SLOVENSKI STANDARD
SIST ISO 9686:2001

01-junij-2001

Neposredno reducirano železo - Določevanje ogljika in/ali žvepla - Metoda z visokofrekvenčnim zgorevanjem z infrardečo meritvijo

Direct reduced iron -- Determination of carbon and/or sulfur content -- High frequency combustion method with infrared measurement

Minerais de fer préréduits -- Dosage du carbone et/ou du soufre -- Méthode par combustion haute fréquence et mesurage par infrarouge

Ta slovenski standard je istoveten z: **ISO 9686:1992**

ICS:

77.040.30	Kemijska analiza kovin	Chemical analysis of metals
77.080.10	Železo	Irons

SIST ISO 9686:2001 **en**

INTERNATIONAL STANDARD

ISO 9686

First edition
1992-12-01

Direct reduced iron — Determination of carbon and/or sulfur content — High frequency combustion method with infrared measurement

Minerais de fer préréduits — Dosage du carbone et/ou du soufre — Méthode par combustion haute fréquence et mesurage par infrarouge

Reference number
ISO 9686:1992(E)

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 voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9686 was prepared by Technical Committee ISO/TC 102, *Iron ores*, Sub-Committee SC 2, *Chemical analysis*.

Annexes A and B form an integral part of this International Standard. Annexes C, D, E and F are for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Direct reduced iron — Determination of carbon and/or sulfur content — High frequency combustion method with infrared measurement

1 Scope

This International Standard specifies a method for the determination of the carbon and/or sulfur content of direct reduced iron by infrared measurement after high frequency combustion.

This method is applicable to carbon contents between 0,05 % (*m*/*m*) and 2,5 % (*m*/*m*) and/or sulfur contents between 0,001 % (*m*/*m*) and 0,05 % (*m*/*m*) in direct reduced iron.

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

ISO 7550:1985, *Laboratory glassware — Disposable micropipettes.*

ISO 7764:1985, *Iron ores — Preparation of predried test samples for chemical analysis.*

3 Principle

Combustion of the test portion in a refractory crucible in a flow of oxygen in the presence of an accelerator, the crucible being inserted in the combustion tube of a high-frequency (HF) furnace.

Conversion of the carbon present into carbon dioxide and the sulfur present into sulfur dioxide. Measurement of each gas by infrared absorption, with calibration using barium carbonate and potassium sulfate.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

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

NOTE 1 The pressure in the furnace should be controlled by a pressure regulator designed specially for the purpose and complying with the manufacturer's specifications.

4.2 Magnesium perchlorate, grain size 0,7 mm to 1,2 mm.

4.3 Accelerator, tungsten (granular form) with known low contents of carbon [< 0,002 % (*m*/*m*)] and sulfur [< 0,000 5 % (*m*/*m*)].

4.4 Pure iron, or iron of known low carbon and sulfur contents as in 4.3.

4.5 Tin capsules, of capacity 0,3 ml, diameter 5 mm, length 17 mm.

4.6 Barium carbonate ($BaCO_3$), fine powder.

Dry at 105 °C for 3 h and cool in a desiccator.

4.7 Sulfur standard solutions.

Dry potassium sulfate (K_2SO_4) at 105 °C for 1 h and cool in a desiccator.

Weigh, to the nearest 0,000 2 g, the amounts of potassium sulfate specified in table 1.

Table 1 — Sulfur standard solutions

Sulfur standard solution	Mass of K_2SO_4 g	Sulfur concentration mg/ml
SS 1	0,2174	0,4
SS 2	0,4348	0,8
SS 3	0,6522	1,2
SS 4	0,8696	1,6
SS 5	2,1740	4,0

Transfer to five 100 ml one-mark volumetric flasks, dissolve with 50 ml of water, dilute to volume and mix.

4.8 Ascarite, used only for carbon determination.

5 Apparatus

Ordinary laboratory apparatus, including micropipettes and one-mark volumetric flasks complying with the specifications of ISO 7550 and ISO 1042 respectively, and

5.1 Commercial carbon/sulfur apparatus

The apparatus required for HF combustion of the samples and the subsequent infrared absorption measurement of evolved carbon dioxide and/or sulfur dioxide may be obtained commercially from a number of manufacturers. Common features of such systems are discussed in annex C.

The manufacturers' instructions for the operation of their equipment shall be followed.

5.2 Ceramic combustion crucibles, required for containing the sample and any additions which may be necessary for the subsequent combustion.

The crucibles shall be of precise dimensions for the system, and shall adapt to the supporting pedestal post so that the sample in the crucible will be positioned at the correct height within the induction coil when it is in the raised position.

These crucibles shall be pre-ignited in an oxygen flow, in a furnace, for not less than 2 h at 1 350 °C (or at 1 100 °C if only sulfur is to be determined), and then stored in a desiccator or closed container before use.

For pre-ignition, a resistance furnace may be used.

5.3 Micropipette, of capacity 50 µl.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 160 µm particle size.

NOTE 2 There is no International Standard for sampling and sample preparation of direct reduced iron, and the application of ISO 3081 [2], ISO 3082 [3] and ISO 3083 [4], which cover the sampling and sample preparation of iron ores, is recommended for materials suitably stabilized against oxidation. For hot briquetted iron, ISO 377-2 [1] could be used.

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample using non-magnetic materials. Taking multiple increments with a non-magnetic spatula, extract a test sample in such a manner that it is representative of the whole contents of the container.

Dry the test sample at 105 °C ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

WARNING — The risks related to combustion analysis are mainly hand burns in pre-igniting the ceramic crucibles, and in the subsequent combustion. Normal precautions for handling oxygen cylinders should be taken. Oxygen from the combustion process should be removed effectively from the apparatus and room, since a too high concentration of oxygen in a confined space may present a fire hazard. HF screening should be effective to avoid radiation hazards.

7.1 General operating instructions

Purify the oxygen supply using tubes packed with ascarite (4.8) and magnesium perchlorate (4.2) and maintain a quiescent flow rate of about 0,5 l/min whilst on standby.

Maintain a glass wool filter between the furnace chamber and the analyser and change as necessary. The furnace chamber, pedestal post and filter trap should be cleaned frequently to remove oxide build-up.

The oxygen flow rate may vary from one instrument to another, but is usually about 2,0 l/min during the combustion period, according to the nature of the material. The temperature reached during the combustion stage depends on the power of the HF generator, the geometry of the furnace chamber, the induction coil and the type and quantity of sample in the crucible. This temperature may be in the order of 1 700 °C, or more.

When the mains supply is switched on after being out of action for any length of time, allow the time recommended by the equipment manufacturer for the stabilization of each item of equipment.

After cleaning the furnace chamber, 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 to the apparatus and adjust the instrument controls to give zero readings.

7.2 Test portion

Weigh 0,400 g of the sample to the nearest 0,001 g.

7.3 Blank test

Carry out a blank test using the same procedure and the same quantities of all reagents as for a determination (7.5) i.e.

1,9 g of tungsten (4.3);

1,3 g of pure iron (4.4);

1 tin capsule (4.5).

To achieve the best accuracy possible, perform at least three blank burns. Use the mean thereof to make a zero adjustment in accordance with the manufacturer's requirements.

7.4 Calibration

7.4.1 Crucible preparation

7.4.1.1 Analysis for carbon only

Using the outline given in annex A, weigh, to the nearest 0,000 2 g, the amounts of barium carbonate (4.6) specified in table 2 into six combustion crucibles (5.2).

Table 2 — Carbon calibration tests

Crucible	Carbon standard	Mass of $BaCO_3$ (4.6) g	C % (m/m)
1	CS 1	0,013 1	0,2
2	CS 2	0,032 9	0,5
3	CS 3	0,065 7	1,0
4	CS 4	0,131 4	2,0
5	CS 5	0,164 3	2,5
6	CS 5	0,164 3	2,5

7.4.1.2 Analysis for sulfur only

Using the micropipette (5.3), introduce 50 µl of each of the sulfur standard solutions (4.7) into seven tin capsules in accordance with table 3.

Table 3 — Sulfur calibration tests

Crucible	Tin capsule	Sulfur standard solutions (4.7)	S % (m/m)
1	1	Pure water (50 µl)	0
2	2	SS 1	0,005
3	3	SS 2	0,010
4	4	SS 3	0,015
5	5	SS 4	0,020
6	6	SS 5	0,050
7	7	SS 5	0,050

Dry the capsules and their contents slowly at 80 °C to 90 °C for 2 h, and cool in a desiccator.

Using the outline given in annex A, prepare seven crucibles containing the tin capsules specified in table 3.

7.4.1.3 Analysis for carbon and sulfur

Using the outline given in annex A, prepare seven crucibles containing tin capsules and the amounts of barium carbonate (4.6) and sulfur standard solutions (4.7) specified in table 4.

Table 4 — Carbon and sulfur calibration tests

Crucible	Carbon (7.4.1.1) and sulfur (7.4.1.2) standards	C + S % (m/m)
1	Pure water (50 µl)	0 + 0
2	CS 1 + SS 1	0,2 + 0,005
3	CS 2 + SS 2	0,5 + 0,010
4	CS 3 + SS 3	1,0 + 0,015
5	CS 4 + SS 4	2,0 + 0,020
6	CS 5 + SS 5	2,5 + 0,050
7	CS 5 + SS 5	2,5 + 0,050

7.4.2 Combustion

With the calibration crucibles prepared as in annex A, burn firstly crucible 7 containing the maximum content of carbon and/or sulfur, then crucible 6 for a check. Adjust the readings to the corresponding value(s).

Burn the other crucibles and note the results to check the linearity.

NOTE 3 For all measurements, the mass compensator is set at 0,400 g.

7.5 Determination

Prepare the tests in accordance with annex A and burn as in the calibration series, in accordance with the manufacturer's instructions.

8 Expression of results

8.1 Calculation of carbon or sulfur content

The carbon and sulfur contents are given directly by the instrument as a function of the calibration (7.4), taking into account the value of the blank test.

NOTE 4 The total blank from all sources (oxygen, iron, tin capsules, tungsten) should not exceed 0,01 % (m/m) of carbon and 0,001 % (m/m) of sulfur.

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equation[1]:

Carbon

$$r = 0{,}020\,3\ X + 0{,}012\,7 \qquad \ldots (1)$$

$$P = 0{,}020\,8\ X + 0{,}024\,4 \qquad \ldots (2)$$

$$\sigma_r = 0{,}007\,2\ X + 0{,}004\,5 \qquad \ldots (3)$$

$$\sigma_L = 0{,}005\,7\ X + 0{,}007\,9 \qquad \ldots (4)$$

Sulfur

$$r = 0{,}037\,3\ X + 0{,}000\,9 \qquad \ldots (5)$$

$$P = 0{,}121\,3\ X + 0{,}001\,5 \qquad \ldots (6)$$

$$\sigma_r = 0{,}013\,3\ X + 0{,}000\,3 \qquad \ldots (7)$$

$$\sigma_L = 0{,}042\,1\ X + 0{,}000\,5 \qquad \ldots (8)$$

where

X is the carbon or sulfur content, expressed as a percentage by mass, of the predried test sample calculated as follows:

- within-laboratory equations [(1), (3), (5) and (7)]: the arithmetic mean of the duplicate values,
- between-laboratories equations [(2), (4), (6) and (8)]: the arithmetic mean of the final results (8.2.3) of the two laboratories;

r is the permissible tolerance within a laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material shall be such that the difference between this result and the certified value of the reference material is statistically insignificant. For a certified reference material that has been analysed by at least 10 laboratories using method(s) that are comparable in both accuracy and precision with this method, the following condition may be used to test the significance of the difference

$$|A_C - A| \leqslant 2\sqrt{\frac{s_{Lc}^2 + \dfrac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (9)$$

where

A_c is the certified value;

A is the result or the mean of results obtained for the certified reference material;

s_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_c is the number of certifying laboratories;

n is the number of replicate determinations on the certified reference material (in most cases $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (9) is satisfied, i.e. if the left-hand side of the condition is less than or equal to the right-hand side, then the difference $|A_c - A|$ is statistically insignificant; otherwise, it is statistically significant.

When the difference is significant, the analysis shall be repeated, simultaneously with an analysis of the test sample. If the difference is again significant, the

1) Additional information is given in annexes D and E.

procedure shall be repeated using a different certified reference material of the same type of material.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (1) or (5) in 8.2.1, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex B, simultaneously with an analysis of a certified reference material of the same type of material.

Acceptability of the results for the test sample shall in each case be subject to the acceptability of the results for the certified reference material.

NOTE 5 The following procedure should be used when the information on the reference material certificate is incomplete:

a) if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression s_{Wc}^2/n_{Wc} and regard s_{Lc} as the standard deviation of the laboratory means;

b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, it is advisable that this material not be used in the application of the standard. In case its use is unavoidable, use the condition

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}}$$

8.2.3 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in annex B, calculated to five decimal places and rounded off to the third decimal place as follows:

a) when the figure in the fourth decimal place is less than 5, it is discarded and the figure in the third decimal place is kept unchanged;

b) when the figure in the fourth decimal place is 5 and there is a figure other than 0 in the fifth decimal place, or when the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by one;

c) when the figure in the fourth decimal place is 5 and the figure 0 is in the fifth decimal place, the 5 is discarded and the figure in the third decimal place is kept unchanged if it is 0, 2, 4, 6 or 8, and is increased by one if it is 1, 3, 5, 7 or 9.

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this International Standard;

d) details necessary for the identification of the sample;

e) the results and the form in which they are expressed;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the result, either for the test sample or for the certified reference material(s).