SLOVENSKI STANDARD
SIST EN ISO 4945:2010

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Jeklo - Določevanje dušika - Spektrometrična metoda (ISO 4945:1977)

Steel - Determination of nitrogen content - Spectrophotometric method (ISO 4945:1977)

Stahl - Bestimmung des Stickstoffgehalts - Spektralphotometrisches Verfahren (ISO 4945:1977)

Acier - Dosage de l'azote - Méthode spectrophotométrique (ISO 4945:1977)

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Steel - Determination of nitrogen content - Spectrophotometric method (ISO 4945:1977)

Acier - Dosage de l'azote - Méthode spectrophotométrique (ISO 4945:1977)

Stahl - Bestimmung des Stickstoffgehalts - Spektralphotometrisches Verfahren (ISO 4945:1977)

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Foreword

The text of ISO 4945:1977 has been prepared by Technical Committee ISO/TC 17 “Steel” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 4945:2009 by Technical Committee ECISS/TC 20 “Methods of chemical analysis of ferrous products” the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2010, and conflicting national standards shall be withdrawn at the latest by April 2010.

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INTERNATIONAL STANDARD 4945

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Steel — Determination of nitrogen content — Spectrophotometric method

Acier — Dosage de l'azote — Méthode spectrophotométrique

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FOREWORD

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International Standard ISO 4945 was developed by Technical Committee ISO/TC 17, *Steel*, and was circulated to the member bodies in March 1976.

It has been approved by the member bodies of the following countries :

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Steel — Determination of nitrogen content — Spectrophotometric method

1 SCOPE

This International Standard specifies a spectrophotometric method for the determination of the nitrogen content of non-alloy and low-alloy steels. This method allows the determination only of the nitrogen content which can be converted to an ammonium salt.

2 FIELD OF APPLICATION

The method is applicable to non-alloy and low-alloy steels containing between 0,002 % and 0,050 % (*m/m*) of nitrogen and less than 0,6 % (*m/m*) of silicon.

3 REFERENCE

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

4 PRINCIPLE

Dissolution of a test portion in dilute sulphuric acid.

After concentration, progressive increasing of the temperature to above 300 °C.

Separation of ammonia from the ammonium salt formed, by displacement and distillation in a boiling sodium hydroxide medium and collecting in an acid medium.

At ambient temperature, formation of a blue-coloured complex between the ammonium ions and phenol in the presence of sodium hypochlorite and sodium pentacyanonitrosylferrate(II) (sodium nitroprusside). Spectrophotometric measurement of the complex at a wavelength of about 640 nm.

5 REAGENTS

During the analysis, use only reagents of recognized analytical grade.

5.1 Distilled or de-ionized water, free from nitrogen compounds, purified by a second passage through ion-exchange resins.

5.2 Potassium sulphate, anhydrous (K_2SO_4).

5.3 Sulphuric acid, ρ approximately 1,84 g/ml, about 96 % (*m/m*) solution, free from nitrogen compounds.

5.4 Sulphuric acid, ρ approximately 1,21 g/ml, about 29 % (*m/m*) solution.

Add in small portions, whilst cooling, 200 ml of sulphuric acid (5.3) to about 700 ml of water (5.1), make up the volume to 1 000 ml with water (5.1) and mix.

5.5 Sodium hydroxide, approximately 12 N solution.

Dissolve, with caution, 480 g of sodium hydroxide pellets in 700 ml of water (5.1) contained in a polytetrafluoroethylene beaker. Heat the solution to boiling and boil for 10 min. Cool, make up the volume to 1 000 ml with water (5.1) and mix. Store in a suitable plastics container.

5.6 Sulphuric acid, approximately 1 N solution.

Add 30 ml of sulphuric acid (5.3) to about 700 ml of water (5.1); after cooling make up the volume to 1 000 ml with water (5.1) and mix.

5.7 Sulphuric acid, approximately 0,04 N solution.

Dilute 40 ml of sulphuric acid solution (5.6) to 1 000 ml with water (5.1) and mix.

5.8 Sodium hydroxide, approximately 0,2 N solution.

Dilute 30 ml of a 250 g/l solution of sodium hydroxide with water (5.1), make up the volume to 1 000 ml with water (5.1) and mix.

5.9 Sodium phenate solution.

Add, whilst agitating and cooling, 5 g of phenol to a mixture of 10 ml of a 250 g/l solution of sodium hydroxide and 80 ml of water (5.1).

Make up the volume to 100 ml with water (5.1) and mix.

Prepare this solution at the time of use.

5.10 *Di*sodium hydrogen phosphate, 0,1 M solution.

Dissolve 36 g of *di*sodium hydrogen phosphate dodecahydrate ($Na_2HPO_4.12H_2O$) in water (5.1), make up the volume to 1 000 ml with water (5.1) and mix.

5.11 *Di*sodium pentacyanonitrosylferrate(II), 0,25 g/l solution.

Dissolve 10 g of *di*sodium pentacyanonitrosylferrate(II) dihydrate (sodium nitroprusside) [$Na_2Fe(CN)_5NO.2H_2O$] in water (5.1), make up the volume to 1 000 ml with water (5.1) and mix.

At the moment of use, dilute 25 ml of this solution to 1 000 ml with water (5.1).

5.12 Sodium hypochlorite, approximately 0,1 N solution (approximately 0,3 % (*m/m*) of active chlorine).

Store this solution at a temperature less than 10 °C.

5.13 Nitrogen, standard solution corresponding to 0,100 0 g of nitrogen (N) per litre.

Weigh, to the nearest 0,1 mg, 0,471 6 g of dry ammonium sulphate, dissolve in water (5.1) and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 100 µg of nitrogen (N).

5.14 Nitrogen, standard solution corresponding to 0,002 0 g of nitrogen (N) per litre.

Transfer 20,0 ml of the standard nitrogen solution (5.13) to a 1 000 ml one-mark volumetric flask, dilute to the mark with water (5.1) and mix.

1 ml of this standard solution contains 2 µg of nitrogen (N).

Prepare this standard solution at the time of use.

5.15 Methyl red, 0,1 g/l solution.

Dissolve 0,1 g of methyl red in water (5.1), make up the volume to 1 000 ml with water (5.1) and mix.

6 APPARATUS

Ordinary laboratory apparatus and

6.1 Semi-micro apparatus for distillation without additional steam (see figure 1) or

6.2 Apparatus for distillation under a current of steam (see figure 2).

6.3 Spectrophotometer.

NOTE — All glassware shall be cleaned prior to use in hot sulphuric-chromic acid prepared from pure ingredients and water (5.1).

7 SAMPLING

Sampling shall be carried out in accordance with ISO/R 377. For wrought steels not complying with ISO/R 377, the appropriate national standard shall be used.

8 PROCEDURE

NOTE — Carry out operations in a well-ventilated room away from all work on nitrogenous products.

8.1 Test portion

Weigh, to the nearest 0,001 g, masses of 1 g and 2 g respectively of the test sample, to be treated concurrently.

8.2 Blank test

The procedure specified in 8.3 and 8.4 eliminates the incidence of the value of the blank test when the same reagents are used with the two test portions indicated in 8.1.

8.3 Determination

8.3.1 *Preparation of the test solution*

In a 150 ml Kjeldahl flask covered with a watch-glass, dissolve the test portion (8.1) with 30 ml of sulphuric acid solution (5.4). Allow to digest, taking care that the temperature of the liquid does not exceed 90 °C, until the release of hydrogen has definitely ceased.

When the release of hydrogen has ceased, remove the watch-glass and heat until white sulphuric fumes begin to appear.

Then add

- — 5 ml of sulphuric acid (5.3) and
- — 1 g of potassium sulphate (5.2).

Heat for 2 h at a temperature above 300 °C, in such a way that the mixture remains liquid. Cool, add 10 ml of water (5.1) and heat to dissolve the majority of the sulphates.

8.3.2 *Distillation*

The distillation may be carried out with or without additional steam.

NOTE — The flasks used in distillation are attacked by the sodium hydroxide solution; change them frequently.

8.3.2.1 DISTILLATION WITHOUT ADDITIONAL STEAM

Use the apparatus shown in figure 1 (6.1).

To collect the distillate, transfer 5 ml of sulphuric acid solution (5.6) to a 100 ml volumetric flask with a ground neck and having a mark at 85 ml. Introduce the tapered tube extension of the condenser into the flask in such a manner that it is immersed in the sulphuric acid solution (5.6).

Pass the test solution (8.3.1) quantitatively into the distillation flask, rinsing with 60 ml of water (5.1), add 50 ml of sodium hydroxide solution (5.5) and rinse the neck of the flask with 30 ml of water (5.1). The final volume of the solution should be approximately 160 to 165 ml. Moisten the ground neck and connect the flask to the condenser immediately after the addition of the sodium hydroxide solution (5.5).

Now begin the distillation. Distil about 80 ml in 25 min. When the distillation is ended, rinse the immersed tube with water (5.1), collecting the washings in the volumetric flask; make up to volume with water (5.1) and mix. Solutions S_1 for the 1 g test portion and S_2 for the 2 g test portion are obtained. Repeat the same operation (8.3.2.1) for each sample to be analysed, taking care, after each distillation, to rinse the flask with plenty of water, then distilled water and finally the water (5.1).

NOTE — To regulate the boiling during the distillation in the apparatus shown in figure 1, it is as well to add some pieces of porous ceramic. These pieces are previously treated as a test sample and collected up after distillation. They are then washed with sulphuric acid solution (5.6) until neutral, then with water (5.1) and finally dried.

8.3.2.2 DISTILLATION UNDER A CURRENT OF STEAM

Use the apparatus shown in figure 2 (6.2).

To collect the distillate, transfer 5 ml of sulphuric acid (5.7) to a beaker of suitable capacity, introduce the tapered tube extension of the condenser into this beaker which has a mark at 85 ml, in such a manner that it is immersed in the 5 ml of sulphuric acid solution (5.7). Pass the test solution (8.3.1) quantitatively into the distillation flask with the aid of the funnel.

Rinse the Kjeldahl flask with 60 ml of water (5.1), add through the funnel 50 ml of sodium hydroxide solution (5.5) and rinse the funnel with 30 ml of water (5.1). The volume of the solution should then be about 160 to 165 ml. The steam generator should be preheated to allow the distillation to commence immediately the sodium hydroxide is introduced.

Distil about 80 ml in 25 min. When the distillation is ended, rinse the immersed tube with water (5.1), collecting the washings in the beaker. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, make up to volume with water (5.1) and mix. Solutions S_1 for the 1 g test portion and S_2 for the 2 g test portion are obtained. Interrupt the heating of the steam generator and allow to cool; the liquid in the flask syphons into the empty flask. Repeat the same operation for each sample to be analysed.

8.3.3 *Development of the colour*

According to the presumed nitrogen content, take the following aliquots of solutions S_1 and S_2 :

- 10,0 ml for nitrogen contents between 0,020 and 0,050 % (*m/m*)
- 25,0 ml for nitrogen contents between 0,010 and 0,020 % (*m/m*)
- 50,0 ml for nitrogen contents between 0,002 and 0,010 % (*m/m*)

and transfer them respectively into two 100 ml volumetric flasks.

Make up to 50 ml with water (5.1) those volumes less than 50 ml. Add 1 drop of methyl red solution (5.15) and neutralize exactly with sodium hydroxide solution (5.8).

Add with a pipette and in the following order :

- 5,0 ml of sodium phenate solution (5.9)
- 5,0 ml of *di*sodium hydrogen phosphate solution (5.10)
- 10,0 ml of sodium pentacyanonitrosylferrate(II) solution (5.11)
- 5,0 ml of sodium hypochlorite solution (5.12).

Make up the volume to 100 ml with water (5.1) and agitate the flasks in an identical manner by alternately turning them upside down (at least ten times).

Allow the colour to develop in the dark for 1 h at ambient temperature.

NOTE — The aliquots indicated are such that in relation to the nitrogen contents, the quantity of nitrogen in the 100 ml flask used for the spectrophotometric measurement is always between 10 and 50 µg for S_1 and 20 and 100 µg for S_2 : thus, the difference is between 10 and 50 µg.

8.3.4 *Spectrophotometric measurement*

Homogenize the coloured solutions S_1 and S_2 and measure the absorbance of solution S_2 in a 1 cm cell, using the spectrophotometer (6.3) at a wavelength corresponding to the maximum absorption — a maximum which is situated at about 640 nm — after having adjusted the apparatus to zero absorbance in relation to solution S_1.

8.4 Plotting of the calibration curve

8.4.1 *Preparation of the standard solutions, related to the spectrophotometric measurement carried out in a 1 cm cell*

To a series of six 100 ml volumetric flasks, transfer the quantities of standard nitrogen solution (5.14) indicated in the following table.

Standard nitrogen solution (5.14)	**Corresponding mass of nitrogen**
ml	µg
0 *	0
5,0	10
10,0	20
15,0	30
20,0	40
25,0	50

* Compensating solution.

Add to each flask 5 ml of sulphuric acid solution (5.7), then add the quantity of water (5.1) necessary to bring the volume to about 50 ml.