SLOVENSKI STANDARD
SIST EN 10136:1997

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Kemična analiza železovih zlitin - Določevanje niklja v jeklih in litinah - Plamenska atomska absorpcijska spektrometrična metoda

Chemical analysis of ferrous materials - Determination of nickel in steels and irons - Flame atomic absorption spectrometric method

Chemische Analyse von Eisenwerkstoffen - Bestimmung von Nickel in Stahl - Flammenatomabsorptionsspektrometrisches Verfahren

Analyse chimique des matériaux sidérurgiques - Dosage du nickel dans les aciers et les fontes - Méthode par spectrométrie d'absorption atomique dans la flamme

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English version

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CEN

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Brief History

This European Standard takes over the content of EURONORM 136-83 "Chemical analysis of ferrous materials - Determination of nickel in steels and irons - flame atomic absorption spectrometric method", prepared by ECISS/TC 20 "Methods of chemical analysis"; the Secretariat of which is allocated to the Dansk Standardiseringsrad (DS).

It has been submitted to the CEN Formal Vote following the decision of the Coordinating Commission (COCOR) of the European Committee for Iron and Steel Standardization on 1987-11-24/25.

It has been adopted and ratified by CEN BT on 1988-11-05.

According to the Common CEN/CENELEC Rules, following countries are bound to implement this European Standard :

Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxemburg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

Note in clauses 1 and 9 EURONORM shall read EUROPEAN STANDARD.

Chemical analysis of ferrous materials

Determination of nickel in steels and irons
Flame atomic absorption spectrometric method

CONTENTS

1. SCOPE AND FIELD OF APPLICATION

This EURONORM specifies a method for the determination of nickel in steels and irons by means of flame atomic absorption spectrometry.

The method is applicable to steels and irons with nickel contents of 0.003 to 2.0% (m/m).

2. REFERENCE

EURONORM 18 - Selection and preparation of samples and test pieces for steel and iron and steel products.

General guidelines for the application of flame atomic absorption spectrometric methods are in course of preparation.

3. PRINCIPLE

Dissolution of a test portion in a mixture of appropriate acids and fuming with perchloric acid.

Spraying of the solution into an air-acetylene flame. Determination of the nickel by means of the spectrometric measurement of the atomic absorption of the 232.0 nm or 352.5 nm line emitted by a nickel hollow cathode lamp.

The instrument is calibrated by addition of a nickel standard solution to a similar matrix to that of the test solution.

NOTE — At the wavelength of 352.5 nm the signal-to-noise ratio is higher than at a wavelength of 232.0 nm. Generally, use of the 352.5 nm line will lead to a better reproducibility.

However, as the sensitivity at 352.5 nm is less than the sensitivity at 232.0 nm, with some instruments the use of the longer wavelength will be impossible when analysing low nickel contents.

4. REAGENTS

During the analysis use only reagents of recognized analytical reagent quality and having a very low nickel content, and only distilled water or water of equivalent purity.

Carefully check the nickel content of all reagents.

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

4.1 Iron of high purity, with a nickel content < 0.0005% (m/m)

4.2 Hydrochloric acid—nitric acid mixture

Mix three volumes of hydrochloric acid, ρ 1.19 g/ml approximately, one volume of nitric acid, ρ 1.40 g/ml approximately and two volumes of water. This mixture is to be prepared immediately before use.

4.3 Nitric acid—perchloric acid mixture

Mix 100 ml of nitric acid, ρ 1.40 g/ml approximately with 300 ml of perchloric acid, ρ 1.54 g/ml approximately. Dilute to 1 l with water and mix.

NOTE — Perchloric acid (ρ 1.67 g/ml approximately) may also be used. 100 ml of perchloric acid (ρ 1.54 g/ml approximately) is equivalent to 79 ml of perchloric acid ρ 1.67 g/ml approximately).

4.4 Nickel stock solution, corresponding to 1 mg of nickel per ml approximately

Weigh, to the nearest 0.001 g, about 0.5 g of high purity nickel ($\geqslant$ 99.9% pure). Transfer the weighed mass to a 400 ml beaker and dissolve in 25 ml of nitric acid (ρ 1.40 g/ml approximately diluted 1 + 1 (v/v)). Boil to remove oxides of nitrogen. Cool and transfer the solution to a 500 ml volumetric flask, dilute to the mark with water and mix. Calculate the concentration of nickel in this stock solution, in mg/ml.

4.5 Nickel reference solution, corresponding to 40 μg of nickel per ml approximately

Transfer 10.0 ml of nickel stock solution (4.4) to a 250 ml volumetric flask, dilute to the mark with water and mix. Calculate the concentration of nickel in the reference solution, in μg/ml.

5. APPARATUS

Ordinary laboratory equipment 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 following performance requirements.

5.1.1 Minimum precision

The standard deviation of 10 measurements of the absorbency of the most concentrated solution shall not exceed 1.0% of the mean absorbance.

The standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero calibration solution) shall not exceed 0.5% of the mean absorbency of the most concentrated calibration solution.

For example, if the top and bottom calibration solutions represent 0.1% and 0.01% nickel in the sample, the precision called for (as two standard deviations) would be 0.002% and 0.001% nickel respectively, assuming curve linearity.

5.1.2 Additional performance requirements

It is also desirable that the instrument should conform to the following additional performance requirements.

(a) Characteristic concentration — The characteristic concentration for nickel in a matrix similar to the final test solution shall be better than 0.10 μg/ml.

(b) Limit of detection — The limit of detection of nickel in a matrix similar to the final test solution shall be better than 0.15 μg/ml.

5.2 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria in 5.1 and for all subsequent measurements.

6. SAMPLING

Sampling shall be carried out in accordance with EURONORM 18.

7. PROCEDURE

WARNING — Perchloric acid vapours may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general. Always use a specially designed fume-hood.

7.1 Test portion

Weigh the mass (m) indicated below to the nearest 0.001 g: m = 1 g ± 5%.

7.2 Blank test

With each analytical run, carry out an analysis on a reagent blank in parallel with the test portion analysis, using identical reagents, conditions, analytical procedures and dilutions throughout.

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml beaker. Add 10 ml of hydrochloric acid—nitric acid mixture (4.2). Heat gently until the reaction ceases.

Add 15 ml of nitric acid—perchloric acid mixture (4.3) and heat until dense white fumes of perchloric acid appear. Continue heating for one minute and allow to cool.

NOTE — If the test portion is readily soluble in the nitric acid—perchloric acid mixture (4.3), the addition of hydrochloric acid—nitric acid mixture (4.2) can be omitted. In that case the test portion is dissolved in the nitric acid—perchloric acid mixture (4.3) and the solution thus obtained is heated as described above.

Dissolve in 25 ml of water by heating gently. Cool again and transfer the solution to a 100 ml volumetric flask, dilute to the mark with water and mix. This is the test solution. If some residue has been left in the solution due to silicon, tungsten, niobium or tantalum, filter the solution through a dry, medium textured filter paper, discarding the first runnings.

If the expected nickel content of the test sample exceeds 0.1% (m/m), dilute the solution as follows:

Transfer 25.0 ml of the solution to a 500 ml volumetric flask, dilute to the mark with water and mix.

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

7.3.2 Preparation of the calibration solutions

Place 10 g of iron (4.1) in a 800 ml beaker. Add 100 ml of hydrochloric acid—nitric acid mixture (4.2) and heat gently to dissolve the iron.

Add 150 ml of nitric acid—perchloric acid mixture (4.3) and heat until dense white fumes of perchloric acid appear. Continue heating for one minute and allow to cool. Dissolve in 100 ml of water by heating gently. Cool again and transfer the solution to a 250 ml volumetric flask, dilute to the mark with water and mix.

7.3.2.1 Nickel content < 0.1% (m/m)

Transfer a series of 25.0 ml aliquots of the iron solution to 100 ml volumetric flasks, add to each flask by means of a burette or pipette respectively 0, 2.5, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of nickel reference solution (4.5), dilute to the mark with water and mix.

7.3.2.2 Nickel content 0.1 to 2.0% (m/m)

Transfer 25.0 ml of the iron solution to a 500 ml volumetric flask, dilute to the mark with water and mix. From this solution transfer 25.0 ml aliquots to 100 ml volumetric flasks. Add to each flask by means of a burette or pipette respectively 0, 2.5, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of nickel reference solution (4.5), dilute to the mark with water and mix.

NOTE — 1 ml of nickel reference solution (4.5) is approximately equivalent to 0.004% (m/m) in the sample in the case of 7.3.2.1 and 0.08% (m/m) in the sample in the case of 7.3.2.2.

7.3.3 Adjustment of atomic absorption spectrometer (5.1)

Type of lamp:	Nickel hollow cathode.
Wavelength:	232.0 nm or 352.5 nm.
Flame:	Air-acetylene clear fuel-lean flame adjusted for maximum nickel response
Lamp current — Slit width	Follow manufacturer's recommendations.

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 UV radiation by means of tinted glass;

(c) the need to keep burner head clear of deposits. A badly clogged burner may cause a flash back;

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

7.3.4 Optimization of the atomic absorption spectrometer settings

Follow the manufacturers instructions for preparing the instrument for use.

When the current to the lamp, the wavelength and flow of gas have been adjusted and the burner lit, spray water until the indication has stabilized. Set the absorbance value to zero. Choose a damping setting or integration time to give a signal steady enough to fulfil the precision requirements (5.1).

Adjust the flame to be clear fuel-lean and the burner height to about 1 cm below the light path. Spraying, alternately, the high- and zero calibration solutions, adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum.

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

7.3.5 Atomic absorption measurements

Set the scale expansion so that the top calibration solution gives nearly full scale deflection. Aspirate the calibration solutions in ascending order repetitively until each gives the acceptable precision (see 5.1.1), thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbency just lower than the test 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 absorbency 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.

Obtain the net mean absorbance of each calibration solution by subtracting the mean absorbance of the zero calibration solution.

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

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

7.4 Establishment of the calibration graph

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

Prepare a calibration graph by plotting the net mean absorbance values of the calibration solutions against micrograms of nickel per millilitre, calculated according to 4.5. Refer the net 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 acceptable.

8. EXPRESSION OF RESULTS

The percentage by mass of nickel (Ni) is given by the expression

$$\text{Ni \% (m/m)} = \frac{(b - c) \cdot \text{D} \cdot 100}{10^6} \cdot \frac{100}{m} = \frac{(b - c) \cdot \text{D}}{100\, m}$$

where:

b is the concentration of nickel in the test solution in µg/ml;

c is the concentration of nickel in the reagent blank solution in µg/ml;

D is the dilution factor in 7.3.1:
(D = 1 for samples with an expected nickel content of 0.1% or less.

D = 20 for samples with an expected nickel content of more than 0.1%);

m is the mass of the test portion, in g.

9. TEST REPORT

The test report shall contain the following particulars:

(a) The method of analysis used by reference to this EURONORM;

(b) the results obtained, as well as the form in which they are expressed;

(c) any particular details which may have been noted during the determination;

(d) any operations not specified in this EURONORM or any optional operations which could have had an influence on the result;

(e) all indications necessary for the identification of the sample;

(f) the laboratory and the date of analysis.

ANNEX

Precision data

Planned trials of this method were carried out by analysts from 6 to 19 laboratories; 2-5 determinations were carried out by each analyst on each sample. From the results obtained the 95% (2s) confidence limits have been calculated in accordance with ISO 5725 and are tabulated as follows: