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

*Minerais de fer pré-réduits — Dosage du carbone et/ou du soufre —
Méthode par combustion haute fréquence et mesurage par infrarouge*

STANDARDSISO.COM : Click to view the full PDF of ISO/TR 9686:2017



STANDARDSISO.COM : Click to view the full PDF of ISO/TR 9686:2017



COPYRIGHT PROTECTED DOCUMENT

© ISO 2017, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

	Page
Foreword	iv
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Principle	1
5 Reagents	1
6 Apparatus	2
7 Sampling and samples	3
7.1 Laboratory sample	3
7.2 Preparation of predried test samples	3
8 Procedure	3
8.1 General operating instructions	3
8.2 Test portion	3
8.3 Blank test	3
8.4 Calibration	4
8.4.1 Crucible preparation	4
8.4.2 Combustion	5
8.5 Determination	5
9 Expression of results	5
9.1 Calculation of mass fraction of carbon or sulfur	5
9.2 General treatment of results	5
9.2.1 Repeatability and permissible tolerance	5
9.2.2 Determination of analytical result	6
9.2.3 Between-laboratories precision	6
9.2.4 Check for trueness	7
9.2.5 Calculation of final result	8
10 Test report	8
Annex A (informative) Crucible loading sequence	9
Annex B (informative) Flowsheet of the procedure for the acceptance of analytical values for test samples	10
Annex C (informative) Features of commercial HF combustion/infrared sulfur analysers	11
Annex D (informative) Derivation of repeatability and permissible tolerance formulae	12
Annex E (informative) Precision data obtained by international analytical trials	13
Bibliography	15

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.

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 documents 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This first edition Technical Report cancels and replaces the second edition International Standard (ISO 9686:2006), which has been technically revised and has been converted to a Technical Report because it is not suitable for determination of carbon or sulfur as a referee method.

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

WARNING — This document may involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices.

1 Scope

This document specifies a method for the determination of the mass fraction of carbon and/or sulfur in direct reduced iron by infrared measurement after high-frequency combustion.

This method is applicable to mass fractions of carbon between 0,05 % and 2,5 %, and/or mass fractions of sulfur between 0,001 % and 0,05 % in direct reduced iron.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

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

4 Principle

The test portion is combusted 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.

The carbon present is converted into carbon dioxide and the sulfur into sulfur dioxide. Each gas is measured by infrared absorption, with calibration using barium carbonate and potassium sulfate.

5 Reagents

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

5.1 Oxygen, minimum purity 99,5 % (mass fraction).

The pressure in the furnace should be controlled by a pressure regulator designed especially for the purpose and complying with the manufacturer's specification.

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

5.3 Accelerator, tungsten (granular form) with known low mass fractions of carbon (<0,002 %) and sulfur (<0,000 5 %).

5.4 Pure iron, or iron of known low mass fractions of carbon and sulfur, as in [5.3](#).

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

5.6 Barium carbonate (BaCO₃), fine powder.

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

5.7 Sulfur standard solutions.

Dry potassium sulfate (K₂SO₄) 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](#).

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

5.8 Ascarite, used only for carbon determination.

Table 1 — Sulfur standard solutions

Sulfur standard solution	Mass of K ₂ SO ₄ g	Sulfur concentration mg/ml
SS 1	0,217 4	0,4
SS 2	0,434 8	0,8
SS 3	0,652 2	1,2
SS 4	0,869 6	1,6
SS 5	2,174 0	4,0

6 Apparatus

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

6.1 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 manufacturer's instruction for the operation of their equipment should be followed.

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

The crucibles should be of precise dimensions for the system, and should 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 should 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.

6.3 Micropipette, of capacity 50 µl.

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of minus 160 µm particle size, which has been taken and prepared in accordance with ISO 10835.

7.2 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 $105\text{ °C} \pm 2\text{ °C}$ as specified in ISO 7764. (This is the predried test sample.)

8 Procedure

WARNING — The risks related to combustion analysis are mainly hand burns when 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.

8.1 General operating instructions

Purify the oxygen supply using tubes packed with ascarite (5.8) and magnesium perchlorate (5.2) 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.

8.2 Test portion

Weigh 0,400 g of the sample to the nearest 0,000 1 g.

8.3 Blank test

Carry out a blank test using the same procedure and the same quantities of all reagents as for a determination (8.5), i.e.:

— 1,9 g of tungsten (5.3);

- 1,3 g of pure iron (5.4);
- 1 tin capsule (5.5).

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.

8.4 Calibration

8.4.1 Crucible preparation

8.4.1.1 Analysis for carbon only

Using the outline given in Annex A, weigh, to the nearest 0,000 2 g, the amount of barium carbonate (5.6) specified in Table 2 into six combustion crucibles (6.2).

Table 2 — Carbon calibration tests

Crucible	Carbon standard	Mass of BaCO ₃ (5.6) g	C % (mass fraction)
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

8.4.1.2 Analysis for sulfur only

Using the micropipette (6.3), introduce 50 µl each of the sulfur standard solutions (5.7) into seven tin capsules in accordance with Table 3.

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.

Table 3 — Sulfur calibration tests

Crucible	Tin capsule	Sulfur standard solutions (5.7)	S % (mass fraction)
1	1	Pure water (50 µl)	0
2	2	SS 1	0,005
3	3	SS 2	0,10
4	4	SS 3	0,015
5	5	SS 4	0,020
6	6	SS 5	0,050
7	7	SS 5	0,050

8.4.1.3 Analysis for carbon and sulfur

Using the outline given in Annex A, prepare seven crucibles containing tin capsules (5.5), and the amounts of barium carbonate (5.6) and sulfur standard solutions (5.7) specified in Table 4.

Table 4 — Carbon and sulfur calibration tests

Crucible	Carbon (8.4.1.1) and sulfur (8.4.1.2)	C + S % (mass fraction)
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

8.4.2 Combustion

With the calibration crucibles prepared as in [Annex A](#), firstly burn 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 For all measurements, the mass compensator is set at 0,400 g.

8.5 Determination

Prepare the test in accordance with [Annex A](#) and burn as in the calibration series, in accordance with the manufacturer's instruction.

9 Expression of results

9.1 Calculation of mass fraction of carbon or sulfur

The mass fractions of carbon and sulfur are given directly by the instrument as a function of the calibration ([8.4](#)), taking into account the value of the blank test.

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

9.2 General treatment of results

9.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the regression [Formulae \(1\) to \(8\)](#).

NOTE Addition information is given in [Annexes D](#) and [E](#).

For carbon:

$$R_d = 0,0203 X + 0,0127 \quad (1)$$

$$P = 0,0208 X + 0,0244 \quad (2)$$

$$\sigma_d = 0,0072 X + 0,0045 \quad (3)$$

$$\sigma_L = 0,0057 X + 0,0079 \quad (4)$$

For sulfur:

$$R_d = 0,0479 X + 0,0010 \quad (5)$$

$$P = 0,1241 X + 0,0014 \quad (6)$$

$$\sigma_d = 0,0169 X + 0,0004 \quad (7)$$

$$\sigma_L = 0,0443 X + 0,0004 \quad (8)$$

where

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

X is the mass fraction of carbon or sulfur, expressed as a percentage, in the pre-dried test sample, calculated as follows:

- within-laboratory [Formulae \(1\), \(3\), \(5\) and \(7\)](#): the arithmetic means of the duplicates values,
- between-laboratories [Formulae \(2\), \(4\), \(6\) and \(8\)](#): the arithmetic mean of the final results [\(9.2.3\)](#) of the two laboratories.

9.2.2 Determination of analytical result

Having computed the independent duplicate results according to [Formula \(1\)](#), compare them with the independent duplicate limit (R_d), using the procedure given in [Annex A](#), and obtain the final laboratory result μ_c (see [9.2.5](#)).

9.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the same procedure as described in [9.2.2](#).

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \quad (9)$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of final results.

Substitute μ_{12} for X in [Formula \(3\)](#) or [\(7\)](#) and calculate P .

If $|\mu_1 - \mu_2| \leq P$, the final results are in agreement.

9.2.4 Check for trueness

The trueness of the analytical method should be checked by applying it to a certified reference material (CRM) or a reference material (RM). Calculate the analytical result (μ_c) for the RM/CRM using the procedures in 9.1 and 9.2, and compare it with the reference or certified value (A_c). There are two possibilities:

- $|\mu_c - A_c| \leq C$, in which case the difference between the reported result and the reference/certified value is statistically insignificant;
- $|\mu_c - A_c| > C$, in which case the difference between the reported result and the reference/certified value is statistically significant.

where

μ_c is the analytical result for the certified reference material;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

C should be calculated using [Formula \(10\)](#):

$$C = \sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_d^2}{n}} \quad (10)$$

where

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 carried out on the CRM/RM;

σ_L and σ_d are as defined in [9.2.1](#).

The following procedure should be used when the information on the reference material certificate is incomplete.

- 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;
- If the certification has been made by only one laboratory or if the interlaboratory results are missing, use [Formula \(11\)](#):

$$C = 2 \sqrt{2\sigma_L^2 + \frac{\sigma_d^2}{n}} \quad (11)$$

A CRM certified by only one laboratory should be avoided unless it is known to have an unbiased certified value.

9.2.5 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](#).

The final result is the arithmetic mean of the acceptable analytical values of 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) Where the final 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) Where 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) Where 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.

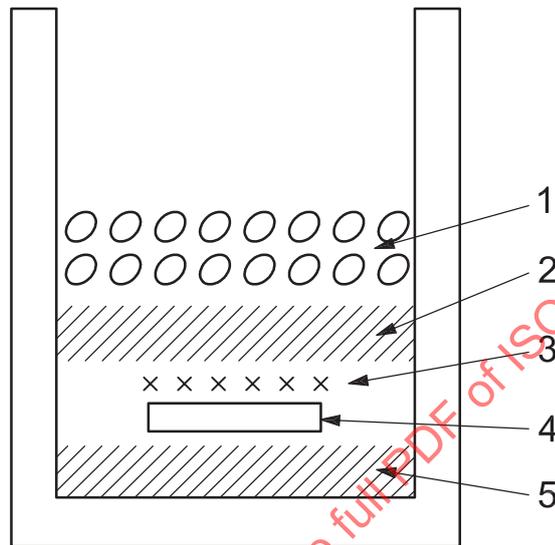
10 Test report

The test report should include the following information:

- a) name and address of the testing laboratory;
- b) date of issue of the test report;
- c) reference to this document, i.e. ISO/TR 9686;
- d) details necessary for the identification of the sample;
- e) results of the analysis;
- f) reference number of the result;
- g) any characteristic noticed during the determination, and any operation not specified in this document which may have had an influence on the result, for either the test sample or the certified reference material(s).

Annex A (informative)

Crucible loading sequence



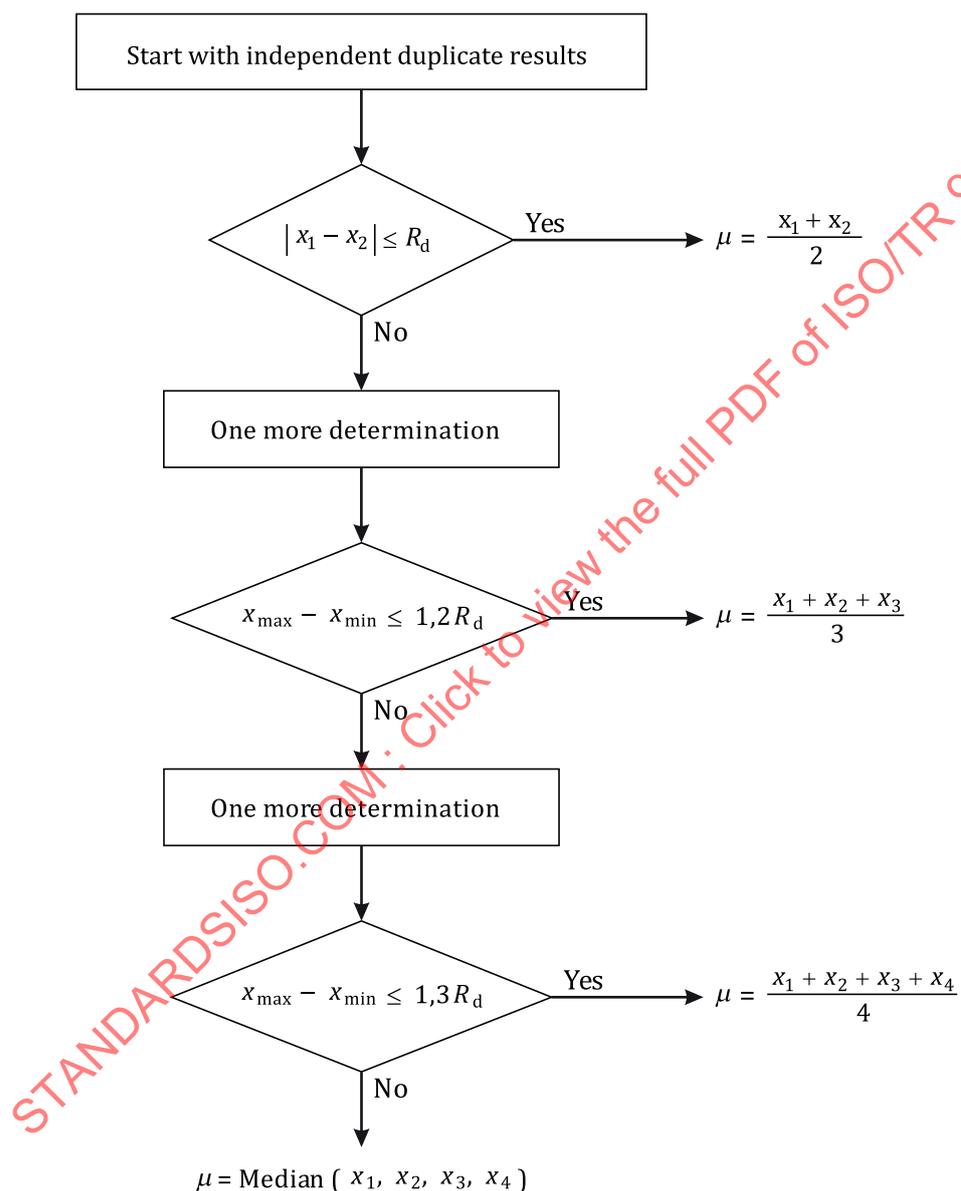
Key

tungsten (5.3):	1,9 g
pure iron (5.4):	0,4 g
test portion (8.2) or barium carbonate (5.6):	0,4 g
tin capsule (5.5)	
pure iron (5.4):	0,9 g

Figure A.1 — Crucible loading sequence

Annex B (informative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



NOTE R_d is as defined in 9.2.1.

Figure B.1 — Flowsheet of the procedure for the acceptance of analytical values for test samples

Annex C (informative)

Features of commercial HF combustion/infrared sulfur analysers

C.1 Combustion

The combustion furnace has an induction coil and HF generator. The furnace chamber consists of a silica tube which fits inside the induction coil. This tube has a metal plate at the top and bottom and is sealed by O-rings. Gas inlet and outlet points are made via the metal plates, with a filter on the outlet to prevent dust particles from reaching the detection system.

The generator is usually a 1,2 kVA to 2,5 kVA unit, but the frequency used by various manufacturers may be different. Values of 2 MHz, 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. The crucible containing the sample and accelerator is supported on a pedestal post, which is precisely positioned when raised, so that the sample in the crucible is correctly placed within the induction coil for effective coupling when the power is applied.

Typical dimensions of combustion crucibles are as follows:

- height of crucibles: 25 mm;
- external diameter: 25 mm;
- internal diameter: 20 mm;
- wall thickness: 2,5 mm;
- thickness of base: 8 mm.

The induction-coil diameter, the number of turns and the furnace geometry determine the degree of HF coupling that can occur, and these factors are determined by the instrument manufacturer. The temperature generated depends in part on these factors, but also on the characteristics of the sample in the crucible, the sample form and the mass of materials. These factors may be varied to some extent by the operator in the light of experience.

It is essential that the oxides formed during combustion be removed by glass-wool filtration, and the filter trap should be cleaned frequently to remove oxide build-up.

C.2 Infrared gas analyser

A given volume of the gaseous products of combustion may be collected at a controlled pressure, and the mixture analysed for CO₂ and/or SO₂; or the CO₂ and/or SO₂ content in a continuous oxygen flow may be integrated during the evolution of gases from the combustion process.

The oxygen carrier-gas containing CO₂ and/or SO₂ is passed to the analyser system, consisting of an infrared cell, usually of the Luft type or equivalent (solid state), where the specific absorption of the infrared radiation is measured.

Electronic amplification of the absorption measurement is usually converted to a digital display of percentage concentration. Means are usually provided for off-setting the zero (blank compensation), adjusting the calibration and linearizing the readout.

Instruments may also be equipped with an integral automatic balance, and a system for applying sample mass correction. In modern instruments, a microprocessor is generally included.

Annex D (informative)

Derivation of repeatability and permissible tolerance formulae

The regression formulae in [9.2.1](#) were obtained by statistical evaluation of the results of international analytical trials carried out in 1986 to 1988 on 4 direct reduced iron (DRI) samples, involving 13 laboratories in 7 countries.

Graphical treatment of the precision data is given in [Annex E](#).

The test samples used are listed in [Table D.1](#).

NOTE 1 A report of the international trials and a statistical analysis of the results (document ISO/TC 102/SC 2 929E, November 1988) is available from the Secretariat of ISO/TC 102/SC 2.

NOTE 2 The statistical analysis was performed in accordance with the principles embodied in ISO 5725-2:1994.

Table D.1 — Mass fractions of carbon and sulfur in test samples

Sample	Carbon content % (mass fraction)	Sulfur content % (mass fraction)
DRI—Gas reduced 16/85	1,838 6	0,001 8
DRI—Lab. produced 17/85	0,365 6	0,001 2
DRI—Lab. produced 18/85	0,096 9	0,001 3
DRI—Coal reduced 19/85	0,096 1	0,039 3