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Steel and iron — Determination of titanium content — Diantipyrylmethane spectrophotometric method

Aciers et fontes — Dosage du titane — Méthode spectrophotométrique au diantipyrylméthane

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Foreword

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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 10280 was prepared by Technical Committee ISO/TC 17, *Steel*.

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

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Steel and iron — Determination of titanium content — Diantipyrylmethane spectrophotometric method

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1 Scope

This International Standard specifies a diantipyrylmethane spectrophotometric method for the determination of titanium in steel and iron.

The method is applicable to titanium contents between 0,002 % (*m*/*m*) and 0,80 % (*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 indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

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 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

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 in hydrochloric, nitric and sulfuric acids.

Fusion of the residue with potassium hydrogen sulfate.

Formation of a yellow complex with 4,4′-diantipyrylmethane.

Spectrophotometric measurement of the coloured complex at a wavelength of about 385 nm.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

4.1 Iron, of high purity containing less than 2 µg Ti/g.

4.2 Potassium hydrogen sulfate ($KHSO_4$).

4.3 Sodium carbonate (Na_2CO_3), anhydrous.

4.4 Hydrochloric acid, ρ about 1,19 g/ml.

4.5 Nitric acid, ρ about 1,40 g/ml.

4.6 Hydrofluoric acid, ρ about 1,15 g/ml.

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

4.8 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 3.

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

4.10 Tartaric acid solution, 100 g/l.

4.11 Ascorbic acid solution, 100 g/l.

Prepare this solution immediately before use.

4.12 Ammonium oxalate solution.

Dissolve 6 g of ammonium oxalate monohydrate $[(COONH_4)_2.H_2O]$ in water and dilute to 200 ml.

4.13 Iron solution, 12,5 g/l.

Dissolve 1,25 g of iron (4.1) in 10 ml of hydrochloric acid (4.7) while heating gently. Add 5 ml of nitric acid (4.5) and boil until the volume of the solution is approximately 10 ml. Cool, transfer to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.14 Reagent blank solution.

Prepare a reagent blank solution in parallel with the determination, using the same quantities of reagents as those used for the determination but no iron. Follow exactly the procedure described in 7.3.1 and 7.3.2, diluting to 100 ml with water.

4.15 Diantipyrylmethane solution.

Dissolve 4 g of 4,4′-methylenebis(2,3-dimethyl-1-phenyl-5-pyrazolone) monohydrate, $C_{23}H_{24}O_2N_4.H_2O$, (diantipyrylmethane) in 20 ml of hydrochloric acid (4.7) and dilute to 100 ml with water.

4.16 Titanium standard solution

4.16.1 Titanium stock solution, corresponding to 1 g of Ti per litre.

Weigh, to the nearest 0,000 1 g, 0,500 g of high purity titanium metal [purity > 99,9 % (*m*/*m*)] and transfer to a 300 ml beaker. Add 180 ml of sulfuric acid, ρ about 1,84 g/ml, diluted 1 + 3, cover with a watchglass, heat gently until the metal has dissolved and oxidize with nitric acid (4.5) added drop by drop. Cool, transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

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

4.16.2 Titanium standard solution, corresponding to 50 mg of Ti per litre.

Transfer 10,0 ml of titanium stock solution (4.16.1) to a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Prepare this solution immediately before use.

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

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus, and

5.1 Crucible, of platinum metal or platinum-gold alloy, of capacity 30 ml.

5.2 Spectrophotometer.

The spectrophotometer shall be equipped to measure absorbance at a wavelength of 385 nm.

Wavelength measurement shall be accurate to ± 2 nm or less. In the absorbance range 0,05 to 0,85, absorbance measurements shall be repeatable to ± 0,003 or better.

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,000 5 g, a test portion according to the presumed titanium content as follows:

a) for titanium contents in the range 0,002 % (*m*/*m*) to 0,125 % (*m*/*m*), a test portion of 1,00 g;

b) for titanium contents in the range 0,125 % (*m*/*m*) to 0,80 % (*m*/*m*), a test portion of 0,50 g.

7.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents and the same cell as in the determination, substituting an equivalent amount of iron (4.1) for the test portion.

7.3 Determination

7.3.1 Dissolution of the test portion

Place the test portion (7.1) in a 250 ml beaker. Add 20 ml of hydrochloric acid (4.4), cover the beaker with a watchglass and digest at 70 °C to 90 °C until the solvent action ceases. Add 5 ml of nitric acid (4.5) and boil until the volume of the solution is approximately 10 ml.

Cool the solution, add 20 ml of sulfuric acid (4.9) and evaporate until fumes of sulfur trioxide appear. Just before fuming occurs, solids will begin to form and

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gentle heating is required to avoid spurting. Once fuming begins the mixture becomes stable and may be fumed briefly at a higher temperature. Avoid overfuming, particularly with chromium-bearing alloys, as the chromium salts deposited are difficult to redissolve.

Cool, add 20 ml of hydrochloric acid (4.8) and warm to redissolve the salts.

Filter through a low ash, medium texture filter paper and wash with hot water. Wash with 10 ml of hydrochloric acid (4.7) and again with hot water. Retain the filtrate.

7.3.2 Treatment of insoluble residue

Transfer the filter paper and residue to a crucible (5.1), dry and ignite at as low a temperature as possible until all carbonaceous matter is removed and finally maintain at about 700 °C for at least 15 min. Cool, add several drops of sulfuric acid (4.9) and 2 ml of hydrofluoric acid (4.6), evaporate to dryness and ignite at 700 °C.

NOTE 1 For test portions containing tungsten proceed as specified in clause 9.

Fuse the residue with 1,0 g of potassium hydrogen sulfate (4.2) over a Bunsen burner and cool. Dissolve by heating with 10 ml of tartaric acid solution (4.10) and add to the original filtrate. Transfer to a 100 ml or 200 ml one-mark volumetric flask according to table 1, dilute to the mark with water and mix.

7.3.3 Colour development

Transfer two aliquots according to table 1 to separate 50 ml one-mark volumetric flasks, to prepare the test solution and the compensating solution. Make the following additions by means of burettes or pipettes, swirling after each addition.

a) Test solution:

- iron solution (4.13) if required (see table 1);
- reagent blank solution (4.14) if required (see table 1);
- 2,0 ml of ammonium oxalate solution (4.12);
- 6,0 ml of hydrochloric acid (4.7);
- 8,0 ml of ascorbic acid solution (4.11), allow to stand for 5 min;
- 10,0 ml of diantipyrylmethane solution (4.15).

b) Compensating solution:

- iron solution (4.13) if required (see table 1);
- reagent blank solution (4.14) if required (see table 1);
- 2,0 ml of ammonium oxalate solution (4.12);
- 8,0 ml of hydrochloric acid (4.7);
- 8,0 ml of ascorbic acid solution (4.11), allow to stand for 5 min.

Dilute solutions a) and b) to the mark with water and mix. Allow to stand for 30 min at room temperature (between 20 °C and 30 °C). If the room temperature is between 15 °C and 20 °C, increase the standing time to 60 min.

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Table 1

Titanium content % (*m*/*m*)	Mass of test portion (m) g	Dilution volume of test solution (7.3.2) (V_0) ml	Volume of aliquot (V_1) ml	Volume of iron solution (4.13) added ml	Volume of reagent blank solution (4.14) added ml	Cell optical path length cm
0,002 to 0,050	1,0	100	10,0	—	—	2
0,050 to 0,125	1,0	100	10,0	—	—	1
0,125 to 0,50	0,5	200	10,0	6,0	5,0	1
0,50 to 0,80	0,5	200	5,0	7,0	7,5	1

7.3.4 Spectrophotometric measurement

Set the wavelength of the spectrophotometer (5.2) to about 385 nm.

Place the optical cell containing water in the spectrophotometer and set the instrument to zero absorbance. Use a size of cell which is suitable for covering the range required (see table 1). When changing the cell size it is necessary to re-zero the spectrophotometer using the new cell.

Measure the absorbances of the coloured test solutions and the compensating solutions of the test sample and the blank test.

For each pair of absorbance readings, determine the net absorbance by subtracting the absorbance of the compensating solution from that of the test solution.

7.4 Establishment of the calibration graph

7.4.1 Preparation of the calibration solutions

Weigh, to the nearest 0,001 g, 1,000 g portions of iron (4.1) into a series of 250 ml beakers. Add titanium standard solution (4.16.2) as indicated in table 2, and treat as described in 7.3.1.

Add 10 ml of hydrochloric acid (4.7), 1,0 g of potassium hydrogen sulfate (4.2) and 10 ml of tartaric acid solution (4.10) to each filtrate. Mix well to dissolve. Cool and transfer to a series of 100 ml one-mark volumetric flasks, dilute to the mark with water and mix.

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Table 2

Titanium content % (*m*/*m*)	Titanium standard solution (4.16.2) ml	Concentration of titanium in the coloured calibration solutions µg/ml	Corresponding titanium content in the test portion % (*m*/*m*)
0,002 to 0,050	0[1]	0	0
	1	0,1	0,005
	3	0,3	0,015
	5	0,5	0,025
	7	0,7	0,035
	10	1,0	0,050
0,050 to 0,125	0[1]	0	0
	5	0,5	0,025
	10	1,0	0,050
	15	1,5	0,075
	20	2,0	0,100
	25	2,5	0,125
0,125 to 0,50	0[1]	0	0
	5	0,5	0,100
	10	1,0	0,200
	15	1,5	0,300
	20	2,0	0,400
	25	2,5	0,500
0,50 to 0,80	0[1]	0	0
	5	0,5	0,20
	10	1,0	0,40
	15	1,5	0,60
	20	2,0	0,80

1) Zero member.

Transfer 10,0 ml aliquots of each calibration solution into separate 50 ml one-mark volumetric flasks and complete the colour development as described in 7.3.3. It is not necessary to add iron solution (4.13) and reagent blank solution (4.14).

NOTE 2 It is not necessary to prepare a compensating solution for each calibration solution. Prepare the compensating solution for the zero member only and use it to compensate for each of the calibration solutions.

7.4.2 Spectrophotometric measurement

Carry out a spectrophotometric measurement of each solution as described in 7.3.4. For expected titanium contents up to 0,050 % (*m*/*m*), carry out the measurements in a cell of 2 cm optical path length. For the remainder, measure in a cell of 1 cm optical path length.

7.4.3 Plotting the calibration graph

Prepare the calibration graphs by plotting net absorbance values against the titanium concentrations, expressed in micrograms per millilitre, in the measured solutions.

8 Expression of results

8.1 Method of calculation

Convert the net absorbance (see 7.3.4) into the corresponding concentration, expressed in micrograms of Ti per millilitre, in the colour-developed test solution by using the calibration graph (7.4.3).

The titanium content, expressed as a percentage by mass, w_{Ti}, is given by the equation

$$w_{\mathrm{Ti}} = (\rho_{\mathrm{Ti},1} - \rho_{\mathrm{Ti},0}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_{\mathrm{t}}}{m} \times 100$$

$$= (\rho_{\mathrm{Ti},1} - \rho_{\mathrm{Ti},0}) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{50}{m} \times 100$$

$$= \frac{V_0(\rho_{\mathrm{Ti},1} - \rho_{\mathrm{Ti},0})}{200 m V_1}$$

where

$\rho_{\mathrm{Ti},0}$ is the concentration, expressed in micrograms per millilitre, of titanium in the blank test solution (corrected for its compensating solution);

$\rho_{\mathrm{Ti},1}$ is the concentration, expressed in micrograms per millilitre, of titanium in the test solution (corrected for its compensating solution);

V_0 is the volume, in millilitres, of the test solution (see 7.3.2 and table 1);

V_1 is the volume, in millilitres, of the aliquot portion (see table 1);

V_{t} is the volume, in millilitres, of colour-developed solution (see 7.3.3);

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

8.2 Precision

A planned trial of this method was carried out by 17 laboratories, at nine levels of titanium, each laboratory making three determinations (see notes 3 and 4) of titanium content at each level.

The test samples used are listed in table A.1.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between titanium content and repeatability (r) and reproducibility (R and R_{w}) of the test results (see note 5) as summarized in table 3. The graphical representation of the figures is given in annex B.

Table 3

Titanium content % (*m*/*m*)	Repeatability r	Reproducibility R	R_{w}
0,002	0,000 35	0,000 80	0,000 68
0,005	0,000 54	0,001 3	0,000 99
0,010	0,000 75	0,002 0	0,001 3
0,025	0,001 2	0,003 3	0,001 9
0,050	0,001 6	0,004 8	0,002 5
0,10	0,002 2	0,007 1	0,003 4
0,25	0,003 4	0,011 9	0,004 9
0,50	0,004 7	0,017 5	0,006 5
0,80	0,005 8	0,022 7	0,007 8

NOTES

3 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.

4 The third determination was carried out at a different time (on a different day) by the same operator as in note 3 using the same apparatus with a new calibration.

5 From the results obtained on day 1 the repeatability (r) and the reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_{w}) was calculated.

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9 Special case

For test portions containing tungsten, fuse the residue from the sulfuric acid-hydrofluoric acid treatment with 5 g of sodium carbonate (4.3) at 950 °C. Cool and dissolve the melt in 200 ml of water. Heat to boiling and filter through a medium texture filter paper while washing with hot water. Discard the filtrate. Transfer the filter paper and residue to a crucible (5.1), dry and ignite at 700 °C.

Proceed as specified in the 2nd paragraph of 7.3.2, from “Fuse the residue with 1,0 g of potassium hydrogen sulfate (4.2) ...” to the end.

Carry out a separate blank test (7.2) and prepare a separate reagent blank solution (4.14) to cover this procedure.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of 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.

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Annex A
(informative)

Additional information on the international cooperative tests

Table 3 was derived from the results of international analytical trials carried out in 1987 and 1988 on eight steel samples and one pig iron sample in eight countries involving 17 laboratories.

The results of the trials were reported in document 17/1 N 807, May 1989. The graphical representation of the precision data is given in annex B.

The test samples used are listed in table A.1.

Table A.1

Sample	Titanium content % (m/m)		
	Certified	Found $\overline{w}_{\mathrm{Ti},1}$	$\overline{w}_{\mathrm{Ti},2}$
BHP-D3 (Mild steel)	0,002[1]	0,001 9	0,001 9
NBS 11h (Mild steel)	0,004	0,003 7	0,003 6
JSS 500-5 (Low alloyed steel)	0,008	0,006 1	0,006 0
JSS 169-5 (Mild steel)	0,012	0,010 7	0,010 8
BCS 453 (Mild steel)	0,016	0,014 1	0,014 4
JSS 171-3 (Mild steel)	0,036	0,035 0	0,034 9
JSS 102-4 (Pig iron)	0,083	0,080 9	0,080 9
NBS 121d (Stainless steel)	0,342	0,339	0,340
BCS 398 (Permanent magnet alloy)	0,79	0,764	0,764

$\overline{w}_{\mathrm{Ti},1}$: general mean within a day
$\overline{w}_{\mathrm{Ti},2}$: general mean between days

1) Non-certified value.

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