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Steel — Determination of nickel — Dimethylglyoxime spectrophotometric method

Aciers — Détermination du nickel — Méthode spectrophotométrique à la diméthylglyoxime

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Foreword

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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).

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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 compound*.

This second edition cancels and replaces the first edition (ISO 4939:1984), which has been technically revised. In particular, the specification of plotting of the calibration graphs shown in 7.4.3 has been corrected.

Steel — Determination of nickel — Dimethylglyoxime spectrophotometric method

1 Scope

This International Standard specifies a spectrophotometric method for the determination of nickel in steel using dimethylglyoxime.

The method is applicable to the determination of nickel mass fractions in the range of 0,10 % and 2,0 %. Cobalt, copper and manganese can cause interferences (see 7.3.2).

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

3 Principle

Dissolution of a test portion in hydrochloric, nitric and perchloric acids.

Formation of a coloured complex of nickel(lll) with dimethylglyoxime in ammoniacal solution containing iodine and potassium iodide.

Spectrophotometric measurement at a wavelength of about 535 nm.

4 Reagents

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

4.1 Acid mixture.

Mix two volumes of hydrochloric acid, ρ approximately 1,19 g/ml, one volume of nitric acid, ρ approximately 1,40 g/ml and two volumes of water.

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

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

Perchloric acid, ρ approximately 1,67 g/ml, may also be used. 100 ml of perchloric acid, ρ approximately 1,54 g/ml is equivalent to 79 ml of perchloric acid, ρ approximately 1,67 g/ml.

4.3 Ammonium citrate, 250 g/l solution.

Dissolve 250 g of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in 250 ml of ammonia solution, ρ approximately 0,91 g/ml, cool, dilute to 1 l with water and mix.

4.4 Iodine, 12,7 g/l solution.

Dissolve 25 g of potassium iodide and 12,7 g of iodine in the minimum volume of water. Dilute to 1 l with water and mix.

4.5 Dimethylglyoxime, 1 g/l solution.

Dissolve 1 g of dimethylglyoxime in 500 ml of ammonia solution, ρ approximately 0,91 g/ml, dilute to 1 l with water and mix.

4.6 Ammonia solution, ρ approximately 0,91 g/ml, diluted 1 + 1.

4.7 Nickel standard solution, 0,5 g/l.

Weigh, to the nearest 0,001 g, 0,500 g of high purity nickel [purity > 99,95 % (mass fraction)] and dissolve in 20 ml of nitric acid, ρ approximately 1,40 g/ml, diluted 2 + 3. Heat to boiling to remove nitrous fumes. Cool and transfer the solution 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 0,5 mg of nickel.

5 Apparatus

All volumetric glassware shall be Class A, in accordance with ISO 648 and ISO 1042.

Ordinary laboratory apparatus and the following shall be used.

Spectrophotometer, suitable for measuring the absorbance of the solution at a wavelength of 535 nm with cells of 1 cm or 4 cm optical path length.

6 Sampling

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

7 Procedure

7.1 Test portion

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

7.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents except the test portion.

7.3 Determination

7.3.1 Preparation of the test solution

Introduce the test portion (7.1) into a 250 ml beaker. Add 10 ml of acid mixture (4.1) and 10 ml of perchloric acid (4.2). Cover the beaker with a watch-glass and heat until acids action ceases.

Evaporate until white fumes of perchloric acid appear and continue fuming at a temperature suitable to maintain a steady reflux of perchloric acid fumes on the walls of the beaker for at least 3 min and until any chromium is oxidized to chromate. Remove from the source of heat and allow to cool.

Add 50 ml of water, heat to dissolve salts, cool and transfer quantitatively to a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Filter by decantation through a dry filter to remove any residue or precipitate and collect the filtrate in a dry beaker, discarding the first fractions of the filtrate.

7.3.2 Colour development

Transfer a 25 ml aliquot portion of the test solution (7.3.1) to a 100 ml one-mark volumetric flask.

If the test solution (7.3.1) contains cobalt, copper or manganese, the aliquot portion taken should be such that the respective contents of these elements do not exceed the following limits: cobalt, 5 mg; copper, 0,5 mg; manganese, 1 mg.

Add 20 ml of the ammonium citrate solution (4.3), mix, then add 3 ml of the iodine solution (4.4) and mix again. Allow to stand for 5 min.

Add 20 ml of the dimethylglyoxime solution (4.5), dilute to the mark with water and mix.

Allow to stand for at least 10 min and at most 20 min at a temperature of 20 °C ± 5 °C.

7.3.3 Preparation of the compensating solution

Transfer a 25 ml aliquot portion of the test solution (7.3.1) to another 100 ml volumetric flask.

Add 20 ml of the ammonium citrate solution (4.3), mix, then add 3 ml of the iodine solution (4.4) and mix again. Allow to stand for 5 min.

Add 20 ml of the ammonia solution (4.6), dilute to the mark with water and mix.

Allow to stand for at least 10 min and at most 20 min at a temperature of 20 °C ± 5 °C.

7.3.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution at a wavelength of about 535 nm in a cell of appropriate optical path length (1 cm or 4 cm) after having adjusted the spectrophotometer (Clause 5) to zero absorbance with the corresponding compensating solution (7.3.3).

7.4 Establishment of the calibration curve

7.4.1 Preparation of the calibration solutions

Introduce into a series of 250 ml beakers containing 10 ml of the acid mixture (4.1) and 10 ml of perchloric acid (4.2), the volumes of the nickel standard solution (4.7) indicated in Table 1, as appropriate for the expected nickel content.

Treat as described in 7.3.1 and 7.3.2, using the calibration solution “0” as the compensating solution.

Table 1 — Composition of the calibration solutions and cell optical path length

Nickel content % (mass fraction)	Nickel standard solution (4.7) ml	Nickel concentration in the solution for spectrophotometric measurement µg/ml	Cell optical path length cm
0,1 to 0,5	0	0	4
	1,0	0,5	
	2,0	1,0	
	3,0	1,5	
	4,0	2,0	
	5,0	2,5	
0,5 to 2,0	0	0	1
	4,0	2,0	
	6,0	3,0	
	8,0	4,0	
	10,0	5,0	
	14,0	7,0	
	16,0	8,0	
	20,0	10,0	

7.4.2 Spectrophotometric measurement

Carry out spectrophotometric measurements of each solution at a wavelength of about 535 nm after having adjusted the spectrophotometer (Clause 5) to zero absorbance with the calibration solution “0” (7.4.1) used as the compensating solution.

7.4.3 Calibration curves

For each range of nickel content and appropriate optical path length of the cells (see Table 1), establish the corresponding calibration graph by plotting the net absorbance values against the nickel concentrations, expressed in micrograms per millilitre, in the calibration solutions.

8 Expression of results

Convert the absorbance (7.3.4) into the corresponding concentration, expressed in micrograms of nickel per millilitre, in the colour-developed test solution by using the calibration curve (7.4.3).

The nickel content (C_{Ni}), expressed as a (%) mass fraction, is given by Formula (1), Formula (2) and Formula (3):

$$C_{\mathrm{Ni}} = \left(\rho_{\mathrm{Ni1}} - \rho_{\mathrm{Ni0}}\right) \times \frac{1}{10^6} \times \frac{V_0}{V_1} \times \frac{V_{\mathrm{t}}}{m} \times 100 \qquad (1)$$

$$C_{\mathrm{Ni}} = \left(\rho_{\mathrm{Ni1}} - \rho_{\mathrm{Ni0}}\right) \times \frac{1}{10^6} \times \frac{250}{25} \times \frac{100}{m} \times 100 \qquad (2)$$

$$C_{\mathrm{Ni}} = \left(\rho_{\mathrm{Ni1}} - \rho_{\mathrm{Ni0}}\right) \times \frac{1}{10m} \qquad (3)$$

where

m is the mass of the test portion (7.1), in grams;

V_0 is the volume of the test solution (7.3.1), in millilitres;

V_1 is the volume of the aliquot portion (7.3.2), in millilitres,;

V_t is the volume of the colour-developed test solution (7.3.2), in millilitres;

ρ_{Ni0} is the concentration of nickel in the blank test solution (corrected for its compensating solution), expressed in micrograms per millilitre;

ρ_{Ni1} is the concentration of nickel in the test solution (corrected for its compensating solution), expressed in micrograms per millilitre.

9 Precision

9.1 General

A planned trial of this method was carried out by five laboratories, at six levels of nickel, each laboratory making six determinations of nickel at each level.

The results obtained were treated statistically in accordance with ISO 5725:1986[1].

The obtained data showed a logarithmic relationship between nickel content and repeatability and reproducibility of the test results. Table 2 shows the smoothed data derived from these relationships. The graphic presentation of the precision data is given in Annex B.

Table 2 — Repeatability and reproducibility limits

Nickel content % (mass fraction)	**Repeatability limit** *r*	**Reproducibility limit** *R*
0,1	0,010	0,013
0,2	0,013	0,018
0,5	0,019	0,027
1,0	0,025	0,038
2,0	0,034	0,053

9.2 Repeatability

The difference between two single and independent results obtained on identical test material by one analyst using the same apparatus within a short time interval in the normal and correct operation of the test method will exceed the repeatability, *r*, only in one case in 20 cases.

9.3 Reproducibility

The difference between two single and independent results obtained by two operators working in different laboratories on identical test material in the normal and correct operation of the test method will exceed the reproducibility, *R*, only in one case in 20 cases.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) method used by reference to this International Standard, i.e. ISO 4939;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard or any optional operation which might have influenced the results.

Annex A
(informative)

Additional information on the international interlaboratory test

Table 2 has been derived from the results of the international trial carried out in 1979 on six steel samples in two countries involving five laboratories.

The results of the trials were reported in document 17/1 N 433, November 1980.

The test samples used are shown in Table A.1.

Table A.1 — Test samples

Sample		**Nickel content** % (mass fraction)	
		Certified	**Found**
BCS 260/4	(high purity iron)	0,003	0,005 5
BCS 431	(plain carbon steel)	0,069	0,066 4
BCS 341	(24 % Cr stainless steel)	0,56	0,556
BCS 226/2	(Ni-Cr-Mo steel)	1,43	1,434
BCS 406	(low alloy steel)	1,69	1,690
BCS 410	(low alloy steel)	2,04	2,034

NOTE 1 The statistical analysis was performed in accordance with ISO 5725:1986[1].

NOTE 2 Six samples were used for the international interlaboratory test. However, as the method is applicable to nickel mass fraction between 0,10 % and 2,0 %, only five points have been illustrated on the figure in Annex B, the data for sample BCS 260/4 (Ni mass fraction: 0,003 %) have been omitted.