INTERNATIONAL STANDARD

ISO 4942

Second edition
2016-07-01

Steels and irons — Determination of vanadium content — N-BPHA spectrophotometric method

Aciers et fontes — Détermination de la teneur en vanadium — Méthode spectrophotométrique au N-BPHA

Reference number
ISO 4942:2016(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4942:1988), which has been technically revised.

Steels and irons — Determination of vanadium content — N-BPHA spectrophotometric method

1 Scope

This document specifies an N-benzoylphenylhydroxylamine (N-BPHA) spectrophotometric method for the determination of vanadium in steels and cast irons.

This document is applicable to vanadium contents between 0,005 % and 0,50 % (mass fraction).

2 Normative references

The following documents are referred to in 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.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

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

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

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:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

Dissolution of a test portion with appropriate acids.

Addition of orthophosphoric acid to an aliquot of the sample solution to prevent the interference of iron, and addition of potassium permanganate to oxidize vanadium to the pentavalent state.

Selective reduction of excess permanganate by sodium nitrite, in the presence of urea and treatment with N-BPHA and hydrochloric acid to form a complex, followed by extraction of the complex with trichloromethane.

Spectrophotometric measurement of the absorbance at approximately 535 nm.

5 Reagents

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

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

5.2 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted 4 + 1.

Add 400 ml of hydrochloric acid (5.1) to 100 ml of water.

5.3 Nitric acid, ρ approximately 1,40 g/ml.

5.4 Perchloric acid, ρ approximately 1,67 g/ml.

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

5.5 Orthophosphoric acid, ρ approximately 1,71 g/ml.

5.6 Orthophosphoric acid, ρ approximately 1,71 g/ml, diluted 1 + 1.

Add 250 ml of orthophosphoric acid (5.5) to 250 ml of water.

5.7 Hydrochloric/nitric acids mixture, 3 + 1.

Mix 300 ml of hydrochloric acid (5.1) with 100 ml of nitric acid (5.3).

Prepare this mixture immediately prior to use.

5.8 Hydrogen peroxide, 300 g/l solution.

5.9 Sodium nitrite, 3 g/l solution.

5.10 Urea, 250 g/l solution.

5.11 Sodium tripolyphosphate ($Na_5P_3O_{10}$), 100 g/l solution.

5.12 Potassium permanganate, 3 g/l solution.

5.13 Trichloromethane (chloroform).

5.14 N-benzoylphenylhydroxylamine [$C_6H_5CON(OH)C_6H_5$], 2,5 g/l solution in trichloromethane.

Dissolve 0,25 g of N-BPHA in 100 ml of trichloromethane (5.13).

This solution shall be stored in a brown bottle. Otherwise, it shall be freshly prepared.

5.15 Iron, 10 g/l solution.

Weigh, to the nearest 1 mg, 5,0 g of pure iron (free from vanadium or with a vanadium content as low as possible and exactly known). Transfer into a 500 ml beaker, cover with a watch-glass and add 100 ml of the hydrochloric/nitric acids mixture (5.7).

After effervescence has ceased, heat gently to complete the dissolution.

Add 100 ml of perchloric acid (5.4) and raise the temperature until white perchloric acid fumes appear and then reflux in the beaker. Continue fuming for about 3 min.

Cool, add 100 ml of hot water and shake to dissolve salts. Add a few drops of hydrogen peroxide (5.8), heat gradually to boiling and maintain at the boil for about 2 min.

Cool and transfer into a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

5.16 **Vanadium standard solution**, 1,0 g/l.

Dry several grams of ammonium metavanadate (NH_4VO_3) in an oven at 100 °C to 105 °C for at least 1 h and cool to room temperature in a desiccator.

A drying temperature over 110 °C will cause the decomposition of ammonium metavanadate. Maintain the drying temperature exactly as specified.

Weigh, to the nearest 1 mg, 2,296 g of the dried product, transfer into a 600 ml beaker, add 400 ml of hot water and heat gently until the product is completely dissolved.

Cool, transfer into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1,0 mg of vanadium.

5.17 **Vanadium standard solution**, 50 mg/l.

Transfer 5,0 ml of the vanadium standard solution (5.16) into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 50 µg of vanadium.

6 Apparatus

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

Ordinary laboratory equipment and the following.

6.1 Spectrophotometer, equipped to measure absorbance at a wavelength of 535 nm, with cells of 1 cm optical path length.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steels and irons.

8 Procedure

8.1 Test portion

Weigh, to the nearest 1 mg, a test portion of the sample according to Table 1.

Table 1 — Test portion

Expected vanadium content % (mass fraction)	**Test portion** (g)
0,005 to 0,10	1,0
0,10 to 0,20	0,50
0,20 to 0,50	0,20

8.2 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all reagents as used for the determination (see 8.3.2 and 8.3.3) but replacing the test solution by the iron solution (5.15).

8.3 Determination

8.3.1 Preparation of the test solution

Transfer the test portion (8.1) (see 10.1) to a 250 ml beaker, cover with a watch-glass and add 20 ml to 30 ml of the hydrochloric/nitric acids mixture (5.7). When effervescence has ceased, heat gently to complete the dissolution.

Add 15 ml to 20 ml of perchloric acid (5.4), raise the temperature so that white perchloric acid fumes appear and reflux in the beaker and continue fuming for about 3 min.

NOTE In the case of cast irons, fuming with perchloric acid for about 3 min is not always sufficient to decompose carbides. Total decomposition is only complete when heating is continued until no more fumes are visible in the beaker and crystallization has occurred. After cooling, add about 30 ml of water and 10 ml of perchloric acid (5.4) before continuing as described below from “Add hydrogen peroxide (5.8)...”.

Cool, add about 30 ml of hot water and shake to dissolve salts. Add hydrogen peroxide (5.8) dropwise to reduce chromium, gradually heat to boiling and continue for 1 min to 2 min to decompose the excess of hydrogen peroxide.

After cooling, filter through a medium texture filter paper and collect the filtrate in a 100 ml one-mark volumetric flask. Wash the filter paper several times with hot water. Dilute to the mark with water and mix.

8.3.2 Oxidation of vanadium

Transfer 25,0 ml of the test solution (8.3.1) into a 125 ml separating funnel. Add 2,0 ml of orthophosphoric acid (5.6) (see 10.2 and 10.3) and 5,0 ml of water and swirl.

Add 0,8 ml of potassium permanganate solution (5.12), swirl and allow to stand for 4 min. Add 5,0 ml of urea solution (5.10) and then add 1,0 ml of sodium nitrite solution (5.9), drop by drop while swirling.

Even if, after the addition of 1,0 ml of sodium nitrite solution (5.9), the solution still appears slightly pink, proceed, without any further addition of sodium nitrite solution, to 8.3.3.

Allow to stand for 1 min.

8.3.3 Colour development and extraction

Add 25,0 ml of hydrochloric acid (5.2) and 10,0 ml of N-BPHA (5.14) and shake for 45 s.

When the layers have separated, draw off the organic phase, filtering through a dry filter paper fitted in an ordinary funnel, or through absorbent cotton fitted in the stem of a separating funnel, into a dry 50 ml one-mark volumetric flask.

Retain the aqueous phase.

Add 10,0 ml of trichloromethane (5.13) to the aqueous phase remaining in the separating funnel and shake for 30 s. Allow to settle, combine the organic phase with the main extract, dilute to the mark with trichloromethane (5.13) and mix (see the following paragraph).

To ensure the same colour development conditions for the test and the calibration solutions, take each solution one by one through the steps from the vanadium oxidation (8.3.2) to the extraction (8.3.3). Avoid batch colour development and carry out each step without delay, unless otherwise specified.

8.3.4 Spectrophotometric measurements

Measure the absorbance of the test solutions at a wavelength of about 535 nm in cells of 1 cm path length, after having adjusted the spectrophotometer (6.1) to the zero absorbance against trichloromethane (5.13).

8.4 Establishment of the calibration curve

8.4.1 Preparation of the calibration solutions

Transfer 25,0 ml portions of iron solution (5.15) into a series of 125 ml separating funnels. Add the volumes of vanadium standard solution (5.17) and of water shown in Table 2, swirl and proceed as specified in 8.3.2 and 8.3.3, but omit the addition of 5 ml of water specified in 8.3.2.

Table 2 — Composition of the calibration solutions

Vanadium standard solution (5.17) ml	Water ml	Corresponding vanadium concentration µg/ml
0	5,0	0
0,5	4,5	0,5
1,0	4,0	1,0
2,0	3,0	2,0
4,0	1,0	4,0
5,0	0	5,0

8.4.2 Spectrophotometric measurements

Measure the absorbance of each solution at a wavelength of about 535 nm, in cells of 1 cm path length, after having adjusted the spectrophotometer (6.1) to the zero absorbance against the zero member of the calibration solutions.

8.4.3 Plotting of the calibration curve

Establish the calibration curve by plotting the absorbance values against the vanadium concentrations, expressed in micrograms per millilitre, in the calibration solutions.

9 Expression of results

9.1 Method of calculation

Convert the absorbance measured in 8.3.4 to the corresponding concentration, expressed in micrograms per millilitre of vanadium in the colour-developed test solution, by using the calibration curve (8.4.3).

The vanadium content, m_{V}, expressed as a mass fraction percentage (%), is given by Formulae (1) to (3):

$$m_{\mathrm{V}} = (C_{\mathrm{V1}} - C_{\mathrm{V0}}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_{\mathrm{t}}}{m} \times 100 + \frac{C_{\mathrm{Fe}}}{m} \quad (1)$$

$$m_{\mathrm{V}} = (C_{\mathrm{V1}} - C_{\mathrm{V0}}) \times \frac{1}{10^6} \times \frac{100}{25} \times \frac{50}{m} \times 100 + \frac{C_{\mathrm{Fe}}}{m} \quad (2)$$

$$m_{\mathrm{V}} = (C_{\mathrm{V1}} - C_{\mathrm{V0}}) \times \frac{1}{50m} + \frac{C_{\mathrm{Fe}}}{m} \quad (3)$$

where

V_0 is the volume of the test solution (8.3.1), in ml;

V_1 is the volume of the aliquot portion (8.3.2), in ml;

V_t is the volume of the colour-developed test solution (8.3.3), in ml;

C_{V0} is the concentration of vanadium in the blank test solution, in µg/ml;

C_{V1} is the concentration of vanadium in the test solution, in µg/ml;

m is the mass of the test portion (8.1), in g;

C_{Fe} is the vanadium content in the iron used in the blank test, expressed as mass fraction in %.

9.2 Precision

A planned trial of this method was carried out by 11 laboratories, at seven levels of vanadium, each laboratory making three determinations at each level (see Notes 1 and 2).

The test samples used are listed in Annex A.

The results obtained were treated statistically in accordance with ISO 5725:1986[1] (see Note 3).

The data obtained showed logarithmic relationships between vanadium content and the repeatability, r, and reproducibilities, R_w and R, of the test results, as summarized in Table 3.

Table 3 — Repeatability limit and reproducibility limits

Vanadium content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,005	0,001 0	0,001 1	0,002 1
0,010	0,001 6	0,001 8	0,003 2
0,020	0,002 4	0,002 8	0,004 9
0,050	0,004 2	0,005 4	0,008 7
0,100	0,006 6	0,008 7	0,013 4
0,200	0,010 2	0,014 1	0,020 7
0,500	0,018 1	0,026 7	0,036 7

A graphical representation of the data is given in Figure B.1.

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725:1986[1], 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 above, using the same apparatus but with a new calibration.

NOTE 3 From the values obtained on day 1, the repeatability, r, and reproducibility, R, were calculated using the procedure specified in ISO 5725:1986[1]. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility, R_w, was calculated.

---

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

10 Special cases

10.1 For test portions containing tungsten, transfer the test portion (8.1) into a 250 ml beaker, cover with a watch-glass and add 15 ml to 20 ml of perchloric acid (5.4), 5 ml of orthophosphoric acid (5.5) and 3 ml to 5 ml of nitric acid (5.3). Heat gently to complete the dissolution, increase the temperature until white perchloric acid fumes reflux in the beaker and continue for about 3 min.

10.2 For test portions containing tungsten, omit the addition of 2,0 ml of orthophosphoric acid (5.6).

10.3 For test solutions containing more than 1 mg of titanium in the aliquot, add 3,0 ml of sodium tripolyphosphate solution (5.11), to prevent the interference of titanium.

11 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;

b) method used by reference to this document, i.e. ISO 4942;

c) results and the unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(informative)

Additional information on the international interlaboratory test

Table 2 was derived from the results of an international trial carried out in 1985 on six steel samples and one pig iron sample in six countries and involving 11 laboratories.

The results of the trial were reported in the ISO/TC 17/SC 1 N 647, March 1986 document. The precision data are presented in graphical form in Figure B.1.

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

Table A.1 — Test samples used for the precision test

Sample	Vanadium content % (mass fraction)		
	Certified	Found	
		m_1	m_2
JSS 513–4 (low-alloy steel)	0,005	0,004 9	0,004 9
JSS 113–2 (pig iron)	0,007	0,007 0	0,007 0
JSS 516–4 (low-alloy steel)	0,010	0,010 2	0,010 6
JSS 652–7 (stainless steel)	0,038[a]	0,038 2	0,038 0
JSS 152–8 (low-alloy steel)	0,10	0,103	0,103
JSS 153–7 (low-alloy steel)	0,21	0,213	0,212
JSS 603–7 (tool steel)	0,46	0,456	0,459

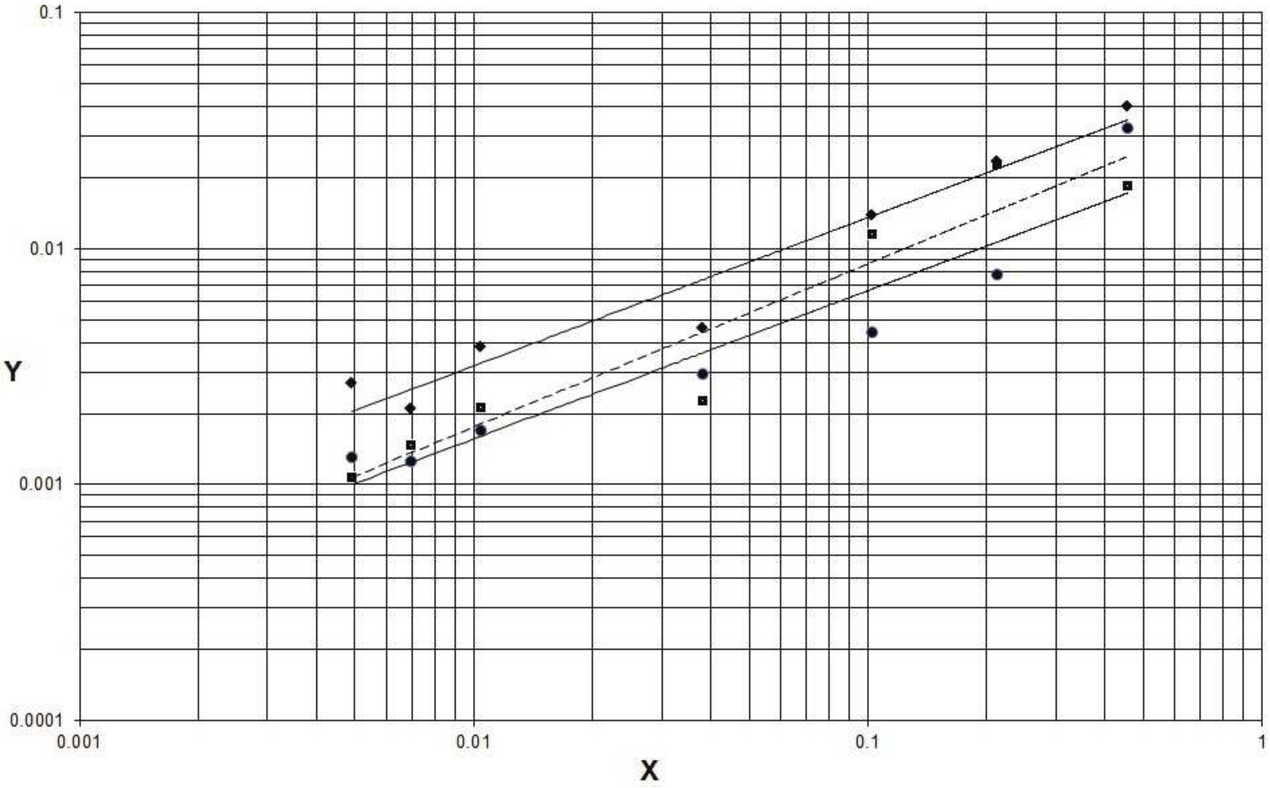
m_1 is the general mean within a day.

m_2 is the general mean between days.

[a] Non-certified value.

Annex B
(informative)

Graphical representation of precision data



Key

- ● r
- ■ R_W
- ◆ R

X vanadium content (mass fraction)
Y precision (%)

Figure B.1 — Relationship between vanadium content and repeatability limit (r) and reproducibility limits (R_W and R)

Bibliography

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

---

[2] Withdrawn. (Replaced by ISO 5725 series.)

ICS 77.080.01

Price based on 10 pages