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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

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Foreword

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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).

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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):

$$m_V = (C_{V1} - C_{V0}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 + \frac{C_{Fe}}{m} \qquad (1)$$

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

$$m_V = (C_{V1} - C_{V0}) \times \frac{1}{50m} + \frac{C_{Fe}}{m} \qquad (3)$$