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МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Steel — Determination of niobium content — PAR spectrophotometric method

Aciers — Dosage du niobium — Méthode spectrophotométrique au PAR

Reference number
ISO 9441 : 1988 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9441 was prepared by Technical Committee ISO/TC 17, *Steel*.

Annexes A and B of this International Standard are for information only.

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Steel — Determination of niobium content — PAR spectrophotometric method

1 Scope

This International Standard specifies a PAR spectrophotometric method for the determination of niobium in steel.

The method is applicable to all types of steel with niobium contents between 0,005 % (*m/m*) and 1,3 % (*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 listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377 : 1985, *Wrought steel — Selection and preparation of samples and test pieces.*

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 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 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 sodium tartrate medium buffered by sodium acetate solution adjusted to pH 6,3.

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

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Iron, of high purity, free from niobium.

4.2 Potassium hydrogen sulfate ($KHSO_4$).

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

4.4 Hydrochloric acid, ϱ approximately 1,19 g/ml, diluted 1 + 9.

4.5 Sulfuric acid, ϱ approximately 1,84 g/ml, diluted 1 + 1.

4.6 Sulfuric acid, ϱ approximately 1,84 g/ml, diluted 1 + 4.

4.7 Hydrogen peroxide, 300 g/l.

4.8 Sodium hydroxide, 120 g/l solution.

Store in a polyethylene bottle.

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

Dissolve 0,3 g of zirconium nitrate in 50 ml of hydrochloric acid, ϱ approximately 1,19 g/ml, diluted 1 + 4. Filter through a fine filter paper, dilute to 100 ml with water and mix.

4.10 Sodium acetate buffer, pH-value 6,3.

Dissolve 350 g of sodium acetate trihydrate in 700 ml of water, add 5,5 ml of glacial acetic acid, ϱ approximately 1,05 g/ml, dilute to 1 000 ml and mix. Adjust the pH-value to 6,3 with small additions of acetic acid or sodium hydroxide solution (4.8), using a pH-meter for measurement.

4.11 Tartaric acid, 100 g/l solution.

4.12 Phenylarsonic acid [$C_6H_5AsO(OH)_2$], 40 g/l solution.

4.13 Phenylarsonic acid [$C_6H_5AsO(OH)_2$], 0,5 g/l solution.

4.14 Disodium dihydrogen(ethylenedinitrilo)-tetraacetate (EDTA.Na_2), 15 g/l solution.

Dissolve 15 g of disodium dihydrogen(ethylenedinitrilo)tetraacetate dihydrate ($C_{10}H_{14}O_8N_2Na_2.2H_2O$) in water, dilute to 1 000 ml and mix.

Store in a polyethylene bottle.

4.15 4-(2-pyridylazo)-resorcinol (PAR) ($C_{11}H_9N_3O_2$), mono- or di-sodium salt, 0,6 g/l solution.

4.16 Niobium, standard solution, corresponding to 0,200 g of Nb per litre.

Weigh, to the nearest 0,000 1 g, 0,143 1 g of niobium(V) oxide (99,5 % minimum) and transfer to a platinum crucible. Fuse with 3,5 g of potassium hydrogen sulfate (4.2). Cool and dissolve in 40 ml of tartaric acid solution (4.11). Add a further 160 ml of tartaric acid solution (4.11). Transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,200 mg of Nb.

5 Apparatus

Ordinary laboratory apparatus and

Spectrophotometer.

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

6 Sampling

Carry out sampling in accordance with ISO 377 or an appropriate national standard.

7 Procedure

WARNING — Phenylarsonic acid contained in solutions 4.12 and 4.13, and in the main solution, filtrate or washings in 7.3.2, can be injurious to health when absorbed into the body.

Inhaling the vapour emitted when the precipitate in 7.3.2 is ignited can be injurious to health.

All solutions, filtrates and washings containing phenylarsonic acid shall be disposed of in a way which conforms with applicable regulations.

7.1 Test portion

Weigh, to the nearest 1 mg, approximately 1,0 g of the test sample (mass *m*).

7.2 Blank test

Parallel with the determination, and following the same procedure, carry out a blank test using the same quantities of all the reagents and the same cell as in the determination, but replacing the test portion by iron (4.1).

7.3 Determination

7.3.1 Dissolution of the test portion

Introduce the test portion (7.1) into a 400 ml squat beaker, add 40 ml of hydrochloric acid (4.3), cover the beaker with a watch-glass and heat until solvent action ceases. Cool slightly and add with caution 5 ml of hydrogen peroxide (4.7). Boil the solution for 1 min, dilute to approximately 200 ml with warm water and add 5 ml of zirconium nitrate solution (4.9).

7.3.2 Separation of the niobium

Heat the solution prepared in 7.3.1 to boiling and add 25 ml of a boiling solution of phenylarsonic acid (4.12). 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 adhering particles from the beaker with a rubber-tipped glass rod. Wash the filter alternately with hot hydrochloric acid (4.4) and cold phenylarsonic acid solution (4.13) until free of iron salts. Finally, wash several times with cold phenylarsonic acid solution (4.13). Transfer the filter and precipitate to a silica crucible. Dry, and then ignite at as low a temperature as possible until all carbonaceous matter is removed, and finally at 800 °C for at least 15 min. Cool in a desiccator, add a few drops of sulfuric acid (4.5) and evaporate to dryness very carefully. Heat to remove sulfur trioxide.

7.3.3 Preparation of the test solution

Add 2 g of potassium hydrogen sulfate (4.2) to the residue obtained and fuse carefully until a clear melt is obtained. Cool, dissolve the fusion products in 50 ml of warm tartaric acid solution (4.11) and transfer to a 400 ml beaker. Add 50 ml of water and mix.

Add 25 ml of sodium hydroxide solution (4.8) and cool. By means of a pH-meter, adjust the pH of the solution to approximately 6,0 with either sulfuric acid (4.6) or sodium hydroxide solution (4.8), as required. Cool to room temperature, transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

7.3.4 Colour development

Take an aliquot of the test solution prepared in 7.3.3, the volume of the aliquot depending on the expected niobium content of the sample as shown in table 1.

Table 1

Niobium % (*m*/*m*)	Volume of aliquot ml
Less than 0,26	25,0
0,26 to 0,65	10,0
0,65 to 1,3	5,0

Introduce the aliquot into a 100 ml one-mark volumetric flask. By means of a pipette, add 10 ml of EDTA,Na_2 solution (4.14), 10 ml of PAR solution (4.15) and 10 ml of sodium acetate buffer solution (4.10), 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 a further 30 min.

7.3.5 Spectrophotometric measurement

Carry out the spectrophotometric measurement at a wavelength of about 550 nm after having set the spectrophotometer (clause 5) to zero absorbance in relation to water. Use 4 cm cells for niobium contents up to 0,06 % (*m/m*) and 1 cm cells for contents greater than 0,06 % (*m/m*).

7.4 Establishment of the calibration graph

7.4.1 Preparation of calibration solutions

Weigh 1,0 g ± 0,05 g portions of iron (4.1) into a series of nine 400 ml beakers. Add volumes of niobium standard solution (4.16) as shown in table 2.

Table 2

Niobium standard solution (4.16) ml	Niobium concentration in cell solution µg/ml	Cell optical path length cm
0	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

Continue as described in 7.3.2 to 7.3.4, but in all cases taking a 25,0 ml aliquot in 7.3.4.

7.4.2 Spectrophotometric measurements

Carry out spectrophotometric measurements on each solution at a wavelength of about 550 nm after having adjusted the spectrophotometer to zero absorbance in relation to water. Use cells with the optical path length indicated in table 2.

Obtain the net absorbance value by subtracting the absorbance of the zero member from the absorbance of each calibration solution in the series.

7.4.3 Plotting of the calibration graph

Allowing for the optical path length of the cell used, prepare the calibration graph by plotting the net absorbance values against the niobium concentrations, expressed in micrograms per millilitre, in the calibration solutions.

8 Expression of results

8.1 Method of calculation

From the calibration graph plotted in 7.4.3, read off the concentration of niobium corresponding to the absorbance, measured in 7.3.5, of the colour-developed test solution.

The niobium (Nb) content, expressed as a percentage by mass, is given by the formula

$$(\varrho_{Nb1} - \varrho_{Nb0}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100$$

$$= (\varrho_{Nb1} - \varrho_{Nb0}) \times \frac{1}{10^6} \times \frac{250}{V_1} \times \frac{100}{m} \times 100$$

$$= (\varrho_{Nb1} - \varrho_{Nb0}) \frac{25}{10 V_1 m}$$

where

m is the mass, in grams, of the test portion (7.1);

V_0 is the volume, in millilitres, of the test solution (see 7.3.3);

V_1 is the volume, in millilitres, of the aliquot portion (see table 1);

V_t is the volume, in millilitres, of the colour-developed test solution (see 7.3.4);

ϱ_{Nb0} is the concentration, in micrograms per millilitre, of niobium in the blank test solution (see 7.2);

ϱ_{Nb1} is the concentration, in micrograms per millilitre, of niobium in the test solution (see 7.3.3).

8.2 Precision

A planned trial of this method was carried out by fifteen laboratories, at seven levels of niobium, each laboratory making three determinations of niobium at each level (see the notes).

The test samples used are listed in annex A.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between niobium content and the repeatability (r) and reproducibility (R_w and R) of the test results, as summarized in table 3. A graphical presentation of the figures is given in annex B.

Table 3

Niobium level % (*m/m*)	Repeatability	Reproducibility	
	r	R_w	R
0,005	0,001 2	0,001 1	0,002 1
0,01	0,001 8	0,001 7	0,003 4
0,02	0,002 7	0,002 7	0,005 5
0,05	0,004 7	0,004 8	0,010 2
0,1	0,007 2	0,007 4	0,016 4
0,2	0,010 8	0,011 4	0,026 4
0,5	0,018 6	0,020 3	0,049 3
1,0	0,028 4	0,031 5	0,079 1
1,3	0,033 3	0,037 2	0,094 3

NOTES

1 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.

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

3 From the values obtained on day 1, the repeatability (r) and reproducibility (R) were calculated, using the procedure specified in ISO 5725. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility (R_w) was determined.

9 Test report

The test report shall include the following information :

a) the method used, by reference to this International Standard;

b) the results, and the form in which they are expressed;

c) any unusual features noted during the determination;

d) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A

(informative)

Additional information on the international co-operative tests

The repeatability and reproducibility data in table 3 were derived from the results of international analytical trials carried out in 1985 on seven steel samples, involving fifteen laboratories in six countries.

The results of the trials were reported in document 17/1 N 653, March 1986. A graphical presentation of the precision data is given in annex B.

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

Table A.1

Sample		Niobium content % (*m/m*)
BCS 431/1	(carbon steel)	0,004
JSS 175-3	(mild steel)	0,011
JSS 174-3	(mild steel)	0,020
JSS 172-5	(mild steel)	0,054
NBS 364	(low-alloy steel)	0,157
JSS 655-7	(stainless steel)	0,60
BCS 467	(high-alloy steel)	1,06

Annex B

(informative)

Graphical representation of precision data

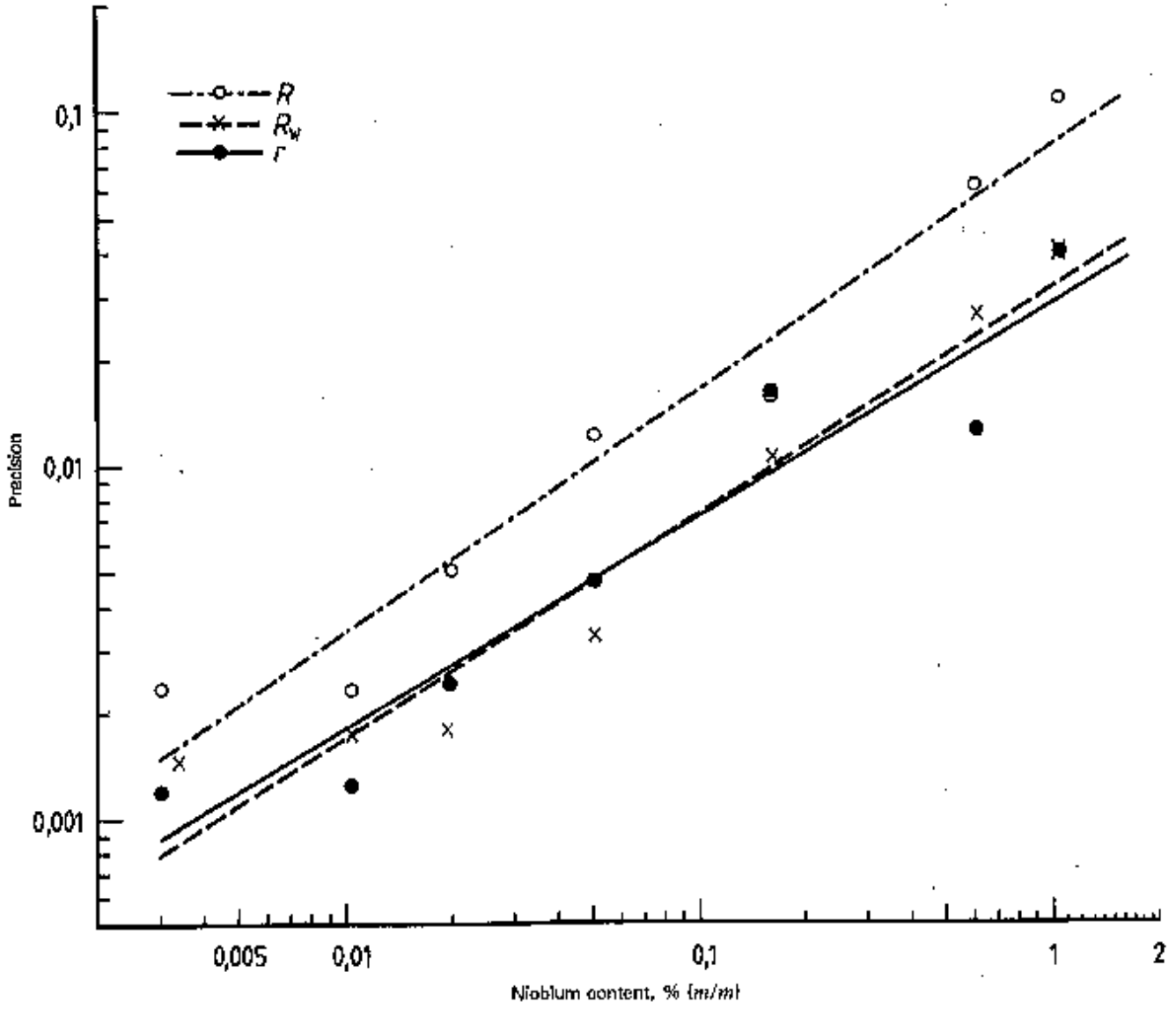

Figure B.1 — Relationship between niobium content and repeatability (r) and between niobium content and reproducibility (R_w and R)

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