INTERNATIONAL STANDARD

ISO 9684

Iron ores — Determination of vanadium content — Flame atomic absorption spectrometric methods

iTeh STANDARD PREVIEW

Minerais de fer — Dosage du vanadium — Méthodes par spectrométrie d'absorption atomique dans la flamme

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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 voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9684 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.

Iron ores — Determination of vanadium content — Flame atomic absorption spectrometric methods

1 Scope

This International Standard specifies two flame atomic absorption spectrometric methods for the determination of the vanadium content of iron ores.

Method 1 is applicable to vanadium contents between 0,005 % (m/m) and 0,05 % (m/m), and Method 2 to vanadium contents between 0,05 % (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

3.1 Dissolution

Decomposition of the test portion by digestion with hydrochloric acid in a polytetrafluoroethylene (PTFE) beaker, addition of hydrofluoric and nitric acids and evaporation to dryness. Addition of hydrochloric and boric acids and evaporation to dryness. Dissolution of the salts in hydrochloric and nitric acids (Method 1), or hydrochloric acid (Method 2), and filtration. Ignition and fusion of the residue with sodium carbonate and dissolution of the cooled melt in the test solution.

3.2 Determination

3.2.1 Extraction (Method 1 only)

Oxidation with cerium(IV) solution and addition of orthophosphoric acid and sodium tungstate solution. Extraction of the vanadium complex with a 1 + 1 mixture of 1-pentanol and methyl isobutyl ketone. Treatment of the solvent phase with water and then ascorbic acid solution to return the vanadium to an aqueous phase.

3.2.2 Measurement (Methods 1 and 2)

Addition of aluminium solution to the test solution and dilution to volume. Aspiration into a dinitrogen oxide-acetylene flame in an atomic absorption spectrometer and measurement of the absorbance at a wavelength of approximately 318,5 nm.

4 Reagents

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

4.1 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

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

4.3 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (m/m), or ρ 1,19 g/ml, 48 % (m/m).

4.4 Nitric acid, ρ 1,4 g/ml.

4.5 Nitric acid, ρ 1,4 g/ml, diluted 1 + 1. (Method 1 only.)

4.6 Orthophosphoric acid, ρ 1,7 g/ml, diluted 1 + 2. (Method 1 only.)

4.7 Sodium carbonate (Na_2CO_3), anhydrous powder.

4.8 Boric acid (H_3BO_3).

4.9 Ammoniun cerium(IV) nitrate $[(NH_4)_2Ce(NO_3)_6]$, 20 g/l solution. (Method 1 only.)

Dissolve 2,0 g of ammonium cerium(IV) nitrate in a mixture of 15 ml of nitric acid (4.5) and 85 ml of water.

4.10 Sodium tungstate ($Na_2WO_4.2H_2O$), 165 g/l solution. (Method 1 only.)

Dissolve 16,5 g of sodium tungstate dihydrate in approximately 70 ml of water, dilute to 100 ml and mix.

4.11 Ascorbic acid ($C_6H_8O_6$), 10 g/l solution. (Method 1 only.)

Prepare freshly for each series of tests.

4.12 Pentan-1-ol (*n*-amyl alcohol, 1-pentanol). (Method 1 only.)

4.13 4-Methylpentan-2-one (methyl isobutyl ketone, MIBK). (Method 1 only.)

4.14 Mixed solvent. (Method 1 only.)

Prepare a 1 + 1 volume ratio mixture of pentan-1-ol (4.12) and MIBK (4.13).

4.15 Aluminium chloride ($AlCl_3.6H_2O$), 220 g/l solution.

Dissolve 220 g of aluminium chloride hexahydrate in water, add 50 ml of hydrochloric acid (4.1), dilute to 1 000 ml with water and mix.

4.16 Iron oxide, high purity (containing less than 0,002 % V).

4.17 Iron background solution. (Method 2 only.)

Dissolve 90 g of high purity iron oxide (4.16) in 750 ml of hydrochloric acid (4.1) while heating. Cool and carefully add a solution of 30 g of sodium carbonate (4.7) in 200 ml of water. Dilute with water to a final volume of approximately 1 000 ml and mix.

NOTE 1 The use of an equivalent quantity of metallic iron (of similarly low vanadium content) in conjunction with a suitable oxidant is permissible.

4.18 Vanadium standard solution, 1 mg V/ml.

Dry ammonium monovanadate (NH_4VO_3) in an air oven at 100 °C for 1 h and cool to room temperature. Dissolve 2,296 g of the dried product in approximately 600 ml of water, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.19 Diluted vanadium standard solution, 0,2 mg V/ml. (Method 1 only.)

Transfer 20,0 ml of vanadium standard solution (4.18) to a 100 ml one-mark volumetric flask, dilute to volume with water and mix.

4.20 Vanadium calibration solutions. (Method 1 only.)

Transfer 1,8 g of high purity iron oxide (4.16) to each of five 100 ml PTFE beakers (5.1). Proceed according to 7.5.1, incorporating the operation in 7.5.2 to dissolve the evaporated salts.

Transfer 0 ml; 1,00 ml; 2,00 ml; 4,00 ml and 6,00 ml of the diluted standard vanadium solution (4.19) respectively to the beakers. Omit the residue processing steps and add 10 ml of nitric acid (4.5) and 25 ml of water. Evaporate to 50 ml and proceed as specified in 7.5.3.

4.21 Vanadium calibration solutions. (Method 2 only.)

Transfer 0 ml; 1,00 ml; 2,00 ml; 4,00 ml and 6,00 ml of vanadium standard solution (4.18) respectively to five 100 ml one-mark volumetric flasks. Add 10 ml of iron background solution (4.17), 4,0 ml of aluminium chloride solution (4.15) and 0,5 g of boric acid (4.8) to each flask. Dilute to volume with water and mix.

5 Apparatus

Ordinary laboratory equipment, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively (unless otherwise indicated), and

5.1 Polytetrafluoroethylene (PTFE) beakers, of capacity 100 ml, preferably low form.

5.2 Platinum crucibles, of minimum capacity 20 ml.

5.3 Muffle furnace.

5.4 Separating funnels, 100 ml (preferably graduated).

5.5 Atomic absorption spectrometer, equipped with a dinitrogen oxide-acetylene burner.

The atomic absorption spectrometer used in this method will be satisfactory if it meets the following criteria:

a) Minimum sensitivity — the absorbance of the most concentrated vanadium calibration solution (4.21) is at least 0,25 (see note 4).

b) Graph linearity — the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) is not less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability — the standard deviation of the absorbance of the most concentrated calibration solution and that of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, are less than 1,5 % and 0,5 % respectively of the mean value of the absorbance of the most concentrated calibration solution.

NOTES

2   The use of a strip-chart recorder and/or digital read-out device is recommended to evaluate criteria a), b) and c) and for all subsequent measurements.

3   Instrument parameters

— V-hollow cathode lamp, mA	10
— Wavelength, nm	318,5
— Dinitrogen oxide flow rate, l/min	9,5
— Acetylene flow rate, l/min	3,8

The slit width should be sufficiently narrow to substantially reject the stronger emitting but weaker absorbing line at 318,4 nm.

In systems where the values shown above for gas flow rates do not apply, the given ratio of the flow rates (5:2) may still be a useful guideline.

4   To check the instrument criteria when only Method 1 is involved, prepare the highest calibration solution specified for Method 2, omitting the iron background solution.

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 5   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 °C ± 2 °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 6   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   Safety precautions

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the dinitrogen oxide-acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the burner is in operation.

7.3   Test portion

Taking several increments, weigh, to the nearest 0,000 5 g, approximately 2 g (Method 1) or 1 g (Method 2) of the predried test sample obtained in accordance with 6.2.

NOTE 7   The test portion should be taken and weighed quickly, in order to avoid reabsorption of moisture.

7.4 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. A predried test sample of the certified reference material shall be prepared as specified in 6.2.

NOTE 8   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.

7.5 Determination Method 1 [vanadium content between 0,005 % (m/m) and 0,05 % (m/m)]

7.5.1 Decomposition of the test portion

Transfer the test portion (7.3) to a 100 ml PTFE beaker (5.1) and add 25 ml of hydrochloric acid (4.1). Cover and mix, and then digest just at the boiling point for 1 h. Add 0,25 ml of nitric acid (4.4), mix and then digest for a further 10 min. Add 10 ml of hydrofluoric acid (4.3) and evaporate to dryness. Add 10 ml of hydrochloric acid (4.1) and 0,5 g of boric acid (4.8), and repeat the evaporation to dryness.

7.5.2 Dissolution of salts and residue treatment

Add 2 ml of hydrochloric acid (4.2), 4 ml of nitric acid (4.5) and 10 ml of water to the PTFE beaker. Add a stirring rod and heat to dissolve the salts. Filter through a close-texture filter paper into a 150 ml low-form beaker marked at the 50 ml capacity point, adding a further 10 ml of nitric acid (4.5) and 25 ml of water to the original PTFE beaker, while heating, to facilitate cleaning of the beaker and transfer of any residue to the paper. Wash the residue with water.

Transfer the residue to a platinum crucible (5.2), dry, ash and ignite the residue at 600 °C to 700 °C, then fuse over a burner or for 30 min in a muffle furnace (5.3) at 1 000 °C in 0,3 g of sodium carbonate (4.7). Transfer the cooled crucible to the main solution using a stirring rod and leach the melt while evaporating the solution. Remove and rinse the crucible as soon as leaching is complete and continue the evaporation to a volume of 50 ml.

NOTE 9   The leach of the fused residue in the main solution may attack the crucible if the evaporation is accidentally carried too far.

7.5.3 Extraction of vanadium

Add 1 ml of ammonium cerium(IV) nitrate solution (4.9) to the solution from 7.5.2, and mix. Cover, heat to boiling, then remove from the heater and add 5 ml of orthophosphoric acid (4.6) and 2,5 ml of sodium tungstate solution (4.10). Replace the cover and heat to maintain gentle boiling for 10 min.

Cool, transfer to a 100 ml separating funnel (5.4) with minimum washing, and retain the beaker for subsequent use. Add 20 ml of mixed solvent (4.14), shake for 40 s and allow to stand for 1 min. Discard the lower aqueous phase, add 20 ml of water to the separating funnel and shake it for 30 s. Allow the phases to separate for 1 min and transfer the lower aqueous phase to the 150 ml beaker calibrated at the 20 ml point. Add a further 20 ml of water to the separating funnel, shake for 30 s and combine this aqueous phase with the first. Add 10 ml of ascorbic acid solution (4.11) to the funnel containing the solvent phase and shake for 30 s. Allow the phases to separate and transfer the lower aqueous phase to the solution in the beaker. Repeat the extraction of vanadium with a second 10 ml portion of ascorbic acid solution and transfer the aqueous phase to the beaker.

NOTES

10   The separation of phases should occur without the formation of emulsion. If any emulsion does form, add 0,1 ml of nitric acid (4.5) and shake for 15 s.

11   Normally the solvent phase will now be colourless, indicating that the vanadium has been effectively removed. However, with ores containing organic matter, a residual colour which is not due to vanadium may remain. This can usually be ignored, but if it is considered excessive it can be prevented by igniting the test portion in a silica or porcelain crucible at 700 °C for 30 min prior to dissolution.

To the combined water and ascorbic acid strip solutions, add 1 ml of aluminium chloride solution (4.15) and evaporate to approximately 20 ml. Cool, transfer to a 25 ml one-mark volumetric flask, dilute to volume with water and mix.

7.5.4 Adjustment of the atomic absorption spectrometer

Set the wavelength for vanadium (318,5 nm) to obtain minimum absorbance and, following the manufacturer's instructions, fit the correct burner and light the flame. After 10 min of preheating the burner, aspirate the calibration solution of highest

vanadium content (4.21, Method 2), and following the manufacturer's instructions concerning the minimum flow rate of acetylene, adjust the gas flows and burner height to obtain maximum absorbance.

Aspirate water and the calibration solution to establish that the absorbance reading is not drifting. Set the reading for water to zero absorbance and evaluate the criteria in 5.5.

7.5.5 Atomic absorption measurements

Aspirate the calibration and test solutions in order of increasing absorption, starting with the blank test solution and the zero calibration solution. Aspirate water between readings, reset to zero if necessary, and record the readings when stable responses are obtained. Repeat the measurements at least twice.

Calculate the average absorbance of the calibration and test solutions. Correct the absorbance values obtained for the calibration solutions by subtracting the absorbance of the zero calibration solution, and prepare a calibration graph by plotting the net absorbance values against micrograms of vanadium per millilitre. If the graph is substantially linear, subtract the absorbance obtained for the blank test from the absorbance obtained for the test solution and, using the graph, convert the net absorbance to micrograms of vanadium per millilitre.

NOTE 12   If any curvature obtained approaches the limit specified in 5.5 b), replot the graph using uncorrected values for all solutions and establish the concentration of the zero calibration solution from the intercept of the graph on the negative side of the concentration axis. Add this value to the nominal concentration values of the calibration solutions and replot the graph to pass through the origin. Determine from the graph the concentration of vanadium, in micrograms per millilitre, in the blank test and test solution respectively and correct the concentration of the test solution with the concentration of the blank test.

7.6 Determination Method 2 [vanadium content between 0,05 % (m/m) and 0,5 % (m/m)]

7.6.1 Decomposition of the test portion

Decompose the test portion as specified in 7.5.1.

7.6.2 Dissolution of salts and residue treatment

Add 10 ml of hydrochloric acid (4.2) and a stirring rod to the PTFE beaker and heat to dissolve the salts. Add 20 ml of water and continue heating for several minutes, if necessary, to complete the dissolution. Filter through a close-texture filter paper

into a 100 ml one-mark volumetric flask and wash the residue with water. Transfer the residue to a platinum crucible (5.2), dry, ash and ignite the residue, then fuse over a burner or for 30 min in a muffle furnace (5.3) at 1 000 °C in 0,3 g of sodium carbonate (4.7). Cool the melt and treat in the covered crucible with 5 ml of water and 5 ml of hydrochloric acid (4.2). Warm to dissolve the fused salts and combine with the main test solution. Cool, add 4 ml of aluminium chloride solution (4.15), dilute to volume with water and mix.

Continue with the determination of vanadium content as specified in 7.5.4 and 7.5.5.

8 Expression of results

8.1 Calculation of vanadium content

The vanadium content, w_V, is calculated as a percentage by mass, from the equations

$$\text{Method 1: } w_V = \frac{2,5\rho_V}{1\,000m} \qquad \ldots (1)$$

$$\text{Method 2: } w_V = \frac{\rho_V}{100m} \qquad \ldots (2)$$

where

ρ_V is the concentration, in micrograms per millilitre, of vanadium in the test solution;

m is the mass, in grams, of the test portion.

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 equations[1]:

Method 1

$$r = 0,026\,0\,X + 0,000\,6 \qquad \ldots (3)$$

$$P = 0,033\,0\,X + 0,001\,5 \qquad \ldots (4)$$

$$\sigma_r = 0,009\,2\,X + 0,000\,2 \qquad \ldots (5)$$

$$\sigma_L = 0,009\,2\,X + 0,000\,5 \qquad \ldots (6)$$

Method 2

$$r = 0,012\,1\,X + 0,005\,9 \qquad \ldots (7)$$

$$P = 0,099\,3\,X - 0,000\,8 \qquad \ldots (8)$$

$$\sigma_r = 0,004\,3\,X + 0,002\,1 \qquad \ldots (9)$$

$$\sigma_L = 0,035\,7\,X - 0,000\,9 \qquad \ldots (10)$$

where

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

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

— within-laboratory equations (3), (5), (7) and (9): the arithmetic mean of the duplicate values,

— between-laboratories equations (4), (6), (8) and (10): 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.

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 insignifiant. For a reference material that has been analysed by at least 10 laboratories using method(s) that are comparable in both accuracy and precision with this method, the following condition may be used to test the significance of the difference:

$$|A_c - A| \leqslant 2\sqrt{\dfrac{s_{Lc}^2 + \dfrac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \dfrac{\sigma_r^2}{n}} \qquad \ldots (11)$$

where

A_c is the certified value;

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

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

s_{Wc} is the within-laborarory 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 certified reference material (in most cases, $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (11) 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 (3) or (7), 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 13   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

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \dfrac{\sigma_r^2}{n}} \qquad \ldots (12)$$

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:

a) when the figure in the fourth decimal place is less than 5, it is discarded and the figure in the third decimal place is kept unchanged;

b) when the figure in the fourth decimal place is 5 and there is a figure other than 0 in the fifth decimal place, or when the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by one;

c) when the figure in the fourth decimal place is 5 and figure 0 is in the fifth decimal place, the 5 is discarded and the figure in the third decimal

place is kept unchanged if it is 0, 2, 4, 6 or 8, and is increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

$$w_{V_2O_5} (\%) = 1{,}785\ 2\ w_V (\%)$$

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this International Standard;

d) details necessary for the identification of the sample;

e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the result, either for the test sample or the certified reference material(s).