



**SLOVENSKI STANDARD**  
**SIST EN 24937:1997**

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**Jeklo in železo - Določevanje kroma - Potenciometrična ali vizualna metoda (ISO 4937:1996)**

Steel and iron - Determination of chromium content - Potentiometric or visual method (ISO 4937:1986)

Stahl und Eisen - Bestimmung des Chromgehalts - Potentiometrische oder visuelle Methode (ISO 4937:1986)

Aciers et fontes - Détermination de la teneur en chrome - Méthode potentiométrique ou visuelle (ISO 4937:1986)

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Steel and iron - Determination of chromium content - Potentiometric or visual method (ISO 4937:1986)

Aciers et fontes - Détermination de la teneur en chrome - Méthode potentiométrique ou visuelle (ISO 4937:1986)

Stahl und Eisen - Bestimmung des Chromgehalts - Potentiometrische oder visuelle Methode (ISO 4937:1986)

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to CEN Central Secretariat has the same status as the official versions.

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### CEN

European Committee for Standardization  
Comité Européen de Normalisation  
Europäisches Komitee für Normung

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### Brief History

On the proposal of the Technical Committee ECISS/TC 20, "Methods of chemical analysis" the Coordinating Commission (COCOR) of the European Committee for Iron and Steel Standardization (ECISS) decided in November 1988 to submit the International Standard

ISO 4937 - 1986      Steel and iron -- Determination of chromium content -- Potentiometric or visual titration method

to the Formal Vote.

This European Standard was adopted by CEN on 1989-11-27

According to the Common CEN/CENELEC Rules, being part of the Internal Regulations of CEN, the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

### Statement

The text of the International Standard ISO 4937, edition 1, 1986 was approved by CEN as a European Standard without any modification.

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# International Standard



# 4937

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## Steel and iron — Determination of chromium content — Potentiometric or visual titration method

*Aciers et fontes — Dosage du chrome — Méthode par titrage potentiométrique ou visuel*

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**Descriptors** : steels, iron, chemical analysis, determination of content, chromium, potentiometric methods, volumetric analysis.

## 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 4937 was prepared by Technical Committee ISO/TC 17, *Steel*.

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.

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# Steel and iron — Determination of chromium content — Potentiometric or visual titration method

## 1 Scope and field of application

This International Standard specifies a method for the determination of chromium in steel and iron by potentiometric or visual titration.

The method is applicable to chromium contents between 0,25 and 35 % (*m/m*).

If vanadium is present, the visual titration is applicable only to test portions containing less than 3 mg of vanadium.

## 2 References

ISO 377, *Wrought steel — Selection and preparation of samples and test pieces*.

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements*.

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

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

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests*.

## 3 Principle

Dissolution of a test portion with appropriate acids.

Oxidation of chromium in an acid medium to chromium(VI) by ammonium peroxydisulfate in the presence of silver sulfate. Reduction of manganese(VII) by hydrochloric acid.

Reduction of chromium(VI) by ammonium iron(II) sulfate standard solution.

In the case of potentiometric detection, determination of the equivalence point by measurement of the potential variation when the ammonium iron(II) sulfate standard solution is being added.

In the case of visual detection, titration of the excess ammonium iron(II) sulfate by potassium permanganate standard solution which also acts as the indicator.

## 4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, free from oxidizing or reducing activity.

### 4.1 Urea.

**4.2 Perchloric acid**,  $\rho$  approximately 1,67 g/ml.

**4.3 Hydrofluoric acid**,  $\rho$  approximately 1,15 g/ml.

**4.4 Orthophosphoric acid**,  $\rho$  approximately 1,70 g/ml.

**4.5 Nitric acid**,  $\rho$  approximately 1,40 g/ml.

**4.6 Hydrochloric acid**,  $\rho$  approximately 1,19 g/ml, diluted 1 + 1.

**4.7 Hydrochloric acid**,  $\rho$  approximately 1,19 g/ml, diluted 1 + 10.

**4.8 Sulfuric acid**,  $\rho$  approximately 1,84 g/ml, diluted 1 + 1.

**4.9 Sulfuric acid**,  $\rho$  approximately 1,84 g/ml, diluted 1 + 5.

**4.10 Sulfuric acid**,  $\rho$  approximately 1,84 g/ml, diluted 1 + 19.

**4.11 Silver sulfate**, 5 g/l solution.

**4.12 Ammonium peroxydisulfate**  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ , 500 g/l solution.

Prepare this solution immediately before use.

**4.13 Manganese sulfate**  $[\text{MnSO}_4 \cdot \text{H}_2\text{O}]$ , 4 g/l solution.

**4.14 Manganese sulfate**  $[\text{MnSO}_4 \cdot \text{H}_2\text{O}]$ , 100 g/l solution.

**4.15 Potassium permanganate**, 5 g/l solution.

**4.16 Sodium nitrite**, 3 g/l solution.

Prepare this solution immediately before use.

**4.17 Sulfamic acid**  $(\text{NH}_2\text{SO}_3\text{H})$ , 100 g/l solution.

This solution remains stable for one week only.

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**4.18 Potassium permanganate, standard solution.****4.18.1 Preparation of the solution**

Dissolve 3,2 g of potassium permanganate in 1 000 ml of water. After storage in complete darkness for 2 weeks, filter through a thick fritted filter without washing. Keep the solution in a coloured glass bottle and avoid contact with organic matter.

**4.18.2 Standardization of the solution**

Boil 250 ml of sulfuric acid (4.10) in a 600 ml beaker for 10 min and allow to cool. Weigh, to the nearest 0,000 1 g, 0,300 0 g of sodium oxalate  $[(\text{COONa})_2]$  previously dried at 105 °C and cooled in a desiccator. Dissolve the salt in boiled sulfuric acid (4.10). Add 39 to 40 ml of potassium permanganate solution (4.18.1) at a rate of 25 to 35 ml/min, stirring gently. The violet colour of the permanganate will disappear in approximately 45 s. Heat to 70 to 75 °C and complete the titration.

Towards the end, titrate very slowly and allow each drop to become colourless before adding the next.

To determine the blank test, titrate 250 ml of sulfuric acid (4.10), as described above, concurrently.

The concentration ( $c_2$ ) of the potassium permanganate standard solution, expressed as milligrams of chromium per millilitre, is given by the formula

$$c_2 = \frac{300,0 \times 1,733}{6,700 \times (V_1 - V_0)}$$

where

$V_1$  is the volume, in millilitres, of potassium permanganate solution (4.18.1) used for titrating sodium oxalate;

$V_0$  is the volume, in millilitres, of potassium permanganate solution (4.18.1) used for titrating the blank test of sulfuric acid (4.10);

6,700 is the molar mass of sodium oxalate divided by 20;

1,733 is the mass, in milligrams, of chromium(VI) contained in 1 ml of the potassium dichromate standard reference solution (4.20);

300,0 is the mass, in milligrams, of sodium oxalate weighed.

**4.19 Ammonium iron(II) sulfate  $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ , standard solution in sulfuric acid medium.**

1 ml of this solution corresponds to about 2 mg of chromium.

**4.19.1 Preparation of the solution**

Dissolve 46 g of ammonium iron(II) sulfate hexahydrate in about 500 ml of water, add 110 ml of sulfuric acid (4.8), cool, dilute to 1 000 ml and mix.

**4.19.2 Potentiometric standardization of the solution** (to be carried out just before use)

Take 30,0 ml of the potassium dichromate standard reference solution (4.20), transfer to a 600 ml beaker, add 45 ml of sulfuric acid (4.9) and make up to about 400 ml with water.

Titrate according to the conditions specified in 7.3.3.1.

The corresponding concentration ( $c_1$ ) of ammonium iron(II) sulfate solution (4.19.1), expressed in milligrams of chromium per millilitre, is given by the formula

$$c_1 = \frac{30,0 \times 1,733}{V_2}$$

where

$V_2$  is the volume, in millilitres, of ammonium iron(II) sulfate solution (4.19.1) used for the standardization;

30,0 is the volume, in millilitres, of the potassium dichromate standard reference solution (4.20) taken for the standardization;

1,733 is the mass, in milligrams, of chromium contained in 1 ml of the potassium dichromate standard reference solution (4.20).

**4.19.3 Visual standardization of the solution** (to be carried out just before use)

Take 25,0 ml of ammonium iron(II) sulfate solution (4.19.1) and add 325 ml of sulfuric acid (4.10). Titrate using the potassium permanganate standard solution (4.18) until a slight violet colour persists.

To determine the blank test, titrate a mixture of 25 ml of water and 325 ml of sulfuric acid (4.10) using the potassium permanganate standard solution (4.18).

The corresponding concentration ( $c'_1$ ) of the ammonium iron(II) sulfate standard solution (4.19), expressed in milligrams of chromium per millilitre, is given by the formula

$$c'_1 = c_2 \times \frac{V_3 - V_0}{25,0}$$

where

$c_2$  is the concentration of the potassium permanganate standard solution (4.18), expressed as milligrams of chromium per millilitre;

$V_3$  is the volume, in millilitres, of the potassium permanganate standard solution (4.18) used to oxidize 25 ml of ammonium iron(II) sulfate solution (4.19.1);

$V_0$  is the volume, in millilitres, of the potassium permanganate standard solution (4.18) used for titrating the blank test of sulfuric acid (4.10);

25,0 is the volume, in millilitres, of ammonium iron(II) sulfate solution (4.19.1) used for the standardization.



#### 4.20 Potassium dichromate, standard reference solution.

Weigh, to the nearest 0,000 1 g, 4,903 1 g of potassium dichromate previously dried at 150 °C to constant mass and cooled in a desiccator.

Dissolve in water, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard reference solution contains 1,733 mg of Cr.

## 5 Apparatus

Ordinary laboratory apparatus (see the note) and

**5.1 Potentiometric titration device**, which permits a difference in potential to be measured with platinum-saturated calomel electrodes.

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

## 6 Sampling

Carry out sampling in accordance with ISO 377 or the appropriate national standards for iron.

## 7 Procedure

**WARNING: Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.**

### 7.1 Test portion

According to the presumed chromium content, weigh, to the nearest 0,000 1 g, the following mass (*m*) of the test portion:

- for chromium contents between 0,25 and 2 % (*m/m*), *m* approximately 2 g;
- for chromium contents between 2 and 10 % (*m/m*), *m* approximately 1 g;
- for chromium contents between 10 and 25 % (*m/m*), *m* approximately 0,5 g;
- for chromium contents between 25 and 35 % (*m/m*), *m* approximately 0,25 g.

### 7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same reagents, as in the determination, but omitting the test portion.

## 7.3 Determination

### 7.3.1 Preparation of the test solution

#### 7.3.1.1 Unalloyed steel and iron

Place the test portion (7.1) in a 600 ml beaker, add 60 ml of sulfuric acid (4.9) and 10 ml of orthophosphoric acid (4.4), and heat to dissolve, then oxidize with 15 ml of nitric acid (4.5). Heat until dense white fumes are given off, cool and then add 100 ml of water.

To accelerate the dissolution of a test portion which has a high silicon content, a few drops of hydrofluoric acid (4.3) may be added (see note 1).

#### 7.3.1.2 Chromium and/or nickel alloyed steel and iron

Place the test portion (7.1) in a 600 ml beaker, add 25 ml of hydrochloric acid (4.6) and heat to dissolve, then oxidize with 15 ml of nitric acid (4.5). If dissolution proves to be particularly difficult, add 1 to 2 ml of hydrofluoric acid (4.3). Then add 20 ml of sulfuric acid (4.8) and 10 ml of orthophosphoric acid (4.4), and heat until dense white fumes appear.

After cooling, add a further 15 ml of nitric acid (4.5) to the fuming solution, if necessary making further additions, until the carbides have completely decomposed. Continue fuming to remove completely oxides of nitrogen then cool and add 100 ml of water (see note 1).

#### 7.3.1.3 Steel containing tungsten

Place the test portion (7.1) in a 600 ml beaker, add 25 ml of hydrochloric acid (4.6) then 20 ml of sulfuric acid (4.8) and 10 ml of orthophosphoric acid (4.4) and heat until effervescence has ceased. If dissolution proves to be particularly difficult add 1 to 2 ml of hydrofluoric acid (4.3). Oxidize with 15 ml of nitric acid (4.5) then heat until dense white fumes appear.

After cooling, add a further 15 ml of nitric acid (4.5) to the fuming solution, if necessary making further additions, until the carbides have completely decomposed. Continue fuming to remove completely oxides of nitrogen then cool and add 100 ml of water (see note 1).

#### 7.3.1.4 High alloyed steel and iron, or steel and iron with high silicon content

Place the test portion (7.1) in a 750 ml conical flask, and add 20 ml of hydrochloric acid (4.6), 10 ml of nitric acid (4.5) and 1 ml of hydrofluoric acid (4.3).

When effervescence has ceased, add 30 ml of perchloric acid (4.2). Heat until white fumes are given off, cover with a watch-glass and continue to heat until the alloy has completely dissolved (the white fumes being retained in the flask). Allow to cool.

Add 30 ml of water, boil for 5 min, and allow to cool (see note 1). Transfer quantitatively into a 600 ml beaker and add 20 ml of sulfuric acid (4.8), 10 ml of orthophosphoric acid (4.4) and 70 ml of water.

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