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Standard

ISO 24476

Steel — Determination of oxygen — Infrared absorption method after fusion under inert gas (Routine method)

Aciers — Détermination de l'oxygène — Méthode par absorption dans l'infrarouge après fusion sous gaz inerte (Méthode de routine)

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

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 oxygen — Infrared absorption method after fusion under inert gas (Routine method)

1 Scope

This document specifies a routine method after fusion under inert gas for the determination of oxygen in steel.

The method is applicable to contents of oxygen between 0,001 % (mass fraction) and 0,02 % (mass fraction).

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 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 terminology databases for use in standardization at the following addresses:

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

4 Principle

Fusing of a test portion in a single-use graphite crucible under an inert gas stream (He or Ar) at a minimum temperature of 2 000 °C. The sample is melted in a graphite crucible. The released oxygen combines with carbon to form carbon monoxide.

Depending on the instrument design, the carbon monoxide is oxidized to carbon dioxide or left as carbon monoxide and swept by the inert gas stream to an infrared detector.

The detector output is compared to that obtained from similar certified reference materials and is displayed as oxygen content of the sample.

The calibration curve is established using steel certified reference materials (CRMs).

5 Reagent and materials

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

5.1 Helium or argon, of ultra-high purity, total impurity content 0,000 5 % (mass fraction) (99,999 % purity minimum by volume).

5.2 Copper(II) oxide, on granulated support.

This reagent is used in some instruments to oxidize carbon monoxide to carbon dioxide. Use the purity specified by the instrument's manufacturer.

5.3 Magnesium perchlorate, (commercial designation: anhydrone), particle size: from 1,2 mm to 2,0 mm.

This reagent is used in the instrument to absorb water. Use the purity specified by the instrument's manufacturer.

5.4 Sodium hydroxide on clay (commercial designation: ascarite), particle size from 0,6 mm to 1,2 mm, for example.

This reagent is used in some instruments to absorb carbon dioxide. Use the purity specified by the instrument's manufacturer.

5.5 Appropriate solvent, suitable for washing greasy or dirty test samples, e.g. high-purity acetone

5.6 Steel reference materials (RMs), material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.

5.7 Steel certified reference materials (CRMs), reference material (RM) characterized by a metrologically valid procedure for one or more specified properties, accompanied a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

6 Apparatus

6.1 Oxygen analyser, 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.

6.2 Graphite crucible, single use. Use high-purity graphite crucibles suitable for use with the instrument.

6.3 Crucible tongs, for handling the graphite crucibles used.

6.4 Glass-wool filters.

7 Sampling

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

8 Procedure

WARNING — The risks involved when using an apparatus for fusing a test portion are mainly burn risks. It is therefore essential to use crucible tongs (6.3) and appropriate containers for the crucibles used.

8.1 General

Assemble the apparatus as recommended by the manufacturer. Make the required power, gas and water connections. Switch on the instrument and allow sufficient warm up time to stabilize.

After changing the filter and/or reagents, 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 blank, calibration and preparation tests as indicated in 8.3 and 8.4 before analysing the sample.

Place a graphite crucible (6.2) on the furnace pedestal and then degas by heating above the degassing temperature of the sample.

The samples are weighed and the mass is transferred automatically or manually to a computer connected to the analyser. The sample is placed in the loading head above the empty degassed graphite crucible placed on the lower electrode tip. Depending on the application, the addition of auxiliary materials which lower the melting point, such as tin or nickel, may be required. When auxiliary materials (tin or nickel) are added, they shall be also added during blank and calibration tests. Check that the glass-wool filters (6.4) are clean and change them as often as necessary.

If the power supply has been switched off for a long time, allow the instrument to stabilize for the time recommended by manufacturer.

NOTE The appropriate degas temperature of the sample and the oxygen extraction temperature are determined by the instrument's manufacturer.

When using computerised instruments for the preparation of the calibration curve, the standardisation (drift correction, and recalibration) and measurement of the oxygen content should be carried out in accordance with the software's operating instructions.

WARNING — Care should be taken when handling hot crucibles and operating furnaces to avoid personal injury by either burn or electrical shock.

8.2 Test sample and sample preparation

Weigh, to the nearest 1 mg, approximately 1 g of the test sample.

Use only solid samples to minimize the potential for errors due to surface oxidation. Samples shall be of the proper size to permit free introduction into the sample loading device, if required, and to fit in the graphite crucible. The samples should be uniform in size. Cut a laboratory sample in the form of a slice of thickness 3 mm to 4 mm.

Cut off a test portion from the laboratory sample to an appropriate size by machining, using no lubricating fluid or by other means that will avoid overheating. Avoid oxide cutting or oxide abrading materials. Thin, flat samples may be stamped using a punch and die. Abrade all surfaces of the samples to remove all traces of surface oxide or other impurities using a clean file, die grinder, or a dry silicon carbide grinding tool. Again, avoid overheating the samples. If wet grinding is used, it is necessary to rinse samples in acetone and air dry completely. If dry grinding is used, avoid overheating the samples.

NOTE 1 For some material, such as plain carbon steel sheet, a rimmed or semi-killed deoxidation practice is used and it is possible that the oxygen is not uniformly distributed throughout the thickness of the sample. In these cases, the removal of too much surface of the material can cause erroneous results.

Do not touch the samples with fingers during and following the final stages of cleaning. Some steel alloys may be prone to oxidation and it may be necessary to store these prepared samples in a desiccator. If oxidation prone alloys are not analysed within four hours after the preparation, it may be necessary to repeat the filing or grinding step prior to analysis.

Careful adherence to the sample preparation procedures described above is critical to obtain accurate results. The use of small and irregular shaped samples requires a diligent effort to ensure that all surface contamination has been removed.

NOTE 2 The mass of the test portion can be dependent on the type of instrument used.

8.3 Blank test

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

Place a graphite crucible (6.2) in the furnace (see Annex A) and then degas by heating at a temperature greater than 2 100 °C. Operate the furnace in accordance with the manufacturer's instructions.

Obtain the reading of the blank test and convert it to micrograms of oxygen by means of the calibration curve.

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

The mean blank value (m_1) is calculated from at least two blank values.

For a mean value above 10 µg/g of oxygen, the mean blank value and the difference between the two blank values shall both not exceed 2 µg/g of oxygen.

If the blank values are abnormally high, investigate and eliminate the source of contamination.

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

8.4 Calibration

8.4.1 General

The calibration of the apparatus shall be carried out before the first sample determination.

Select CRMs (5.7) having a matrix as close as possible to the matrix of the material to be analysed and covering the range of oxygen contents to be determined.

8.4.2 Plotting the calibration curve

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

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

NOTE The calibration curve can be automatically established by computerised apparatus by using these data.

8.5 Determination

Assemble the apparatus and calibrate it.

Clean the electrode with a brush and vacuum cleaner before each determination.

Place a graphite crucible (6.2) in the furnace and then degas it at a temperature greater than 2 100 °C.

Put the test portion into the graphite crucible and record the mass of the test portion.

Operate the furnace in accordance with the manufacturer's instructions for fusion, extraction of oxygen and measurement of the infrared absorption.

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

During the sample analysis run, analysis of a RM or a CRM sample at regular intervals is recommended for monitoring possible drifts from the initial calibration.

9 Expression of results

9.1 Method of calculation

Convert the analyser reading for the test portion to micrograms of oxygen, w_O, (mass fraction) by means of the calibration curve (see 8.4).

The oxygen content, expressed as a percentage by mass, is given by the Formula (1):

$$w_O = \frac{m_0 - m_1}{m \times 10^6} \times 100 \qquad (1)$$

where

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

m_1 is the mass of oxygen, expressed in micrograms, in the blank test (see 8.3);

m is the mass, in grams, of the test portion (see 8.2).

9.2 Precision

A planned trial of this method was carried out by 9 laboratories in 4 countries, at 11 levels of oxygen content.

Each laboratory carried out three determinations (see NOTES 1 and 2) of the oxygen content on each level.

Table 1 — Experimental precision data

Oxygen content % mass fraction		**Repeatability** r % mass fraction	**Reproducibility**	
Certified	Found		R_w % mass fraction	R % mass fraction
0,000 96	0,000 93	0,000 15	0,000 31	0,000 36
0,001 6	0,001 84	0,000 32	0,000 41	0,000 75
0,002 2	0,002 21	0,000 51	0,000 51	0,000 95
0,006 6	0,006 62	0,000 43	0,000 71	0,000 71
0,006 9	0,007 03	0,000 20	0,000 72	0,001 25
0,009 9	0,009 91	0,000 54	0,000 75	0,001 32
0,010 0	0,010 72	0,000 77	0,000 78	0,001 27
0,012 0	0,012 36	0,000 78	0,000 78	0,001 42
0,015 1	0,014 82	0,000 65	0,000 89	0,002 12
0,017 3	0,016 69	0,000 35	0,001 09	0,002 04
0,019 4	0,019 83	0,000 89	0,000 89	0,002 97

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 the results obtained are listed in Table B.1 and Table 1, respectively.

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

Since the coefficients of correlation of the relations between m and r, and R are lower than 0,9 only the experimental precision data are presented (see Table 1).

The graphical representations of the data are shown in Annex C.

10 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 or of the test report;

b) method used by reference to this document, i.e. ISO 24476;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(informative)

Features of commercial resistive electrode furnaces and oxygen analysers

A.1 Helium or argon source

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

A.2 Purifying unit

The purifying unit contains sodium hydroxide-impregnated attapulgite and magnesium perchlorate in a dehydration tube.

A.3 Flowmeter

The flowmeter is used for measuring the flow of helium or argon 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 or other materials depending on the instrument's manufacturer 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 the 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 Infrared (IR) absorption detector

The sample, contained in a small, single use graphite crucible, is fused under a flowing inert gas stream at a temperature sufficient to release oxygen. The oxygen combines with carbon from the crucible to form carbon monoxide (CO) and is carried by the flowing inert gas stream to an infrared detector. In some instruments the CO is converted to carbon dioxide (CO_2) and detected in an infrared cell as CO_2. CO or CO_2 absorbs IR energy at a precise wavelength within the IR spectrum. The energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is prevented from reaching the detector by use of a precise wavelength filter. Thus, the absorption of IR energy can only be attributed to CO_2 or CO and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measuring chamber. The detector output is compared to that obtained from similar certificate reference materials and is displayed as oxygen content of the sample.