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Steel and iron — Determination of high sulfur content — Infrared absorption method after combustion in an induction furnace

Aciers et fontes — Dosage du soufre en fortes teneurs — Méthode par absorption dans l'infrarouge après combustion dans un four à induction

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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 13902 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 high sulfur content — Infrared absorption method after combustion in an induction furnace

1 Scope

This International Standard specifies a method for the determination of the sulfur content in steel and iron using an infrared absorption method after combustion in an induction furnace.

The method is applicable to a sulfur content of between 0,10 % (*m/m*) and 0,35 % (*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 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet— Nominal sizes of openings.*

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

Combustion of a test portion with accelerator at a high temperature in a high-frequency induction furnace in a current of pure oxygen.

Transformation of sulfur into sulfur dioxide.

Measurement by infrared absorption of the sulfur dioxide carried by a current of oxygen.

4 Reagents and materials

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

4.1 Oxygen, 99,5 % (*m/m*) minimum.

It is essential that an oxidation catalyst, copper(II) oxide or platinum for example, in a tube heated to a temperature above 450 °C is used prior to a purifying unit (see annex A), when the presence of organic contaminants is suspected in the oxygen.

4.2 Pure iron, of a known (or determined by the procedure given in 7.4) low sulfur content of less than 0,000 5 % (*m/m*).

4.3 Suitable solvent, appropriate for washing greasy or dirty test samples, for example, acetone.

4.4 Magnesium perchlorate, anhydrous, [$Mg(ClO_4)_2$], particle size: from 0,7 mm to 1,2 mm.

4.5 Accelerator, tungsten, free from sulfur, or of a known sulfur content of less than 0,000 5 % (*m/m*).

NOTE 1 The mesh size of the accelerator may be dependent on the type of apparatus used.

4.6 Anhydrous barium sulfate [minimum assay: 99,5 % (*m/m*)], dried at 105 °C to 110 °C for 3 h and cooled in a desiccator before use.

4.7 Inert ceramic (attapulgus clay), impregnated with sodium hydroxide, particle size: from 0,7 mm to 1,2 mm.

5 Apparatus

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

The apparatus required for combustion in a high-frequency induction furnace and the subsequent infrared absorption measurement of the evolved sulfur dioxide may be obtained commercially from a number of manufacturers. Follow the manufacturer's instructions for the operation of the equipment.

Features of commercial instruments are given in annex A.

5.1 Microbalance, weighing to the nearest 0,001 mg.

5.2 Ceramic crucible, capable of withstanding combustion in an induction furnace.

Ignite crucibles in an electric furnace in air or in a current of oxygen, for not less than 2 h at 1 100 °C, and store in a desiccator before use.

5.3 Glass-fibre filter, cut to the diameter of the crucible and ignited for 12 h at 450 °C.

6 Sampling and preparation of the test samples

Sampling and preparation of the samples shall be carried out in accordance with ISO 14284. The sample for analysis shall be homogenized before weighing the test portion. Powders can be homogenized by stirring (see clause 9).

7 Procedure

SAFETY INSTRUCTIONS — The risks related to combustion analysis are mainly burns in pre-igniting the ceramic crucibles and in the fusion. Use crucible tongs at all times and suitable containers for the used crucibles. Normal precautions for handling oxygen cylinders shall be taken. Oxygen from the combustion process shall be removed effectively from the apparatus since a high concentration of oxygen in a confined space can present a fire hazard.

7.1 Apparatus conditioning

Purify the oxygen supply using tubes packed with the inert ceramic (attapulgus clay) impregnated with sodium hydroxide (4.7) and magnesium perchlorate (4.4), and maintain a quiescent flow rate whilst on standby. Maintain a glass-wool filter or a stainless steel net as a dust collector. Clean and change as necessary. The furnace chamber, pedestal post and filter trap shall be cleaned frequently to remove oxide build-up.

Allow each item of equipment to stabilize for the time recommended by the equipment manufacturers when the main supply is switched on after being out of action for any length of time.

After cleaning the furnace chamber and/or changing filters or after the equipment has been inoperative for a period, stabilize the apparatus by burning several samples, of similar type to the samples to be analysed, prior to setting up for analysis.

Flush oxygen through the apparatus and adjust the instrument controls to give a zero reading.

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

Select the certified reference material with a sulfur content close to the maximum sulfur content in the calibration series, and measure the sulfur content of the certified reference material in the same manner as specified in 7.4.

Adjust the reading of the instrument to the certified value.

It is essential that this adjustment is made before the calibration as specified in 7.5. It cannot replace or correct the calibration.

7.2 Test portion

Degrease the test sample by washing in a suitable solvent (4.3). Evaporate the last traces of the solvent by heating.

Weigh, to the nearest 1 mg, 0,5 g of the test sample (see clause 9) and add 0,5 g ± 0,001 g of the pure iron (4.2) (see note 2).

NOTE 2 The mass of the test portion and accelerator 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.

Prepare a ceramic crucible (5.2), place a glass-fibre filter (5.3) at the bottom by using a small pair of tweezers. Add 1,000 g of the pure iron (4.2) and 1,5 g ± 0,1 g of the accelerator (4.5).

Treat the crucible and contents as specified in the second and third paragraphs of 7.4.

Obtain the readings of the blank tests and convert them to milligrams of sulfur by means of the calibration graph (7.6).

The mean blank value (m_1) is calculated from the two blank values (see note 3).

NOTE 3 It is essential that the mean blank value does not exceed 0,005 mg of sulfur and the difference between the two blank values does not exceed 0,003 mg of sulfur. If this value is abnormally high, it should be investigated and the source of contamination eliminated.

7.4 Sulfur content in the pure iron (4.2)

Determine the sulfur content in the pure iron (4.2) as follows.

Prepare two ceramic crucibles(5.2). Place a glass-fibre filter (5.3) at the bottom of each of them by using a small pair of tweezers.

Add 0,500 g of the pure iron (4.2) to one ceramic crucible and 1,000 g to the other. Cover each with 1,5 g ± 0,1 g of the accelerator (4.5).

Treat the crucible and contents as specified in the second and third paragraphs of 7.5.

Convert the values obtained into milligrams of sulfur by means of the calibration graph (7.6).

The mass (m_2) of sulfur, with 0,500 g of pure iron added, is obtained by subtracting the value (m_3) corresponding to 0,500 g of the pure iron from that(m_4) of 1,000 g of pure iron. The mass (m_5) of sulfur with 1,000 g of pure iron added is twice the mass (m_2) of the sulfur with 0,500 g of pure iron added:

$$m_5 = 2 \times m_2 = 2 \times (m_4 - m_3)$$

7.5 Determination

Prepare a ceramic crucible (5.2) and place a glass-fibre filter (5.3) at the bottom by using a small pair of tweezers. Add the test portion (7.2) and the pure iron (4.2) (see 7.2), and cover with 1,5 g ± 0,1 g of the accelerator (4.5).

Place the ceramic crucible and contents on the pedestal post, raise to the combustion position and lock the system. Operate the furnace in accordance with the manufacturer's instructions.

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

7.6 Establishment of the calibration graph

7.6.1 Preparation of the calibration series

Prepare eight ceramic crucibles (5.2) and place a glass-fibre filter (5.3) at the bottom of each of them by using a small pair of tweezers.

Weigh, with the microbalance (5.1), to the nearest 0,001 mg, the masses of barium sulfate (4.6) as near as possible to those indicated in table 1.

Add 1,000 g of the pure iron (4.2) and cover with 1,5 g ± 0,1 g of the accelerator (4.5).

7.6.2 Measurements

Treat the crucible and contents as specified in the second and third paragraphs of 7.5.

Table 1 — Calibration series

Mass of barium sulfate (4.6) mg	**Mass of sulfur taken in the ceramic crucible** mg	**Sulfur content in the test portion** % (*m*/*m*)
0 [1]	0	0
3,64	0,50	0,10
5,46	0,75	0,15
7,28	1,00	0,20
9,10	1,25	0,25
10,92	1,50	0,30
12,74	1,75	0,35
14,56	2,00	0,40

1) Zero member

7.6.3 Plotting the calibration graph

The net reading is obtained by subtracting the reading of the zero member from that of each member of the calibration series.

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

8 Expression of results

8.1 Method of calculation

Convert the analyser reading of the test portion (see 7.5) to milligrams of sulfur (m_0) by means of the calibration graph.

The sulfur content, w_S, expressed as a percentage by mass, is given by the equation

$$w_S = \frac{(m_0 - m_1 + m_2)}{m \times 10^3} \times 100$$

$$= \frac{(m_0 - m_1 + m_2)}{10_m}$$

where

m_0 is the mass, expressed in milligrams, of sulfur in the test portion;

m_1 is the mass, expressed in milligrams, of sulfur in the blank test (7.3);

m_2 is the mass, expressed in milligrams, of sulfur in 0,5 g of pure iron (4.2), (see 7.4);

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

8.2 Precision

A planned trial of this method was carried out by 18 laboratories in seven countries, at eight levels of sulfur content, each laboratory making three determinations (see notes 4 and 5) of sulfur content on each level.

NOTES

4 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.

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

The test samples used and mean/precision results obtained are listed in table 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 sulfur content and repeatability limit (r) and reproducibility limits (R and R_w) of the test results (see note 6) as summarized in table 2. The graphical representation of the data is shown in figure C.1.

NOTE 6 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 2 — Results for repeatability and reproducibility

Sulfur content % (m/m)	Repeatability r	Reproducibility R	 R_w
0,10	0,004 0	0,017 7	0,009 6
0,15	0,005 9	0,018 8	0,011 3
0,20	0,007 8	0,020 0	0,012 6
0,25	0,009 7	0,020 7	0,013 8
0,30	0,011 6	0,021 3	0,015 0
0,35	0,013 4	0,021 9	0,015 9

9 Procedure for samples containing fine powder

In the case of a sample for analysis which does contain fine powder, that is , particles of size less than 500 µm, sieve into coarse and fine fractions using a test sieve (500 µm size) specified in ISO 565. Weigh proportionate parts of each fraction to obtain a representative sample for analysis, and determine the sulfur content separately for each fraction.

In this case, the sulfur content, w_S, expressed as a percentage by mass, is given by the equation

$$w_S = \frac{(w_{S,1} \times m_{\mathrm{cf}}) - (w_{S,2} \times m_{\mathrm{ff}})}{m_{\mathrm{cf}} + m_{\mathrm{ff}}}$$

where

$w_{S,1}$ is the sulfur content, expressed as a percentage by mass, in the coarse fraction;

$w_{S,2}$ is the sulfur content, expressed as a percentage by mass, in the fine fraction;

m_{cf} is the mass of the coarse fraction, expressed in grams, in the test sample;

m_{ff} is the mass of the fine fraction, expressed in grams, in the test sample.

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;

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 high-frequency induction furnaces and infrared carbon analysers

A.1 Source of oxygen, fitted with a fine regulating valve and a pressure gauge. A pressure regulator is required to control the oxygen pressure to the furnace according to the manufacturer's specification. This is usually 28 kN/m^2.

A.2 Purifying unit, containing the inert ceramic impregnated with sodium hydroxide in a carbon dioxide absorbing tube, and the magnesium perchlorate in a dehydration tube.

A.3 Flowmeter, capable of measuring a flow of oxygen of 0 l/min to 4 l/min.

A.4 High-frequency induction furnace

A.4.1 The combustion furnace consists of an induction coil and a high-frequency generator. The furnace chamber consists of a silica tube (e.g. 30 mm to 40 mm in outer diameter, 26 mm to 36 mm in inner diameter, 200 mm to 220 mm in length) which fits inside the induction coil. This tube has metal plates at the top and bottom which are sealed to the tube by O-rings.

Gas inlet and outlet points are made through the metal plates.

A.4.2 The generator is usually a 1,5 kVA to 2,5 kVA apparent power unit, but the frequency used by certain manufacturers may be different. Values of 2 MHz to 6 MHz, 15 MHz, and 20 MHz have been used. The power from the generator is fed to the induction coil which surrounds the silica furnace tube and is usually air-cooled.

A.4.3 The crucible containing the sample, flux and accelerator is supported on a pedestal post which is precisely positioned so that, when raised, the metal in the crucible is correctly placed within the induction coil for effective coupling when the power is supplied.

A.4.4 The induction coil diameter, the number of turns, the furnace chamber geometry and the power of the generator determine the degree of coupling which can occur. These factors are determined by the instrument manufacturer.

A.4.5 The temperature attained during the combustion depends in part on the factors indicated in A.4.4, but also on the characteristics of the metal in the crucible, the form of the test portion and the mass of materials. Certain of these factors may be varied to some extent by the operator.

A.5 Dust collector, capable of collecting metal oxide dust in a current of oxygen from the furnace.

A.6 Infrared gas analyser

A.6.1 In most instruments the gaseous products of combustion are transferred in a continuous flow of oxygen to the analyser system. The gases flow through an infrared cell, for example of the Luft type, where the absorption of the infrared radiation due to sulfur dioxide is measured and integrated over a pre-programmed time period. The signal is amplified and converted to a digital display of the percentage concentration of sulfur.

A.6.2 In some analysers, the products of combustion may be collected in oxygen in a fixed volume at controlled pressure and the mixture analysed for sulfur dioxide.

A.6.3 Electronic controls are usually provided for adjusting the instrument zero, compensating for the blank, adjusting the slope of the calibration line and correcting for non-linear response. The analyser generally has a means of entering the mass of standard or test portion for automatic correction of the read-out. Instruments may also be equipped with an integrated automatic balance for weighing the crucible, weighing the test portion and transferring the value of mass to the calculator.

Annex B
(informative)

Additional information on the international cooperative tests

Table 2 was derived from the results of international analytical trials carried out in 1993 on three steel samples and five iron samples in seven countries involving 18 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 1035, March 1994. The graphical representation of the precision data is given in annex C.

The test samples used and mean results obtained are listed in table B.1.

Table B.1 — Detailed results obtained in interlaboratory tests

	Sulfur content % (*m/m*)			**Precision data**		
Sample	**Certified**	**Found**		**Repeatability**	**Reproducibility**	
		$\overline{w}_{S,1}$	$\overline{w}_{S,2}$	r	R	R_w
ACS 2 (cast iron)	0,125	0,122	0,120	0,006 3	0,017	0,007 7
ECRM 489-1(cast iron)	0,155	0,153	0,153	0,005 7	0,021	0,014
ECRM 485-2(cast iron)	0,165	0,147	0,146	0,006 6	0,018	0,011
ECRM 486-1(cast iron)	0,168 1)	0,146	0,146	0,005 0	0,021	0,012
SWEDEN STEEL (stainless steel)	0,19 1)	0,199	0,200	0,006 6	0,016	0,014
ECRM 484-1(cast iron)	0,230	0,238	0,239	0,006 8	0,027	0,012
JSS S26 (unalloyed steel)	0,304	0,291	0,290	0,012	0,021	0,016
ECRM 085-1 (unalloyed steel)	0,336	0,336	0,338	0,016	0,020	0,012

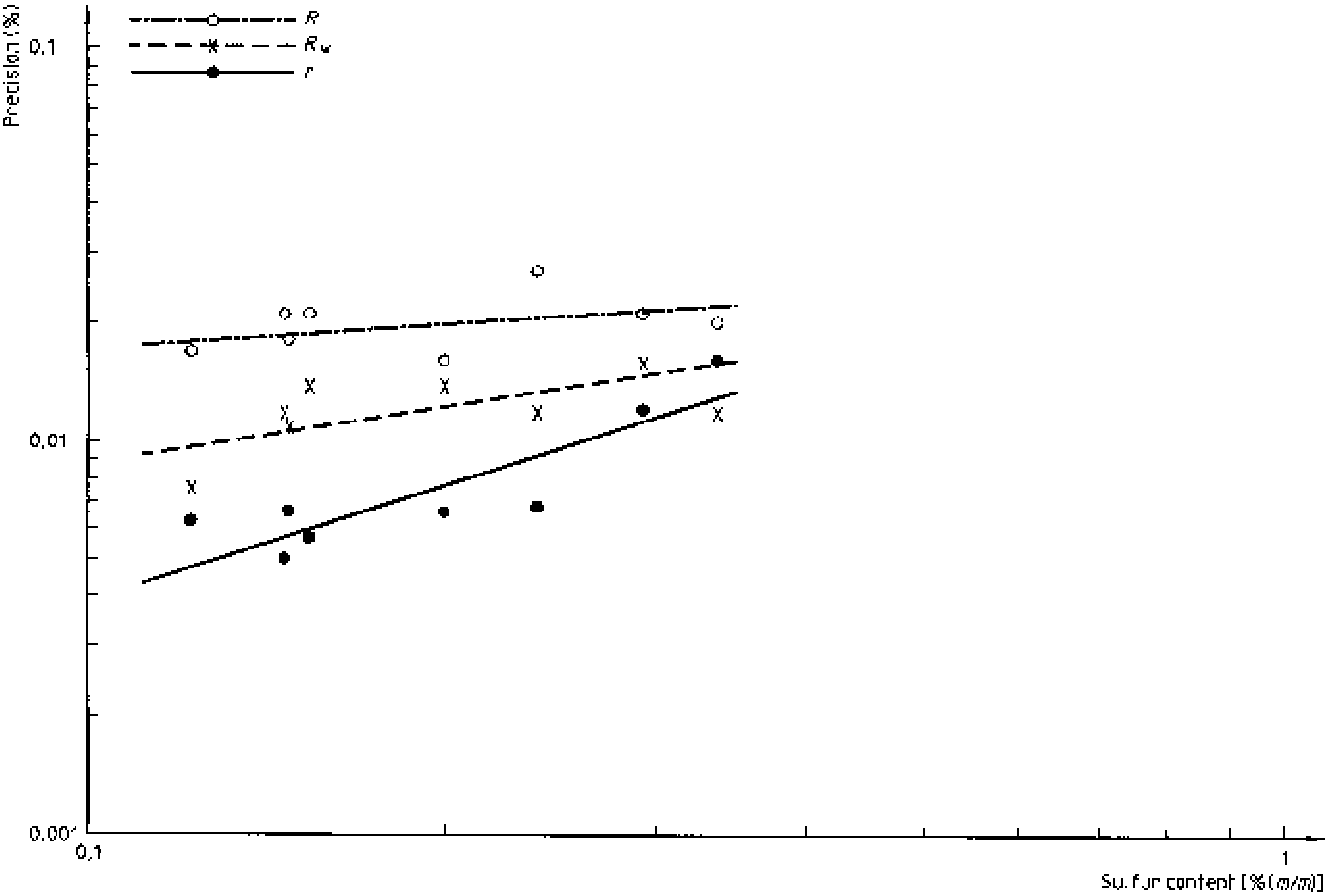
$\overline{w}_{S,1}$, general mean within a day

$\overline{w}_{S,2}$, general mean between days

1) Non-certified value.

Annex C
(informative)

Graphical representation of precision data



$$\lg r = 0{,}951\,4 \lg \overline{w}_{S,1} - 1{,}441$$

$$\lg R_w = 0{,}392\,8 \lg \overline{w}_{S,2} - 1{,}624$$

$$\lg R = 0{,}177\,7 \lg \overline{w}_{S,1} - 1{,}574$$

where

$\overline{w}_{S,1}$ is the average sulfur content, expressed as a percentage by mass, obtained within a day;

$\overline{w}_{S,2}$ is the average sulfur content, expressed as a percentage by mass, obtained between days.

Figure C.1 — Logarithmic relationship between sulfur content ($\overline{w}_S$) and repeatability limit (*r*) or reproducibility limits(*R* and R_w)

ICS 77.080.01

Descriptors: steels, iron, chemical analysis, determination of content, sulphur, combustion analysis, spectroscopic analysis.

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