# INTERNATIONAL STANDARD

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# Steel and iron — Determination of nitrogen content — Thermal conductimetric method after fusion in a current of inert gas (Routine method)

*Aciers et fontes — Dosage de l'azote — Méthode par conductibilité thermique après fusion sous gaz inerte (Méthode pratique)*

Reference number
ISO 15351:1999(E)

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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15351 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Annexes A, B and C of this International Standard are for information only.

# Steel and iron — Determination of nitrogen content — Thermal conductimetric method after fusion in a current of inert gas (Routine method)

## 1 Scope

This International Standard specifies a thermal conductimetric method after fusion under inert gas for the determination of nitrogen in steel and iron.

The method is applicable to nitrogen contents between 0,002 % ($m/m$) and 0,6 % ($m/m$).

## 2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO Guide 31:1981, *Contents of certificates of reference materials.*

ISO Guide 35:1989, C*ertification of reference materials — General and statistical principles.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions.*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method.*

ISO 10702:1993, *Steel and iron — Determination of nitrogen content — Titrimetric method after distillation.*

ISO 10720:1997, *Steel and iron — Determination of nitrogen content — Thermal conductimetric method after fusion in a current of inert gas.*

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition.*

## 3 Principle

Fusion of a test portion in a single-use graphite crucible under helium gas at a high temperature (e.g. 2 200 °C). Extraction of the nitrogen in the form of molecular nitrogen in the stream of helium.

Separation from the other gaseous extracts and measurement by thermal conductimetric method.

Calibration graph established using steel or iron certified reference materials (CRM).

NOTE The accuracy of the method is largely dependant upon the accuracy of the method used to certify the nitrogen concentration of CRMs as well as upon their homogeneity. These calibration specimens shall be ECRM, NIST, JK, JSS, CMSI and other national or international CRMs.

## 4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 3 water as specified in ISO 3696.

**4.1 Water**, prepare just before use.

**4.2 Helium**, high purity, total impurity content 0,000 5 % (*m*/*m*).

An oxidation reagent or catalyst [copper(II) oxide or platinum] tube heated to a temperature above 450 °C shall be used prior to a purifying unit, when the presence of organic contaminants is suspected in the helium.

**4.3 Copper (II) oxide**, on granulated support.

**4.4 Magnesium perchlorate** $Mg(ClO_4)_2$ (commercial designation: anhydrone), particle size: from 1,2 mm to 2 mm, or anhydrous calcium sulfate, (commercial designation: drierite), particle size from 0,6 mm to 0,85 mm.

**4.5 Sodium hydroxide**, on granulated support (commercial designation: ascarite), particle size: from 0,7 mm to 1,2 mm.

**4.6 Appropriate solvent**, suitable for washing greasy or dirty test samples, e.g. acetone.

**4.7 Steel or iron reference materials (RM)**, one or more of whose property values are sufficiently homogeneous as described in ISO Guide 35 and well-established for use in the calibration of an apparatus, the assessment of a measurement method or for assigning values to materials.

**4.8 Steel or iron certified reference materials (CRM),** steel or iron reference materials (4.7), accompanied by a certificate in accordance with ISO Guide 31 and one or more of whose chemical element concentrations have been established, in accordance with ISO Guide 35, by a referee method (e.g. ISO 10702 and 10720) which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

## 5 Apparatus

During the analysis, unless otherwise stated, use only ordinary laboratory apparatus.

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

The apparatus required for fusion of the test portion and separation and measurement of the extracted nitrogen may be obtained commercially from a number of manufacturers. Follow the manufacturer's instructions for the operation of the instrument.

Features of commercial instruments are given in annex A.

**5.1 Graphite crucible**, single-use.

Use high purity crucibles suitable for use with the apparatus.

**5.2 Crucible tongs**, for handling the crucibles used.

**5.3 Glass-wool filters.**

## 6 Sampling

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

## 7 Procedure

**WARNING — The risks involved when using an apparatus for fusing the test portion are mainly risks of burns. It is therefore essential to use crucible tongs (5.2) and appropriate containers for the crucibles used.**

### 7.1 General

Keep the glass-wool filters (5.3) clean. Using a certified reference material, verify the effectiveness of the installed reagents (4.3, 4.4 and 4.5) and change them if necessary.

In certain instruments, it is necessary to clean the sample introduction pipe in the furnace after each analysis in order to eliminate carbon deposits. If the electricity supply has been switched off for a long time, allow time for the instrument to stabilize as recommended by the manufacturer.

After changing the filters (5.3) and/or reagents (4.3, 4.4 and 4.5), or when the apparatus has been inoperative for a period, stabilize the instrument by carrying out trial analyses, the results of which are to be disregarded, then proceed with calibration as indicated in 7.5 before analysing the sample.

If the instrument used provides a direct reading in percentage of nitrogen, adjust the instrument reading for each calibration range as follows.

Read the content of a certified reference material of high nitrogen content at various power settings. The required heating power for the determination of test samples is that at which the reading levels off.

In order to determine a high alloy test sample a high alloy certified reference material shall be used to know the required heating power.

### 7.2 Test portion

Degrease the test sample by washing in a suitable solvent (4.6). Evaporate the last traces of the washing liquid by heating.

Weigh, to the nearest 1 mg, approximately 1 g of the test sample for nitrogen contents up to 0,1 % ($m/m$) and approximately 0,5 g for nitrogen contents greater than 0,1 % ($m/m$).

NOTE The mass of the test portion may be dependent on the type of instrument used.

### 7.3 Blank test

Prior to the determination, carry out the following blank tests in duplicate.

Place a graphite crucible (5.1) in the furnace (see annex A) and then degas by heating at a temperature greater than 2 200 °C. Operate the furnace in accordance with the manufacturer's instructions.

Obtain the reading of the blank tests and convert it to micrograms of nitrogen by means of the calibration graph (see 7.5).

The mean blank value ($m_1$) is calculated from the two blank values.

NOTE It is essential that neither the mean blank value nor the difference between the two blank values exceed 10 µg of nitrogen. If these values are abnormally high, the source of contamination should be investigated and eliminated.

## 7.4 Determination

Place a graphite crucible (5.1) in the furnace (see annex A) and then degas by heating at a temperature greater than 2 200 °C.

Put the test portion (see 7.2) into the degassed graphite crucible.

Operate the furnace in accordance with the manufacturer's instructions.

At the end of the fusion and measuring cycle, remove and discard the crucible, and record the analyser reading.

## 7.5 Establishment of the calibration graph

### 7.5.1 Preparation of the calibration series

#### 7.5.1.1 Selection of reference materials for nitrogen contents up to 0,1 % ($m/m$)

Select five CRMs (4.8) having a matrix as close as possible to the matrix of the material to be measured and containing approximately 0,002 %, 0,01 %, 0,03 %, 0,05 % and 0,1 % ($m/m$) of nitrogen and designate them as standards A, B, C, D and E respectively.

#### 7.5.1.2 Selection of reference materials for nitrogen between 0,1 % ($m/m$) and 0,5 % ($m/m$)

Select three CRMs (4.8) having a matrix as close as possible to the matrix of the material to be measured and containing approximately 0,10 %, 0,30 % and 0,50 % ($m/m$) of nitrogen and designate them as standards AA, BB and CC.

### 7.5.2 Test portion

Treat reference materials as indicated in 7.2.

### 7.5.3 Blank test

Carry out blank test as indicated in 7.3.

### 7.5.4 Measurements

Treat the samples for calibration as indicated in 7.4.

### 7.5.5 Plotting the calibration graph

Obtain the net reading by subtracting the reading of the blank from that of each member of the calibration series.

Prepare a calibration graph by plotting the net reading in micrograms of nitrogen for each member of the calibration series.

# 8 Expression of results

## 8.1 Method of calculation

Convert the analyser reading for the test portion to micrograms of nitrogen ($m_0$) by means of the calibration graph (see 7.5).

The nitrogen content, $w_N$ (%), expressed as a percentage by mass, is given by the equation:

$$w_N = \frac{(m_0 - m_1)}{m \times 10^6} \times 100$$

$$= \frac{(m_0 - m_1)}{10^4 m}$$

where

$m_0$ is the mass of nitrogen, expressed in micrograms, in the test portion;

$m_1$ is the mass of nitrogen, expressed in micrograms, in the blank test (see 7.3);

$m$ is the mass, in grams, of the test portion (see 7.2).

## 8.2 Precision

A planned trial of this method was carried out by 23 laboratories in ten countries, at 14 levels of nitrogen content, each laboratory making three determinations (see notes 1 and 2) of nitrogen content on each level.

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in note 1, using the same apparatus with a new calibration.

The test samples used and mean/precision results obtained are listed in Tables B.1 and B.2 respectively.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between nitrogen content and repeatability limit ($r$) and reproducibility limits ($R_w$ and $R$) of the test results (see note 3) as summarized in Table 1. The graphical representation of the data is shown in Figure C.1.

NOTE 3 From the two values obtained on day 1, the repeatability ($r$) and reproducibility ($R$) were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility limit ($R_w$) was calculated using the procedure given in ISO 5725-3.

**Table 1 — Results for repeatability and reproducibility**

| **Nitrogen content** | **Repeatability** | **Reproducibility limits** | |
|---|---|---|---|
| % ($m/m$) | $r$ | $R_w$ | $R$ |
| 0,002 | 0,000 45 | 0,000 60 | 0,001 1 |
| 0,005 | 0,000 45 | 0,000 60 | 0,001 1 |
| 0,010 | 0,000 49 | 0,000 66 | 0,001 1 |
| 0,020 | 0,000 83 | 0,001 1 | 0,001 4 |
| 0,050 | 0,001 7 | 0,002 3 | 0,003 1 |
| 0,100 | 0,002 8 | 0,003 8 | 0,005 6 |
| 0,200 | 0,004 8 | 0,006 5 | 0,010 |
| 0,50 | 0,009 7 | 0,013 | 0,022 |
| 0,60 | 0,011 | 0,015 | 0,026 |

## 9 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) the method used, by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

# Annex A
(informative)

# Features of commercial resistive electrode furnaces and nitrogen analysers

## A.1 Helium source

Fitted with a fine adjustment valve and a pressure gauge. The pressure control valve is used to check the helium inlet pressure in the furnace in accordance with the manufacturer's instructions; this is usually 28 kN/m$^2$.

## A.2 Purifying unit

Containing sodium hydroxide-impregnated attapulgite, and magnesium perchlorate in a dehydration tube.

## A.3 Flowmeter

For measuring the flow of helium in the range 0 l/min to 4 l/min.

## A.4 Resistive electrode furnace

**A.4.1** The furnace used for fusion of the test portion by the Joule effect is composed of two solid copper or copper alloy electrodes which fit together tightly while providing an adequate volume to accommodate a graphite crucible. The graphite crucible is used as an electrical connection between the two electrodes.

Tightness is generally ensured by an O-ring.

The electrodes are generally cooled by means of water circulation so that the O-rings are not damaged during the fusion of the test portion.

**A.4.2** A transformer supplies the necessary amperage for fusion to be performed satisfactorily.

**A.4.3** The graphite crucible containing the test portion and a nickel capsule, if required, is placed on the lower electrode to ensure a good electrical connection.

**A.4.4** The temperature reached during fusion is dependent partly on the parameters in A.4.1 and partly on the metal properties, the test portion shape and mass and sometimes on the crucible geometry.

## A.5 Thermal conductivity gas analyser (catharometer)

**A.5.1** In most current apparatus, the gaseous fusion emissions are transferred into the analyser by a continuous flow of helium.

An apparatus, after the oxidation furnace, in which reagents (4.3, 4.4 and 4.5) are installed makes it possible to convert carbon monoxide and hydrogen into carbon dioxide and water and to absorb them.

The helium-nitrogen stream flow is led to the catharometer. The difference in thermal conductivity of the pure gas and of the mixture is recorded and integrated over a pre-programmed time interval.

Signal amplification and conversion with digital display make it possible to obtain the percentage nitrogen concentration.

**A.5.2** Electronic controls are used to set the instrument at zero, to compensate for the blank value, to adjust the calibration curve slope and to correct non-linear responses.

Provision is generally incorporated in the analyser to take into account the mass of the reference sample or test portion, and to automatically correct readings.

Some equipment may also be fitted with integrated automatic scales to weigh the test portion and to transfer the corresponding value to the analyser.

# Annex B
(informative)

## Additional information on the international cooperative tests

Table 1 was derived from the results of the international analytical trial carried out in 1996 on 14 steel samples in ten countries involving 23 laboratories.

Statistical calculation was conducted using selected laboratories which satisfied the requirements of 7.5.1 for a calibration procedure in which the tested sample was sandwiched between at least two CRMs.

The results of the trial were reported in document ISO/TC 17/SC 1 N 1126, 1996-06-26 and N 1130, 1996-07-03. The graphical representation of the precision data is given in annex C.

The test samples used and the results obtained are listed in Tables B.1 and B.2.

**Table B.1 — Test samples used in the interlaboratory tests**

| **Sample** | **Chemical composition,** % (*m*/*m*) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | N | C | Si | Mn | Cr | Mo | Ni | Others |
| ECRM 285-1<br>(High alloy steel) | 0,002 3 | 0,003 | | 0,013 | | 5,07 | 18,46 | Co:9,22 |
| ECRM 077-2<br>(Low alloy steel) | 0,005 4 | 0,151 | 0,293 | 1,28 | | | | V:0,058 |
| ECRM 008-2<br>(Low alloy steel) | 0,009 | 0,613 | 0,366 | 0,552 | | | | |
| NIST 50c<br>(Tool steel) | 0,012 | 0,719 | 0,311 | 0,342 | 4,13 | | | W:18,44<br>V:1,16 |
| ECRM 281-1<br>(High alloy steel) | 0,023 | 0,048 | 0,929 | 0,786 | 18,17 | | 9,37 | |
| ECRM 227-1<br>(High alloy steel) | 0,040 | 0,950 | 0,272 | 0,236 | 4,25 | 2,64 | 0,114 | Cu:0,124<br>V:2,44 |
| JK 8F<br>(Stainless steel) | 0,071 5 | | 0,424 | 1,552 | 16,91 | 2,775 | 11,01 | Co:0,125 |
| MBH NSA 20<br>(Stainless steel) | 0,15 | 0,11 | 0,54 | 0,69 | 17,8 | 2,05 | 10,04 | |
| ECRM 230-1<br>(High alloy steel) | 0,159 8 | 0,077 5 | 0,524 | 8,450 | 18,05 | 0,298 | 5,558 | |
| MBH NSB 20<br>(Stainless steel) | 0,19 | 0,17 | 0,66 | 0,52 | 18,0 | 0,37 | 10,6 | |
| DAIDO<br>(Heat resisting steel) | 0,23 [a] | 0,2 | 0,1 | 1 | 21 | | 11 | Ti:0,01 |
| NIST 346a<br>(Heat resisting steel) | 0,442 | 0,502 | 0,219 | 9,16 | 21,08 | 0,237 | 3,34 | Cu:0,375 |
| DAIDO<br>(Heat resisting steel) | 0,45 [a] | 0,5 | 0,1 | 9,8 | 21 | | 4 | |
| MBH NSC 30<br>(High alloy steel) | 0,62 | 0,71 | 1,119 | 9,5 | 24,8 | 6 | 3,34 | Nb+Ta:0,62 |

[a] Non-certified value.