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Steel and irons — Determination of nickel content — Gravimetric or titrimetric method

Aciers et fontes — Dosage du nickel — Méthode gravimétrique ou titrimétrique

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This draft has been developed within the International Organization for Standardization (ISO), and processed under the **ISO lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

To expedite distribution, this document is circulated as received from the committee secretariat. ISO Central Secretariat work of editing and text composition will be undertaken at publication stage.



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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.

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The main task of technical committees is to prepare International Standards. 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.

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ISO 4938 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second/third/... edition cancels and replaces the first/second/... edition (ISO 4938:1988), [clause(s) / subclause(s) / table(s) / figure(s) / annex(es)] of which [has / have] been technically revised.

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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, either by gravimetry or by titrimetry.

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

2 Normative references

The following referenced documents are indispensable for the application 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.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — One mark 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.*

3 Principle

Dissolution of a test portion with appropriate acids,

Precipitation of the nickel as nickel-diméthylglyoxime.

— 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 diméthylglyoxime.

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

In the case of the titrimetric determination, acid dissolution of the precipitate, addition of excess EDTA.Na₂ solution and back titration of the excess EDTA.Na₂ by zinc solution using xylenol orange as an indicator.

In both cases, determination of residual nickel in the filtrate(s) by atomic absorption spectrometry.

4 Reagents

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

4.1 Sodium hydrogen sulphate (NaHSO₄)

4.2 Ethanol, 95 % (V/V)

4.3 Acetic acid, glacial, ρ approximately 1,05 g/ml

4.4 Hydrofluoric acid, ρ 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 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.

4.5 Nitric acid, ρ approximately 1,40 g/ml

4.6 Perchloric acid, ρ approximately 1,54 g/ml

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

4.7 Sulphuric acid, ρ approximately 1,84 g/ml

4.8 Ammonia solution, ρ approximately 0,90 g/ml

4.9 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted 1 + 1

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

4.10 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted 1 + 99

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

4.11 Nitric acid, ρ 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, ρ 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, ρ 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, ρ 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 (ρ 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 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.Na₂ 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.Na₂ solution (4.24.1), expressed in milligrams of nickel per millilitre, is given by the equation:

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

where

- m*₁ is the mass, in milligrams, of nickel contained in 1 ml of the nickel standard solution (4.24.3);
- m*₂ is the mass, in milligrams, of nickel corresponding to 1 ml of the zinc standard solution (4.25);
- V*₁ is the volume, in millilitres, of the zinc standard solution (4.25) used for the titration;
- V*₂ is the volume, in millilitres, of the EDTA.Na₂ solution (4.24.1) used for the standardization.

4.24.3 Nickel standard solution

Weigh, to the nearest 0,1 mg, 1,000 g of nickel [Ni > 99,95 % (m/m)]. 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 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, 1,1140 g of zinc [purity > 99,9 % (m/m)] and transfer to a 300 ml beaker. If the zinc metal is oxidized, it should be cleaned with hydrochloric acid (4.9), water and acetone, respectively, 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 acetic acid (4.3). Adjust the pH of the solution to 6,0 ± 0,2 with ammonia solution (4.14). Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution corresponds to 1,0 mg of Ni and also approximately to 1 ml of the EDTA.Na₂ standard volumetric solution (4.24).

4.26 Xylenol orange, 1 g/l solution

5 Apparatus

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

The apparatus consists of ordinary laboratory equipment, and

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 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 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 weightings 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.

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

Remove the beaker from the heat 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, collecting the filtrate in an 800 ml beaker and washing 8 to 10 times with hot perchloric acid (4.12) followed by two washings with water.

NOTE This solution is a 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 fuse the residue by carefully heating the crucible with a small amount of sodium hydrogen sulphate (4.1).

Cool the melt, dissolve it in hot water and add to the main solution.

7.2.2 First nickel precipitation

7.2.2.1 For 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 every 10 mg of nickel present.

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

Filter through a rapid 12,5 cm hardened paper and wash 6 to 8 times with the cold washing water (4.23).

7.2.2.2 For test portions containing more than 5 mg of copper

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

7.2.2.3 For 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 every 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. Stand the solution at room temperature for 4 hours, checking that the solution remains at pH 8.

Filter through a rapid 12,5 cm hardened paper and wash 6 to 8 times with the cold washing water (4.23).

7.2.2.4 For 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 the solution at controlled potential, commencing the deposition with a cathode potential of -0,15 V (vs. standard calomel electrode), and gradually reducing to -0,30 V (vs. standard calomel electrode). Copper deposition should be complete after about 40 minutes 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 minutes. 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 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 indicated in 7.2.2.3.