
**Kemična analiza železovih zlitin - Določevanje dušika (v sledih) v jeklih -
Spektrofotometrična metoda**

Chemical analysis of ferrous materials - Determination of nitrogen (trace mounts) in steel
- Spectrophotometric method

Chemische Analyse von Eisen- und Stahlwerkstoffen - Bestimmung von Stickstoff
(Spuren-Gehalte) in Stahl - Photometrisches Verfahren

Analyse chimique des matériaux sidérurgiques - Dosage de l'azote (à l'état de traces)
dans les aciers - Méthode spectrophotométrique

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English version

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CEN

European Committee for Standardization
 Comité Européen de Normalisation
 Europäisches Komitee für Normung

Central Secretariat : Rue Bréderode 2, B-1000 Brussels

Brief History

This European Standard takes over the content of EURONORM 179-85 "Chemical analysis of ferrous materials - Determination of nitrogen (trace amounts) in steels - Spectrophotometric 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, Luxembourg, 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 nitrogen (trace amounts) in steels

Spectrophotometric method

CONTENTS

1. SCOPE AND FIELD OF APPLICATION	7. PROCEDURE
2. REFERENCE	7.1 Test portion
3. PRINCIPLE	7.2 Blank test
4. REAGENTS	7.3 Preparation of the steam distillation apparatus
5. APPARATUS	7.4 Determination
6. SAMPLING	7.5 Establishment of the calibration graph
	8. EXPRESSION OF RESULTS
	9. TEST REPORT
	ANNEX: Precision data

1. SCOPE AND FIELD OF APPLICATION

This EURONORM specifies a method for the spectrophotometric determination of nitrogen in steels.

The method is primarily intended for the determination of total nitrogen in very low nitrogen non-alloy steels. It may be used, however, for any low nitrogen ferrous alloy that is soluble in hydrochloric acid provided that the acid-resistant form of silicon nitride is not present. This highly resistant nitride has been found only in samples of silicon steels manu-

factured without aluminium addition and then only in sheet material.

The method is applicable to nitrogen contents from 0.0005 to 0.005% (m/m).

NOTE — The method has also been successfully applied to a pure iron with a nitrogen content of 0.0038% (m/m) — see Annex.

2. REFERENCE

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

3. PRINCIPLE

Dissolution of the test portion with hydrochloric acid and separation of the acid-insoluble residue by means of a centrifuge.

Decomposition of the acid-insoluble residue by intense fuming with sulphuric acid and addition of the extract to the solution of the test portion containing the acid-soluble nitrogen.

Recovery of the total nitrogen as ammonia by steam distillation over sodium hydroxide.

Spectrophotometric measurement of the coloured complex produced by the indophenol blue reaction.

4. REAGENTS

During the analysis use only reagents of recognized analytical reagent quality and which are known to give a very low nitrogen blank. The same batch of each reagent shall be used for every test and blank determination in a given series of tests.

All references to 'water' relate to ammonia-free water. Ammonia-free water shall be prepared by passing distilled water

through the cation exchange column (5.1). It is essential that the resin column shall be acid washed before use to ensure its conversion to the hydrogen form (H⁺). This is most conveniently done by passing 2 litres of hydrochloric acid ρ 1.19 g/ml approximately, diluted 1 + 9 (V/V), through the column, then washing with water until freed from acid.

4.1 Iron of high purity or steel of very low nitrogen content

NOTE — High purity iron powder or very low nitrogen mild steel (< 0.001% nitrogen) may be used for this purpose. It should be washed in the same way as the sample.

4.2 Hydrochloric acid, ρ 1.19 g/ml approximately (12 mol/l approximately)

4.3 Sulphuric acid, ρ 1.84 g/ml approximately, (18 mol/l approximately)

Sulphuric acid supplies shall be tested individually and selected for a low content of combined nitrogen in any form (less than 0.5 ppm). Nitrogen as ammonia will usually be the major source of contamination and this may be tested by the normal methods, but nitrates may also be present and may be detected by the following method.

Add 6 ml of the sulphuric acid to 2 ml of water and cool to 60 °C. Add one drop of hydrochloric acid (4.2) and one drop of diphenylamine reagent (4.8). No blue colour should develop. Less than 0.1 ppm can be detected by this test.

4.4 Sulphuric acid, ρ 1.84 g/ml approximately, diluted 1 + 4 (V/V) (3.6 mol/l approximately)

4.5 Sodium hydroxide, 400 g/l solution

Dissolve 400 g of sodium hydroxide in water, dilute to 1 000 ml and mix. This solution should be prepared in a polyethylene beaker (water-cooled if necessary) and stored in a polyethylene bottle.

4.6 Barium chloride, 100 g/l solution

Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water, dilute to 1 000 ml and mix.

4.7 Chromic-sulphuric acid*

Dissolve 2 g of chromium trioxide in 50 ml of water, and add slowly 100 ml of sulphuric acid (4.3) with constant stirring.

4.8 Diphenylamine reagent*

To 25 ml of water, whilst stirring, cautiously add 75 ml of sulphuric acid (4.3) then add 0.1 g diphenylamine, stir until dissolved and cool.

4.9 Phenol, 50 g/l solution

Dissolve 50 g of phenol in water, transfer to a 1 000 ml volumetric flask, dilute to the mark with water and mix. (Store out of direct sunlight in an amber coloured bottle).

4.10 Sodium hydroxide—sodium hypochlorite solution

4.10.1 Determination of available chlorine in commercial sodium hypochlorite solution

By means of a burette, transfer 10 ml of the sodium hypochlorite solution to a 250 ml volumetric flask, dilute to the mark with water and mix.

Transfer, by means of a safety pipette, 10 ml of this solution to a 100 ml conical beaker, add 2 g of potassium iodide and 10 ml of glacial acetic acid, ρ 1.048–1.050 g/ml approximately. Titrate the liberated iodine using sodium thiosulphate (4.12) until the colour is almost discharged. Add 2 ml of starch solution (4.13), and continue the titration until the blue colour is discharged.

Available chlorine per cent (w/v) = $0.886 \cdot V$

where V is the volume in millilitres of sodium thiosulphate (4.12) used in the titration.

4.10.2 Calculation

The volume of sodium hypochlorite solution required for the preparation of 1 l of sodium hydroxide-sodium hypochlorite solution (4.10) is

$$\frac{2.1 \cdot 100 \cdot 70.91}{0.886 \cdot V \cdot 74.44} = \frac{225.7}{V} \text{ ml}$$

This volume is equivalent to 2.1 g of available chlorine.

4.10.3 Preparation of solution 4.10

Dissolve 25 g of sodium hydroxide in about 400 ml of water. Add the calculated volume of sodium hypochlorite solution (4.10.2) from a burette, dilute to 1 000 ml and mix. (Store out of direct sunlight in an amber bottle).

4.11 Sodium pentacyanonitrosylferrate (sodium nitroprusside) ($\text{Na}_2 [\text{Fe}(\text{CN})_5\text{NO}] 2\text{H}_2\text{O}$)

Dissolve 0.1 g of sodium pentacyanonitrosylferrate in water, dilute to 100 ml and mix. Prepare freshly each day, store in an amber coloured bottle but do not use until at least 60 min. after preparation.

4.12 Sodium thiosulphate, 0.05 mol solution*

Dissolve 24.821 g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in water containing 0.1 g of sodium carbonate. Transfer to a 1 000 ml volumetric flask, dilute to the mark with water and mix.

4.13 Starch, 5 g/l solution*

Make a suspension of 0.5 g of starch in 10 ml of water. Add to 90 ml of boiling water. Cool, dilute to 100 ml and mix.

4.14 Ammonium chloride reference solution corresponding to 1 μg of nitrogen per millilitre

Dissolve 0.382 g of ammonium chloride (previously dried to constant weight at 105 °C) in water, transfer to a 1 000 ml

volumetric flask, dilute to the mark and mix. Transfer 10 ml of this solution to a 1 000 ml volumetric flask, dilute to the mark and mix.

* Reagents marked with an asterisk are not used in the determination itself but only for auxiliary purposes, e.g. the preparation of other reagent solutions.

5. APPARATUS

Ordinary laboratory equipment and

5.1 Cation exchange column

A column packed with a sulphonated polystyrene cation exchange resin (Fig. 1).

5.2 Aluminium alloy heating block

An aluminium alloy block containing a number of sockets for the purpose of supporting 50 ml centrifuge tubes (Fig. 2) and heated by contact with the surface of a hotplate.

NOTE — It is essential that the hot plate is capable of heating the test solutions to a temperature of at least 320 °C. This should be checked by inserting a thermometer in sulphuric acid under test conditions.

5.3 Steam distillation apparatus

The distillation unit illustrated in Fig. 3 has been found suitable.

5.4 Centrifuge

An electrically driven centrifuge capable of taking tubes of 50 ml capacity and attaining a steady speed of 3 500 revolutions per minute.

5.5 A spectrophotometer suitable for measuring the absorbance of the solution at a wavelength of 635 nm together with 1 cm cells

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6. SAMPLING

Sampling shall be carried out in accordance with EURONORM 18.

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7. PROCEDURE

NOTE — It is essential that nitrogen determinations shall be carried out in a laboratory reserved for the purpose and it is particularly important that ammonium salts and ammonia fumes should be excluded. In addition, the glassware should be reserved for this work only and should be cleaned with the chromic-sulphuric acid solution (4.7), and thoroughly washed with ammonia-free water before use.

7.1 Test portion

NOTE — Sample millings or drillings should be washed in ether to remove any contamination by oil. If the drillings or millings have been stored in the chemical laboratory they should be washed in hot water and dried immediately before determining the nitrogen content.

Weigh the mass (m) indicated below to the nearest 0.001 g :

$m = 1.0 \text{ g} \pm 5\%$ and also to the same accuracy 0.25 g of high purity iron (4.1).

7.2 Blank test

With each analytical run, carry out an analysis on a 0.25 g portion of high purity iron (4.1) in parallel with the test portion analysis, using identical reagents and conditions throughout.

7.3 Preparation of the steam distillation apparatus

Ammonia-free water shall be used exclusively in the steam generating flask A (Fig. 3). Any water left over from a previous day should be rejected and the flask rinsed before refilling.

Prepare the apparatus (Fig. 3) for use as follows: Fill the steam generator A with water, replace stopper G, open the screw clip K, and raise the funnel plug D. Heat the steam generator and boil the water vigorously, allowing the steam to escape for 30 min. via funnel C and the drain tube from steam trap B. Close the screw clip K, transfer 5 ml of sodium hydroxide solution (4.5) to the distillation vessel E via funnel C and lower the funnel plug D. Collect and discard about 50 ml of distillate and rinse the condenser tip with water. Place a 100 ml volumetric flask under the condenser and distil until about 35 ml of distillate have been collected. Turn off the source of heat to the steam generator A allowing the contents of the distillation vessel E to syphon into trap B, then open the screw clip K to discard the solution.

To the volumetric flask add 8 ml of phenol solution (4.9), 8 ml of the sodium hydroxide-hypochlorite solution (4.10) and 2 ml of sodium pentacyanonitrosylferrate solution (4.11), mixing the solutions after each addition. Dilute to the mark and mix. To a second 100 ml volumetric flask add about 35 ml of water and make the same reagent additions as to the distillate. Dilute to the mark and mix.

NOTE — The addition of phenol, sodium hypochlorite and sodium pentacyanonitrosylferrate solutions should be made by means of burettes. Since these reagents are photosensitive the burettes should be filled immediately before use. They should be emptied and washed out immediately after use.

Allow both solutions to stand away from direct sunlight, preferably in a dark cupboard, for a period of 40 min. Measure the absorbance of each solution at 20 ± 1 °C, using the conditions specified in clause 7.4.4.

Convert both absorbance readings to micrograms of nitrogen by means of the calibration graph (7.5). If the difference

indicates more than $3 \mu\text{g}$ ($\neq 0.0003\%$) nitrogen from the steam distillation, the source of contamination should be identified and steps taken to reduce it to an acceptable value.

7.4 Determination

7.4.1 Preparation of the test solution

Transfer the test portion (sample and pure iron) (7.1) to a centrifuge tube.

Add 5 ml of hydrochloric acid (4.2), cover and insert in the aluminium alloy heating block (5.2). Heat gently, avoiding loss by evaporation until solvent action has apparently ceased.

Remove from the heating block and add, by means of safety pipettes or micro-burettes, 0.25 ml of sulphuric acid (4.4) and 0.5 ml of barium chloride solution (4.6). Mix by swirling the tube and allow to cool.

Transfer to the centrifuge and spin for 5 min. at 3 500 revolutions per minute.

Decant the supernatant liquid into a 50 ml squat beaker. Rinse the walls of the tube very carefully with about 5 ml of water and transfer the washings to the 50 ml beaker. Cover the beaker and reserve.

Add 5 ml of sulphuric acid (4.3) to the residue in the centrifuge tube then cover and insert the tube in the aluminium alloy heating block (5.2). Evaporate to fuming and continue heating at a minimum temperature of 320°C for 50 min. Cool and cautiously transfer the contents of the centrifuge tube to the reserved solution in the 50 ml beaker, washing any deposit from the cover and walls of the tube into the beaker with water. Heat to dissolve soluble salts, then cool.

7.4.2 Distillation

Place a 100 ml volumetric flask under the condenser and close screw clip K (Fig. 3). Transfer the sample solution to the distillation vessel E, rinsing the beaker and funnel several times with a few millilitres of water. Add 35 ml of sodium hydroxide solution (4.5) and lower the funnel plug D. Heat the steam generator A and distil at such a rate that no frothing takes place, collecting about 35 ml of distillate.

Turn off the source of heat to the steam generator A, allowing the contents of the distillation vessel to syphon into trap B, then open the screw clip K to discard the solution. The still is now ready for the next determination. Cover the flask and reserve the distillate until the complete batch has been distilled so that all can be treated for colour development at the same time.

7.4.3 Development of the colour

Add to the distillate 8 ml of phenol solution (4.9), 8 ml of sodium hydroxide-sodium hypochlorite solution (4.10) and 2 ml of sodium pentacyanonitrosylferrate solution (4.11) mixing the solutions after each addition. See Note in clause 7.3.

Dilute to the mark, allow to stand away from direct sunlight, preferably in a dark cupboard, for a period of 40 minutes.

7.4.4 Spectrophotometric measurement

Carry out the spectrophotometric measurement in 1 cm cells at a wavelength of 635 nm, at a temperature of $20 \pm 1^\circ\text{C}$ having set the spectrophotometer to zero absorbance in relation to water.

Convert the readings for the test portion solution and for the reagent blank solution to micrograms of nitrogen by reference to the calibration graph (7.5).

7.5 Establishment of the calibration graph

7.5.1 Preparation of the calibration solutions

To a series of seven 100 ml volumetric flasks make additions of ammonium chloride reference solution (4.14) as follows:

Ammonium chloride solution (4.14) ml	Nitrogen added μg	Equivalent nitrogen on 1 g sample %
0	0	0
5	5	0.0005
10	10	0.001
20	20	0.002
30	30	0.003
40	40	0.004
50	50	0.005

Dilute, if necessary, to 50 ml with water and mix.

Continue as described in clause 7.4.3.

7.5.2 Spectrophotometric measurements

Carry out spectrophotometric measurements according to the method described in clause 7.4.4., after having adjusted the spectrophotometer to zero absorbance in relation to water.

7.5.3 Plotting the calibration curve

From each of the absorbance readings subtract the reading obtained on the test portion with no added ammonium chloride. Prepare a calibration graph by plotting the net absorbance readings against micrograms of nitrogen.

8. EXPRESSION OF RESULTS

The percentage by mass of nitrogen (N) is given by the expression

$$\text{N \% (m/m)} = \frac{m_1 - m_0}{m} \cdot 10^4$$

where

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

m_1 is the mass, in micrograms, of nitrogen found in the test portion solution;

m_0 is the mass, in micrograms, of nitrogen found in the blank test solution.

9. TEST REPORT

The test report shall contain the following particulars:

- (a) the method of analysis used by reference to this EURO-NORM;
- (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 7 analysts from different laboratories; 6 determinations were carried out by each analyst on each of 7 samples. From the results

obtained the 95% (2s) confidence limits have been calculated in accordance with ISO 5725, and are tabulated as follows:

Alloy type	Nitrogen % (m/m)	Repeatability r	Reproducibility R
Non-alloy steel	0.0009	0.00022	0.00027
Non-alloy steel	0.0012	0.00033	0.00038
Non-alloy steel	0.0019	0.00025	0.00028
Non-alloy steel	0.0027	0.00027	0.00033
Non-alloy steel	0.0032	0.00029	0.00035
Pure iron	0.0038	0.00031	0.00043
Non-alloy steel	0.0043	0.00026	0.00035

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Repeatability

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

Reproducibility

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.