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# International Standard



# 4939

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## Steel and cast iron — Determination of nickel content — Dimethylglyoxime spectrophotometric method

*Aciers et fontes — Dosage du nickel — Méthode spectrophotométrique à la diméthylglyoxime*

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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.

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 4939 was prepared by Technical Committee ISO/TC 17, *Steel*.

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# Steel and cast iron — Determination of nickel content — Dimethylglyoxime spectrophotometric method

## 1 Scope and field of application

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

The method is applicable to nickel contents between 0,10 and 4 % (*m/m*). Cobalt, copper and manganese may cause interferences. (See the note to 7.3.2.)

## 2 Reference

ISO/R 377, *Selection and preparation of samples and test pieces for wrought steel*.

## 3 Principle

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

Formation of a coloured complex of nickel(III) 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 distilled water or water of equivalent purity.

### 4.1 Acid mixture.

Mix 2 volumes of hydrochloric acid,  $\rho$  approximately 1,19 g/ml, 1 volume of nitric acid,  $\rho$  approximately 1,40 g/ml, and 2 volumes of water.

### 4.2 Perchloric acid, $\rho$ approximately 1,54 g/ml.

NOTE — Perchloric acid,  $\rho$  approximately 1,67 g/ml, may also be used. 100 ml of perchloric acid,  $\rho$  approximately 1,54 g/ml is equivalent to 79 ml of perchloric acid,  $\rho$  approximately 1,67 g/ml.

### 4.3 Ammonium citrate solution.

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

### 4.4 Iodine solution.

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

### 4.5 Dimethylglyoxime solution.

Dissolve 1 g of dimethylglyoxime in 500 ml of ammonia solution,  $\rho$  approximately 0,91 g/ml, dilute to 1 litre and mix.

### 4.6 Ammonia solution $\rho$ approximately 0,91 g/ml, diluted 1 + 1.

### 4.7 Nickel, standard solution, corresponding to 0,5 g of Ni per litre.

Weigh, to the nearest 0,000 1 g, 0,500 0 g of high purity nickel and dissolve in 20 ml of nitric acid,  $\rho$  approximately 1,40 g/ml, diluted 2 + 3. Boil to remove fumes and 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 0,5 mg of Ni.

## 5 Apparatus

Ordinary laboratory apparatus and

Spectrophotometer.

## 6 Sampling

Carry out sampling in accordance with ISO/R 377 or appropriate national standards for cast 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**

Weigh, to the nearest 0,001 g, approximately 0,5 g (*m*) of the test sample.

**7.2 Blank test**

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents.

**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 the acid mixture (4.1) and 10 ml of the perchloric acid (4.2), cover the beaker with a watch-glass and heat until solvent action ceases.

Evaporate until white fumes of perchloric acid appear and continue fuming at such a temperature as 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, warm to dissolve salts, cool and transfer quantitatively to a 250 ml one-mark volumetric flask. Dilute to the mark 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 or 10 ml aliquot portion of the test solution (7.3.1), as appropriate for the required content range, to a 100 ml one-mark volumetric flask, according to table 1.

**Table 1**

Nickel content	Volume of aliquot	Cell optical path length
% ( <i>m/m</i> )	ml	cm
0,1 to 0,5	25	4
0,5 to 1,6	25	1
1,6 to 4,0	10	1

NOTE — 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 and mix.

Allow to stand for at least 10 min and not more than 20 min at a temperature of 20 °C.

**7.3.3 Preparation of the compensating solution**

Transfer an aliquot portion, of the same volume as that taken for the test solution (7.3.2), to another 100 ml one-mark 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 and mix.

Allow to stand for at least 10 min and not more than 20 min at a temperature of 20 °C.

**7.3.4 Spectrophotometric measurement**

Carry out the spectrophotometric measurement of the test solution at a wavelength of about 535 nm with a cell of appropriate optical path length (see table 1) after having adjusted the spectrophotometer (clause 5) to zero absorbance in relation to the compensating solution (7.3.3).

**7.4 Establishment of the calibration graph**

**7.4.1 Preparation of calibration solutions**

Introduce into a series of 250 ml beakers containing 10 ml of the acid mixture (4.1) and 10 ml of the perchloric acid (4.2), the volumes of the nickel standard solution (4.7) indicated in table 2, 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.

**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 in relation to the calibration solution "0" (7.4.1) used as the compensating solution.

**7.4.3 Plotting of the calibration graph and calculation of the angular coefficient  $\alpha$**

Prepare the calibration graph by plotting the net absorbance values, converted to measurement in a 1 cm optical path length cell, against the nickel concentrations, expressed in micrograms per millilitre, in the measured solutions. Calculate the angular coefficient  $\alpha$  from the slope of the calibration graph, if it is a straight line.

Table 2

Nickel content (7.3.2)	Nickel standard solution (4.7)	Corresponding nickel concentration	Cell optical path length
% (m/m)	ml	µg/ml	cm
0,1 to 0,5	0	0	4
	1,0	5	
	2,0	10	
	3,0	15	
	4,0	20	
	5,0	25	
0,5 to 1,6	0	0	1
	2,0	10	
	4,0	20	
	8,0	40	
	10,0	50	
	14,0	70	
	16,0	80	
1,6 to 4,0	0	0	1
	5,0	25	
	10,0	50	
	15,0	75	
	20,0	100	
	25,0	125	
	30,0	150	
	35,0	175	
	40,0	200	

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## 8 Expression of results

### 8.1 When the calibration graph is not a straight line

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

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

$$\begin{aligned} & (e_{\text{Ni}1} - e_{\text{Ni}0}) \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 \\ &= (e_{\text{Ni}1} - e_{\text{Ni}0}) \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{250}{V_1} \times \frac{100}{m} \times 100 \\ &= (e_{\text{Ni}1} - e_{\text{Ni}0}) \frac{25}{10bV_1m} \end{aligned}$$

where

- $b$  is the optical path length, in centimetres, of the cell used for the measurements;
- $m$  is the mass, in grams, of the test portion (7.1);
- $V_0$  is the volume, in millilitres, of the test solution (7.3.1);
- $V_1$  is the volume, in millilitres, of the aliquot portion (table 1);

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

$e_{\text{Ni}0}$  is the concentration, expressed in micrograms per millilitre, of nickel in the blank test solution (corrected for its compensating solution);

$e_{\text{Ni}1}$  is the concentration, expressed in micrograms per millilitre, of nickel in the test solution (corrected for its compensating solution).

### 8.2 When the calibration graph is a straight line

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

$$\begin{aligned} & \frac{A_1 - A_0}{a} \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{V_0}{V_1} \times \frac{V_t}{m} \times 100 \\ &= \frac{A_1 - A_0}{a} \times \frac{1}{10^6} \times \frac{1}{b} \times \frac{250}{V_1} \times \frac{100}{m} \times 100 \\ &= \left( \frac{A_1 - A_0}{a} \right) \frac{25}{10bV_1m} \end{aligned}$$

where

- $a$  is the angular coefficient or the absorbance per microgram of Ni per millilitre of solution measured with an optical path length of 1 cm;

$A_0$  is the absorbance of the blank test solution measured in relation to its compensating solution (7.2);

$A_1$  is the absorbance of the test solution measured in relation to its compensating solution (7.3.3);

$b$  is the optical path length, in centimetres, of the cell used for the measurements;

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

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

$V_1$  is the volume, in millilitres, of the aliquot portion (table 1);

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

### 9 Precision

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, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests*.

The data obtained showed a logarithmic relationship between nickel content and repeatability and reproducibility of the test results, as summarized in table 3. The graphic presentation of the figures is given in annex B.

**Table 3**

Level nickel % (m/m)	$r$	$R$
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
4,0	0,046	0,075

The difference between two independent single results found on identical test material by one analyst using the same apparatus within a short time interval will exceed the repeatability  $r$ , on average not more than once in 20 cases, in the normal and correct operation of the method.

The difference between two single and independent results found by two operators working in different laboratories on identical test material will exceed the reproducibility  $R$ , on average not more than once in 20 cases, in the normal and correct operation of the method.

### 10 Test report

The test report shall include the following information:

- a) the method used by reference to this International Standard;
- b) the results, and the form in which they are expressed;
- c) any unusual features noted during the determination;
- d) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

## Annex A

### Additional information on the international co-operative tests

(Not an integral part of this International Standard.)

The table 3 in clause 9 has been derived from the results of the international analytical trials 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. Graphical treatment of the precision data is given in annex B.

The test samples used were:

Sample	Nickel content % (m/m)	
	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	0,558
BCS 225/2 (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

#### NOTES

- 1 The statistical analysis has been performed in accordance with ISO 5725.
- 2 Six samples were used for the international co-operative test. However, as the method is applicable to nickel contents between 0,10 and 4 % (m/m), only five points have been illustrated on the figures in annex B, the data for sample BCS 260/4 [Ni: 0,003 % (m/m)] having been omitted.

### Annex B

## Graphical representation of precision data

(Not an integral part of this International Standard.)

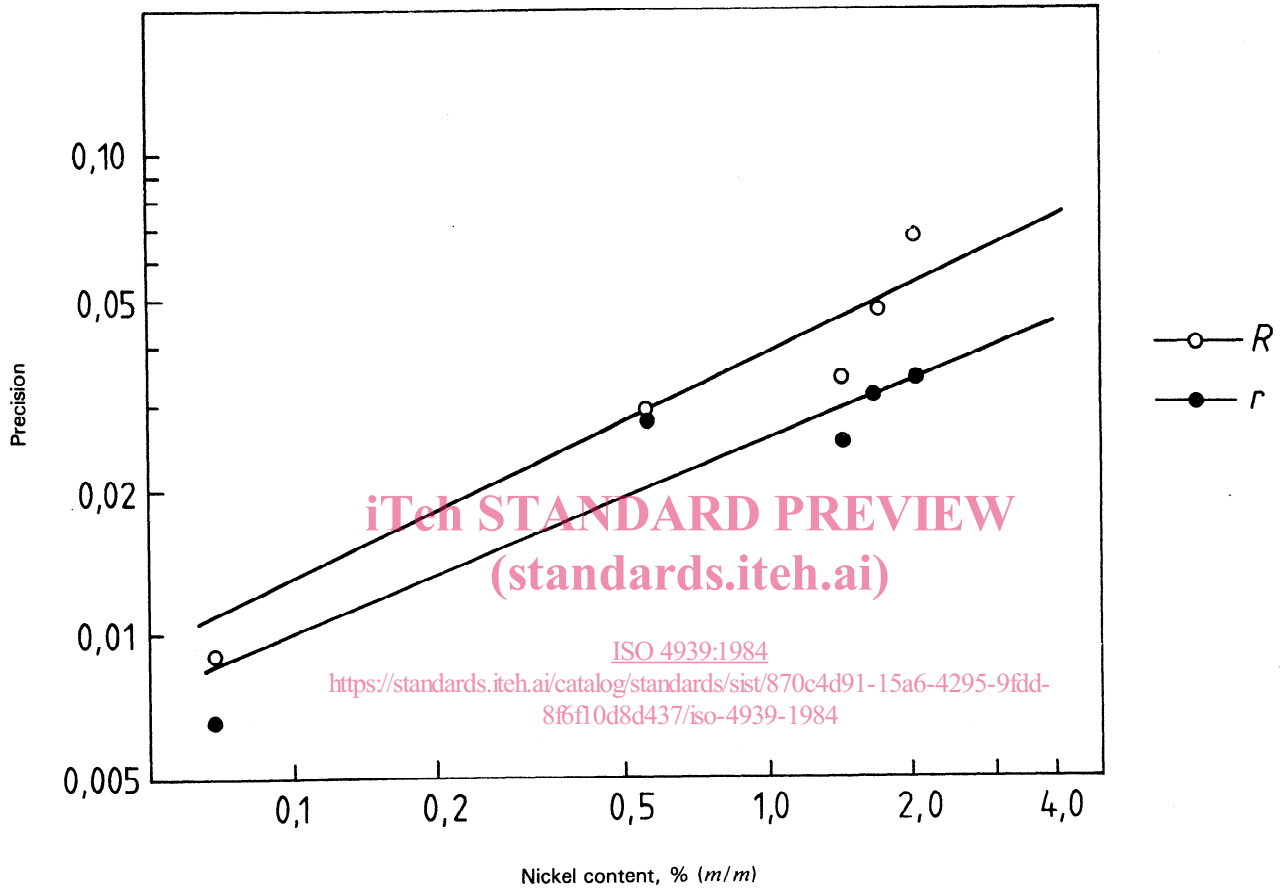


Figure — Relationship between nickel content and repeatability  $r$  or reproducibility  $R$