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

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

Reference number
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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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4935 was prepared by Technical Committee ISO/TC 17, *Steel*.

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

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

1 Scope

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

The method is applicable to sulfur contents between 0,002 % (m/m) and 0,10 % (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 listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377 : 1985, *Wrought steel — Selection and preparation of samples and test pieces.*

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

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

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725 : 1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

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 and only distilled water or water of equivalent purity.

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

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

4.2 Pure iron, of known low sulfur contents 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 [$Mg(ClO_4)_2$], particle size: from 0,7 mm to 1,2 mm.

4.5 Accelerator, tungsten, free of sulfur, or of known sulfur contents less than 0,000 5 % (m/m). The mesh size of the accelerator may be dependent on the type of apparatus used.

4.6 Sulfur, standard solutions.

Weigh, to the nearest 0,1 mg, the mass described in table 1 of potassium sulfate [minimum assay: 99,9 % (m/m)] previously dried at 105 °C to 110 °C for 1 h or to constant mass and cooled in a desiccator.

Table 1

Reference of sulfur standard solution	Mass of potassium sulfate g	Concentration of sulfur mg/ml
4.6.1	0,217 4	0,40
4.6.2	0,380 4	0,70
4.6.3	0,543 4	1,00
4.6.4	1,086 9	2,00
4.6.5	1,902 2	3,50
4.6.6	2,717 2	5,00
4.6.7	4,347 5	8,00

Transfer to seven 100 ml beakers and dissolve in water.

Transfer quantitatively into seven 100 ml one-mark volumetric flasks. Dilute to the mark with water and mix.

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.

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

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 C.

5.1 Micropipettes, 50 µl and 100 µl, limit of error shall be less than 1 µl.

5.2 Tin capsule, about 6 mm in diameter, 18 mm in height, 0,3 g in mass and approximately 0,4 ml in volume.

5.3 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.

NOTE — For the determination of low sulfur contents it is advisable to ignite crucibles at 1 350 °C in a current of oxygen.

6 Sampling

Sampling shall be carried out in accordance with ISO 377 or appropriate national standards for iron.

7 Procedure

SAFETY INSTRUCTIONS — The risks related to combustion analysis are mainly burns in pre-igniting the ceramic crucibles and in the fusions. 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, 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.

NOTE — This adjustment shall be 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 washing liquid by heating.

Weigh, to the nearest 1 mg, 1 g of the test sample for sulfur contents less than 0,04 % (m/m) and 0,5 g for sulfur contents greater than 0,04 % (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.

Transfer a tin capsule (5.2) to a ceramic crucible (5.3), press the tin capsule lightly against the bottom of the crucible. Add the same quantity of the pure iron (4.2) as the test portion (7.2) 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 (7.5).

The blank value is obtained by subtracting the mass of sulfur in the pure iron (4.2) used (see note 1) from the mass of sulfur in the blank tests.

The mean blank value $(\overline{m}_1)$ is calculated from the two blank values (see note 2).

NOTES

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

Prepare two ceramic crucibles (5.3). Transfer a tin capsule (5.2) to each and press the capsule lightly against the bottom of the crucible.

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 7.4.

Convert the values obtained into milligrams of sulfur by means of the calibration graph (7.5).

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 of 1,000 g of pure iron added is twice the mass (m_2) of the sulfur with 0,500 g of pure iron added:

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

2 The mean blank value shall not exceed 0,005 mg of sulfur and the difference between the two blank values shall not exceed 0,003 mg of sulfur. If this value is abnormally high, investigate and eliminate the source of contamination.

7.4 Determination

Transfer a tin capsule (5.2) to a ceramic crucible (5.3), press the tin capsule lightly against the bottom of the ceramic crucible, add the test portion (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.

7.5 Establishment of the calibration graph

7.5.1 Samples having sulfur contents less than 0,005 % (m/m)

7.5.1.1 Preparation of the calibration series

Using the 50 µl micropipette (5.1), transfer water (zero member) and sulfur standard solutions (4.6) as indicated in table 2 to four separate tin capsules (5.2).

Evaporate slowly at 90 °C until completely dry and then cool to room temperature in a desiccator.

Table 2

Reference of sulfur standard solution	Mass of sulfur µg	Sulfur content in the test portion % (m/m)
Water	0	0,000 0
4.6.1	20	0,002 0
4.6.2	35	0,003 5
4.6.3	50	0,005 0

7.5.1.2 Measurements

Transfer the tin capsule from 7.5.1.1 to a ceramic crucible (5.3), press the tin capsule lightly against the bottom of the ceramic crucible, add 1,000 g of the pure iron (4.2) and cover 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 7.4.

7.5.1.3 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.

7.5.2 Samples having sulfur contents between 0,005 % (m/m) and 0,04 % (m/m)

7.5.2.1 Preparation of the calibration series

Using the 50 µl micropipette (5.1), transfer water (zero member) and sulfur standard solutions (4.6) as indicated in table 3 to five separate tin capsules (5.2).

Evaporate slowly at 90 °C until completely dry and then cool to room temperature in a desiccator.

Table 3

Reference of sulfur standard solution	Mass of sulfur µg	Sulfur content in the test portion % (m/m)
Water	0	0,000 0
4.6.3	50	0,005 0
4.6.4	100	0,010 0
4.6.6	250	0,025 0
4.6.7	400	0,040 0

7.5.2.2 Measurements

As specified in 7.5.1.2.

7.5.2.3 Plotting the calibration graph

As specified in 7.5.1.3.

7.5.3 Samples having sulfur contents between 0,04 % (m/m) and 0,1 % (m/m)

7.5.3.1 Preparation of the calibration series

Using the 100 µl micropipette (5.1), transfer water (zero member) and sulfur standard solutions (4.6) as indicated in table 4 to five separate tin capsules (5.2).

Evaporate slowly at 90 °C until completely dry and then cool to room temperature in a desiccator.

Table 4

Reference of sulfur standard solution	Mass of sulfur µg	Sulfur content in the test portion % (m/m)
Water	0	0,000 0
4.6.3	100	0,020 0
4.6.4	200	0,040 0
4.6.5	350	0,070 0
4.6.6	500	0,100 0

7.5.3.2 Measurements

Transfer the tin capsule from 7.5.3.1 to a ceramic crucible (5.3), press the tin capsule lightly against the bottom of the ceramic crucible, add 0,500 g of the pure iron (4.2) and cover 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 7.4.

7.5.3.3 Plotting the calibration graph

As specified in 7.5.1.3.

8 Expression of results

8.1 Method of calculation

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

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

$$w_S = \frac{(m_0 - \overline{m}_1)}{m \times 10^3} \times 100$$

$$= \frac{(m_0 - \overline{m}_1)}{10m}$$

where

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

$\overline{m}_1$ is the mass, expressed in milligrams of sulfur, in the blank test (7.3);

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 22 laboratories, at 15 levels of sulfur, each laboratory marking three determinations of sulfur content at each level (see notes 1 and 2).

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

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between sulfur content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 3) as summarized in table 5. The graphical representation of the precision data is given in annex B.

Table 5

Sulfur content % (m/m)	Repeatability r	Reproducibility R	R_w
0,002	0,000 21	0,000 59	0,000 25
0,005	0,000 37	0,001 11	0,000 48
0,010	0,000 57	0,001 79	0,000 77
0,020	0,000 88	0,002 89	0,001 26
0,050	0,001 56	0,005 43	0,002 39
0,100	0,002 41	0,008 75	0,003 89

NOTES

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

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.

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

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 the 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)

Additional information on the international cooperative tests

Table 5 was derived from the results of international analytical trials carried out in 1985 on 11 steel and four iron samples in five countries involving 22 laboratories.

The results of the trials were reported in document ISO/TC 17/1 N 673, April 1986. The graphical representation of the precision data is given in annex B.

The test samples used are listed in table A.1.

Table A.1

Sample		Sulfur content % (m/m)		
		Certified	Found	
			$\overline{w}_1$	$\overline{w}_2$
IRSID 487-1	Cast iron	0,000 7	0,000 58	0,000 70
BAS 088-1	High-purity iron	0,001 9	0,002 06	0,002 09
BAM 885-1	18Ni.5Mo.9Co steel	0,002 4	0,002 12	0,002 10
BAM 184-1	Low alloy steel	0,003 2	0,002 87	0,002 88
BAM 129-2	Low alloy steel	0,004 4	0,003 56	0,003 56
BAM 128-1	Carbon steel	0,007	0,007 09	0,007 04
CTIF C 76	Cast iron	(0,009)	0,008 14	0,008 03
BAS 281-1	Stainless steel	0,016	0,016 7	0,016 6
JSS 241-7	Carbon steel	0,020	0,018 8	0,018 8
JSS 150-8	Low alloy steel	0,030	0,030 0	0,030 0
JSS 245-1	Carbon steel	0,060	0,061 2	0,061 3
CTIF FB 10-1	Cast iron	0,089	0,090 2	0,090 8
CTIF FB 12	Cast iron	0,155	0,160 3	0,160 7
BAM 286-1	Sulfur-free cutting stainless steel	0,280	0,286 8	0,286 2
IRSID 022-1	Sulfur-free cutting steel	0,300	0,313 2	0,312 3

$\overline{w}_1$: General mean of within a day

$\overline{w}_2$: General mean of between days

( ): Non-certified value

Annex B
(informative)

Graphical representation of precision data

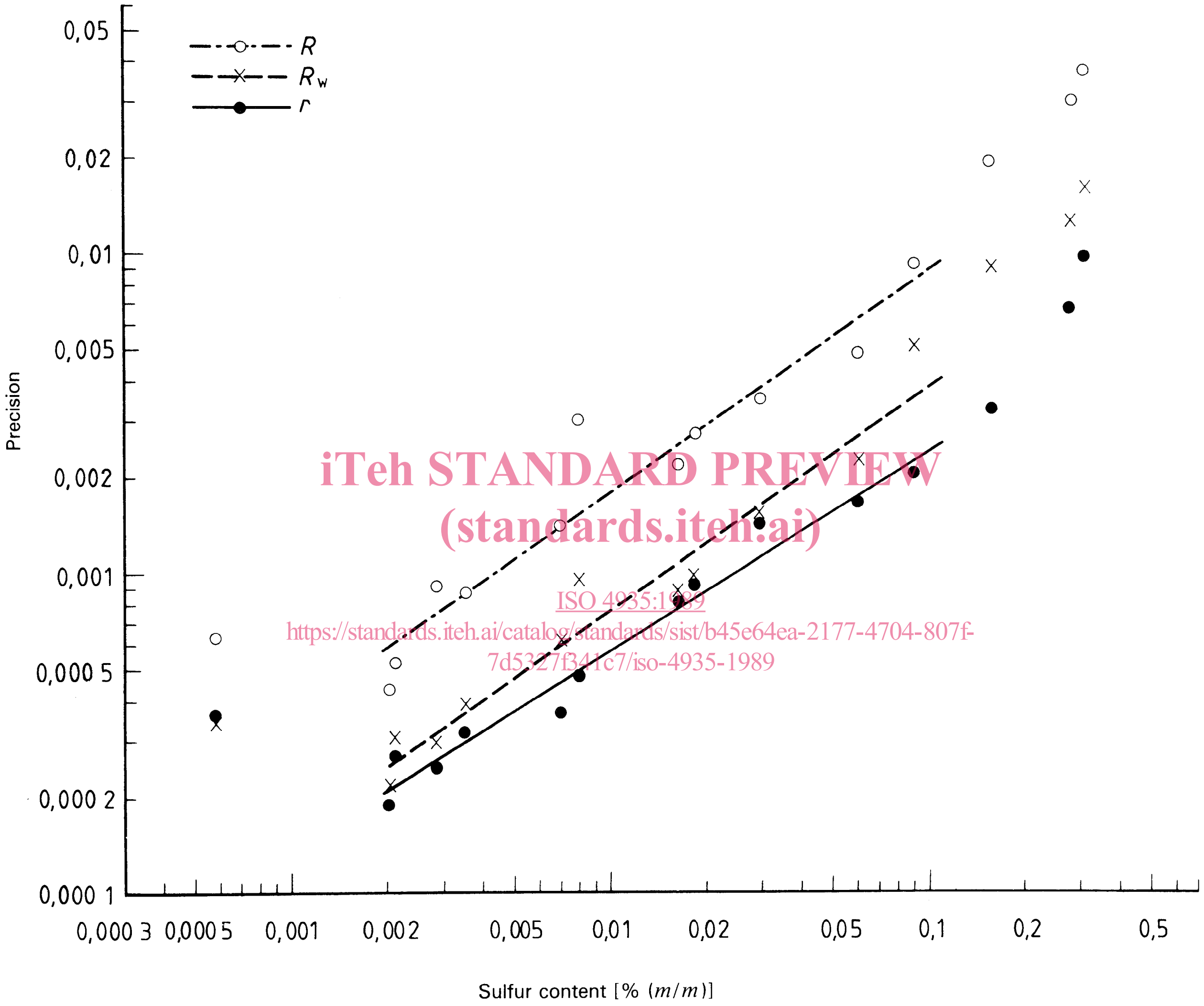

Figure B.1 — Logarithmic relationship between sulfur content [% (m/m)] and repeatability (r) or reproducibility $(R$ and $R_w)$

$\lg r = 0{,}622\,12 \lg w - 1{,}996\,5$

$\lg R_w = 0{,}700\,66 \lg w - 1{,}709\,4$

$\lg R = 0{,}688\,78 \lg w - 1{,}369\,3$

Annex C
(informative)

Features of commercial high-frequency induction furnaces and infrared sulfur analysers

C.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.

C.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.

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

C.4 High-frequency induction furnace

C.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 the bottom which are sealed to the tube by 0-rings.

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

C.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 20,0 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.

C.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.

C.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.

C.4.5 The temperature attained during the combustion depends in part on the factors indicated in C.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.

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

C.6 Infrared gas analyser

C.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.

C.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.

C.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 the 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.