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Steel and iron — Determination of vanadium content — N-BPHA spectrophotometric method

Aciers et fontes — Dosage du vanadium — Méthode spectrophotométrique au N-BPHA

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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 4942 was prepared by Technical Committee ISO/TC 17, *Steel*.

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

Steel and iron — Determination of vanadium content — N-BPHA spectrophotometric method

1 Scope

This International Standard specifies an N-BPHA spectrophotometric method for the determination of vanadium in steel and iron.

The method is applicable to vanadium contents between 0,005 % (*m/m*) and 0,50 % (*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 with appropriate acids.

Addition of orthophosphoric acid to an aliquot of the solution thus obtained 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 into trichloromethane.

Spectrophotometric measurement of the absorbance at approximately 535 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 Hydrochloric acid, ρ about 1,19 g/ml.

4.2 Hydrochloric acid, ρ about 1,19 g/ml, diluted 4 + 1.

4.3 Nitric acid, ρ about 1,40 g/ml.

4.4 Perchloric acid, ρ about 1,67 g/ml.

4.5 Orthophosphoric acid, ρ about 1,71 g/ml.

4.6 Orthophosphoric acid, ρ about 1,71 g/ml, diluted 1 + 1.

4.7 Hydrochloric acid/nitric acid mixture.

Mix three volumes of hydrochloric acid (4.1) with one volume of nitric acid (4.3). Prepare fresh as needed.

4.8 Hydrogen peroxide, 300 g/l solution.

4.9 Sodium nitrite, 3 g/l solution.

4.10 Urea, 250 g/l solution.

4.11 Sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), 100 g/l solution.

4.12 Potassium permanganate, 3 g/l solution.

4.13 Trichloromethane (chloroform).

4.14 N-BPHA, 2,5 g/l solution in trichloromethane.

Dissolve 0,25 g of *N*-benzoylphenylhydroxylamine [$\text{C}_6\text{H}_5\text{CON}(\text{OH})\text{C}_6\text{H}_5$] in 100 ml of trichloromethane (4.13). Prepare fresh, or store in a brown bottle.

4.15 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 known exactly. Transfer to a 500 ml beaker, cover with a watch-glass and add 100 ml of hydrochloric acid/nitric acid mixture (4.7). After effervescence has ceased, heat gently to complete the dissolution.

Add 100 ml of perchloric acid (4.4) and raise the temperature until white perchloric acid fumes 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 (4.8), heat gradually to boiling and maintain at the boil for about 2 min. Cool, transfer to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

4.16 Vanadium, standard solutions.

4.16.1 Vanadium stock solution corresponding to 1,0 g of V per litre.

Dry several grams of ammonium metavanadate (NH_4VO_3) in an air oven at 100 °C to 105 °C (see the note) for at least 1 h and cool to room temperature in a desiccator. Weigh, to the nearest 1 mg, 2,296 g of the dried product, transfer to a 600 ml beaker, add 400 ml of hot water and gently simmer to dissolve. Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this stock solution contains 1,0 mg of V.

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

4.16.2 Vanadium standard solution, containing 50 mg of V per litre.

Transfer 5,0 ml of the stock solution (4.16.1) to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

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

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 appropriate national standards for iron.

7 Procedure

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

7.1 Test portion

Weigh, to the nearest 1 mg, the mass given below as a function of expected vanadium content :

- a) vanadium content from 0,005 % (*m/m*) to 0,10 % (*m/m*), mass of test portion approximately 1,0 g;
- b) vanadium content from 0,10 % (*m/m*) to 0,20 % (*m/m*), mass of test portion approximately 0,50 g;
- c) vanadium content from 0,20 % (*m/m*) to 0,50 % (*m/m*), mass of test portion approximately 0,20 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure and using the same quantities of all the reagents in the determination, as specified in 7.3.2 and 7.3.3, but replacing the test solution by iron solution (4.15).

7.3 Determination

7.3.1 Preparation of the test solution

Transfer the test portion (7.1) (see 9.1) to a 250 ml beaker, cover with a watch-glass and add 20 ml to 30 ml of hydrochloric acid/nitric acid mixture (4.7). After effervescence has ceased, heat gently to complete the dissolution.

Add 15 ml to 20 ml of perchloric acid (4.4), raise the temperature so that white perchloric acid fumes reflux in the beaker and continue for about 3 min.

Cool, add about 30 ml of hot water and shake to dissolve salts. Add hydrogen peroxide (4.8) dropwise to reduce chromium, gradually heat to boiling and maintain at the boil for 1 min to 2 min to decompose excess hydrogen peroxide.

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

7.3.2 Oxidation of vanadium

Transfer 25,0 ml of the test solution (see 7.3.1) to a 125 ml separating funnel. Add 2,0 ml of orthophosphoric acid (4.6) (see 9.2 and 9.3) and 5,0 ml of water and swirl.

Add 0,8 ml of potassium permanganate solution (4.12), swirl and allow to stand for 4 min. Add 5,0 ml of urea solution (4.10) and then add 1,0 ml of sodium nitrite solution (4.9) drop by drop while swirling (see 9.4). Allow to stand for 1 min.

7.3.3 Colour development and extraction

Add 25,0 ml of hydrochloric acid (4.2) and 10,0 ml of N-BPHA trichloromethane solution (4.14) 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, retaining the aqueous phase.

Add 10,0 ml of trichloromethane (4.13) 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 (4.13) and mix (see the note).

NOTE — To ensure the same colour development conditions for the test and calibration solutions, take each solution one by one through the steps from vanadium oxidation (7.3.2) to extraction (7.3.3), avoiding batch colour development, and carrying out each procedure without delay unless otherwise specified.

7.3.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution at a wavelength of about 535 nm with a cell of 1 cm path length after having adjusted the spectrophotometer (see clause 5) to zero absorbance in relation to trichloromethane (4.13).

7.4 Establishment of the calibration graph

7.4.1 Preparation of calibration solutions

Introduce 25,0 ml portions of iron solution (4.15) into a series of 125 ml separating funnels. Add volumes of vanadium standard solution (4.16.2) and water as shown in table 1, swirl and proceed as specified in 7.3.2 and 7.3.3, but omit the addition of 5 ml of water specified in 7.3.2.

7.4.2 Spectrophotometric measurement

Carry out spectrophotometric measurements of each solution at a wavelength of about 535 nm after having adjusted the spectrophotometer to zero absorbance in relation to the zero member of the calibration solutions.

7.4.3 Plotting of the calibration graph

Prepare the calibration graph by plotting the absorbance values against the vanadium concentrations, expressed in micrograms per millilitre, in the measured solutions.

8 Expression of results

8.1 Method of calculation

Convert the absorbance measured in 7.3.4 into the corresponding concentration, expressed in micrograms per millilitre, of vanadium in the colour-developed test solution by using the calibration graph plotted in 7.4.3.

The vanadium (V) content, expressed as a percentage by mass, is given by the formula

$$\begin{aligned}
 & (e_{V1} - e_{V0}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 + \frac{C}{m} \\
 &= (e_{V1} - e_{V0}) \times \frac{1}{10^6} \times \frac{100}{25} \times \frac{50}{m} \times 100 + \frac{C}{m} \\
 &= (e_{V1} - e_{V0}) \times \frac{1}{50m} + \frac{C}{m}
 \end{aligned}$$

where

V_0 is the volume, in millilitres, of the test solution (see 7.3.1);

V_1 is the volume, in millilitres, of the aliquot portion (see 7.3.2);

V_t is the volume, in millilitres, of the colour-developed test solution (see 7.3.3);

e_{V0} is the concentration, expressed in micrograms per millilitre, of vanadium in the blank test solution;

e_{V1} is the concentration, expressed in micrograms per millilitre, of vanadium in the colour-developed test solution;

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

C is the vanadium content, expressed as a percentage by mass, in the iron used in the blank test and the calibration.

Table 1

Vanadium standard solution (4.16.2) ml	Water ml	Corresponding vanadium concentration µg/ml
0	5,0	0
0,50	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

8.2 Precision

A planned trial of this method was carried out by eleven laboratories, at seven levels of vanadium, each laboratory making three determinations of vanadium 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 (see note 3).

The data obtained showed a logarithmic relationship between vanadium content and the repeatability (*r*) and reproducibility (*R_w* and *R*) of the test results, as summarized in table 2. A graphical representation of the data is given in annex B.

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 calculated.

9 Special cases

9.1 For test portions containing tungsten, transfer the test portion (7.1) to a 250 ml beaker, cover with a watch-glass and add 15 ml to 20 ml of perchloric acid (4.4), 5 ml of

orthophosphoric acid (4.5) and 3 ml to 5 ml of nitric acid (4.3). Heat gently to complete the dissolution, increase the temperature until white perchloric acid fumes reflux in the beaker and continue for about 3 min.

9.2 For test portions containing tungsten, omit the addition of 2,0 ml of orthophosphoric acid (4.6).

9.3 For test solutions containing more than 1 mg of titanium in the aliquot, add 3,0 ml of sodium tripolyphosphate solution (4.11), to prevent the interference of titanium.

9.4 Even if, after the addition of 1,0 ml of sodium nitrite solution (4.9), the solution still appears slightly pink, proceed, without any further addition of sodium nitrite solution, to 7.3.3.

10 Test report

The test report shall include the following particulars :

- a) all information necessary for the identification of the sample, the laboratory and the date of the analysis;
- b) the method used, by reference to this International Standard;
- c) the results, and the form in which they are expressed;
- d) any unusual features noted during the determination;
- e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Table 2

Level of vanadium % (m/m)	Repeatability	Reproducibility	
	<i>r</i>	<i>R_w</i>	<i>R</i>
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