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

Aciers et fontes — Dosage 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.

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 4938 was prepared by Technical Committee ISO/TC 17, *Steel*.

Annexes A and B of this International Standard are for information only.

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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, using either a gravimetric or titrimetric finish.

The method is applicable to nickel contents from 0,5 % (*m/m*) to 30 % (*m/m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377 : 1985, *Wrought steel — Selection and preparation of samples and test pieces*.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1 : General requirements*.

ISO 648 : 1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks*.

ISO 4793 : 1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*.

ISO 5725 : 1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*.

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 finish, weighing of the dried nickel dimethylglyoxime precipitate.

In the case of the titrimetric finish, 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.

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 Sodium hydrogen sulfate (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.

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

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

4.7 Sulfuric 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.

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

4.11 Nitric acid, ρ approximately 1,40 g/ml, diluted 2 + 3.

4.12 Perchloric acid, ρ approximately 1,54 g/ml, diluted 1 + 49.

4.13 Ammonia solution, ρ approximately 0,90 g/ml, diluted 1 + 1.

4.14 Ammonia solution, ρ approximately 0,90 g/ml, diluted 1 + 3.

4.15 Hydrochloric-nitric acid mixture.

Mix 3 volumes of hydrochloric acid, ρ approximately 1,19 g/ml, and 1 volume of nitric acid (4.5).

Prepare this solution immediately before 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 1 000 ml with water. Filter before use.

4.18 Citric acid, solution.

Dissolve 500 g of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in water and dilute to 1 000 ml 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 1 000 ml 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 Hydrazinium(2+) sulfate ($N_2H_6SO_4$), 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 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 Disodium(ethylenedinitrilo)tetraacetate ($EDTA.Na_2$), standard volumetric solution.

4.24.1 Preparation of the solution

Dissolve 6,33 g of disodium(ethylenedinitrilo)tetraacetate dihydrate ($C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$) 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 reference 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 from the third paragraph of 7.2.5.

The corresponding concentration c of the $EDTA.Na_2$ 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 reference 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 $EDTA.Na_2$ solution (4.24.1) used for the standardization.

4.24.3 Preparation of nickel reference solution

Weigh, to the nearest 0,1 mg, 1,000 0 g of high-purity nickel [purity > 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 reference solution contains 1,0 mg of Ni.

4.25 Zinc, standard solution.

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

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 to decomposition. 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 $6,0 \pm 0,2$ 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 $EDTA.Na_2$ standard volumetric solution (4.24).

4.26 Xylenol orange, 1 g/l solution.

Triturate 0,1 g of xylenol orange ($C_{31}H_{28}N_2O_{13}SNa_4$) with a little water to make a paste. Dilute to 100 ml. Filter and store in an amber-coloured glass-stoppered bottle.

This solution is stable for one week.

5 Apparatus

All volumetric glassware shall be grade A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

The apparatus consists of ordinary laboratory equipment (see preceding paragraph), 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 377, or 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

The test portion shall be selected so that the amount of nickel to be precipitated falls within the range 25 mg to 70 mg for the gravimetric finish and 25 mg to 40 mg for the titrimetric finish. For example, if 3,5 % (*m/m*) nickel is expected, weigh approximately 1 g of the test sample. 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 acid 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, 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 is completely oxidized. 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 washes with water. (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 sulfate (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 reacidify slightly with hydrochloric acid (4.9). Heat to 90 °C and pour directly 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 h. 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 to 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 washings 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 $\text{pH } 8,0 \pm 0,2$ 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 h, 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 solution prepared in 7.2.1 add hydrazinium(2+) sulfate solution (4.21) drop by drop until the chromium is completely reduced.

Remove the copper by electrolysis of the solution at controlled potential, commencing deposition with a cathode potential of $-0,15 \text{ V}$ (vs. standard calomel electrode), and gradually reducing to $-0,30 \text{ V}$ (vs. 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 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.

7.2.3 Second nickel precipitation (see note 1)

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 sulfuric 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 2). Cool and dilute with water to about 400 ml.

Add 10 ml of citric acid solution (4.18), neutralize with ammonia solution (4.13) and reacidify with hydrochloric acid (4.9). Heat the solution to $90 \text{ }^\circ\text{C}$ and add 10 ml of dimethylglyoxime solution (4.20) for every 10 mg of nickel present.

Neutralize with ammonia solution (4.13) and add 2 ml excess. Stir well and allow to stand at $80 \text{ }^\circ\text{C}$ for 2 h. Allow the solution to cool slowly to $50 \text{ }^\circ\text{C}$, add 50 ml of ethanol (4.2) (see note 3), mix well and allow to cool to $35 \text{ }^\circ\text{C}$.

NOTES

- 1 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 finish is to be used, in which case proceed in accordance with 7.2.5.
- 2 The elimination of the organic content of the precipitate and filter normally takes 20 min to 30 min.
- 3 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 finish

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

Dry the crucible and precipitate at $110 \text{ }^\circ\text{C}$ for 2 h, cool in a desiccator and weigh at 10-minute intervals to constant mass.

7.2.5 Titrimetric finish

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

NOTE — 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_2 standard volumetric solution (4.24) for every 10 mg of nickel present and then add 3 ml in excess. Record the total volume of the EDTA.Na_2 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 xylene orange solution (4.26) as indicator, mix and titrate with the zinc standard solution (4.25) to a red-purple end point.

8 Expression of results

8.1 Methods of calculation

8.1.1 Gravimetric finish

The nickel content, expressed as a percentage by mass, is given by the formula

$$20,32 \times \frac{(m_4 - m_3)}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_3 is the mass, in grams, of the empty crucible;

m_4 is the mass, in grams, of the crucible and the nickel dimethylglyoxime precipitate;

20,32 is the conversion factor, multiplied by 100, for nickel dimethylglyoxime to nickel.

8.1.2 Titrimetric finish

The nickel content, expressed as a percentage by mass, is given by the formula

$$\frac{(c \times V_4) - (m_2 \times V_3)}{m_0 \times 10^3} \times 100$$

$$= \frac{(c \times V_4) - (m_2 \times V_3)}{10 m_0}$$

where

c is the nickel equivalent, in milligrams per millilitre, of the EDTA.Na₂ standard volumetric solution;

V_3 is the volume, in millilitres, of the zinc standard solution consumed;

V_4 is the total volume, in millilitres, of the EDTA.Na₂ standard volumetric solution added;

m_0 is the mass, in grams, of the test portion;

m_2 is the mass, in milligrams, of nickel corresponding to 1 ml of the zinc standard solution used.

8.2 Precision

A planned trial of this method was carried out by 12 laboratories on the gravimetric finish and by 10 laboratories on the titrimetric finish, at seven levels of nickel, each laboratory making four determinations of nickel at each level.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a linear relationship between nickel content and repeatability and reproducibility of the test results, as summarized in table 1. Information on the samples used is shown in annex A and a graphic presentation of the data is given in annex B.

9 Test report

The test report shall include the following particulars:

- all information necessary for the identification of the sample, the laboratory and the date of the analysis;
- a reference to this International Standard;
- the type of finish used (gravimetric or titrimetric);
- 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 any optional operation which may have influenced the results.

Table 1

| Nickel level % (m/m) | Gravimetric finish | | Titrimetric finish | |
|-------------------------|----------------------|------------------------|----------------------|------------------------|
| | Repeatability r | Reproducibility R | Repeatability r | Reproducibility R |
| 0,5 | 0,032 | 0,025 | 0,011 | 0,012 |
| 1,0 | 0,035 | 0,030 | 0,015 | 0,018 |
| 5,0 | 0,063 | 0,071 | 0,049 | 0,070 |
| 10,0 | 0,098 | 0,123 | 0,092 | 0,134 |
| 15,0 | 0,132 | 0,174 | 0,135 | 0,198 |
| 20,0 | 0,167 | 0,226 | 0,178 | 0,262 |
| 25,0 | 0,202 | 0,278 | 0,220 | 0,326 |
| 30,0 | 0,236 | 0,329 | 0,263 | 0,390 |

Annex A (informative)

Additional information on the international co-operative tests

Table 1 in sub-clause 8.2 has been derived from the results of international analytical trials carried out in 1983 on one pig iron and six steel samples in five countries, involving 12 (gravimetric finish) and 10 (titrimetric finish) laboratories.

The results of the trials were reported in document 17/1 N 598, March 1984. Graphical treatment of the precision data is given in annex B.

The test samples used are given in table A.1.

Table A.1

| Sample | Nickel content % (m/m) | | |
|-----------------------------|---------------------------|-------------|-------------|
| | Certified | Found | |
| | | Gravimetric | Titrimetric |
| ECRM 481-1 (pig iron) | 1,19 | 1,183 | 1,190 |
| JSS 151-7 (low-alloy steel) | 2,99 | 2,959 | 2,985 |
| BAM 230-1 (stainless steel) | 5,55 | 5,555 | 5,576 |
| JSS 653-1 (stainless steel) | 13,91 | 13,897 | 13,935 |
| BCS 334 (stainless steel) | 20,60 | 20,478 | 20,560 |
| NBS 348 (high-alloy steel) | 25,8 | 25,719 | 25,751 |
| JK 37 (stainless steel) | 30,82 | 30,743 | 30,802 |

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Annex B
(informative)

Graphical representation of precision data

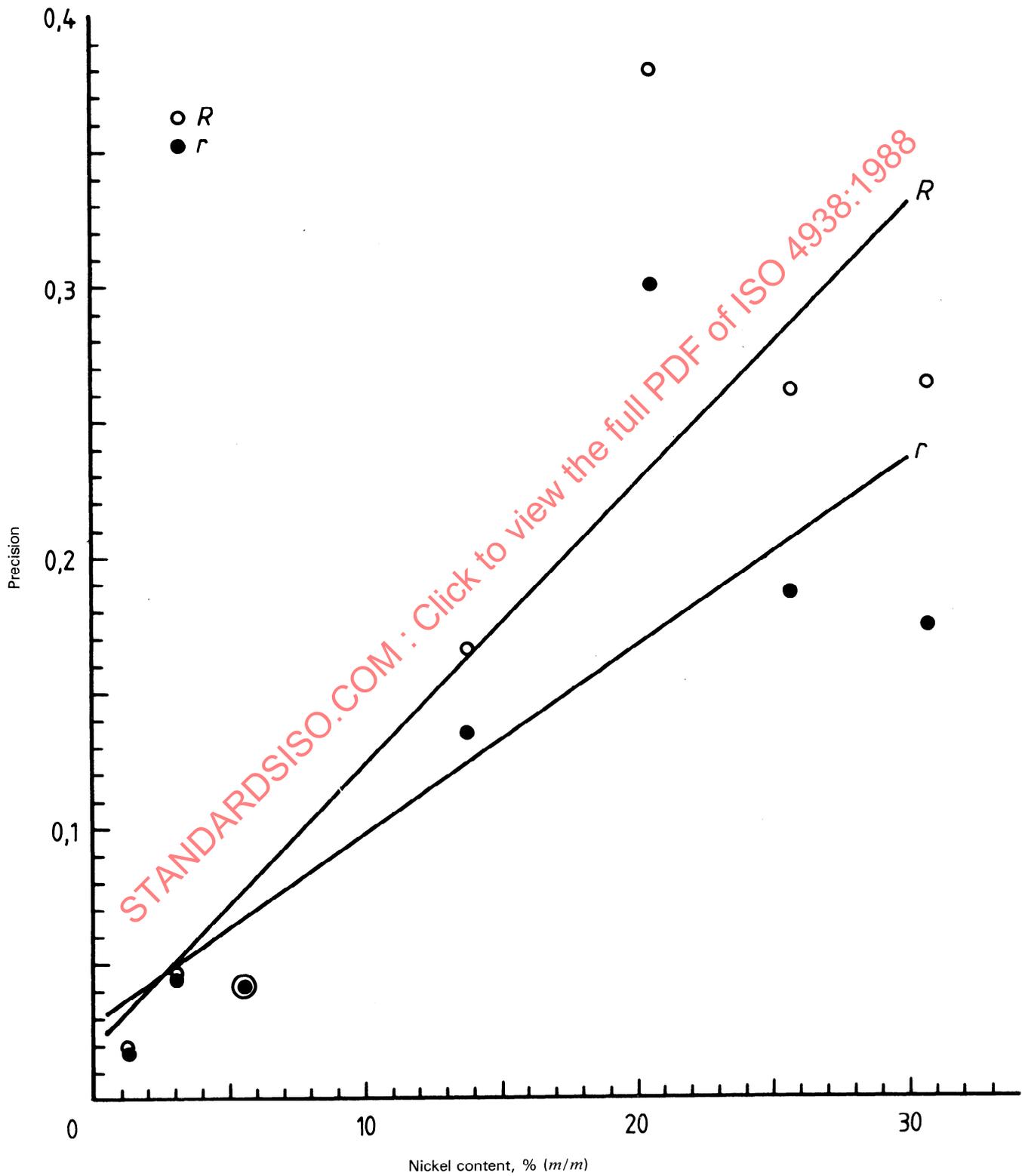


Figure B.1 — Relationship between nickel content and repeatability *r* and between nickel content and reproducibility *R* (gravimetric finish)