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Steel and cast iron — Determination of nickel content — Flame atomic absorption spectrometric method

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Foreword

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Steel and cast iron — Determination of nickel content — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a method for the determination of nickel in steel and cast iron by means of flame atomic absorption spectrometry.

The method is applicable to nickel contents in the range 0,002 to 0,5 % (m/m).

2 Reference

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

3 Principle

Dissolution of a test portion in a mixture of appropriate acids followed by evaporation to fuming with perchloric acid.

Spraying of the solution into an air-acetylene flame. Spectrometric measurement of the atomic absorption of the 352,5 nm spectral line emitted by a nickel hollow cathode lamp.

NOTE — With some instruments it is not possible to obtain sufficient sensitivity at the wavelength of 352,5 nm for low concentrations of nickel near the bottom end of the application range and in such cases the alternative wavelength of 232,0 nm must be used.

At the wavelength of 352,5 nm, the signal-to-noise ratio is higher than at a wavelength of 232,0 nm. In general, use of the 352,5 nm line will give better reproducibility.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and having a very low nickel content and only distilled water or water of equivalent purity.

If possible, use only freshly prepared distilled or deionized water.

4.1 Iron of high purity, nickel content < 0,000 5 % (m/m).

4.2 Hydrochloric acid-nitric acid mixture.

Mix three parts by volume of hydrochloric acid (ϱ about 1,19 g/ml), one part by volume of nitric acid (ϱ about 1,40 g/ml), and two parts by volume of water.

Prepare this mixture immediately before use.

4.3 Nitric acid-perchloric acid mixture.

Mix 100 ml of nitric acid (ϱ about 1,40 g/ml) with 800 ml of perchloric acid (ϱ about 1,54 g/ml). Dilute to 1 litre and mix.

NOTE — Perchloric acid (ϱ about 1,67 g/ml) may also be used. 100 ml of perchloric acid (ϱ about 1,54 g/ml) is equivalent to 79 ml of perchloric acid (ϱ about 1,67 g/ml).

4.4 Nickel, standard solution.

4.4.1 Stock solution, corresponding to 1 g of Ni per litre.

Weigh, to the nearest 0,000 1 g, 0,500 0 g of high purity nickel [$\geqslant$ 99,9 % (m/m) pure], and dissolve in 25 ml of nitric acid (ϱ about 1,40 g/ml, diluted 1 + 1). Boil to remove nitrous fumes. Cool and transfer the solution to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

4.4.2 Standard solution, corresponding to 40 mg of Ni per litre.

Transfer 10,0 ml of the stock solution (4.4.1) into a 250 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 40 µg of Ni.

Prepare this standard solution immediately before use.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Atomic absorption spectrometer

A nickel hollow cathode lamp; supplies of air and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from nickel.

The atomic absorption spectrometer used will be satisfactory if after optimization according to 7.3.4 the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the precision criteria given in 5.1.1.

5.1.1 Minimum precision

Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. The standard deviation shall not exceed 1,0 % of the mean absorbance.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). The standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

It is also desirable that the instrument should conform to the additional performance requirements given in 5.1.1.1 to 5.1.1.3.

5.1.1.1 Characteristic concentration

The characteristic concentration for nickel in a matrix similar to the final test portion solution shall be better than 0,50 µg of Ni per millilitre for wavelength 352,5 nm and better than 0,10 µg of Ni per millilitre for wavelength 232,0 nm.

5.1.1.2 Limit of detection

This is defined as twice the standard deviation of 10 measurements of the absorbance of a solution containing the appropriate element of a concentration level selected to give an absorbance just above that of the zero member.

The limit of detection of nickel in a matrix similar to the final test portion solution shall be better than 0,30 µg of Ni per millilitre for wavelength 352,5 nm and better than 0,15 µg of Ni per millilitre for wavelength 232,0 nm.

5.1.1.3 Graph linearity

The slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range (expressed as a change in absorbance) determined in the same way.

For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

5.2 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria in 5.1.1 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the read-out error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring a suitable solution with and without scale expansion and simply dividing the signal obtained.

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 matter in general.

Ensure that the spray system and drainage system are washed free from perchloric acid after use.

NOTE — All glassware shall first be washed in hydrochloric acid (ϱ about 1,19 g/ml, diluted 1 + 1), then in water. The quantity of nickel present in the beakers and flasks can be checked by measuring the absorption of the distilled water introduced into the glassware after the acid wash.

7.1 Test portion

Weigh, to the nearest 0,001 g, approximately 1 g 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 including iron (4.1).

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml beaker. Add, in small portions, 15 ml of the nitric acid-perchloric acid mixture (4.3), cover the beaker with a watch-glass and heat gently until solvent action ceases. Evaporate until dense white fumes of perchloric acid appear. Continue fuming for 1 min at such a temperature as to maintain a steady reflux of white perchloric acid fumes on the walls of the beaker.

NOTE — For samples not readily soluble in the nitric acid-perchloric acid mixture (4.3), first dissolve in 10 ml of the hydrochloric acid-nitric acid mixture (4.2) before adding the 15 ml of the nitric acid-perchloric acid mixture (4.3).

Allow to cool, add 25 ml of water and heat gently to dissolve salts. Cool again and transfer quantitatively to a 100 ml one-mark volumetric flask. Dilute to the mark and mix.

Filter by decantation through a dry medium filter paper to remove any residue or precipitate, for example graphite, silica or tungstic acid, and collect the filtrate in a dry beaker after discarding the first runnings.

If the expected nickel content of the test sample exceeds 0,1 % (*m*/*m*), the solution shall be diluted as follows.

Transfer 20,0 ml of the solution to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

NOTE — If the solution has to be diluted to give the test solution, the blank test (7.2) must be diluted in the same way.

7.3.2 Preparation of the calibration solutions

Place 10 ± 0,01 g of the iron (4.1) in an 800 ml beaker. Add 100 ml of the hydrochloric acid-nitric acid mixture (4.2) and heat until dissolved.

When dissolution is complete, add 150 ml of the nitric acid-perchloric acid mixture (4.3) and evaporate until dense white fumes of perchloric acid appear. Continue fuming for 1 min at such a temperature as to maintain a steady reflux of white perchloric acid fumes on the walls of the beaker.

Allow to cool, add 100 ml of water and heat gently to dissolve salts. Cool again and transfer the solution quantitatively to a 250 ml one-mark volumetric flask. Dilute to the mark and mix.

7.3.2.1 Nickel content < 0,1 % (*m*/*m*)

Transfer a series of 25,0 ml aliquots of the iron solution (7.3.2) to 100 ml one-mark volumetric flasks. Add to the flasks from a pipette or burette respectively 0 (the zero member); 2,5; 5,0; 10,0; 15,0; 20,0; and 25,0 ml of nickel standard solution (4.4.2). Dilute to the mark and mix.

7.3.2.2 Nickel content 0,1 to 0,5 % (*m*/*m*)

Transfer a series of 5,0 ml aliquots of the iron solution (7.3.2) to 100 ml one-mark volumetric flasks. Add to the flasks from a pipette or burette respectively 0 (the zero member); 2,5; 5,0; 10,0; 15,0; 20,0; and 25,0 ml of nickel standard solution (4.4.2). Dilute to the mark and mix.

NOTE — 1 ml of nickel standard solution (4.4.2) diluted to 100 ml is equivalent to 0,004 % (*m*/*m*) Ni in the case of 7.3.2.1 and 0,02 % (*m*/*m*) Ni in the case of 7.3.2.2.

7.3.3 Adjustment of atomic absorption spectrometer

See table 1.

Table 1

Type of lamp	Nickel hollow cathode
Wavelength	352,5 or 232,0 nm
Flame	Air-acetylene slightly lean flame adjusted for maximum nickel response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations

In the absence of the bandwidth recommendations mentioned in table 1 the following guidelines are suggested:

nickel 352,5 nm — bandwidth within the range 0,2 to 0,4 nm

nickel 232,0 nm — bandwidth within the range 0,15 to 0,25 nm

NOTE — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:

a) the explosive nature of acetylene, and regulations concerning its use;

b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;

c) the need to keep the burner head clear of deposits caused by perchloric salts, etc. A badly clogged burner may cause a flash back;

d) make sure that the liquid trap is filled with water.

7.3.4 Optimizing the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.

When the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, spray water until the indication has stabilized.

Set the absorbance value at zero using the zero member (7.3.2.1 or 7.3.2.2).

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision requirements (5.1.1).

Adjust the flame to be slightly lean and the burner height to about 1 cm below the light path. Spraying alternately the calibration solution of highest concentration and the zero member, adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum. Check that the spectrometer is set accurately on the required wavelength.

Evaluate the criteria of 5.1.1 to ensure that the instrument is suitable for the determination.

7.3.5 Spectrometric measurements

Set the scale expansion so that the calibration solution of highest concentration gives nearly full scale deflection. Aspirate the calibration solutions in ascending order repetitively until each gives the specified precision, thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Aspirate these first in ascending order, then in descending order, with the test solution as the middle solution in each case, measuring the absorption in relation to water. Aspirate the complete range of calibration solutions again.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case it is suggested that the two "sandwiching" solutions should not be used for the primary calibration but should be analysed alternately with the test solution.

Spray calibration solutions at frequent intervals during the measurement of a batch of determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the absorbance of each calibration solution.

Obtain the absorbance of the test solution and the mean absorbance of the blank test.

Convert the absorbances of the test solution and of the blank test to micrograms of Ni per millilitre by means of the calibration graph (7.4).

7.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations, and for the range of nickel contents expected.

Before plotting the graph, it is necessary to determine the concentration (real or apparent) of the zero member of the calibration series. This concentration is obtained by plotting the absorbances of the first three calibration solutions and extrapolating the curve to the concentration axis. The concentration, expressed in micrograms of Ni per millilitre, is added to the concentration value of each of the calibration solutions prior to the preparation of the calibration graph.

Prepare a calibration graph by plotting the absorbance values of the calibration solutions against nickel content, expressed in micrograms per millilitre. Refer the absorbances of the two adjacent calibration solutions to the graph. If these two calibration readings do not deviate from the graph by more than the permitted precision criteria then the test solution readings are also acceptable.

8 Expression of results

8.1 Method of calculation

The nickel content, expressed as a percentage by mass, w_{Ni} (%), is given by the equation

$$w_{\mathrm{Ni}}(\%) = \frac{(\varrho_0 - \varrho_1)\, D \times 100}{10^6} \times \frac{100}{m}$$

$$= \frac{(\varrho_0 - \varrho_1)\, D}{100\, m}$$

where

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

ϱ_0 is the concentration expressed in micrograms per millilitre, of nickel in the test solution derived from the calibration graph (7.4);

ϱ_1 is the concentration, expressed in micrograms per millilitre, of nickel in the blank test;

D is the dilution factor in 7.3.1;

$D = 1$ for samples with an expected nickel content of 0,1 % (m/m) or less

$D = 5$ for samples with an expected nickel content of more than 0,1 % (m/m)

8.2 Precision

A planned trial of this method was carried out involving from six to 18 laboratories and six levels of nickel, each laboratory making from two to five determinations at each level. A further trial was carried out involving from 13 to 19 laboratories at seven levels of nickel, each laboratory making two determinations 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 2, derived from 10 sets of results for nickel contents between 0,003 and 0,95 % (m/m) appropriate to the working range of 0,002 to 0,5 % (m/m) specified for the method.

Table 2

Nickel content [% (m/m)]	**Repeatability,** r	**Reproducibility,** R
0,002	0,000$_7$	0,001$_0$
0,005	0,001$_1$	0,001$_9$
0,01	0,001$_7$	0,003$_1$
0,02	0,002$_6$	0,004$_9$
0,05	0,004$_5$	0,009$_1$
0,10	0,006$_6$	0,014$_6$
0,20	0,0010$_2$	0,023$_3$
0,50	0,017$_6$	0,043$_5$

The difference between two 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 independant 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.

9 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

(This annex does not form part of this International Standard.)

Table 2 was derived from the results of international analytical trials on three steel samples (five countries involving 18 laboratories), five cast iron samples (France, 14 to 19 laboratories) and two steel samples (Netherlands, six to seven laboratories), namely on 10 samples in all.

The results of the international analytical trials were reported in document 17/1 N 432, July 1981 and French results on cast iron were reported in Document 17/1 N 546, October 1982. Graphical treatment of the precision data is given in annex B.

The test samples used are listed in table 3.

Table 3

Sample		Nickel content [% (*m*/*m*)]
BCS 260/4	(High purity iron)	0,003
EURO 077-1	(Plain carbon steel)	0,031
BCS 431	(Plain carbon steel)	0,069
E 80	(Cast iron)	0,070
C 82	(Low alloy cast iron)	0,080
C 79	(Low alloy cast iron)	0,112
EURO 278/1	(Cr-Mo steel)	0,236
A 80	(Low alloy cast iron)	0,329
A 82	(Low alloy cast iron)	0,423
BCS 341	(24 % Cr steel)	0,56-

NOTE — The statistical analysis was performed in accordance with ISO 5725

Annex B

Graphical representation of precision data

(This annex does not form part of this International Standard.)

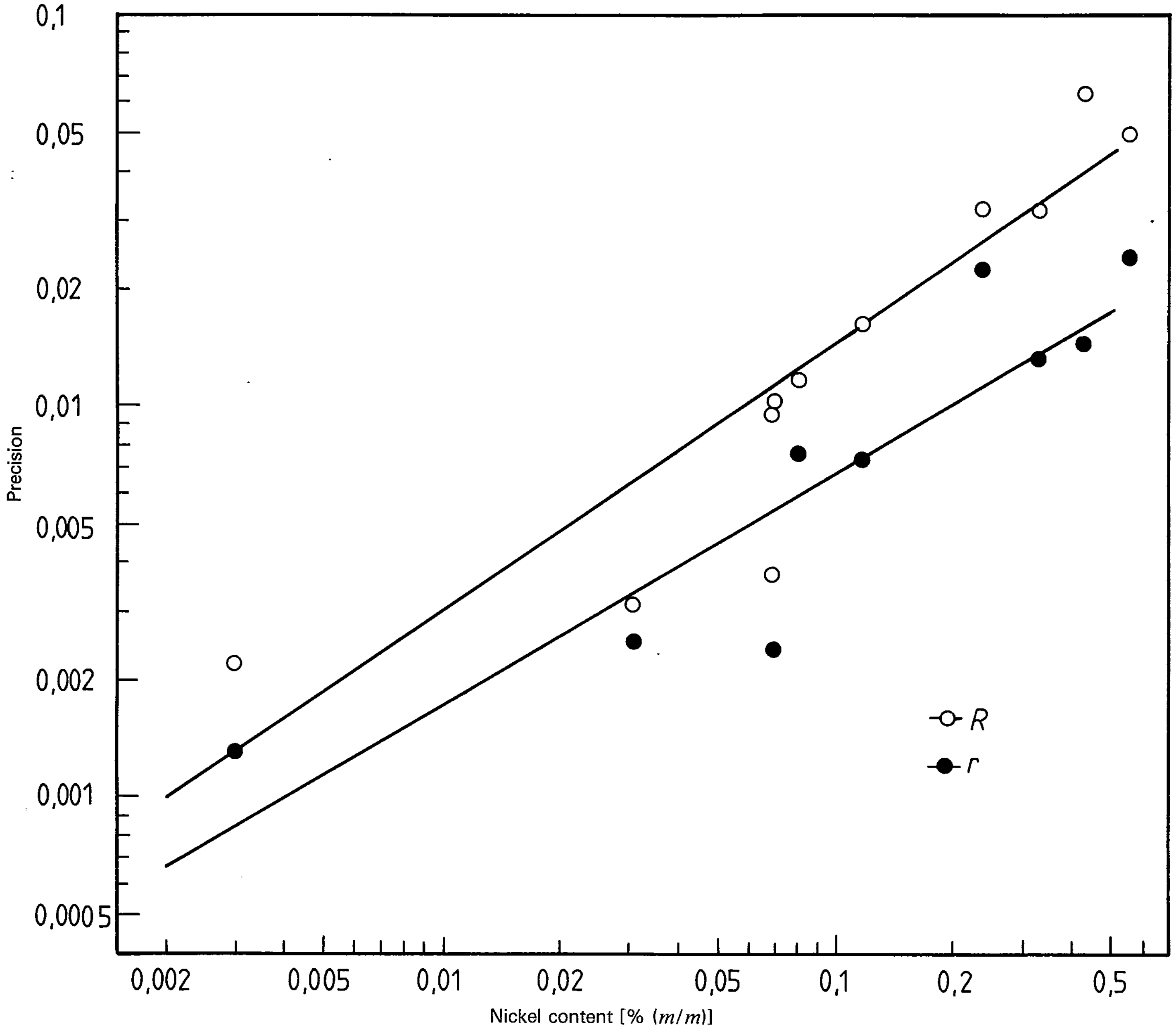

Figure — Relationship between nickel content and repeatability, *r*, or reproducibility, *R*