Chemical analysis of ferrous materials — Determination of oxygen content in steel and iron —

Part 2: Infrared method after fusion under inert gas

The European Standard EN 10276-2:2003 has the status of a
British Standard

ICS 77.040.30

National foreword

This British Standard is the official English language version of EN 10276-2:2003.

The UK participation in its preparation was entrusted to Technical Committee ISE/18, Sampling and analysis or iron and steel, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

This British Standard, was published under the authority of the Standards Policy and Strategy Committee on 9 July 2003

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 13 and a back cover.

The BSI copyright date displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

ISBN 0 580 42239 9

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 10276-2

July 2003

ICS 77.040.30

English version

Chemical analysis of ferrous materials - Determination of oxygen content in steel and iron - Part 2: Infrared method after fusion under inert gas

Analyse chimique des matériaux ferreux - Détermination de la teneur en oxygène de l'acier et de la fonte - Partie 2: Méthode par absorption dans l'infrarouge après fusion sous gaz inerte

Chemische Analyse von Eisenwerkstoffen - Bestimmung des Sauerstoffgehalts von Stahl und Eisen - Teil 2: Messung der Infrarotabsorption nach Aufschmelzen unter Inertgas

This European Standard was approved by CEN on 7 May 2003.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 10276-2:2003 E

Contents

Foreword 3
1 Scope 4
2 Normative references 4
3 Principle 4
4 Reagents and materials 4
5 Apparatus 6
6 Sampling 6
7 Procedure 7
7.1 General 7
7.2 General instructions 7
7.3 Test portion 7
7.4 Blank test 7
7.5 Calibration 8
7.6 Preparation test 8
7.7 Determination 8
7.7.1 Method 1 8
7.7.2 Method 2 8
8 Expression of results 9
8.1 Method of calculation 9
8.2 Precision 10
9 Test report 12
Bibliography 13

Foreword

This document EN 10276-2:2003 has been prepared 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 January 2004, and conflicting national standards shall be withdrawn at the latest by January 2004.

This document includes a Bibliography.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies an infrared method after fusion under inert gas for the determination of oxygen in steel and iron.

The method is applicable to oxygen contents between 0,0005 % (m/m) and 0,01 % (m/m).

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 10276-1	*Chemical analysis of ferrous materials – Determination of oxygen in steel and iron – Part 1: Sampling and preparation of steel samples for oxygen determination.*
EN ISO 14284	*Steel and iron – Sampling and preparation of samples for the determination of chemical composition (ISO 14284:1996).*

3 Principle

Fusion of a test portion in a single-use graphite crucible under helium gas at a minimum temperature of 2000 ° C. Combination of the oxygen from the sample with carbon from the crucible to form carbon monoxide. Eventually transformation of carbon monoxide into carbon dioxide.

Measurement of infrared absorption of the carbon monoxide or dioxide and use of a calibration curve plotted using the measurements obtained with potassium nitrate.

4 Reagents and materials

During the analysis, unless otherwise stated, only reagents of recognised analytical grade shall be used. The following reagents and materials shall be used:

4.1 Helium, high purity, total impurity content 0,0005 % (m/m).

An oxidation 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.

4.2 Magnesium perchlorate, Mg $(ClO_4)_2$, (commercial designation: anhydrone), particle size from 1,2 mm to 2,0 mm, or **Anhydrous Calcium sulphate, $(CaSO_4)$**, (commercial designation: drierite), particle size from 0,6 mm to 0,85 mm.

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

4.4 Copper oxide, CuO

4.5 Platinum, Pt

4.6 Tin or nickel capsules, For example ∅ 5 mm, length 13 mm, weight 160 mg, with low oxygen content, less than 0,1 µg/mg of oxygen.

Cut off the upper part of the tin capsule to reduce the weight to 50 mg or the length to 8 mm.

4.7 Water, high purity, deionized, prepared just before use.

4.8 Potassium nitrate, KNO3, high purity, maximum total impurity content 0,0005 % (m/m).

Dry before use at 100 °C to 105 °C for 2 h and allow to cool in a dessicator.

4.9 Potassium nitrate stock solution, corresponding to 4 mg/ml of oxygen.

Weigh, to the nearest 0,1 mg, 8,416 g of potassium nitrate (4.8).

Place in a 100 ml beaker and dissolve in about 50 ml of water (4.7).

Transfer quantitatively to a 1000 ml volumetric flask, dilute to the mark with water (4.7), and mix.

1 ml of the potassium nitrate stock solution contains 4 mg of oxygen as potassium nitrate.

4.10 Potassium nitrate diluted stock solution, corresponding to 0,4 mg/ml of oxygen.

This solution shall be prepared freshly before use.

Transfer 10 ml of the potassium nitrate stock solution in a 100 ml volumetric flask, dilute to the mark with water (4.7), and mix.

1 ml of the potassium nitrate stock solution contains 0,4 mg of oxygen as potassium nitrate.

4.11 Potassium nitrate standard solutions.

These solutions shall be prepared freshly before use.

Transfer the volume listed in Table 1 of the potassium nitrate stock solution (4.9) and of the potassium nitrate diluted stock solution (4.10) in a series of nine 100 ml volumetric flasks, dilute to the mark with water (4.7), and mix.

100 µl of each of the potassium nitrate standard solutions contain the mass of oxygen (as potassium nitrate) listed in the last column of Table 1.

Table 1 — Potassium nitrate standard solutions

Potassium nitrate standard solution	Volume of potassium nitrate stock solution (4.9) added (except for solution 4.11.2)	Mass of oxygen in 1 ml of the potassium nitrate standard solution	Mass of oxygen in 100 µl of the potassium nitrate standard solution
4.11.1	0 ml [a]	0 mg	0 µg
4.11.2	3 ml of potassium nitrate diluted stock solution (4.10)	0,012 mg	1,2 µg
4.11.3	1,0 ml	0,04 mg	4 µg
4.11.4	2,0 ml	0,08 mg	8 µg
4.11.5	3,0 ml	0,12 mg	12 µg
4.11.6	5,0 ml	0,20 mg	20 µg
4.11.7	10,0 ml	0,40 mg	40 µg
4.11.8	20,0 ml	0,80 mg	80 µg
4.11.9	30,0 ml	1,20 mg	120 µg

[a] zero member: The standard solution (4.11.1) is in fact the water (4.7) used for preparing the solutions.

4.12 Graphite powder, high purity, with low oxygen content.

5 Apparatus

The apparatus required for fusion of the test portion and measurement of the carbon monoxide or dioxide extracted may be obtained commercially from a number of manufacturers. The manufacturer's instructions for the operation of the instrument shall be followed.

5.1 Graphite crucible, single-use

High purity crucibles suited to the apparatus shall be used.

5.2 Crucible tongs shall be used for handling the crucibles.

5.3 Glass wool filters

5.4 Micropipette, 100 µl, shall be used, limit of error shall be less than 1 µl.

6 Sampling

Sampling shall be carried out in accordance with EN ISO 14284 and EN 10276-1.

7 Procedure

7.1 General

The risk involved when using an apparatus for fusing the test portion are mainly risks of burns. Crucible tongs (5.2) and appropriate containers for the used crucibles shall be used.

7.2 General instructions

It shall be checked that glass wool filters (5.3) are clean and they shall be changed as often as necessary.

If the electricity supply has been switched off for a long time, the instrument shall be allowed to stabilise for the time recommended by the manufacturer.

After changing the filters (5.3) and/or reagents (4.2, 4.3 and 4.4), or when the apparatus has been inoperative for a period, the instrument shall be allowed to stabilise by carrying out trial analyses, the result of which are to be disregarded, then proceed with blank calibration and preparation tests as indicated in 7.4, 7.5 and 7.6 before analysing the sample.

If the instrument used provides a direct reading in percentage of oxygen, the instrument reading shall be adjusted for each calibration range as follows:

Using a CRM with a high oxygen content, record the contents measured at different levels of furnace heating power. 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 CRM shall be used to know the required heating power.

7.3 Test portion

Prepare the test portion of approximately 1 g in accordance with EN 10276-1.

Weigh the test portion to the nearest 1 mg.

7.4 Blank test

Prior to the determination, the following blank test shall be carried out in duplicate.

Proceed as in 7.7 without test portion, entering a weight of 1 g, and setting the blank subtraction of the instrument to zero.

Obtain the reading of the blank test.

The mean value of the blank test shall be sufficiently low when compared to the oxygen content to be determined in the test portion.

For mean values below 8 µg/g of oxygen, neither the mean blank value nor the difference between the two blank values should exceed 0,5 µg/g of oxygen. For mean values above 8 µg/g of oxygen, neither the mean blank value nor the difference between the two blank values should exceed 2 µg/g of oxygen.

If the blank values are abnormally high, the source of contamination shall be investigated and eliminated.

If the mean value of the blank is satisfactory, it may then be introduced in the blank subtraction device of the instrument.

7.5 Calibration

Prior to the determination, the following calibration shall be carried out.

Prepare according to 4.11 at least five solutions chosen from solutions 4.11.1 to 4.11.9 indicated in Table 1, according to the level of oxygen content to be determined.

Using the micropipette (5.4), transfer 100 µl of each of the freshly prepared potassium nitrate standard solutions (4.11.1 to 4.11.9) to each tin or nickel capsule (4.6) respectively and dry at 90°C to 95°C for 2 h.

NOTE The drying of the calibration solutions in the tin or nickel capsules should be done stepwise, in order to avoid splashing and loss of calibration material due to over-rapid heating before complete vaporisation of the water.

Carefully press the tin or nickel capsule and proceed as in 7.7, using the tin or nickel capsule as a test portion, entering a sample weight of one gram, and setting the sample fusion temperature to 2000°C to limit tin vaporisation.

Prepare a calibration graph by plotting the reading obtained from the instrument against oxygen content expressed in micrograms from the last column of Table 1.

7.6 Preparation test

Prior to the determination, the following preparation test in duplicate shall be carried out.

Choose a CRM or routine sample (to be prepared just before determination) with an oxygen content close to that expected in the samples to be analysed.

Proceed as in 7.3 for the preparation of this preliminary sample.

Proceed as in 7.7 for the determination on the preliminary sample.

The results shall be within the limits of a control chart for the preliminary sample.

If not, check the preparation conditions and repeat the sample preparation test.

7.7 Determination

7.7.1 Method 1

The electrode shall be cleaned with a brush and vacuum cleaner before each determination.

Place a graphite crucible (5.1) in the furnace and then degas by heating above 2100 °C to 2800 °C.

After a cooling period of five to ten seconds, put the test portion with an empty tin or nickel capsule (4.6) into the degassed crucible, entering a sample weight of one gram.

Analyse in accordance with the apparatus manufacturer's instructions.

At the end of the fusion and measuring cycle, remove and discard the crucible and record the value displayed by the analyser.

7.7.2 Method 2

The electrode shall be cleaned with a brush and vacuum cleaner before each determination.

Place a graphite crucible (5.1) in the furnace and then degas by heating above 2100°C to 2800 °C. Repeat degassing once if possible with the apparatus used.

NOTE The addition of 0,3 g of graphite powder (4.12) before degassing can lead to a faster reduction of surface contamination and therefore give a better separation of the two surface contamination and bulk oxygen peaks.

After a cooling period of five to ten seconds, put the test portion with an empty tin or nickel capsule (4.6) into the degassed crucible, entering a sample weight of one gram.

Select the suitable heating rate to separate a first peak corresponding to surface contamination (signal 1) and a second peak corresponding to the bulk oxygen (signal 2), analysing in accordance with the apparatus manufacturer's instructions.

The separation of surface contamination and bulk oxygen can be achieved by a two stage fusion, with parameters which can depend on the equipment used in accordance with the laboratory experience and the manufacturer's instructions, for example:

- an increase of the furnace temperature with a heating rate of less than one degree centigrade per second by a dial reading, until a first peak corresponding to surface contamination appears,

- followed by a rapid increase of the furnace temperature to 2000 °C to 2800 °C, giving a second peak corresponding to bulk oxygen evolution.

At the end of the fusion and measuring cycle, the crucible shall be removed and discarded and the analyser reading corresponding to signal 2 (bulk oxygen) shall be recorded.

8 Expression of results

8.1 Method of calculation

Using the calibration curve (see 7.5), convert the reading corresponding to the test portion, displayed by the analyser (total signal for method 1, and core oxygen signal (signal 2) for method 2) into micrograms of oxygen (m_0).

The oxygen content, expressed as a percentage mass by mass, w_O (expressed in microgram/gram) is given by the equation:

$$w_O = m_0 / m$$

where

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

m is the mass, in grams, of the test portion (see 7.3).

The result is the mean value of at least two determinations made on the same sample.

The individual values may be given in order to provide additional information.

For mean values below 8 µg/g of oxygen, the difference between two individual determinations shall not exceed 2 µg/g of oxygen.

For mean values below 50 µg/g of oxygen, the difference between two individual determinations shall not exceed 5 µg/g of oxygen.

For mean values above 50 µg/g of oxygen, the difference between two individual determinations shall not exceed 10 percent of the mean value.

If the difference is too high, additional determinations shall be performed until obviously outlying values can be discarded.

The decision of discarding an outlying result is more efficiently taken when a chart recorder is fitted to the apparatus.

For example, a faulty preparation of the sample surface will produce an important peak at the beginning of the fusion.

8.2 Precision

An inter-laboratory precision test was carried out by 15 laboratories using nine samples according to Table 2. The results obtained were treated statistically in accordance with ISO 5725-2 and the results are summarised in Table 3. A graphical representation is showed in Figure 1.

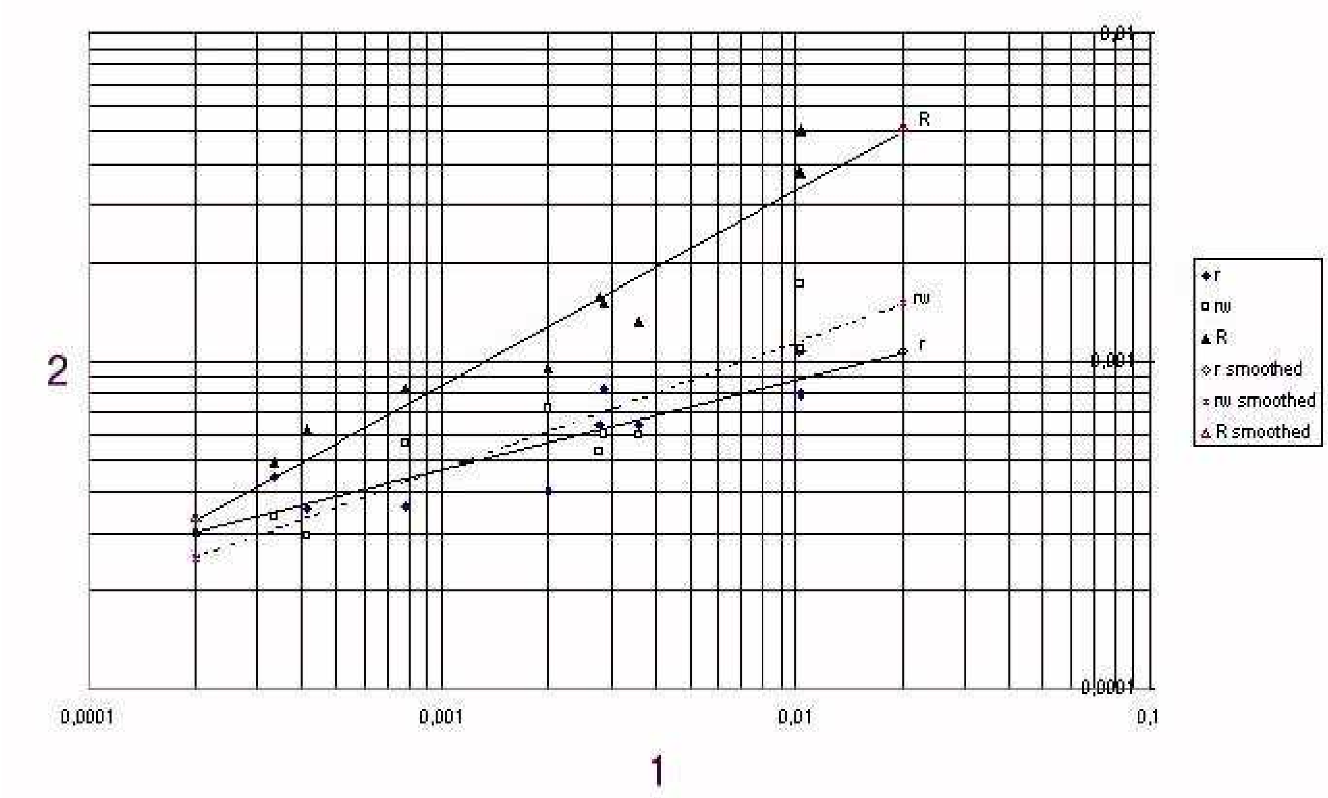
Table 2 — Determined mean concentrations in the precision test samples and the certified values

Sample n°	Name	Certified value or expected value [a]	Found value
Sample K	IRSID 1749	2 ppm [a]	4,1 ppm
Sample A	151KH	3 to 6 ppm [a]	7,8 ppm
Sample G	JSS GS6b	3,4 ppm	3,0 ppm
Sample B	IRSID 1748	17 ppm [a]	20 ppm
Sample E	JK 32	28 ppm	26,7 ppm
Sample H	JSS GS-3c	34,6 ppm	35,9 ppm
Sample C	ETS64	40 ppm [a]	28,4 ppm
Sample D	ETS59	94 ppm [a]	102,4 ppm
Sample F	ECRM 284-2	99 ppm [a]	103,6 ppm

[a] not certified

Table 3 — The relationships between the oxygen content and the precision parameters: smoothed values for r, R_w and R together with the coefficients of variations (CV)

Content (%)	r	Rw	R	R/r	CV(R)	Aimed CV(R)	Max CV(R)
0,0002	0,00030	0,00025	0,00034	1,11	48,88	28,28	62,15
0,0005	0,00039	0,00036	0,00058	1,49	33,77	20,58	45,24
0,001	0,00047	0,00047	0,00087	1,86	25,53	16,19	35,58
0,002	0,00057	0,00062	0,00132	2,32	19,30	12,73	27,98
0,005	0,00073	0,00088	0,00228	3,11	13,34	9,27	20,37
0,01	0,00089	0,00115	0,00344	3,88	10,08	7,29	16,02
0,02	0,00107	0,00151	0,00520	4,84	7,62	5,73	12,60



Key

1 Oxygen content (% m/m)

2 Precision (%)

Figure 1 — Graphical representation of precision data

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 part of EN 10276,

c) the result and the form in which they are expressed,

d) any unusual features noted during the determination,

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

Bibliography

[1] ISO 5725-2, *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.*

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover.
Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001.
Fax: +44 (0)20 8996 7001. Email: orders@bsi-global.com. Standards are also available from the BSI website at http://www.bsi-global.com.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre.
Tel: +44 (0)20 8996 7111. Fax: +44 (0)20 8996 7048. Email: info@bsi-global.com.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration.
Tel: +44 (0)20 8996 7002. Fax: +44 (0)20 8996 7001.
Email: membership@bsi-global.com.

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsi-global.com/bsonline.

Further information about BSI is available on the BSI website at http://www.bsi-global.com.

Copyright

Details and advice can be obtained from the Copyright & Licensing Manager.
Tel: +44 (0)20 8996 7070. Fax: +44 (0)20 8996 7553.
Email: copyright@bsi-global.com.

BSI
389 Chiswick High Road
London
W4 4AL