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**Steel and iron — Determination of  
nickel content — Gravimetric or  
titrimetric method**

*Aciers et fontes — Détermination du nickel — Méthode gravimétrique  
ou titrimétrique*

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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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#).

The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition ~~and replaces the first edition (ISO 4938:1988)~~, which has been technically revised.

# Steel and iron — Determination of nickel content — Gravimetric or titrimetric method

## 1 Scope

This International Standard specifies a method for the determination of nickel in steel and iron by gravimetry or titrimetry.

The method is applicable to nickel contents from 1 % to 30 % (mass fraction).

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

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

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## 3 Principle

Dissolution of a test portion with appropriate acids.

Precipitation of the nickel as nickel-dimethylglyoxime.

- Cobalt, if present, is oxidized by potassium hexacyanoferrate(III).
- Copper, if present with cobalt, preferably is removed by controlled potential electrolysis.

Acid dissolution of the precipitate and filtration of the solution, followed by a second precipitation of the nickel as nickel dimethylglyoxime.

In the case of the gravimetric determination, weighing the dried dimethylglyoxime precipitate.

In the case of the titrimetric determination, acid dissolution of the precipitate, addition of excess EDTA.Na<sub>2</sub> solution and back titration of the excess EDTA.Na<sub>2</sub> by zinc solution using xylenol orange as an indicator.

In both cases, determination of residual nickel in the filtrate(s) by atomic absorption spectrometry (see [Annex C](#)).

## 4 Reagents

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

### 4.1 Sodium hydrogen sulphate (NaHSO<sub>4</sub>).

4.2 **Ethanol**, 95 % (volume fraction).

4.3 **Acetic acid**, glacial,  $\rho$  approximately 1,05 g/ml.

4.4 **Hydrofluoric acid**,  $\rho$  approximately 1,15 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 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.

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

4.6 **Perchloric acid**,  $\rho$  approximately 1,54 g/ml.

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

4.7 **Sulphuric acid**,  $\rho$  approximately 1,84 g/ml.

4.8 **Ammonia solution**,  $\rho$  approximately 0,90 g/ml.

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

Add 500 ml of hydrochloric acid ( $\rho$  approximately 1,19 g/ml) to 500 ml of water.

4.10 **Hydrochloric acid**,  $\rho$  approximately 1,19 g/ml, diluted 1 + 99.

Add 10 ml of hydrochloric acid ( $\rho$  approximately 1,19 g/ml) to 990 ml of water.

4.11 **Nitric acid**,  $\rho$  approximately 1,40 g/ml, diluted 2 + 3.

Add 200 ml of nitric acid (4.5) to 300 ml of water.

4.12 **Perchloric acid**,  $\rho$  approximately 1,54 g/ml, diluted 1 + 49.

Add 10 ml of perchloric acid (4.6) to 490 ml of water.

4.13 **Ammonia solution**,  $\rho$  approximately 0,90 g/ml, diluted 1 + 1.

Add 500 ml of ammonia solution (4.8) to 500 ml of water.

4.14 **Ammonia solution**,  $\rho$  approximately 0,90 g/ml, diluted 1 + 3.

Add 100 ml of ammonia solution (4.8) to 300 ml of water.

4.15 **Hydrochloric/nitric acids mixture.**

Mix three volumes of hydrochloric acid ( $\rho$  approximately 1,19 g/ml) with one volume of nitric acid (4.5).

Prepare this mixture immediately prior to use.

4.16 **Ammonium acetate**, 200 g/l solution.

**4.17 Ammonium citrate buffer solution.**

Dissolve 500 g of citric acid monohydrate ( $C_6H_8O_7 \cdot H_2O$ ) in 675 ml of ammonia solution (4.8) and dilute to 1 l with water.

Filter before use.

**4.18 Citric acid, 500 g/l solution.**

Dissolve 500 g of citric acid monohydrate ( $C_6H_8O_7 \cdot H_2O$ ) in water and dilute to 1 l with water.

Filter before use.

**4.19 Dimethylglyoxime, 30 g/l solution in alkaline medium.**

Dissolve 20 g of potassium hydroxide in 400 ml of water, add 30 g of dimethylglyoxime ( $C_4H_8N_2O_2$ ) and stir until dissolution is complete. Dilute to 1 l with water and mix.

Filter before use.

**4.20 Dimethylglyoxime, 10 g/l solution in ethanol.**

Dissolve 10 g of dimethylglyoxime ( $C_4H_8N_2O_2$ ) in 1 000 ml of ethanol (4.2).

Filter before use.

**4.21 Hydrazine dihydrogen sulphate ( $N_2H_6SO_4$ ), 100 g/l solution.****4.22 Potassium hexacyanoferrate(III),  $K_3[Fe(CN)_6]$ , 100 g/l solution.**

This solution is stable for approximately 30 days.

1 ml of this solution corresponds approximately to 0,02 g of cobalt and manganese, respectively.

**4.23 Washing water, adjusted to pH 8 with a few drops of ammonia solution (4.13).****4.24 Ethylenediaminetetraacetic acid disodium salt ( $EDTA.Na_2$ ), standard-volumetric solution.****4.24.1 Preparation of the solution**

Dissolve 6,33 g of ethylenediaminetetraacetic acid disodium salt ( $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$ ) in water, transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds approximately to 1 mg of nickel.

**4.24.2 Standardization of the solution**

Transfer 25,0 ml of the nickel standard solution (4.24.3) to a 250 ml beaker and add 33 ml of  $EDTA.Na_2$  solution (4.24.1). Add 15 ml of ammonium acetate solution (4.16) and dilute to about 150 ml with water. Continue as described in the third paragraph of 7.2.5.

The corresponding concentration,  $c$ , of the EDTA.Na<sub>2</sub> solution (4.24.1), expressed in milligrams of nickel per millilitre, is given by Formula (1):

$$c = \frac{(m_1 \times 25) + (m_2 \times V_1)}{V_2} \quad (1)$$

where

$m_1$  is the mass of nickel contained in 1 ml of the nickel standard solution (4.24.3), in milligrams;

$m_2$  is the mass of nickel corresponding to 1 ml of the zinc standard solution (4.25), in milligrams;

$V_1$  is the volume of the zinc standard solution (4.25) used for the titration, in millilitres;

$V_2$  is the volume of the EDTA.Na<sub>2</sub> solution (4.24.1) used for the standardization, in millilitres.

#### 4.24.3 Nickel standard solution

Weigh, to the nearest 0,1 mg, 1,000 g of nickel [Ni > 99,95 % (mass fraction)]. Dissolve in 20 ml of nitric acid (4.11). Boil to remove nitrous fumes, cool, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

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

#### 4.25 Zinc standard solution

Weigh, to the nearest 0,1 mg, 1,114 0 g of zinc [purity > 99,9 % mass fraction] and transfer to a 300 ml beaker. If the zinc is oxidized, it should be cleaned with hydrochloric acid (4.9), water and acetone, and dried for 5 min at 110 °C before use.

Add about 50 ml of water, 20 ml of hydrochloric acid (4.9) and five drops of bromine-saturated water. Cover with a watch glass and heat until the metal is completely dissolved. Continue the heating until the colour of the bromine disappears, cool to room temperature and add 20 ml of glacial acetic acid (4.3). Adjust the pH of the solution to  $6,0 \pm 0,2$  with ammonia solution (4.14). Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds to 1,0 mg of Ni and also approximately to 1 ml of the EDTA.Na<sub>2</sub> standard volumetric solution (4.24).

#### 4.26 Xylenol orange, 1 g/l solution.

Pulverize 0,1 g of xylenol orange (C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O<sub>13</sub>SN<sub>4</sub>) with a little portion of water to make a paste. Dilute to 100 ml with water. Filter and store in a brown glass stoppered bottle.

This solution is stable for one week.

## 5 Apparatus

All volumetric glassware shall be Class A in accordance with ISO 648 or ISO 1042, as appropriate.

Ordinary laboratory equipment and the following shall be used.

**5.1 Sintered-glass filter**, complying with porosity grade P16 of ISO 4793.

**5.2 pH-meter**.

**5.3 Apparatus for controlled-potential electrolysis**, with a saturated calomel reference electrode and a platinum electrode.



## 6 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel and iron.

## 7 Procedure

### 7.1 Test portion

The test portion shall be selected so that the amount of nickel to be precipitated is within the range of 25 mg to 70 mg for the gravimetric determination and 25 mg to 40 mg for the titrimetric determination.

For example, if 3,5 % (mass fraction) nickel content is expected, weigh approximately a 1 g test portion. All weighings shall be to the nearest 0,1 mg.

### 7.2 Determination

#### 7.2.1 Preparation of the test solution

Place the test portion (7.1) in a beaker of suitable capacity (e.g. 400 ml for test portions up to 2,5 g and 600 ml for test portions above 2,5 g). Add 30 ml of hydrochloric/nitric acids mixture (4.15) for test portions up to 2,5 g and 50 ml for other test portions. Cover the beaker with a watch-glass and heat at 50 °C to 60 °C until reaction is complete and then add 0,5 ml to 1 ml of hydrofluoric acid (4.4). Add 30 ml of perchloric acid (4.6) for test portions up to 2,5 g and 50 ml for other test portions.

Increase the temperature to approximately 180 °C and evaporate the solution until copious white fumes of perchloric acid are evolved. (standards.iteh.ai)

Cover the beaker with a dry watch-glass and continue fuming until the chromium, if present, is completely oxidized (at this stage, the solution gets the orange dichromate colour).

Remove the beaker from the heat source and allow to cool. Add 100 ml of water and heat to dissolve the salts. Boil for about 5 min to eliminate chlorine compounds.

Filter through a rapid filter paper to remove graphite and oxides of silicon, tungsten, niobium and tantalum. Collect the filtrate in an 800 ml beaker and wash eight to ten times with hot perchloric acid (4.12) and then, wash twice with water.

NOTE This solution is the main solution.

Transfer the filter and residue to a platinum crucible. Dry, ash and ignite at a temperature of 900 °C. Treat the residue with hydrofluoric acid (4.4), evaporate and then fuse the residue by carefully heating the crucible with a small amount of sodium hydrogen sulphate (4.1).

Allow the crucible to cool, dissolve the melted residue in hot water and add the solution obtained to the main solution.

#### 7.2.2 First nickel precipitation

7.2.2.1 The following applies to test portions containing less than 5 mg of copper and less than 5 mg of cobalt.

Dilute the test solution prepared in 7.2.1 to approximately 400 ml with water and add 50 ml of citric acid solution (4.18). Neutralize with ammonia solution (4.13) and re-acidify slightly with hydrochloric acid (4.9). Heat to 90 °C and directly pour into the solution, 10 ml of dimethylglyoxime solution (4.20) for each 10 mg of nickel present.

Neutralize the solution with ammonia solution (4.13), add 2 ml excess and stir well. Let the solution stand at approximately 65 °C for about 2 h. Cool rapidly to room temperature.

Filter through a rapid 12,5 cm hardened paper and wash six to eight times with the cold washing water (4.23).

**7.2.2.2** The following applies to test portions containing more than 5 mg of copper.

Follow the procedure as described in 7.2.2.1 but increase the amount of dimethylglyoxime solution (4.20) for the precipitation. Add 10 ml for each 10 mg of nickel present and add 30 ml in excess.

**7.2.2.3** The following applies to test portions containing more than 5 mg of cobalt.

Evaporate the test solution prepared in 7.2.1 or 7.2.2.4 to 100 ml approximately.

Transfer the solution into a 600 ml beaker containing 100 ml of the ammonium citrate buffer solution (4.17) and 65 ml of ammonia solution (4.8). After rinsing the original beaker with water, wash once with 15 ml of ammonia solution (4.13) and add the washing to the test solution.

Add an amount of potassium hexacyanoferrate(III) solution (4.22) sufficient to oxidize the cobalt and manganese present (6 ml for each 0,1 g of cobalt and manganese) plus 10 % excess. Stir well (the solution should now be red) and, using a pH-meter (5.2), adjust the solution to pH  $8,0 \pm 0,2$  with ammonia solution (4.8) or acetic acid (4.3). Add 50 ml of ethanol (4.2) and 100 ml of dimethylglyoxime solution (4.19) and stir well. Let the solution stand at room temperature for 4 h, checking that the solution remains at pH 8.

Filter through a rapid 12,5 cm hardened paper and wash six to eight times with the cold washing water (4.23).

**7.2.2.4** The following applies to test portions containing cobalt and high concentrations of copper.

To the test portion prepared in 7.2.1, add hydrazine dihydrogen sulphate solution (4.21) drop by drop until the chromium is completely reduced.

Remove the copper by electrolysis of the solution at controlled potential, commencing the deposition with a cathode potential of  $-0,15$  V (against standard calomel electrode) and gradually reducing to  $-0,30$  V (against standard calomel electrode). Copper deposition should be complete after about 40 min when the current remains constant at a very low value.

Completion of deposition can be checked by adding about 20 ml of water to the test solution and continuing the electrolysis. Deposition is complete if no copper is deposited on the freshly submerged portion of the cathode after 5 min. Switch off the current to the calomel electrode circuit. Remove the calomel electrode, then remove the platinum electrodes and rinse with water.

Add about 5 ml of nitric acid (4.5) and evaporate the solution until copious white fumes are evolved. Cover the beaker with a dry watch-glass and continue heating until the chromium is completely oxidized. Remove the beaker from the heat source and allow to cool. Dilute the solution with 100 ml of water, heat to dissolve the salts and boil for about 5 min to eliminate chlorine compounds.

Proceed as described in 7.2.2.3.

### 7.2.3 Second nickel precipitation

The second nickel precipitation may be omitted for test portions containing less than 20 mg of copper and less than 25 mg of cobalt if the titrimetric determination is to be used, in which case, proceed as described in 7.2.5.

Place the filter and precipitate obtained in 7.2.2 in the precipitation beaker and cover with a watch glass. Add 15 ml of nitric acid (4.5), 10 ml of sulphuric acid (4.7) and 4 ml of perchloric acid (4.6), and then heat. Increase the temperature to evaporate the solution until there is a strong emission of white fumes (see Note 1). Cool and dilute with water to about 400 ml.

NOTE 1 The elimination of the organic content of the precipitate and filter normally takes 20 min to 30 min.

Add 10 ml of citric acid solution (4.18), neutralize with ammonia solution (4.13) and re-acidify with hydrochloric acid (4.9). Heat the solution to 90 °C and add 10 ml of dimethylglyoxime solution (4.20) for each 10 mg of nickel present.

Neutralize with ammonia solution (4.13) and add 2 ml excess. Stir well and allow to stand at 80 °C for 2 h. Allow the solution to cool slowly to 50 °C, add 50 ml of ethanol (4.2) (see Note 2), mix well and allow to cool to 35 °C.

NOTE 2 Ethanol is added to compensate for the loss due to evaporation and to prevent the possible separation of dimethylglyoxime at lower temperatures.

#### 7.2.4 Gravimetric determination

Collect the precipitate obtained in 7.2.3 on a sintered-glass filter (5.1) which has been dried previously at 110 °C, cooled in a desiccator and weighed at 10 min intervals to constant mass. Wash the beaker and crucible 15 times with the washing water (4.23) at 45 °C. Do not allow the precipitate to become dry at any time during the washing procedure.

Dry the crucible and precipitate at 110 °C for 2 h, cool in a desiccator and weigh at 10 min intervals to constant mass.

Combine the filtrates from 7.2.2 and 7.2.4. Evaporate to a viscous consistency. Add 50 ml of hydrochloric acid ( $\rho$  approximately 1,19 g/ml), in 10 ml to 15 ml portions and heat. Add 50 ml of hot water and bring to the boil. Allow to cool and transfer to a 200 ml one-mark volumetric flask. Make up to the mark with water and mix.

Determine the nickel content of the combined filtrates by atomic absorption spectrometry (see Annex C).

The nickel content of the combined filtrates should not exceed 0,2 % (mass fraction) nickel in the original sample.

NOTE 1 High levels of nickel in the filtrates might indicate a faulty crucible.

NOTE 2 If the nickel concentration in the filtrates is high or the sensitivity of the atomic absorption spectrometer is very high, it might be necessary to dilute the solution before the atomic absorption measurements.

#### 7.2.5 Titrimetric determination

Dissolve the precipitate obtained in 7.2.2 or 7.2.3 (see the following paragraph) from the paper with alternate small additions of nitric acid (4.11) and warm water and collect the solution in the original precipitation beaker.

When continuing from 7.2.3, carry out the following filtration before proceeding in 7.2.5.

Filter through a rapid 12,5 cm hardened filter paper and wash thoroughly with the cold washing water (4.23).

Transfer to a 250 ml beaker and boil for several minutes. After cooling, add 12 ml of the EDTA.Na<sub>2</sub> standard volumetric solution (4.24) for each 10 mg of nickel present and then add 3 ml in excess. Record the total volume of the EDTA.Na<sub>2</sub> solution added. Add 15 ml of ammonium acetate solution (4.16) and dilute to about 150 ml with water.

Adjust the pH of the solution to  $6,0 \pm 0,2$  with ammonia solution (4.14) or hydrochloric acid (4.10) and keep for about 10 min. Add several drops of xylenol orange solution (4.26) as indicator, mix and titrate with the zinc standard solution (4.25) to a red-purple end point.

Take the filtrate from 7.2.2 or combine the filtrates from 7.2.2 and 7.2.4. Proceed as described in 7.2.4 from "Add 50 ml of hydrochloric acid ( $\rho$  approximately 1,19 g/ml), ...".