TECHNICAL
REPORT

ISO/TR
15349-1

First edition
1998-10-15

Unalloyed steel — Determination of low carbon content —

Part 1:
Infrared absorption method after combustion in an electric resistance furnace (by peak separation)

Acier non allié — Détermination des faibles teneurs en carbone —

Partie 1: Méthode par absorption dans l'infrarouge après combustion dans un four électrique à résistances (par séparation de pics)

Reference number
ISO/TR 15349-1:1998(E)

Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

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 main task of technical committees is to prepare International Standards. In exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

- type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;
- type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;
- type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 15349-1, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition.*

This document is being issued in the Technical Report (type 2) series of publications (according to subclause G.3.2.2 of part 1 of the ISO/IEC Directives, 1995) as a "prospective standard for provisional application" in the field of determination of carbon content in steel because there is an urgent need for guidance on how standards in this field should be used to meet an identified need.

This document is not to be regarded as an "International Standard". It is proposed for provisional application so that information and experience of its use in practice may be gathered. Comments on the content of those documents should be sent to the ISO Central Secretariat.

A review of this Technical Report (type 2) will be carried out not later than three years after its publication with the options of: extension for another three years; conversion into an International Standard; or withdrawal.

ISO/TR 15349 consists of the following parts, under the general title *Unalloyed steel — Determination of low carbon content*:

- *Part 1: Infrared absorption method after combustion in an electric resistance furnace (by peak separation)*
- *Part 2: Infrared absorption method after combustion in an induction furnace (with preheating)*
- *Part 3: Infrared absorption method after combustion in an electric resistance furnace (with preheating)*

Annexes A to C of this part of ISO/TR 15349 are for information only.

This page intentionally left blank

Unalloyed steel — Determination of low carbon content —

Part 1:
Infrared absorption method after combustion in an electric resistance furnace (by peak separation)

1 Scope

This part of ISO 15349 describes an infrared absorption method with peak separation procedure after combustion in an electric resistance furnace for the determination of the low carbon content in unalloyed steel.

The method is applicable to carbon contents between 0,000 3 % (m/m) and 0,010 % (m/m).

2 Normative references

The following standards contain provisions which, through references in this text, constitute provisions of this part of ISO 15349. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 15349 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 1042:1998, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

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.*

ISO 15349-2:—[1], *Unalloyed steel — Determination of low carbon content — Part 2: Infrared absorption method after combustion in an induction furnace (with preheating).*

3 Principle

Combustion of a test portion with accelerator at a high temperature in an electric resistance furnace in a current of pure oxygen. Transformation of carbon into carbon dioxide and/or carbon monoxide.

Measurement, by peak separation process, of infrared absorption of the carbon dioxide and carbon monoxide evolved from steel and carried by a current of pure oxygen.

---

[1] To be published.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 3 water as specified in ISO 3696.

4.1 Water, free from carbon dioxide.

Boil water for 30 min, cool to room temperature and bubble with oxygen (4.2) for 15 min. Prepare just before use.

4.2 Oxygen, 99,95 % (*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, when the presence in the oxygen of organic contaminants is suspected.

4.3 Suitable solvent, appropriate for washing greasy or dirty test samples; e.g. acetone.

4.4 Accelerator, copper plate(see note 1) or granular tin (see note 2) of known very low carbon content less than 0,000 1 % (*m*/*m*).

NOTE 1 Copper plate (about 0,1 g/plate) should be used after the following treatment: heat the copper plate at 450 °C to 600 °C for 10 min in a current of oxygen and cool in a desiccator without grease. This treatment shall be carried out just before use.

NOTE 2 Granular tin should be used after the following treatment: rinse the granular tin in hydrochloric acid (ρ about 1,19 g/ml, diluted 1 + 1) for 5 min using an ultrasonic wave washer, wash it thoroughly with water and dry. Stock it in a clean glass bottle with ground-in stopper.

4.5 Standard substances

4.5.1 Sucrose, standard solution

Weigh, to the nearest 0,1 mg, the masses of sucrose, indicated in table 1, (analytical standard grade) previously dried at 100 °C to 105 °C for 2,5 h then cooled in a desiccator and transfer to seven 100 ml beakers.

Add 30 ml of water (4.1) to dissolve, transfer to seven 100 ml one-mark volumetric flasks quantitatively, dilute to the mark with water (4.1) and mix.

4.5.2 Calcium carbonate

Dry calcium carbonate [minimum assay 99,9 % (*m*/*m*)] at 180 °C for 1 h and cool in a desiccator before use.

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

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

Table 1 — Standard solution series of sucrose

Standard solution reference number	Mass of sucrose g	Corresponding mass of carbon added µg	Carbon content in 1 g of the test portion % (*m*/*m*)
1	0 [1]	0	0
2	0,010 0	4,21	0,000 42
3	0,025 0	10,53	0,001 05
4	0,060 0	25,26	0,002 53
5	0,120 0	50,53	0,005 05
6	0,180 0	75,79	0,007 58
7	0,240 0	101,1	0,010 11

1) Zero member.

5 Apparatus

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

All laboratory glassware shall be class A, in accordance with ISO 1042 as appropriate.

The apparatus required for combustion in an electric resistance furnace and subsequent infrared absorption measurement with peak separation procedure of the evolved carbon dioxide and/or carbon monoxide from steel may be obtained commercially, for example, Trace carbon analyser Model EMIA - U610, HORIBA, LTD[2].

Follow the manufacturer's instructions for the operation of the instrument.

5.1 **Ceramic boat**, 80 mm × 13,5 mm × 10 mm

Ignite a ceramic boat in an electric resistance furnace in a current of oxygen for not less than 2 h at 1 200 °C and store in a desiccator without grease.

Just before use, ignite the ceramic boat at 1 300 °C for several minutes and use the hot boat.

5.2 **Quartz boat**, 30 mm × 9 mm × 8 mm

Rinse a quartz boat in the washing solution [mix nine volumes of nitric acid (ρ about 1,40 g/ml, diluted 1 + 6) and one volume of hydrogen peroxide (30 % V/V)] for 2 h to 3 h, wash it thoroughly with water and dry. Stock in a desiccator without grease.

Just before use, place the quartz boat on the ceramic boat, ignite it at 1 200 °C for 10 min and cool in a desiccator without grease.

5.3 **Micropipette**, 100 µl, limit of error shall be less than 1 µl.

6 Sampling and preparation of the test samples

Sampling and preparation of the samples shall be carried out in accordance with ISO 14284.

Prepare the chip size of test sample between 0,75 mm and 2,0 mm.

7 Procedure

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

7.1 Preparation of the apparatus

Raise the temperature of the combustion furnace to 1 300 °C.

After having verified the highest temperature (more than 1 200 °C) at the centre of the heating zone in the combustion tube by use of a thermocouple, measure the distance, L, from the inlet of combustion tube to the centre of the heating zone in millimetres. Prepare two rigid nickel bars. Fix the stopper of a rigid nickel bar, A at the point

---

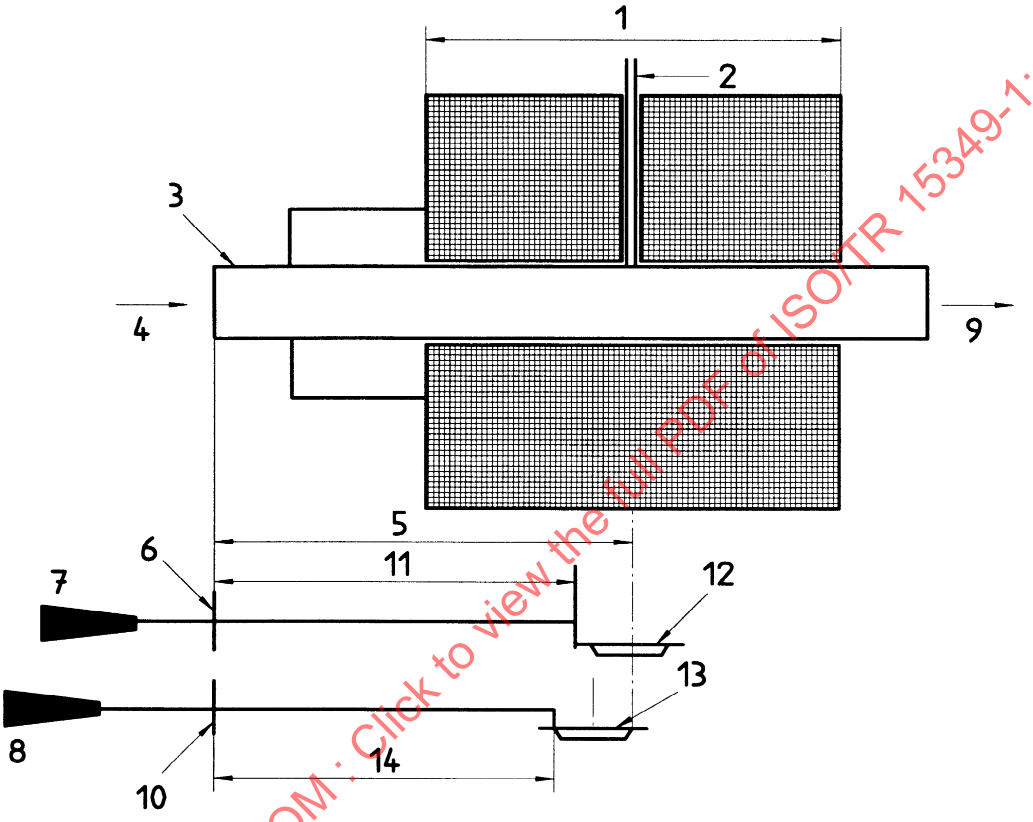
[2] Model EMIA - U610, HORIBA is the tradename of a product supplied by HORIBA LTD. This information is given for the convenience of users of this part of ISO/TR 15349 and does not constitue an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

where L = (the length of the ceramic boat used)/2 (mm) distance from the bar end. This is used to set the ceramic boat containing the test portion or calcium carbonate (see note below and figure 1).

NOTE 1 e.g., for model EMIA — U610, L is 290 mm and boat length is 80 mm. In this case the stopper is 250 mm distant from the bar end.

Fix the stopper of another rigid nickel bar, B at the point where L = the length of the ceramic boat used (mm) distance from the bar end. This is used to set the ceramic boat containing sucrose (see note below and figure 1).

NOTE 2 e.g., for model EMIA — U610, L is 290 mm and boat length is 80 mm. In this case the stopper is 210 mm distant from the bar end.



Key:

1	Heating zone
2	Thermocouple
3	Combustion tube
4	Oxygen
5	L mm
6	Stopper A
7	Rigid nickel bar A
8	Rigid nickel bar B
9	Evolved gases carried by oxygen to measuring system
10	Stopper B
11	L – (length of ceramic boat) /2 mm
12	Ceramic boat (test portion or calcium carbonate)
13	Ceramic boat containing quartz boat (sucrose)
14	L – (length of ceramic boat) mm

Figure 1 — Combustion furnace

Purify the oxygen supply using tubes packed with the inert ceramic (4.7) (attapulgus clay) impregnated with sodium hydroxide and magnesium perchlorate (4.6), and maintain a quiescent flowrate whilst on standby. Maintain a glass wool filter. Clean and charge as necessary.

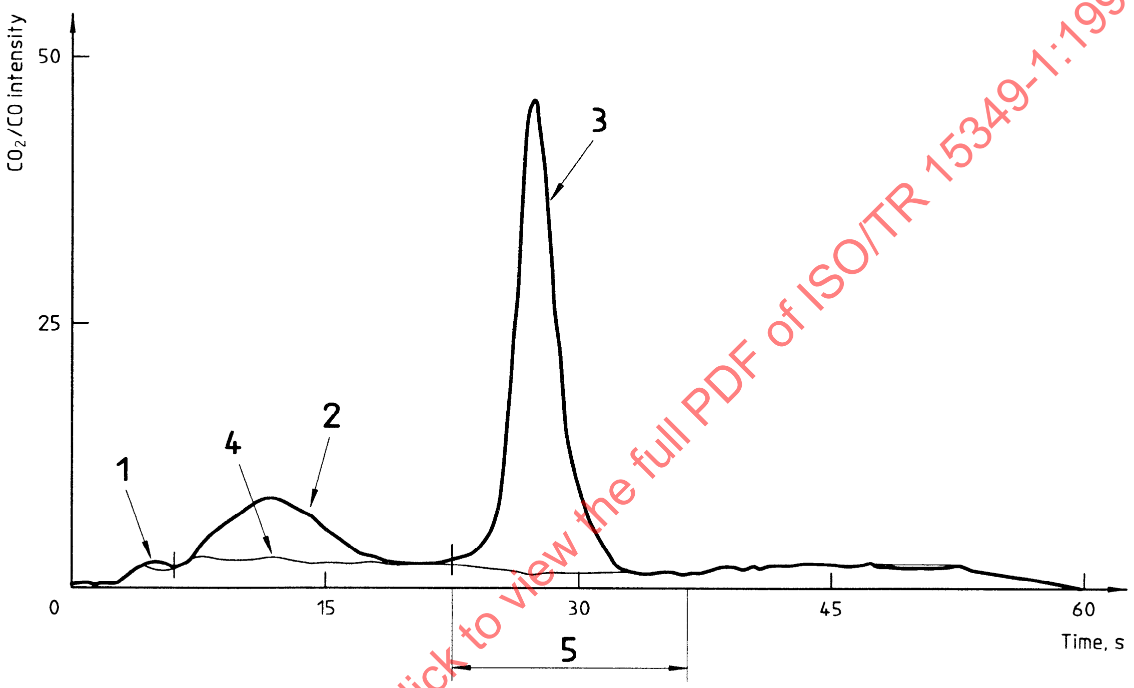
When the main supply is switched on after being out of action for any length of time, allow each item of equipment to stabilize for the time recommended by the equipment manufacturers.

After 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 of carbon, adjust the instrument reading for each calibration range as follows.

Make a choice of an appropriate steel-CRM (certified reference materials) carry out as described in 7.4 and obtain a time-CO_2/CO intensity chart. After having verified the extraction peak attributed to carbon content in the metal, set a duration for integration corresponding to the extraction peak attributed to carbon content in the metal (see figure 2) and integrate the signal of the infrared absorption for this duration. (Carbon in air and any contamination is excluded from integration. This is peak separation procedure).

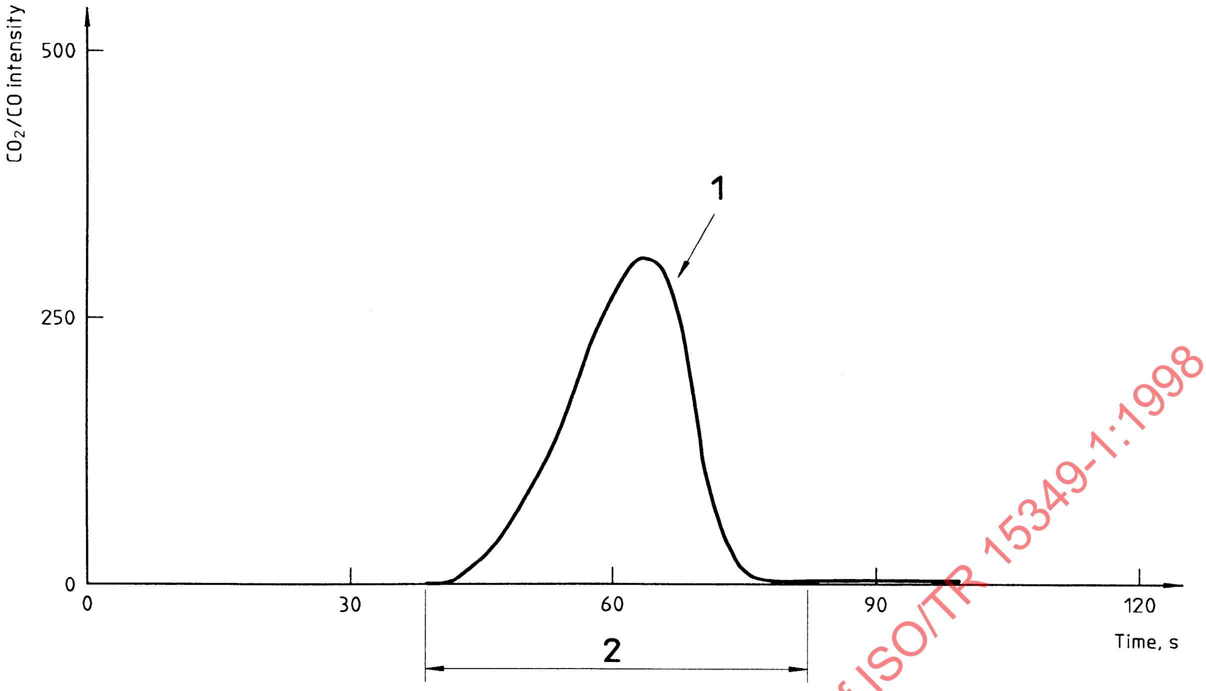


Key

1 Carbon in air
2 Contaminated carbon content
3 Carbon in steel
4 Blank (boat + Sn)
5 Duration for integration

Figure 2 — Time-CO_2/CO intensity chart of steel sample

For the preparation of a calibration graph using the calcium carbonate, carry out as described in 7.4 and obtain a time-CO_2/CO intensity chart. After having verified the extraction peak attributed to carbon content in the calcium carbonate, set a duration for integration corresponding to the extraction peak attributed to carbon content in the calcium carbonate (see figure 3) and integrate the signal of the infrared absorption at this duration for integration.



Key

1 Calcium carbonate

2 Duration for integration

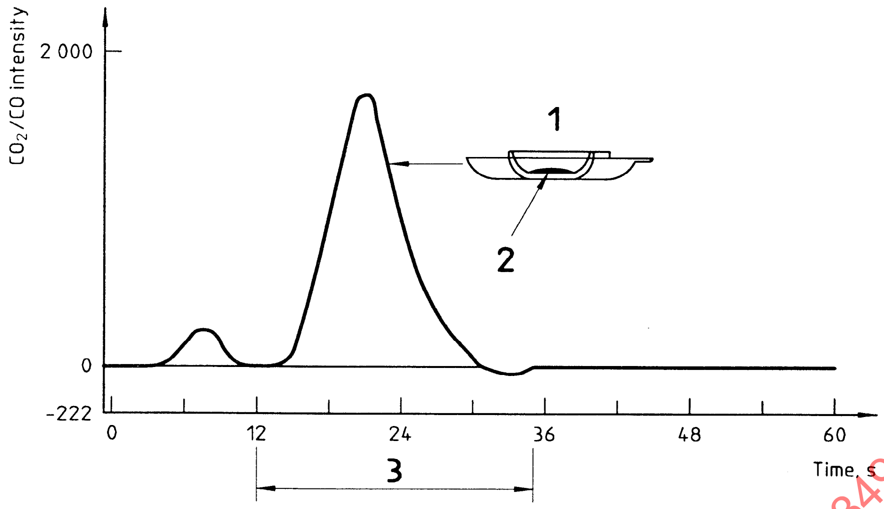
Figure 3 — Time-CO_2/CO intensity chart of calcium carbonate

For the preparation of a calibration graph using the sucrose standard solution, carry out as described in 7.5.1.1 to 7.5.1.2 and obtain a time-CO_2/CO intensity chart. After having verified the extraction peak attributed to carbon content in the sucrose, set a duration for integration corresponding to the extraction peak attributed to carbon content in the sucrose (see figure 4) and integrate the signal of the infrared absorption at this duration for integration.

Select the steel-CRM with a carbon content close to the maximum carbon content in the calibration series, measure the carbon content of the certified reference material in the manner described in 7.4.

Adjust the reading of the instrument to the certified value.

NOTE This adjustment shall be made before the calibration as described in 7.5. It cannot replace or correct the calibration.



Key

1 Combustion boat + quartz boat
2 Sucrose
3 Duration for integration

Figure 4 — Time-CO_2/CO intensity chart of sucrose combustion

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 0,1 mg, approximately 1,0 g of the test sample.

7.3 Blank test

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

Add the 0,50 g of the accelerators (4.4) to the ceramic boat.

Treat the boat and contents as described in the second and third paragraph of 7.4.

Obtain the reading of the blank tests and convert it to micrograms, to the nearest 0,1 µg, of carbon by means of the calibration graph (see 7.5).

The mean blank value is calculated from the two blank values to the nearest 0,1 µg.

NOTE The mean blank value and the difference between the two blank values shall both not exceed 1,0 µg of carbon. If these values are abnormally high, investigate and eliminate the source of contamination.

7.4 Determination

Transfer the test portion (see 7.1) to the middle zone of ceramic boat (5.1) and cover with the 0,50 g of the accelerator (4.4).

Place the ceramic boat and contents in the inlet of the combustion tube, using the rigid nickel bar A, insert the boat until it is stopped and lock the system. (In this case the centre of boat is at the centre of heating zone — see figure 1). Operate the instrument in accordance with the manufacturer's instructions.

At the end of the combustion and measuring cycle (see figure 2), remove and discard the boat, and record the analyser reading.

7.5 Establishment of the calibration graph

7.5.1 In the case where the sucrose standard solution is used

7.5.1.1 Preparation of the calibration series

Using a micropipette (5.3), introduce 100 µl, to the nearest 1 µl, of each of the sucrose standard solutions (4.5.1) into a series of seven quartz boats and dry at 90 °C to 95 °C in an air-oven.

NOTE Confirm the weight of 100 µl sucrose standard solution by weighing to the nearest 1 mg, if necessary.

7.5.1.2 Measurement

Transfer the quartz boat containing sucrose to the middle of the ceramic boat (5.1).

Place the ceramic boat and contents in the inlet of the combustion tube, using the rigid nickel bar B, insert the boat until it is stopped and lock the system. (In this case the centre of boat is the length of the ceramic boat used inlet side from the centre of heating zone — see figure 1).

Operate the instrument in accordance with the manufacturer's instructions.

At the end of the combustion and measuring cycle (see figure 4), remove and discard the boat, and record the analyser reading.

7.5.1.3 Plotting the calibration graph

Obtain the net reading 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 micrograms, to the nearest 0,1 µg, of carbon for each member of the calibration series.

7.5.2 In the case where calcium carbonate is used

7.5.2.1 Preparation of the calibration series

Using a microbalance, weigh, to the nearest 0,1µg, the masses of calcium carbonate (4.5.2) indicated in table 2 and transfer to seven ceramic boats (5.1), respectively.

Table 2 — Calibration series of calcium carbonate

Mass of calcium carbonate (4.5.2) µg	Corresponding mass of carbon added µg	Carbon content in 1 g of the test portion % (*m/m*)
0 [1]	0	0
40	4,8	0,000 48
85	10,2	0,001 02
210	25,2	0,002 52
420	50,4	0,005 04
630	75,6	0,007 56
850	102,0	0,010 20

[1] Zero member

7.5.2.2 Measurement

Place the ceramic boat and contents in the inlet of the combustion tube, using the rigid nickel bar A; insert the boat until it is stopped and lock the system. (In this case the centre of boat is at the centre of heating zone — see figure 1).

Operate the instrument in accordance with the manufacturer's instructions.

At the end of the combustion and measuring cycle (see figure 3), remove and discard the boat, and record the analyser reading.

7.5.2.3 Plotting the calibration graph

Obtain the net reading 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 micrograms, to the nearest 0,1 µg, of carbon for each member of the calibration series.

8 Expression of results

8.1 Method of calculation

Convert the analyser reading of the test portion to micrograms of carbon by means of the calibration graph (see 7.5).

The carbon content, expressed as a percentage by mass, w_C, is given by the equation:

$$w_C = \frac{\left(m_{C,1} - m_{C,0}\right)}{m \times 10^6} \times 100$$

$$= \frac{\left(m_{C,1} - m_{C,0}\right)}{10^4 m}$$

where

$m_{C,1}$ is the mass, expressed in micrograms of carbon, in the test portion;

$m_{C,0}$ is the mass, expressed in micrograms of carbon, in the blank test (see 7.3);

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

8.2 Precision

A planned trial of this method was carried out by five laboratories, using 11 levels of carbon contents, as described in ISO 15349-2, each laboratory making three determinations of cobalt content at each level.

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 above, using the same apparatus with a new calibration.

The details of the test samples used and the mean results obtained are given in tables B.1 and B.2.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3 without Cochran's and Grubbs' outlier tests (all data included for calculation).

The data obtained showed a logarithmic relationship between the carbon content and the repeatability limit (r) and reproducibility limits (R_W and R) of the test results as summarized in table 3. The graphical representation of the data is shown in figure C.1.

NOTE 3 From the two values obtained on day 1, the repeatability limit (r) and reproducibility limit (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 specified in ISO 5725-3.

Table 3 — Results for repeatability limit and reproducibility limits

Carbon content	Repeatability limit	Reproducibility limits	
% (m/m)	r	R_W	R
0,000 3	0,000 044	0,000 082	0,000 13
0,000 5	0,000 056	0,000 099	0,000 16
0,001 0	0,000 076	0,000 13	0,000 21
0,002 0	0,000 10	0,000 17	0,000 27
0,005 0	0,000 16	0,000 23	0,000 39
0,010 0	0,000 22	0,000 30	0,000 51

Annex A
(informative)

Features of commercial electric resistant furnaces and infrared carbon analysers

A.1 Source of oxygen

This is 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

This contains the inert ceramic impregnated with sodium hydroxide in a carbon dioxide absorbing tube, and the magnesium perchlorate in a dehydration tube.

A.3 Flowmeter

This is capable of measuring a flow of oxygen of 0 l/min to 5 l/min.

A.4 Electric resistant furnace

A.4.1 The combustion furnace consists of a furnace chamber and a heating unit. The furnace chamber consists of a ceramic tube (e.g. 25 mm to 50 mm in outer diameter, 20 mm to 40 mm in inner diameter and 400 mm to 600 mm in length) which fits inside the heating unit. The tube has metal flanges at the front and rear which are sealed to the tube by the packing.

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

A.4.2 The heating unit is usually 4 kVA apparent power, and the heating temperature of tube is measured by thermocouple. The tube is resistant up to 1 450 °C.

A.4.3 The boat containing the sample and accelerator is inserted at the front of the furnace. The boat should be placed correctly at the centre of the heating zone by the inserting rod (rigid nickel bar). The shutter of the furnace should be closed soon after inserting the boat.

A.4.4 The temperature attained during combustion depends on the characteristics of the metal in the boat, the form of the test portion and the mass of materials. The importance of these factors may be varied to some extent by the operator. Maximum temperature of tube during carbon determination is almost 1 250 °C.

A.5 Dust collector

This is capable of collecting metal oxide dust in a current of oxygen from the furnace.

A.6 Desulfurization tube

This consists of a heated oxidation tube containing a platinum foil or platinized silica and a sulfur trioxide collector containing cellulose cotton.

A.7 Infrared gas analyser

A.7.1 In most instruments the gaseous products of combustion are transferred in a continuous flow of oxygen to the analyser stream. The gases flow through an infrared cell, for example of the Luft type, where the absorption of the infrared radiation due to carbon dioxide and/or carbon monoxide 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 carbon.

A.7.2 In some analysers, the products of combustion may be collected in oxygen in a fixed volume at controlled pressure and the mixture analysed for carbon dioxide and/or carbon monoxide.

A.7.3 Electric controls are usually provided for adjusting the instrument zero, compensating for the blank, adjusting the slope of the calibration line and correcting for non-liner 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 automatic balance for weighing the boat, weighing the test portion and transferring the value of mass to the calculator.