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

*Aciers et fontes — Dosage de l'azote — Méthode par conductibilité thermique après fusion sous un courant de gaz inerte*

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## Foreword

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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.

International Standard ISO 10720 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition.*

Annexes A to C of this International Standard are for information only.

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

## 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 0,000 8 % (*m*/*m*) and 0,5% (*m*/*m*).

## 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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

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

ISO 1042:—[1], *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 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.

## 4 Reagents and materials

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

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1) To be published. (Revision of ISO 1042:1983)

**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 Pure iron,** of known low nitrogen contents less than 0,001 % (*m*/*m*).

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

**4.5 Anhydrous magnesium perchlorate,** $Mg(ClO_4)_2$, particle size from 1,2 mm to 2,0 mm, or anhydrous calcium sulfate, particle size from 0,60 mm to 0,85 mm.

**4.6 Sodium hydroxide,** on granulated support.

Particle size from 0,7 mm to 1,2 mm.

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

**4.8 Potassium nitrate,** standard solution.

After drying at between 100 °C and 105 °C for 2 h and allowing to cool in a desiccator, weigh, to the nearest 0,1 mg, the masses of potassium nitrate [purity > 99,9 % (*m*/*m*)] indicated in table 1.

Dissolve the potassium nitrate in about 50 ml of water (4.1), transfer quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark with water (4.1) and mix.

1 ml of each standard solution contains the mass of nitrogen indicated in table 1.

**Table 1 — Standard solutions**

| Name of the standard solution | Mass of potassium nitrate used<br>g | Corresponding concentration of nitrogen<br>mg/ml |
|---|---|---|
| 4.8.1 | 9,022 8 | 12,5 |
| 4.8.2 | 7,218 2 | 10,0 |
| 4.8.3 | 5,413 8 | 7,5 |
| 4.8.4 | 3,609 1 | 5,0 |
| 4.8.5 | 1,804 6 | 2,50 |
| 4.8.6 | 0,902 3 | 1,25 |
| 4.8.7 | 0,360 9 | 0,50 |
| 4.8.8 | [4.8.5 x 1/10] 1) | 0,25 |
| 4.8.9 | [4.8.6 x 1/10] | 0,125 |
| 4.8.10 | [4.8.7 x 1/10] | 0,050 |

1) e.g. .transfer 10,0 ml of the standard solution (4.8.5) into a 100 ml one-mark volumetric flask, dilute to the mark with water (4.1) and mix.

## 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, separation and measurement of the nitrogen extracted 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 Micropipette,** 100 µl and 200 µl, limit of error shall be less than 1 µl.

**5.3 Nickel capsule.**

For example, about 6 mm in diameter; 8 mm in height; 0,2 g in mass and 0,23 ml in volume, or about 6 mm in diameter; 12,5 mm in height; 0,5 g in mass and 0,35 ml in volume. In any case, the nitrogen content shall be less than 0,000 2 % (*m*/*m*).

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

**5.5 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 (5.4) and appropriate containers for the used crucibles.**

### 7.1 General instructions

Keep the glass-wool filters (5.5) clean. Using a certified reference material, verify the effectiveness of the installed reagents (4.4, 4.5 and 4.6) 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 (5.5) and/or reagents (4.4, 4.5 and 4.6), 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 (4.7). Evaporate the last traces of the washing liquid by heating.

Weigh, to the nearest 1 mg, approximately 1,0 g of the test sample for nitrogen contents up to 0,1 % (*m*/*m*) and approximately 0,50 g for nitrogen contents greater than 0,1 % (*m*/*m*) (see note 1).

NOTE 1 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.

### 7.3.1 Sample with nitrogen contents up to 0,10 % (*m*/*m*)

**7.3.1.1** Using the micropipette (5.2), transfer 200 µl of water (4.1) to a nickel capsule (5.3) and dry at 90 °C to 95 °C for 2 h. Treat the nickel capsule as specified in 7.4.1, and add the same quantity of the pure iron (4.3) in place of the test portion.

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

The blank value is obtained by subtracting the mass of nitrogen in the pure iron used (4.3) from the mass of nitrogen in the blank tests.

The mean blank value ($m_1$) is calculated from the two blank values (see note 2).

NOTE 2 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.

### 7.3.2 Sample with nitrogen contents between 0,10 % (*m*/*m*) and 0,50 % (*m*/*m*)

Using the micropipette (5.2), transfer 200 µl of water (4.1) to a degassed graphite crucible (5.1) and dry at 90 °C to 95 °C for 2 h. Add the same quantity of the pure iron (4.3) instead of the test portion and proceed as specified in 7.3.1.2.

## 7.4 Determination

### 7.4.1 Sample with nitrogen contents up to 0,10 % (*m*/*m*)

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

**7.4.1.2** Flatten a nickel capsule (5.3) by pressing, insert it and add the test portion (see 7.2) to the degassed graphite crucible.

**7.4.1.3** 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.

### 7.4.2 Sample with nitrogen contents between 0,10 % (*m*/*m*) and 0,50 % (*m*/*m*)

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

Add the test portion (see 7.2) to the degassed graphite crucible (5.1) and continue as specified in 7.4.1.3.

## 7.5 Establishment of the calibration graph

### 7.5.1 Preparation of the calibration series

### 7.5.1.1 Sample with nitrogen contents up to 0,10 % (*m*/*m*)

Using the micropipette (5.2), transfer 200 µl of each of the potassium nitrate standard solutions (4.8) indicated in table 2, to the respective nickel capsule (5.3), and dry at 90 °C to 95 °C for 2 h.

### 7.5.1.2 Sample with nitrogen contents between 0,10 % (*m*/*m*) and 0,50 % (*m*/*m*)

Using the micropipette (5.2), transfer 200 µl of each of the potassium nitrate standard solutions (4.8) indicated in table 3, to the respective degassed graphite crucible(5.1), and dry at 90 °C to 95 °C for 2 h.

### 7.5.2 Measurements

### 7.5.2.1 Sample with nitrogen contents up to 0,10 % (*m*/*m*)

Treat the nickel capsule (5.3) containing potassium nitrate as specified in 7.4.1. Add the same quantity of the pure iron (4.3) in place of the test portion.

### 7.5.2.2 Sample with nitrogen contents between 0,10 % (*m*/*m*) and 0,50 % (*m*/*m*)

Add, to each dried graphite crucible, the same quantity of the pure iron (4.3) as that of the test portion used, and continue as specified in 7.4.1.3

### 7.5.3 Plotting the calibration graph

Obtain the net reading by subtracting the reading of the zero member (see tables 2 and 3) from that of each member of the calibration series.

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

**Table 2 — Calibration solutions, nitrogen contents up to 0,10 % (*m*/*m*)**

Test portion: 1,0 g — Standard solutions added: 200 µl

| Standard solution (4.8) used | Concentration of nitrogen<br>mg/ml | Mass of nitrogen taken in the nickel capsule or the graphite crucible<br>µg | Nitrogen content in the test portion<br>% (*m*/*m*) |
|---|---|---|---|
| water(4.1) | 0[1] | 0 | 0 |
| 4.8.10 | 0,050 | 10 | 0,001 0 |
| 4.8.9 | 0,125 | 25 | 0,002 5 |
| 4.8.8 | 0,250 | 50 | 0,005 0 |
| 4.8.7 | 0,500 | 100 | 0,010 |
| 4.8.6 | 1,25 | 250 | 0,025 |
| 4.8.5 | 2,50 | 500 | 0,050 |
| 4.8.4 | 5,00 | 1 000 | 0,100 |

1) Zero member

**Table 3 — Calibration solutions, nitrogen contents between 0,10 % (*m*/*m*) and 0,50 % (*m*/*m*)**

Test portion: 0,5 g — Standard solutions added: 200 µl

| **Standard solution (4.8) used** | **Concentration of nitrogen** mg/ml | **Mass of nitrogen taken in the nickel capsule or the graphite crucible** µg | **Nitrogen content in the test portion** % (*m*/*m*) |
|---|---|---|---|
| water(4.1) | 0[1] | 0 | 0 |
| 4.8.5 | 2,5 | 500 | 0,100 |
| 4.8.4 | 5,0 | 1 000 | 0,200 |
| 4.8.3 | 7,5 | 1 500 | 0,300 |
| 4.8.2 | 10,0 | 2 000 | 0,400 |
| 4.8.1 | 12,5 | 2 500 | 0,500 |

[1] Zero member

## 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, expressed in micrograms, of nitrogen in the test portion;

$m_1$ is the mass, expressed in micrograms, of nitrogen 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 14 laboratories, at eleven levels of nitrogen, each laboratory making three determinations (see notes 3 and 4) of nitrogen at each level.

NOTES

3 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.

4 The third determination was carried out at a different time (on a different day) by the same operator as in note 3, using the same apparatus with a new calibration.

The test samples used are listed in annex B.1.

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

The data obtained showed a logarithmic relationship between nitrogen content and repeatability (*r*) and reproducibility (*R* and $R_w$) of the test results (see note 5) as summarized in table 4. The graphical representation of the data is shown in annex C.

**Table 4 — Results for repeatability and reproducibility limits**

| **Nitrogen content**<br>% (*m*/*m*) | **Repeatability limit**<br>*r* | **Reproducibility limits**<br>*R* | <br>$R_w$ |
|---|---|---|---|
| 0,000 8 | 0,000 24 | 0,000 39 | 0.000 27 |
| 0,001 0 | 0,000 27 | 0,000 45 | 0,000 30 |
| 0,002 0 | 0,000 36 | 0,000 71 | 0,000 44 |
| 0,005 0 | 0,000 54 | 0,001 30 | 0,000 71 |
| 0,010 0 | 0,000 73 | 0,002 07 | 0,001 03 |
| 0,020 0 | 0,000 98 | 0,003 28 | 0,001 49 |
| 0,050 0 | 0,001 46 | 0,006 03 | 0,002 42 |
| 0,100 | 0,001 97 | 0,009 56 | 0,003 50 |
| 0,200 | 0,003 07 | 0,014 4 | 0,006 26 |
| 0,500 | 0,005 54 | 0,024 9 | 0,013 5 |

NOTE 5 From the two values obtained on day 1, the repeatability limit (*r*) and reproducibility limit (*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.

## 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.