



SLOVENSKI STANDARD
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Legirana jekla - Določevanje kroma - Optična emisijska spektrometrija z induktivno sklopljeno plazmo (ICP/OES)

Alloyed steels - Determination of chromium content - Inductively coupled plasma optical emission spectrometric method

Stahl - Bestimmung des Chromgehaltes - Optischer Emissionsspektrometrie mit induktiv gekoppeltem Plasma Verfahren

Aciers alliés - Détermination du chrome - Méthode par spectrométrie d'émission optique avec source à plasma induit

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**Alloyed steels - Determination of chromium content -
Inductively coupled plasma optical emission spectrometric
method**

Aciers alliés - Détermination du chrome - Méthode par
spectrométrie d'émission optique avec source à plasma
induit

Stahl - Bestimmung des Chromgehaltes - Optischer
Emissionsspektrometrie mit induktiv gekoppeltem
Plasma Verfahren

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (FprCEN/TR 10367:2019) has been prepared by Technical Committee ECISS/TC 102 “Methods of Chemical analysis of iron and steel”, the secretariat of which is held by SIS.

This document is currently submitted to the Vote on TR.

iTeh STANDARD PREVIEW
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<https://standards.iteh.ai/catalog/standards/sist/6c5c7a02-fc35-4b9b-823a-dcbe8ec918bb/sist-tp-cen-tr-10367-2019>

1 Scope

This document specifies an inductively coupled plasma optical emission spectrometric method for the determination of the chromium content (mass fraction) between 5,0% (m/m) and 27,0% (m/m) in alloyed steels.

The method doesn't apply to alloyed steels having carbon contents higher than 1% and niobium and/or tungsten contents higher than 0,1%.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 648, *Laboratory glassware — Single-volume pipettes*

EN ISO 1042, *Laboratory glassware — One mark volumetric flasks*

EN ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

4 Principle

Dissolution of a test portion with hydrochloric and nitric acids. Filtration and ignition of the acid insoluble residue. Removal of silica with hydrofluoric acid. Fusion of the residue with potassium hydrogen sulphate (or with potassium disulphate), acid dissolution of the melt and addition of this solution to the reserved filtrate.

After suitable dilution and, if necessary, addition of an internal reference element, nebulisation of the solution into an inductively coupled plasma emission spectrometer and measurement of the intensity of the emitted light (including, where appropriate, that of the internal reference element).

The method uses a calibration based on a very close matrix matching of the calibration solutions to the sample and bracketing of the mass fractions between 0,95 to 1,05 of the approximate content of chromium in the sample to be analysed. The content of all elements in the sample has, therefore, to be approximately known. If the contents are not known, the sample has to be analysed by some semi-quantitative method. The advantage with this procedure is that all possible interferences from the matrix will be compensated, which will result in high accuracy. This is most important for spectral interferences, which can be severe in very highly alloyed matrixes. All possible interferences shall be kept at a minimum level. Therefore, it is essential that the spectrometer used meets the performance criteria specified in the method for the selected analytical lines.

The wavelengths reported in Table 1 have been investigated and the strongest possible interferences are given. If other wavelengths are used, they shall be carefully checked. The wavelength for the internal reference element should be selected carefully. The use of scandium at 363,1 nm or yttrium at 371,0 nm is recommended. These wavelengths are interference-free for the elements and contents generally found in alloyed steels.

5 Reagents

5.1 General

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

The same reagents should be used for the preparation of calibration solutions and of sample solutions.

5.2 Hydrochloric acid, HCl ($\rho_{20} = 1,19$ g/ml)

5.3 Nitric acid, HNO₃ ($\rho_{20} = 1,33$ g/ml)

5.4 Hydrofluoric acid, HF ($\rho_{20} = 1,13$ g/ml)

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes, producing severe skin burns which are slow to heal. In the case of contact with skin, wash well with water, apply a topical gel containing 2,5% (mass fraction) calcium gluconate, and seek immediate medical treatment.

5.5 Sulphuric acid, H₂SO₄ ($\rho_{20} = 1,84$ g/ml)

5.6 Sulphuric acid, solution 1 + 1

While cooling, add 25 ml of sulphuric acid (5.5) to 25 ml of water.

5.7 Potassium hydrogen sulphate [KH₂SO₄] or potassium disulphate [K₂S₂O₇]

FprCEN/TR 10367:2019 (E)**5.8 Chromium standard solution, 10 g/l**

Weigh, to the nearest 0,001 g, 2 g of high purity chromium [min 99,9% (mass fraction)], place it in a beaker and add 100 ml of hydrochloric acid (5.2). Cover with a watch glass and heat gently until chromium is completely dissolved. After cooling, transfer the solution quantitatively into a 200 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 10 mg of chromium.

5.9 Chromium standard solution, 5 g/l

Weigh, to the nearest 0,001 g, 1 g of high purity chromium [min 99,9% (mass fraction)], place it in a beaker and add 50 ml of hydrochloric acid (5.2). Cover with a watch glass and heat gently until chromium is completely dissolved. After cooling, transfer the solution quantitatively into a 200 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 5 mg of chromium.

5.10 Standard solutions of matrix elements

Prepare standard solutions for each element whose content (mass fraction) in the test sample is higher than 1%. Use pure metals or chemical substances with chromium contents (mass fractions) less than 100 µg/g.

5.11 Internal reference element solution, 1 g/l

Choose a suitable element to be added as internal reference and prepare a 1 g/l solution.

NOTE Elements such as Sc and Y are often used for this purpose.

6 Apparatus**6.1 General**

All volumetric glassware shall be class A and calibrated, in accordance with EN ISO 648 or EN ISO 1042 as appropriate.

6.2 Fine texture filter paper**6.3 Platinum crucibles****6.4 Optical emission spectrometer, equipped with inductively coupled plasma**

This shall be equipped with a nebulisation system. The instrument used will be satisfactory if, after optimizing in accordance with the manufacturer's instructions, it meets the performance criteria given in Annex A.

The spectrometer can be either a simultaneous or a sequential one. If a sequential spectrometer can be equipped with an extra arrangement for simultaneous measurement of the internal reference element intensity, it can be used with the internal reference method. If the sequential spectrometer is not equipped with this arrangement, an internal reference cannot be used and an alternative measurement technique without internal reference element shall be used.

7 Sampling

Sampling shall be carried out in accordance with EN ISO 14284 or with an appropriate national standard for steels.

8 Procedure

8.1 Test portion

Weigh 0,5 g of the test sample to the nearest 0,001 g.

8.2 Preparation of the test solution, T_{Cr}

Transfer the test portion (8.1) into a 250 ml beaker.

Add 15 ml of hydrochloric acid (5.2), cover with a watch glass, heat gently until the attack reaction ceases, and then add dropwise, 10 ml of nitric acid (5.3).

Depending on the composition of each sample, larger amounts of hydrochloric acid can be necessary. Addition of hydrogen peroxide (H_2O_2) may advantageously help dissolution. The same quantities of the dissolution reagents shall be added to the corresponding calibration solutions.

Boil until nitrous fumes have been expelled. After cooling, add about 20 ml of water, filter the solution through a fine texture filter paper (6.2) and collect the filtrate into a 200 ml one-mark volumetric flask.

Wash the filter paper and its content with hot water slightly acidified with nitric acid (5.3) several times and collect the washings in the 200 ml one-mark volumetric flask.

Transfer the filter into a platinum crucible (6.3), dry and ignite first at a relatively low temperature (until all carbonaceous matter is removed) and then at about 800 °C for at least 15 min.

Allow the crucible to cool. Add into the crucible 0,5 to 1,0 ml of sulphuric acid solution (5.6) and 2 ml of hydrofluoric acid (5.4). Evaporate to dryness and cool.

Add into the crucible 1,00 g of potassium hydrogen sulphate or potassium disulphate (5.7) and fuse carefully by means of a Meker burner, until a clear melt is obtained.

NOTE 1 For residues containing substantial amounts of chromium carbides, prolonged heating could be necessary for complete fusion. The potassium hydrogen sulphate or potassium disulphate (5.7) can be regenerated by allowing the melt to cool, adding some drops of sulphuric acid (5.5) and repeating the fusion until the residue is fused.

NOTE 2 Depending on the composition of each sample, larger amounts of potassium hydrogen sulphate or potassium disulphate (5.7) can be used, provided the same amount is added to the corresponding calibration solutions.

Allow the crucible to cool and add about 10 ml of water and 2 ml of hydrochloric acid (5.2) to the solidified melt. Heat gently, in order to dissolve the fusion products. Allow the crucible to cool and quantitatively add the solution to the filtrate in the 200 ml one-mark volumetric flask.

NOTE 3 The volume of hydrochloric acid (5.2) can be increased, provide the same volume is added to the corresponding calibration solutions.

NOTE 4 If an internal reference element is used, an appropriate volume of the internal reference element solution (5.11) can be added at this stage. In this case, omit this operation when diluting the sample solution.

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Dilute to the mark with water and mix.

Transfer 20 ml of this sample solution into a 100 ml one-mark volumetric flask and add 10 ml of hydrochloric acid (5.2).

NOTE 5 Depending on the instrument performances, the final concentration of the test solution can be lower (or higher), provide the corresponding calibration solutions have the same final concentration.

If an internal reference element is used, add, with a calibrated pipette, 10 ml of the internal reference element solution (5.11).

NOTE 6 Depending on the instrument performances, the volume and/or the concentration of the internal reference element solution could be different.

Dilute to the mark with water and mix.

8.3 Predetermination of the test solution

Prepare two calibration solutions labelled K_{28} and K_0 , matrix matched to the test sample solution as follows:

Add 14 ml of the chromium standard solution (5.8) in a 400 ml beaker, labelled K_{28} .

In each 400 ml beaker, K_{28} and K_0 , add the volumes of the standard solutions (5.10) necessary to match the sample matrix to be tested, for each element whose content is above 1%.

The matrix shall be matched to the nearest percent.

Add in each 400 ml beaker, 15 ml of hydrochloric acid (5.2) and 10 ml of nitric acid (5.3). Cover with a watch glass and boil until nitrous fumes have been expelled and, if necessary, until the volume of the solutions is sufficiently reduced. After cooling, add about 20 ml of water and transfer each solution into a 200 ml one-mark volumetric flask.

Dissolve into each flask 1,00 g of potassium hydrogen sulphate or potassium disulphate (5.7) and add 2 ml of hydrochloric acid (5.2).

Dilute to the mark with water and mix.

Transfer 20 ml of each solution K_{28} and K_0 into two 100 ml one-mark volumetric flasks and add 10 ml of hydrochloric acid (5.2).

If an internal reference element is used add 10 ml of the internal reference element solution (5.11).

NOTE Depending on the instrument performances, the volume and/or the concentration of the internal reference element solution could be different.

Dilute to the mark with water and mix.

Measure the absolute intensities I_{28} and I_0 for the solutions K_{28} and K_0 .

Measure the absolute intensity I_{Cr} of the solution of test T_{Cr} .

Calculate the approximate concentration of chromium K_{Cr} in % (mass fraction), in the test solution using Formula (1):

$$K_{Cr} (\%) = I_{Cr} \frac{(K_{28} - K_0)}{I_{28} - I_0} \quad (1)$$