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železove rude -- Določitev vsebnosti titana -- Diantipirilmetanov spektrofotometrični postopek

Iron ores -- Determination of titanium content -- Diantipyrylmethane spectrophotometric method

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Minerais de fer -- Dosage du titane -- Méthode spectrophotométrique au diantipyrylméthane

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International Standard



4691

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**Iron ores — Determination of titanium content —
Diantipyrylmethane spectrophotometric method**

Minerais de fer — Dosage du titane — Méthode spectrophotométrique au diantipyrylméthane

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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.

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 4691 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Iron ores — Determination of titanium content — Diantipyrylmethane spectrophotometric method

1 Scope and field of application

This International Standard specifies a spectrophotometric method using diantipyrylmethane for the determination of titanium content in iron ores.

This method is applicable to a concentration range of 0,01 to 6,0 % (*m/m*) of titanium in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

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

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

ISO 3081, *Iron ores — Increment sampling — Manual method.*¹⁾

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.*²⁾

ISO 3083, *Iron ores — Preparation of samples — Manual method.*³⁾

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

3 Principle

Decomposition of the test portion:

a) By treatment with hydrochloric, nitric and sulfuric acids, filtration and ignition of the residue, followed by treatment with hydrofluoric and sulfuric acids and fusion with potassium pyrosulfate. Dissolution of the melt in the main solution.

b) By sintering with sodium peroxide, followed by treatment with hydrochloric and sulfuric acids, filtration and ignition of the residue, followed by treatment with hydrofluoric and sulfuric acids and fusion with potassium pyrosulfate. Dissolution of the melt in the main solution.

c) By fusion with sodium tetraborate/sodium carbonate mixture, followed by treatment with hydrochloric acid. Not applicable to samples containing more than 8 % (*m/m*) silicon.

Reduction of the iron with ascorbic acid. Colour development with diantipyrylmethane, and measurement of the absorbance at approximately 385 nm.

4 Reagents

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

4.1 Potassium pyrosulfate ($K_2S_2O_7$).

4.2 Sodium peroxide (Na_2O_2), fine powder.

4.3 Sodium tetraborate, anhydrous ($Na_2B_4O_7$), first dried at 60 to 70 °C, then at 160 °C, and finally calcined at 400 °C.

4.4 Sodium carbonate, anhydrous (Na_2CO_3).

4.5 Fusion mixture: 1 part by mass of the sodium tetraborate (4.3) mixed with 1 part by mass of the sodium carbonate (4.4) and stored in a closed vessel.

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

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

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

4.9 Nitric acid, ρ 1,4 g/ml.

4.10 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (*m/m*) solution.

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

1) At present at the stage of draft. (Revision of ISO 3081-1973).

2) At present at the stage of draft.

3) At present at the stage of draft. (Revision of ISO 3083-1973.)

4.12 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 9.

4.13 Sulfuric acid, ρ 1,84 g/ml, diluted 2 + 98.

4.14 Diantiprylmethane, solution, 15 g/l.

Dissolve 15 g of diantiprylmethane monohydrate ($C_{23}H_{24}O_2N_4 \cdot H_2O$) in about 300 ml of water and 30 ml of sulfuric acid (4.11) and dilute with water to 1 litre. If a residue remains in the solution, filter off the residue. Store the solution in a brown bottle.

4.15 Ascorbic acid, 100 g/l solution.

The solution should be freshly prepared.

4.16 Ammonium iron(III) sulfate, 100 g/l solution.

Dissolve 100 g of ammonium iron(III) sulfate in 500 ml of water acidified with 5 ml of sulfuric acid (4.11). Dilute to 1 litre and mix.

4.17 Titanium, standard solution corresponding to 0,1 g of Ti per litre.

Weigh 0,167 g of titanium dioxide (TiO_2) calcined previously at 900 to 950 °C for about 40 min in a platinum crucible and fuse with 3 to 4 g of the potassium pyrosulfate (4.1) at a temperature of 650 to 700 °C until the clear melt is obtained. After cooling, place the crucible in a 100 ml beaker, add 50 to 60 ml of sulfuric acid (4.12) and dissolve the cooled melt with moderate heating. After washing the platinum crucible with sulfuric acid (4.12), transfer the solution to a 1 000 ml volumetric flask, dilute with sulfuric acid (4.12) to volume and mix.

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

4.18 Titanium, standard solution corresponding to 20 mg of Ti per litre.

Pipette a 50 ml aliquot of the titanium standard solution (4.17) into a 250 ml volumetric flask, dilute with sulfuric acid (4.12) to volume and mix.

1 ml of this standard solution contains 0,02 mg of Ti.

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, and

Spectrophotometer, suitable for the measurement of absorbance at a wavelength of 385 nm, together with 10 mm cells.

6 Sampling and samples

6.1 Laboratory samples

For analysis, use a laboratory sample of minus 100 μ m 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 μ m.

NOTE — 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 manner that it is representative of the whole contents of the container. Dry the test sample at 105 ± 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 — 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 either case, appropriate recalibration.

7.2 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 — 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 either case no significant changes in the analytical procedure would 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 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.

7.3 Test portion

Taking several increments, weigh, to the nearest 0,000 1 g, approximately the amount of the predried test sample (6.2) according to table 1.

Table 1

Ti content, w_{Ti} % (m/m)	Mass of test portion g	Aliquot (7.4.2) ml
$0,01 < w_{Ti} \leq 0,1$	0,5	30,0
$0,1 < w_{Ti} \leq 0,3$	0,5	20,0
$0,3 < w_{Ti} \leq 1,0$	0,5	5,0
$1,0 < w_{Ti} \leq 6,0$	0,13	5,0

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

7.4 Determination

7.4.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as instructed in 7.4.1.1. If it is on alkali sintering, proceed as instructed in 7.4.1.2, and if it is on fusion, proceed as instructed in 7.4.1.3, respectively.

7.4.1.1 Acid attack

Place the test portion (7.3) in a 300 ml beaker, moisten with a few drops of water, add 30 ml of hydrochloric acid (4.6), cover with a watch-glass, and heat gently to decompose. Add 5 ml of the nitric acid (4.9) and 10 ml of sulfuric acid (4.11), remove the watch-glass, heat cautiously to dense white fumes, and continue heating for about 10 min. Allow the beaker to cool, add 20 ml of hydrochloric acid (4.7) and about 50 ml of water, and heat to dissolve the soluble salts.

Filter the solution through a medium-texture filter paper, scrub the wall of the beaker with a rubber-tipped glass rod, and transfer the residue to the filter paper. Wash the residue two or three times with hot sulfuric acid (4.13) and two or three times with hot water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution.

Place the filter paper and the residue in a platinum crucible, dry, char, ignite and cool. Moisten the residue in the crucible with sulfuric acid (4.11), add 5 ml of the hydrofluoric acid (4.10) and heat gently to expel the silicon tetrafluoride and sulfuric acid. Allow the crucible to cool, add about 2 g of the potassium pyrosulfate (4.1), cover with a platinum lid, and heat first gently, then finally to dull red heat to fuse the residue.

NOTE — If necessary for complete fusion, the amount of potassium pyrosulfate may be increased to 5 g in all.

After cooling, transfer the crucible and lid to the 300 ml beaker containing the main solution, heat to dissolve the cooled melt, and take out the crucible and lid after washing with water. Transfer the solution to a 200 ml volumetric flask, dilute to volume and mix.

7.4.1.2 Alkali sintering

Place the test portion in a nickel crucible, add 3 g of the sodium peroxide (4.2), mix well using a platinum or nickel spatula, and tamp the mixture. Place the crucible for 1 or 2 min at the entrance of a muffle furnace, the temperature of which is regulated at 400 ± 20 °C, and then into the furnace for about 1 h to effect sintering. Take the crucible out of the furnace and cool. Transfer the sintered mass to a 300 ml beaker, cover the beaker with a watch-glass and add about 30 ml of water.

NOTE — If the volume of water added is insufficient, bumping may occur on subsequent heating. As a safety precaution, the volume may be increased up to 100 ml.

Rinse the crucible first with water and then once with hydrochloric acid (4.8), and add the washings to the mass in the beaker. Acidify slowly with 30 ml of hydrochloric acid (4.6), cover the beaker with a watch-glass and heat the solution gently to decompose the excess of peroxide. Remove the watch-glass, add 10 ml of sulfuric acid (4.11), heat cautiously to dense white fumes and continue heating for about 10 min. Allow the beaker to cool, add 20 ml of hydrochloric acid (4.7) and about 50 ml of water, and heat to dissolve the soluble salts.

Filter the solution through a medium-texture filter paper, scrub the wall of the beaker with a rubber-tipped glass rod, and transfer the residue to the filter paper. Wash the residue two or three times with hot sulfuric acid (4.13) and two or three times with hot water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution.

Place the filter paper and the residue in a platinum crucible, dry, char, ignite and cool. Moisten the residue in the crucible with sulfuric acid (4.11), add 5 ml of hydrofluoric acid (4.10) and heat gently to expel the silicon tetrafluoride and sulfuric acid. Allow the crucible to cool, add about 2 g of the potassium pyrosulfate (4.1), cover with a platinum lid, and heat first gently, then finally to dull red heat to fuse the residue.

NOTE — If necessary for complete fusion, the amount of potassium pyrosulfate may be increased to 5 g in all.

After cooling, transfer the crucible and lid to the 300 ml beaker containing the main solution, heat to dissolve the cooled melt, and take out the crucible and lid after washing with water. Transfer the solution to a 200 ml volumetric flask, dilute to volume and mix.

7.4.1.3 Alkali fusion

Mix the test portion with 5 g of fusion mixture (4.5) in a platinum crucible, cover with a platinum lid, heat gently, and after melting fuse at a temperature of 1 000 to 1 050 °C for about 10 min. Remove from the heat and swirl cautiously to cause the cooling melt to solidify in a thin layer on the wall of the crucible. Allow the crucible to cool, place the crucible and lid and the contents in a 300 ml beaker and add 100 ml of hydrochloric acid (4.8). Dissolve the melt, take out the crucible and lid and wash into the beaker.

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NOTE — If an undissolved residue remains, such residue should be filtered and discarded.

Transfer the solution into a 200 ml volumetric flask, dilute to volume and mix.

7.4.2 Spectrophotometric determination

Pipette an aliquot, given in table 1, of the test solution and the blank solution, respectively, into 100 ml volumetric flasks, add 5 ml of ammonium iron(III) sulfate solution (4.16), add 10 ml of the ascorbic acid solution (4.15) and shake. Add 15 ml of hydrochloric acid (4.7) and 30 ml of the diantipyrylmethane solution (4.14), dilute to volume with water and mix (the final test solution).

Allow to stand for at least 20 min and measure the absorbance at a wavelength of approximately 385 nm in a 10 mm cell using the blank test solution as a reference.

NOTES

1 20 mm cells may be used, if necessary, for test solutions of lowest titanium contents.

2 When the fusion decomposition is applied to samples containing more than 1 % (*m/m*) silicon, the test solution, after colour development and just before measuring the absorbance, should be filtered to remove possible precipitates of silica.

3 The colour is stable for at least 24 h.

Determine the concentration, expressed in micrograms per millilitre, of titanium from the absorbance using the calibration graph prepared as instructed in 7.4.3.

7.4.3 Preparation of calibration graph

Take 0,0; 1,0; 3,0; 5,0; 7,0; and 10,0 ml of the titanium standard solution (4.18) into six 100 ml volumetric flasks, add 5 ml of the ammonium iron(III) sulfate solution (4.16) and 10 ml of the ascorbic acid solution (4.15), and shake. Add 15 ml of hydrochloric acid (4.7) and 30 ml of the diantipyrylmethane solution (4.14) to each flask, dilute to volume and proceed as instructed in 7.4.2. Plot the relationship between the concentration, expressed in micrograms per millilitre, of titanium and the absorbance to prepare the calibration graph.

8 Expression of results

8.1 Calculation of titanium content

The titanium content, w_{Ti} , as a percentage by mass, is calculated to five decimal places for contents lower than 1 % (*m/m*) and to four decimal places for contents higher than 1 % (*m/m*), using the equation

$$w_{Ti} (\%) = \frac{c \times 100}{m_1 \times 1\,000\,000} \times 100 = \frac{c}{100 m_1} \quad \dots (1)$$

where

c is the concentration, in micrograms per millilitre, of titanium in the final test solution;

m_1 is the mass, in grams, of sample represented in the 100 ml of final test solution calculated from the equation

$$m_1 = \frac{m_0 \times V}{200}$$

in which

m_0 is the mass of the test portion (table 1);

V is the volume of the aliquot (table 1).

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⁾

Decomposition method

Regression formulae

Acid attack $r = 0,020\,4x + 0,004\,5 \quad \dots (2)$

$P = 0,044\,7x + 0,007\,0 \quad \dots (3)$

$\sigma_r = 0,007\,2x + 0,001\,6 \quad \dots (4)$

$\sigma_L = 0,015\,0x + 0,002\,2 \quad \dots (5)$

Alkali sintering $r = 0,022\,3x + 0,001\,5 \quad \dots (6)$

$P = 0,074\,1x - 0,001\,8 \quad \dots (7)$

for $0,01 < x < 0,024\,3 \quad P = 1,96 \sigma_r$

$\sigma_r = 0,007\,9x + 0,000\,5 \quad \dots (8)$

$\sigma_L = 0,025\,6x - 0,000\,8 \quad \dots (9)$

Alkali fusion $r = 0,020\,2x + 0,004\,1 \quad \dots (10)$

$P = 0,051\,9x + 0,007\,6 \quad \dots (11)$

$\sigma_r = 0,007\,1x + 0,001\,5 \quad \dots (12)$

$\sigma_L = 0,017\,6x + 0,002\,5 \quad \dots (13)$

where

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;

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

— within laboratory equations (2, 4, 6, 8, 10, 12); the arithmetic mean of the duplicate values,

— between laboratory equations (3, 5, 7, 9, 11, 13); the arithmetic mean of the final results (8.2.3) of the two laboratories.

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

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 certificate 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 precision with this method, the following condition may be used to test the significance of the difference:

$$|A_c - A| \leq 2 \sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \quad \dots (14)$$

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;

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 sample (in most cases $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (14) 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 equations (2) or (6) or (10) as appropriate, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with a corresponding blank test and 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 — The following procedure should be used when the information on the reference material certificate is incomplete:

- 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;

- if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the formula

$$|A_c - A| \leq 2 \sqrt{2 \sigma_L^2 + \frac{\sigma_r^2}{n}}$$

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 for contents of titanium lower than 1 % (m/m) and to four decimal places for contents higher than 1 % (m/m).

For contents of titanium lower than 1 % (m/m) the value calculated to five decimal places is rounded off to the third decimal place as follows:

- 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;
- 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;
- when the figure in the fourth decimal place is 5 and there is no figure other than 0 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 increased by one if it is 1, 3, 5, 7 or 9.

In a similar manner, with the ordinal numbers decreased by one, the value for contents of titanium higher than 1 % (m/m) is rounded off to the second decimal place.

8.3 Oxide factor

$$w_{TiO} (\%) = 1,668 w_{Ti} (\%)$$

9 Test report

The test report shall include the following information:

- reference to this International Standard;
- details necessary for the identification of the sample;
- result of the analysis;
- reference number of the result;
- 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).