



SLOVENSKI STANDARD
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Iron ores -- Determination of vanadium content -- BPHA spectrophotometric method

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Minerais de fer -- Dosage du vanadium -- Méthode spectrophotométrique à la BPHA

Ta slovenski standard je istoveten z: **ISO 9683:1991**

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INTERNATIONAL STANDARD

ISO
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Iron ores — Determination of vanadium content — BPHA spectrophotometric method

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spectrophotométrique à la BPHA*
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Reference number
ISO 9683:1991(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 voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9683 was prepared by Technical Committee ISO/TC 102, *Iron ores*, Sub-Committee SC 2, *Chemical analysis*.

Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

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Iron ores — Determination of vanadium content — BPHA spectrophotometric method

1 Scope

This International Standard specifies a spectrophotometric method using N-benzoyl-phenylhydroxylamine (BPHA) for the determination of the vanadium content of iron ores.

This method is applicable to vanadium contents between 0,005 % (*m/m*) and 0,5 % (*m/m*) in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

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 indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks*.

ISO 3081:1986, *Iron ores — Increment sampling — Manual method*.

ISO 3082:1987, *Iron ores — Increment sampling and sample preparation — Mechanical method*.

ISO 3083:1986, *Iron ores — Preparation of samples — Manual method*.

ISO 7764:1985, *Iron ores — Preparation of predried test samples for chemical analysis*.

3 Principle

Decomposition of a test portion by fusion with sodium peroxide and leaching with water and sulfuric acid.

Addition of orthophosphoric acid to an aliquot and oxidization of vanadium to the pentavalent state by potassium permanganate. Reduction of the excess permanganate by sodium nitrite in the presence of urea.

Treatment with BPHA and hydrochloric acid to form a complex, followed by extraction of the complex with chloroform.

Spectrophotometric measurement of the absorbance at approximately 535 nm.

4 Reagents

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

4.1 Sodium peroxide, fine powder.

4.2 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 4 + 1.

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

4.4 Orthophosphoric acid, ρ 1,7 g/ml, diluted 1 + 1.

4.5 Hydrogen peroxide, 300 g/l solution.

4.6 Sodium nitrite, 3 g/l solution.

4.7 Urea, 250 g/l solution.

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4.8 Potassium permanganate, 3,2 g/l solution.

Dissolve 3,2 g of potassium permanganate in 100 ml of water. Boil gently for about 1 h, filter through a carefully cleaned fine-texture glass filter funnel into a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix. Store the solution in a brown bottle.

4.9 Sodium tripolyphosphate (Na₅P₃O₁₀), 100 g/l solution.

Dissolve 25 g of sodium tripolyphosphate in 170 ml of water, dilute to 250 ml and mix.

4.10 Background solution.

Place 1,300 g of pure iron (containing less than 0,001 % V) in a zirconium or vitreous carbon crucible (5.1) containing 4,0 g of sodium peroxide (4.1). Add another 4,0 g of sodium peroxide, mix thoroughly with a glass rod or nickel spatula and tamp the mixture. Place the crucible for 1 min or 2 min at the entrance of a muffle furnace (5.2), the temperature of which is regulated at 420 °C ± 10 °C, and then transfer it to the closed furnace for at least 1 h to effect sintering.

Remove the crucible from the furnace and cool to room temperature. Place the crucible containing the sintered mass in a dry 400 ml beaker, cover with a watch-glass and, momentarily lifting the cover, add 5 ml of water around the sinter cake. When the reaction has subsided, add a further 15 ml of water in the same way. After several minutes, when the reaction has subsided again, empty the crucible into the 400 ml beaker, rinsing with approximately 10 ml of water. Cautiously pour 30 ml of sulfuric acid (4.3) into the crucible, heat gently, if necessary, to dissolve any residue, and transfer the solution to the beaker, rinsing with about 10 ml of water.

Cautiously add 100 ml of sulfuric acid (4.3) and mix with a glass rod. Add 1 to 2 drops of hydrogen peroxide (4.5) while stirring, until a clear yellow solution is obtained. Boil for about 2 min, cool, transfer to a 200 ml one-mark volumetric flask, dilute to volume with water and mix.

4.11 Chloroform.**4.12 N-benzoyl-phenylhydroxylamine (BPHA), 2,5 g/l chloroform solution.**

Prepare freshly, or store in a brown bottle.

4.13 Vanadium standard solutions.**4.13.1 Vanadium stock solution, 1 000 µg V/ml.**

Dry several grams of ammonium metavanadate (NH₄VO₃) in an air oven at 100 °C for 1 h and cool to

room temperature in a desiccator. Weigh, to the nearest 0,000 2 g, 2,296 3 g of the dried product into a 600 ml beaker, add 400 ml of hot water and heat gently to dissolve. Cool, carefully add 50 ml of sulfuric acid (4.3), transfer to a 1 000 ml one-mark volumetric flask, quantitatively, dilute to volume with water and mix.

4.13.2 Vanadium standard solution, 50 µg V/ml.

Transfer 5,0 ml of vanadium stock solution (4.13.1) to a 100 ml one-mark volumetric flask containing 70 ml of water and 5 ml of sulfuric acid (4.3). Cool, dilute to volume with water and mix.

4.14 Calibration solutions.

To each of six 125 ml separating funnels, add 25,0 ml of background solution (4.10) and 7 ml of orthophosphoric acid (4.4). Using pipettes, add the quantities of vanadium standard solution (4.13.2) and water as described in table 1 to the respective separating funnels, and mix by swirling.

Table 1 Calibration solutions

Vanadium standard solution (4.13.2) ml	Water ml	Vanadium concentration in the measured solution (7.4.2) µg/ml
0	5,0	0
0,5	4,5	0,5
1,0	4,0	1,0
2,0	3,0	2,0
3,5	1,5	3,5
5,0	0	5,0

For colour development and extraction, proceed as directed in 7.4.2, beginning at "Add 0,8 ml of potassium permanganate solution (4.8), ..."

5 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively, and

5.1 Zirconium metal or vitreous carbon crucible, of approximately 50 ml capacity.

5.2 Muffle furnace, capable of being regulated at 420 °C ± 10 °C.

5.3 Spectrophotometer.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 μm particle size which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082 or ISO 3083. In the case of ores with significant contents of combined water or oxidizable compounds, use a particle size of minus 160 μm .

NOTE 1 A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container. Dry the test sample at $105\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with annex A, independently, on one predried test sample.

NOTE 2 The expression "independently" means that the second and any subsequent result is not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure shall be carried out either by the same operator at a different time or by a different operator including, in both cases, appropriate recalibration.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,0002 g, approximately 0,5 g of the predried test sample obtained in accordance with 6.2.

NOTE 3 The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.3 Blank test and check test

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. In a

blank test, 25 ml of the background solution shall be used in place of the aliquot of the test solution. A predried test sample of the certified reference material shall be prepared as specified in 6.2.

NOTE 4 The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that in both cases no significant changes in the analytical procedure will become necessary.

When the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents used are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

7.4 Determination

7.4.1 Decomposition of the test portion

Place 2,00 g of sodium peroxide (4.1) in a zirconium or vitreous carbon crucible (5.1). Immediately add the test portion (7.2) and mix well using a glass rod or a nickel spatula. Fuse over a burner and swirl the crucible until the melt is cherry red and clear. Remove from the heat and swirl cautiously to cause the cooling melt to solidify in a thin layer on the wall of the crucible. Now place the crucible and contents in a dry 300 ml beaker. Cover with a watch-glass and, momentarily lifting the cover, add 5 ml of water to the crucible. When the effervescence has ceased, empty the crucible into the beaker, rinsing with approximately 5 ml of water.

Add 32 ml of sulfuric acid (4.3) to the beaker via the crucible, wash the crucible with 5 ml of water and remove the crucible.

Add 1 to 2 drops of hydrogen peroxide (4.5) until a clear yellow solution appears. Boil for about 2 min, cool, transfer to a 50 ml one-mark volumetric flask, dilute to volume with water and mix. (This is the test solution.)

7.4.2 Colour development and extraction

Using a pipette, introduce appropriate aliquots (see table 2) of the test solution and background solution into a 125 ml separating funnel, add 7 ml of orthophosphoric acid (4.4) and 5 ml of water and mix by swirling.

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Table 2 — Dilution guide for test solution

Vanadium content % (m/m)	Alliquot of the test solution (7.4.1) ml	Alliquot of the background solution (4.10) ml	Vanadium content of the aliquot µg
0,005 to 0,10	25	0	12,5 to 250
0,10 to 0,20	10	15	100 to 200
0,20 to 0,50	5	20	100 to 250

Add 0,8 ml of potassium permanganate solution (4.8), mix by swirling and stand for 4 min. Add 5 ml of urea solution (4.7), then add 1 ml of sodium nitrite solution (4.6) drop by drop while swirling and allow to stand for 1 min. Add 25 ml of hydrochloric acid (4.2) and 10 ml of BPHA solution (4.12), and shake for 45 s. Allow the two layers to separate, draw off the organic layer (main extract) by filtering through absorbent cotton inserted into the stem of the funnel or through a dry filter paper fitted in an ordinary funnel, into a dry 50 ml one-mark volumetric flask, retaining the aqueous layer.

Add 10 ml of chloroform (4.11) to the separating funnel and shake for 30 s. Allow the two layers to separate, draw off the organic layer by filtering through the absorbent cotton or dry filter paper. Combine it with the main extract, dilute to volume with chloroform and mix.

CAUTION — Operations involving the use of chloroform should be conducted in a cool, well ventilated area.

NOTES

5 To ensure the same colour developing conditions in the test solution and the calibration solutions, each solution should be taken separately through the colour development and extraction steps, and batch colour development should be avoided.

6 For the test solution containing more than 1 mg of titanium in the aliquot, 10 ml of sodium tripolyphosphate solution (4.9) should be added before the addition of potassium permanganate solution (4.8).

7.4.3 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution at a wavelength of about 535 nm, in a cell of 1 cm optical path length, after adjusting the spectrophotometer (5.3) to zero absorbance in relation to chloroform (4.11).

7.4.4 Calibration

7.4.4.1 Spectrophotometric measurement

Carry out the spectrophotometric measurement of absorbance of each calibration solution (4.14), using

the calibration solution with 0 ml of vanadium standard solution (4.13) as the reference in accordance with the directions given in 7.4.3.

7.4.4.2 Plotting the calibration graph

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

8 Expression of results

8.1 Calculation of vanadium content

Convert the absorbance (7.4.3) of the colour-developed test solution and the blank test solution into the corresponding concentration, expressed in micrograms of vanadium per millilitre, by means of the calibration graph (7.4.4.2).

The vanadium content, w_v , expressed as a percentage by mass, is calculated from the equation

$$\begin{aligned}
 w_v &= (\rho_{v,1} - \rho_{v,0}) \times \frac{1}{10^6} \times \frac{V_1}{V_2} \times \frac{V_3}{m} \times 100 \\
 &= (\rho_{v,1} - \rho_{v,0}) \times \frac{1}{10^6} \times \frac{50}{V_2} \times \frac{50}{m} \times 100 \\
 &= (\rho_{v,1} - \rho_{v,0}) \times \frac{1}{4V_2m} \dots (1)
 \end{aligned}$$

where

$\rho_{v,0}$ is the concentration, in micrograms per millilitre, of vanadium in the blank test solution (7.3);

$\rho_{v,1}$ is the concentration, in micrograms per millilitre, of vanadium in the test solution (7.4.1);

V_1 is the volume, in millilitres, of the test solution;

V_2 is the volume, in millilitres, of the aliquot portion (table 1);

V_3 is the volume, in millilitres, of the colour-developed test solution (7.4.2);

m is the mass, in grams, of the test portion (7.2).

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed

by the following regression equations¹⁾:

$$r = 0,034\ 4\ X + 0,001\ 6 \quad \dots (2)$$

$$P = 0,068\ 9\ X + 0,001\ 0 \quad \dots (3)$$

$$\sigma_r = 0,012\ 2\ X + 0,000\ 6 \quad \dots (4)$$

$$\sigma_L = 0,022\ 9\ X + 0,000\ 2 \quad \dots (5)$$

where

X is the vanadium content, expressed as a percentage by mass, of the test sample, calculated as follows:

- within-laboratory equations (2) and (4): the arithmetic mean of the duplicate values,
- between-laboratory equations (3) and (5): the arithmetic mean of the final results (8.2.3) of the two laboratories;

r is the permissible tolerance within a laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation.

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_c is the number of certifying laboratories;

n is the number of replicate determinations on the reference material (in most cases $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (6) is satisfied, i.e. if the left-hand side is less than or equal to the right-hand side, then the difference, $|A_c - A|$ is statistically insignificant; otherwise it is statistically significant.

When the difference is significant, the analysis shall be repeated simultaneously with an analysis of the test sample. If the difference is again significant, the procedure shall be repeated using a different certified reference material of the same type of ore.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2), one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of ore.

Acceptability of the results for the test sample shall in each case be subject to the acceptability of the results for the certified reference material.

NOTE 7 The following procedure should be used when the information on the reference material certificate is incomplete:

- a) if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression s_{Wc}^2/n_{Wc} and regard s_{Lc} as the standard deviation of the laboratory means;
- b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, it is advisable that this material not be used in the application of the standard. In case its use is unavoidable, use the equation

$$|A_c - A| \leq 2 \sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \quad \dots (7)$$

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material shall be such that the difference between this result and the certified value of the reference material is statistically insignificant. For a reference material that has been analysed by at least 10 laboratories using method(s) that are comparable both in accuracy and in precision with this method, the following condition may be used to test the significance of the difference

$$|A_c - A| \leq 2 \sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \quad \dots (6)$$

where

A_c is the certified value;

A is the result or the mean of results obtained for the reference material;

s_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

8.2.3 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in annex A, calculated to five decimal places and rounded off to the third decimal place as follows:

1) Additional information is given in annexes B and C.