

TC 17

International Standard



4936

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Steel and cast iron — Determination of chromium content — Diphenylcarbazide spectrophotometric method

Aciers et fontes — Dosage du chrome — Méthode spectrophotométrique à la diphenylcarbazide

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Foreword

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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 4936 was prepared by Technical Committee ISO/TC 17, *Steel*.

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Steel and cast iron — Determination of chromium content — Diphenylcarbazide spectrophotometric method

1 Scope and field of application

This International Standard specifies a diphenylcarbazide spectrophotometric method for the determination of chromium in steel and cast iron.

The method is applicable to chromium contents between 0,01 and 0,25 % (m/m).

2 Reference

ISO/R 377, *Selection and preparation of samples and test pieces for wrought steel.*

3 Principle

Dissolution of a test portion in nitric and perchloric acids.

Oxidation of chromium in a phosphoric perchloric medium by potassium permanganate.

Oxidation of diphenylcarbazide by chromium(VI).

Spectrophotometric measurement of the oxidized form of diphenylcarbazide at a wavelength of about 540 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 Phosphoric acid, ρ about 1,71 g/ml, diluted 1 + 9.

4.2 Acid mixture.

Mix 30 ml of perchloric acid (ρ about 1,67 g/ml), 15 ml of nitric acid (ρ about 1,40 g/ml) and 15 ml of water.

Prepare fresh as needed. Do not store.

4.3 Potassium permanganate, 3,16 g/l solution.

4.4 Sodium azide (NaN_3), 10 g/l solution.

4.5 Diphenylcarbazide, 2,5 g/l solution in acetone.

Dissolve 0,25 g of diphenylcarbazide in 100 ml of acetone. Prepare this solution immediately before use.

4.6 Iron, standard solution corresponding to 5 g of Fe per litre.

Weigh, to the nearest 0,001 g, 1,000 g of pure iron free from chromium or with a chromium content as low as possible and known exactly. Proceed with the dissolution as specified in 7.3.1.

1 ml of this standard solution contains 5 mg of Fe.

4.7 Chromium, standard solution.

4.7.1 Chromium, stock solution corresponding to 1 g of Cr per litre.

Weigh, to the nearest 0,1 mg, 2,829 0 g of potassium dichromate, previously dried in an oven at 105 to 110 °C for 3 to 4 h and cooled to room temperature in a desiccator, and dissolve in water. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this stock solution contains 1 mg of Cr.

4.7.2 Chromium, standard solution corresponding to 5 mg of Cr per litre.

Take 5,0 ml of the stock solution (4.7.1), introduce into a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 5 μg of Cr.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrophotometer, or

5.2 Photometer, fitted with filters, with maximum transmission at 530 nm.

6 Sampling

Carry out sampling in accordance with ISO/R 377 or appropriate national standards for cast iron.

7 Procedure

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

7.1 Test portion

Weigh, to the nearest 0,001 g, approximately 1 g of the test sample.

7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure using the same quantities of all reagents and the same cell in the determination, as specified in 7.3.2, but replacing the test solution by the iron solution (4.6).

7.3 Determination

7.3.1 Preparation of the test solution

Introduce the test portion (7.1) into a 250 ml beaker and add 25 to 30 ml of the acid mixture (4.2). Cover the beaker with a watch-glass. After effervescence ceases, heat gently to complete the attack and increase the temperature until white perchloric fumes reflux in the beaker. Continue fuming for about 3 min.

Allow the perchloric acid to evaporate until crystallization of iron perchlorate occurs (see the note).

Cool, add 100 ml of hot water, swirl to dissolve the salts, gradually heat to boiling and gently boil for about 1 min.

After cooling, transfer the solution quantitatively to a 200 ml one-mark volumetric flask. Dilute to the mark and mix.

If necessary, filter through a dry filter of medium texture and collect the filtrate into a dry beaker. Discard the first fraction.

NOTE — Do not continue the heating, otherwise the salts are difficult to dissolve.

7.3.2 Colour development

Take 10,0 ml of the test solution (7.3.1) and introduce into a 100 ml conical flask. Add 20 ml of the phosphoric acid solution (4.1) and 1 ml of the potassium permanganate solution (4.3).

Cover the flask with a watch-glass, heat and gently boil the solution for 5 min. Discontinue heating and immediately add, drop by drop, the sodium azide solution (4.4), waiting 5 to 10 s between the drops until the discoloration of the permanganate, and then cool rapidly to the ambient temperature.

Transfer this solution quantitatively to a 100 ml one-mark volumetric flask, dilute to about 80 ml and add 10 ml of the diphenylcarbazide solution (4.5). Dilute to the mark and mix.

7.3.3 Spectrophotometric measurement

After 10 min, carry out the spectrophotometric measurement at a wavelength of about 540 nm with an appropriate optical path cell, after having adjusted the spectrophotometer (5.1) or the photometer (5.2) to zero absorbance against the blank test solution (7.2).

NOTE — The colour is stable for 30 min.

7.4 Establishment of the calibration graph

7.4.1 Preparation of calibration solutions

Introduce into a series of seven 100 ml conical flasks the 0 — 2,0 — 5,0 — 10,0 — 15,0 — 20,0 and 25,0 ml of the chromium standard solution (4.7.2) resulting in chromium concentrations in the colour-developed solutions of 0 — 0,10 — 0,25 — 0,50 — 0,75 — 1,00 and 1,25 μg of Cr per millilitre respectively.

Add to each flask 10,0 ml of the iron solution (4.6), 20 ml of the phosphoric acid solution (4.1) and then 1 ml of the potassium permanganate solution (4.3).

Continue as specified in 7.3.2 from the second paragraph, "Cover the flask with a watch-glass...".

7.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurements for each flask according to the procedure specified in 7.3.3, but replacing the blank test solution by the calibration solution zero (7.4.1).

7.4.3 Plotting of the calibration graph and calculation of the angular coefficient a

Plot the absorbance against the known mass of chromium, in micrograms per millilitre.

Calculate the angular coefficient a from the slope of the calibration graph, if it is a straight line.

NOTE — The absorbance of a solution containing 1 $\mu\text{g}/\text{ml}$ of chromium, measured at 540 nm in a 1 cm optical path length cell, is $0,80 \pm 0,02$.

8 Expression of results

8.1 When the calibration graph is not a straight line

Convert the absorbance (7.3.3) into the corresponding concentration of chromium in the colour-developed test solution in micrograms per millilitre by using the calibration curve (7.4.3).

Calculate the chromium (Cr) content, expressed as a percentage by mass from the following formula:

$$\begin{aligned} & \frac{200}{10} \times \frac{1}{10^6} \times c \times 100 \times \frac{100}{m} + C \\ & = \frac{c}{5m} + C \end{aligned}$$

where

c is the concentration, in micrograms per millilitre, of chromium in the colour-developed test solution;

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

C is the percentage by mass of chromium present in the iron used in the blank test solution and for the calibration.

8.2 When the calibration graph is a straight line

The chromium (Cr) content, expressed as a percentage by mass, is calculated from the following formula:

$$\frac{200}{10} \times \frac{1}{10^6} \times \frac{A}{a} \times 100 \times \frac{1}{d} \times \frac{100}{m} + C$$

$$= \frac{A}{5adm} + C$$

where

A is the absorbance of the test solution corrected with the absorbance of the blank test solution;

a is the angular coefficient or the absorbance of a solution containing 1 µg/ml per centimetre cell path length;

d is the optical path length, in centimetres, of the cell used for the measurements;

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

C is the percentage by mass of chromium present in the iron used in the blank test solution and for the calibration.

9 Test report

The test report shall include the following particulars:

- the method used by reference to this International Standard;
- the results, and the form in which they are expressed;
- any unusual features noted during the determination;
- any operation not specified in this International Standard or in the International Standard to which reference is made, or any optional operation which may have influenced the result.

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