8.3.2 Separation of the niobium

Heat the solution to boiling and add 25 ml of a boiling solution of phenylarsonic acid (5.11). Boil for 5 min, add a small amount of filter paper pulp, mix well and allow to stand for 10 min.

Filter through a pulp pad prepared from macerated filter paper and remove the adhering particles from the beaker with a rubber-tipped glass rod. Wash the filter alternately with hot hydrochloric acid solution (5.6) and cold phenylarsonic acid solution (5.12) until freed from iron salts. Finally wash several times with cold phenylarsonic acid solution (5.12). Transfer the filter and its content into a silica crucible. Dry, ignite at a temperature as low as possible until all carbonaceous matter is removed, and finally at

800 °C for at least 15 min. Allow to cool in a desiccator, add a few drops of sulphuric acid solution (5.7) and evaporate to dryness very carefully, in order to remove sulphur trioxide.

Add 2 g of potassium hydrogen sulphate (5.3) and fuse carefully until a clear melt is obtained. Allow to cool, dissolve the fusion products with 50 ml of hot tartaric acid (5.17) and transfer the solution into a 400 ml beaker. Add 50 ml of water and mix.

Add 25 ml of sodium hydroxide solution (5.16) and allow to cool. Using a pH meter (6.2) adjust the pH of the solution to approximately 6,0 with either sulphuric acid solution (5.8) or sodium hydroxide (5.16) as required. Allow to cool to room temperature, transfer into a 250 ml volumetric flask, dilute to the mark with water and mix.

8.3.3 Development of the colour

Take an aliquot volume of the solution obtained in 8.3.2, according to the instructions given in Table 1.

Table 1 — Volume of the aliquot

Niobium % (by mass)	**Volume of the aliquot** (ml)
< 0,26	25,0
0,26 to 0,65	10,0
0,65 to 1,30	5,0

Transfer the aliquot into a 100 ml volumetric flask. By means of a pipette add 10 ml of EDTA Na_2 (5.9), 10 ml of PAR (5.13) and 10 ml of buffer solution (5.15), mixing well after each addition. Allow to stand for 15 min at approximately 20 °C, then dilute to the mark with water and mix. Allow to stand for 30 min.

8.3.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement at a wavelength of 550 nm after having set the spectrophotometer to zero absorbance with water. Use 4 cm path length cells for niobium contents up to 0,06 % and 1 cm path length cells for contents greater than 0,06 %.

Convert the readings corresponding to the test solution and to the blank test solution to milligrams of niobium by reference to the calibration curve (8.4).

8.4 Establishment of the calibration curve

8.4.1 Preparation of the calibration solutions

Weigh 1,0 g portions of pure iron (5.2) into a series of 400 ml beakers. Add the volumes of the niobium standard solution (5.19) given in Table 2.

Table 2 — Calibration solutions

Niobium standard solution (5.18) ml	Corresponding niobium mass mg	Cell path length cm
0 [a]	0	1 and 4
1,0	0,2	4
2,0	0,4	4
3,0	0,6	1 and 4
5,0	1,0	1
7,0	1,4	1
9,0	1,8	1
11,0	2,2	1
13,0	2,6	1
[a] Zero member		

Continue as described in 8.3.1 to 8.3.3 but in all cases by taking a 25 ml aliquot in 8.3.3.

8.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurements according to the first paragraph of 8.3.4, after having adjusted the spectrophotometer to zero absorbance with water.

8.4.3 Plotting the calibration curve

From each of the absorbance readings, subtract the reading corresponding to the zero member.

Prepare the calibration curve by plotting the net absorbance readings against the mass of niobium, expressed in milligrams.

For samples containing more than 0,26 % (by mass) of niobium and for which 10 ml or 5 ml aliquots are used the relationships with the calibration curve based on 25 ml aliquots is given in Table 3.

Table 3 — Relationships with the calibration curve for 10 ml and 5 ml aliquots

Niobium content % (by mass) in 1 g test portion			Cell path length
25 ml aliquot	**10 ml aliquot**	**5 ml aliquot**	cm
0	0	0	1 and 4
0,02	-	-	4
0,04	-	-	4
0,06	-	-	1 and 4
0,10	0,25	-	1
0,14	0,35	0,70	1
0,18	0,45	0,90	1
0,22	0,55	1,10	1
0,26	0,65	1,30	1

9 Expression of results

The niobium content, W_{Nb}, expressed as a percentage (%) by mass, is given by Formulae (1) and (2):

$$W_{\mathrm{Nb}} = \frac{m_1 - m_0}{m \times 1\,000} \times \frac{250}{V} \times 100 \quad (1)$$

$$W_{\mathrm{Nb}} = \frac{m_1 - m_2}{m} \times \frac{25}{V} \quad (2)$$

where

m is the mass of the test portion, expressed in grams;

m_1 is the mass of niobium in the aliquot of the test solution, expressed in milligrams;

m_0 is the mass of niobium in the blank test solution, expressed in milligrams;

V is the volume of the aliquot (8.3.3), expressed in ml.

10 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) test method used by reference to the present document;

c) results as well as the unit in which they are expressed;

d) any unusual characteristics noted during the determination;

e) any operation not included in this document 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

Planned trials of this method were carried out by 10 analysts from different laboratories.

Five determinations were carried out by each analyst on 4 different samples.

Five determinations were also carried out by 7 of the analysts on a fifth sample, marked by a (*) in Table A.1.

From the results obtained the 95 % confidence limits have been calculated in accordance with ISO 5725:1986 and are summarized in Table A.1.

Table A.1 — Statistical information

Alloy type	Niobium % (by mass)	Repeatability r	Reproducibility R
Non-alloy steel	0,029	0,002 0	0,002 4
Non-alloy steel	0,099	0,005 1	0,007 6
Magnet alloy, 13 % Ni, 8 % Al, 3 % Cu, 25 % Co	0,589	0,012 7	0,021 2
Niobium stabilized steel 18 % Cr, 9,5 % Ni	1,035	0,022 9	0,040 8
Niobium stabilized steel 17,5 % Cr, 13 % Ni (*)	0,906	0,017 5	0,041 6

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.

Reproducibility, R

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

Bibliography

[1] ISO 5725:1986[1], *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*

[1] Withdrawn. (Replaced by the ISO 5725 series.)

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