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Steel — Determination of nitrogen — Spectrophotometric method

Acier — Détermination de l'azote — Méthode spectrophotométrique

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www. iso. org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www. iso .org/iso/foreword. html.

This document was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4945:1977), which has been technically revised. The following changes have been made:

— the scope and applicable range has been expanded as a result of the interlaboratory test;

— addition of copper(II) sulfate pentahydrate for the treatment of the insoluble residue.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Steel — Determination of nitrogen — Spectrophotometric method

1 Scope

This document specifies a spectrophotometric method for the determination of nitrogen in steel.

The method is applicable to the determination of nitrogen mass fraction between 0,000 6 % and 0,050 % in low alloy steels and between 0,010 % and 0,050 % in high alloy steels.

The method does not apply to samples containing silicon nitrides or having silicon contents higher than 0,6 %.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Dissolution of a test portion in hydrochloric acid.

Fuming of the acid-insoluble residue in sulphuric acid with potassium sulfate and copper(II) sulfate.

Distillation of the solution made alkaline with sodium hydroxide, and collection of ammonia in a receiver containing diluted sulphuric acid.

Formation of a blue-coloured complex between the ammonium ions and phenol in the presence of sodium hypochlorite and disodium pentacyanonitrosylferrate(III) (sodium nitroprusside).

Spectrophotometric measurement of the complex at a wavelength of about 640 nm.

5 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade and only freshly prepared grade 2 water as specified in ISO 3696.

5.1 Hydrochloric acid solution, 1 + 1.

Add 500 ml of hydrochloric acid (ρ approximately 1,19 g/ml) to 500 ml of water and mix.

5.2 Sulphuric acid, ρ approximately 1,84 g/ml, free from nitrogen compounds.

It is preferable to prepare the acid by evaporating until the fume of sulphuric acid appears and to continue fuming for 20 min to 30 min at the time of use.

5.3 Sulphuric acid solution, approximately 0,02 mol/l.

Add 30 ml of sulphuric acid (5.2) little by little into about 700 ml of water. After cooling, make up the volume to 1 l with water, and mix. Dilute 40 ml of this solution to 1 l with water and mix.

5.4 Sodium hydroxide, 500 g/l solution.

Add cautiously, while stirring and cooling, about 900 ml of water into a polyethylene bottle containing 500 g of sodium hydroxide pellets. Cool, dilute to 1 l with water and mix.

5.5 Sodium hydroxide, 7,5 g/l solution.

Dilute 15 ml of sodium hydroxide (5.4) to 1 l with water and mix.

5.6 Potassium sulfate, K_2SO_4.

5.7 Copper(II) sulfate pentahydrate, $CuSO_4{\cdot}5H_2O$.

5.8 Disodium hydrogenphosphate, 0,1 mol/l solution.

Dissolve 36 g of disodium hydrogenphosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$) in water, make up the volume to 1 l with water, and mix.

5.9 Sodium hypochlorite, NaClO, approximately 0,1 mol/l solution, with approximately 0,3 % (mass fraction) of active chlorine.

Store this solution at a temperature less than 10 °C for at least 3 d or more before use.

5.10 Sodium phenoxide, solution.

Add, while stirring and cooling, 5 g of phenol (C_6H_6O) to a mixture of 10 ml of a 250 g/l solution of sodium hydroxide and 80 ml of water. Make up the volume to 100 ml with water, and mix.

Prepare this solution at the time of use.

5.11 Sodium pentacyanonitrosylferrate(III), 0,25 g/l solution.

Dissolve 10 g of sodium pentacyanonitrosylferrate(III) dihydrate (sodium nitroprusside dihydrate) [$Na_2Fe(CN)_5NO{\cdot}2H_2O$] in water, make up the volume to 1 l with water, and mix.

Dilute 25 ml of this solution to 1 l with water at the time of use.

5.12 **Nitrogen stock solution**, corresponding to 0,1 mg/ml of nitrogen.

Weigh, to the nearest 0,1 mg, 0,382 0 g of ammonium chloride, which is previously dried in a sulfuric acid desiccator under a reduced pressure, dissolve in water and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water, and mix.

1 ml of this stock solution contains 0,1 mg of nitrogen.

5.13 **Nitrogen standard solution**, corresponding to 2 µg/ml of nitrogen.

Transfer 20,0 ml of the nitrogen stock solution (5.12) to a 1 000 ml one-mark volumetric flask, dilute to the mark with water, and mix.

Prepare this standard solution at the time of use.

1 ml of this standard solution contains 2 µg of nitrogen.

5.14 **Methyl red**, 0,1 g/l solution.

Dissolve 0,005 g of methyl red in ethanol, make up the volume to 50 ml with ethanol and mix.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 648 and ISO 1042.

Ordinary laboratory apparatus and the following shall be used.

6.1 **Spectrophotometer**, suitable for measuring absorbances at a wavelength of 640 nm with 10 mm optical path length cells.

6.2 **Steam distillation apparatus** (see Annex A).

The apparatus consists of a steam generator, a distillation flask, a funnel, a condenser and a receiver. A trap can be used between the steam generator and the distillation flask.

Examples of the recommended form of apparatus are illustrated in Figures A.1, A.2 and A.3.

The steam generator should be preheated to allow starting the distillation immediately after the introduction of the test solutions.

6.3 **Hot water bath**, suitable for boiling water.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel.

8 Procedure

CAUTION — Carry out operations in a well-ventilated room away from all sources of nitrogen compounds.

8.1 Test portion

Weigh, to the nearest 0,1 mg, a test portion in accordance with Table 1.

Table 1 — Mass of test portion

Expected nitrogen content % (mass fraction)	Test portion g
0,000 6 to 0,005 0	2,0
0,005 0 to 0,050	1,0

8.2 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all reagents as used for the determination, except the test portion.

8.3 Determination

8.3.1 Dissolution

8.3.1.1 Place the test portion (8.1) in a 300 ml beaker or conical flask. Add 30 ml of hydrochloric acid (5.1), cover with a watch-glass or a funnel and heat until acid action has apparently ceased.

8.3.1.2 Filter the solution through a filter paper (see 8.3.1.3) and collect the filtrate in a 300 ml beaker. Rinse the beaker or the conical flask with water, remove adherent particles with a rubber-tipped rod, and filter the rinsing through the same filter paper. Wash the filter paper with a minimum quantity of water. Keep the filtrate and the washings in the beaker (this is test solution S1).

8.3.1.3 A medium-texture filter paper is suitable for sample solutions that do not contain fine nitrides. However, a close-texture filter paper is recommended if the sizes of nitrides are unknown. Vacuum filtration, using a membrane filter with pore size less than 0,2 µm, is necessary for samples which are known to contain fine nitrides such as boron nitride.

8.3.2 Treatment of insoluble residue

Transfer the filter paper and the insoluble residue to a 500 ml conical flask and add 10 g of potassium sulfate (5.6), 1 g of copper(ll) sulfate pentahydrate (5.7) and 20 ml of sulphuric acid (5.2).

Heat gently until the water into the flask has evaporated and the first white sulphuric fumes appear, cover the flask with a funnel and continue fuming (between 335 °C to 350 °C) for about 60 min to decompose the residue.

Cool to room temperature, add 50 ml of water and boil thoroughly for 5 min to remove sulfur dioxide from the solution (this is test solution S2).

8.3.3 Steam distillation (see **Figure A.1**, **A.2** or **A.3**)

To collect the distillate, transfer 5 ml of sulphuric acid (5.3) to a 100 ml volumetric flask with a ground neck and having a mark at 90 ml. Introduce the tapered tube extension of the condenser into the flask in such a manner that it is immersed in the 5 ml of sulphuric acid (5.3) solution.

Add 110 ml of sodium hydroxide solution (5.4) to the distillation flask (b) through the funnel (f) and rinse the funnel with a minimum quantity of water.

Add sample solutions S1 and S2 (see 8.3.1 and 8.3.2) to the distillation flask (b) through the funnel (f) and rinse the vessels of sample solutions and the funnel with a minimum quantity of water.

Add water to the distillation flask through the funnel to make up the volume of the solution to about 250 ml.

Begin the distillation and continue until the distillate has reached the 90 ml mark. Rinse the immersed tube with water and collect the rinsings in the 100 ml volumetric flask. Make up to volume with water and mix.

The distillation should take about 25 min.

8.3.4 Formation of the coloured complex

Transfer to a 100 ml one-mark volumetric flask an aliquot of the solution from 8.3.3, chosen in accordance with Table 2. Add 100 µl of methyl red solution (5.14), and neutralize exactly with sodium hydroxide solution (5.5). Make up the volume of the solution to about 50 ml with water if needed.

Table 2 — Aliquots

Expected nitrogen content % (mass fraction)	Aliquots ml
0,000 6 to 0,010	50
0,010 to 0,020	25
0,020 to 0,050	10

Add 5,0 ml of sodium phenoxide solution (5.10), 5,0 ml of disodium hydrogenphosphate solution (5.8) and agitate the flask in an identical manner by alternately turning it upside down (at least 10 times). Add 10,0 ml of disodium pentacyanonitrosylferrate(III) solution (5.11) and 5,0 ml of sodium hypochlorite solution (5.9) and agitate the flask in an identical manner by alternately turning it upside down (at least 10 times). Place the flask in the boiling water of the hot water bath (6.3) for 5 min. After cooling to room temperature, make up to volume with water and mix (this is the test solution).

8.3.5 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each test solution at a wavelength of about 640 nm after having adjusted the spectrophotometer to zero absorbance by reference to water using 10 mm cells.

8.4 Establishment of the calibration curve

8.4.1 Preparation of the calibration solutions

The preparation of the calibration solutions shall be carried out in parallel to that of the sample solutions.

Transfer 30 ml of hydrochloric acid (5.1) and the volumes of nitrogen standard solution (5.13) given in Table 3 into a series of seven 200 ml beakers.

To collect the distillate, transfer 5 ml of sulphuric acid (5.3) to a 100 ml volumetric flask with a ground neck and having a mark at 90 ml. Introduce the tapered tube extension of the condenser into the flask in such a manner that it is immersed in the 5 ml of sulphuric acid (5.3) solution.

Add 55 ml of sodium hydroxide solution (5.4) to the distillation flask (b) through the funnel (f) and rinse the funnel with a minimum quantity of water.

Add the content of the 200 ml beaker to the distillation flask (b) through the funnel (f) and rinse the beaker and the funnel with a minimum quantity of water.

Add water to the distillation flask through the funnel to make up the volume of the solution about 250 ml.

Begin the distillation and continue until the distillate has reached the 90 ml mark. Rinse the immersed tube with water and collect the rinsings in the 100 ml volumetric flask. Make up to volume with water and mix.

Transfer 50 ml of the solution to a 100 ml one-mark volumetric flask. Add 1 drop of methyl red solution (5.14), and neutralize exactly with sodium hydroxide solution (5.5).

Add 5,0 ml of sodium phenoxide solution (5.10) and 5,0 ml of disodium hydrogenphosphate solution (5.8) and agitate the flask in an identical manner by alternately turning it upside down (at least 10 times). Add 10,0 ml of disodium pentacyanonitrosylferrate(III) solution (5.11) and 5,0 ml of sodium hypochlorite solution (5.9) and agitate the flask in an identical manner by alternately turning it upside down (at least 10 times). Place the flask in the boiling water of the hot water bath (6.3) for 5 min. After cooling to room temperature, make up to volume with water and mix.

Table 3 — Calibration solutions

Volume of nitrogen standard solution (5.13) ml	**Corresponding mass of nitrogen in the test solution** µg	**Nitrogen content of the test sample** % (mass fraction)			
		Test portion			
		2 g	1 g	1 g	1 g
		Aliquot			
		50 ml	50 ml	25 ml	10 ml
0[a]	0	0	0	0	0
5	5	0,000 5	0,001 0	0,002 0	0,005 0
10	10	0,001 0	0,002 0	0,004 0	0,010 0
20	20	0,002 0	0,004 0	0,008 0	0,020 0
30	30	0,003 0	0,006 0	0,012 0	0,030 0
40	40	0,004 0	0,008 0	0,016 0	0,040 0
50	50	0,005 0	0,010 0	0,020 0	0,050 0

[a] Zero member.

8.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each calibration solution (8.4.1) at a wavelength of about 640 nm (see 8.3.5), in a cell of 10 mm optical path length, using water as the reference medium.

Subtract the absorbance of the zero member solution from the absorbance of each calibration solution.

8.4.3 Plotting the calibration curve

Establish the calibration curve, which passes through the origin, by plotting the net absorbance values against the mass of nitrogen, expressed in micrograms per millilitre, in the calibration solutions.

9 Expression of results

9.1 Method of calculation

Convert the absorbance of the test solution and of the blank test solution to micrograms of nitrogen by means of the calibration curve (see 8.4.3).

The nitrogen content, w_N, expressed as a mass fraction (%), is given by Formula (1):

$$w_N = \frac{m_1 - m_0}{m \times \frac{B}{100}} \times 100 \qquad (1)$$

where