TECHNICAL
SPECIFICATION

ISO/TS
10719

First edition
2016-12-01

Cast irons — Determination of non-combined carbon content — Infrared absorption method after combustion in an induction furnace

Fontes — Détermination du carbone non combiné — Méthode par absorption dans l'infrarouge après combustion dans un four à induction

Reference number
ISO/TS 10719:2016(E)

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

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Foreword

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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 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.

The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This first edition Technical Specification replaces the first edition Technical Report (ISO/TR 10719:1994), which has been technically revised. The following changes have been made:

- steels have been deleted from the scope;
- the possibility to establish the calibration curve by means of certified reference materials has been added;
- assessment of the precision data has been revised.

Cast irons — Determination of non-combined carbon content — Infrared absorption method after combustion in an induction furnace

1 Scope

This document specifies an infrared absorption method after combustion in an induction furnace for the determination of non-combined carbon content in cast irons.

The method is applicable to non-combined carbon contents between 1,0 % (mass fraction) and 3,0 % (mass fraction).

Elements ordinarily present do not interfere. However, some alloyed cast irons, when extensively heat treated, contain carbides that are not soluble when using this method and may give high values for non-combined carbon.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

3.1
non-combined carbon
graphitic carbon
carbon that is not dissolved by methanol and nitric and hydrofluoric acids

4 Principle

Decomposition of a test portion with nitric acid in the presence of methanol and treatment with hydrofluoric acid. Removal of the non-combined carbon by filtering through a glass-fibre filter.

Combustion of the glass-fibre filter containing the non-combined carbon in a flow of oxygen at a high temperature, using a high-frequency induction furnace, in the presence of pure iron and an accelerator. Transformation of carbon into carbon dioxide and/or carbon monoxide.

Measurement by infrared absorption of the carbon dioxide and/or carbon monoxide, carried by the current of oxygen.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only water with a low content of organic matter, i.e. grade 2 or grade 1 water as specified in ISO 3696.

5.1 **Water,** free from carbon dioxide.

Boil water for 30 min, cool to room temperature and allow oxygen (5.2) to bubble through it for 15 min. Prepare just before use.

5.2 **Oxygen,** minimum purity 99,5 % (volume fraction).

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

5.3 **Iron**, containing less than 0,001 0 % of carbon (mass fraction).

5.4 **Solvent,** appropriate for cleaning greasy or dirty test samples, for example, acetone.

5.5 **Methanol**, minimum purity 99,5 % (volume fraction).

5.6 **Barium carbonate**.

Dry barium carbonate [minimum purity > 99,5 % (mass fraction)] at 105 °C to 110 °C for 3 h and cool in a desiccator before use.

5.7 **Cast iron certified reference materials (CRMs)**, containing 1 % to 3 % (mass fraction) carbon.

The cast irons to be used for this purpose shall have white structure.

5.8 **Accelerator**.

Copper, tungsten-tin mixture or tungsten containing less than 0,001 0 % carbon (mass fraction).

5.9 **Nitric acid**, ρ about 1,40 g/ml.

5.10 **Hydrofluoric acid**, ρ about 1,15 g/ml.

5.11 **Hydrochloric acid**, ρ about 1,19 g/ml, diluted 1 + 1.

5.12 **Sodium hydroxide**, 120 g/l solution.

Cautiously dissolve 60 g of sodium hydroxide in about 200 ml of water (5.1). When dissolution is complete, cool, dilute to 500 ml with water, mix and store in a plastic bottle.

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

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

6 Apparatus

The apparatus required for combustion in a high frequency induction furnace and the subsequent infrared absorption measurement of the evolved carbon dioxide and/or carbon monoxide may be obtained commercially from a number of manufacturers. Follow the manufacturer's instructions for the operation of the instrument. A pressure regulator is required to control the oxygen pressure to the furnace according to the manufacturer's specification.

Ordinary laboratory apparatus and the following shall be used.

6.1 Filter, made of glass fibre, 47 mm in diameter, pore size 0,3 µm.

6.2 Vacuum filtering apparatus, for use with 47 mm glass-fibre filters (6.1) and suitable for use with acids.

6.3 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.

7 Sampling

Sampling shall be carried out in accordance with ISO 14284 or with an appropriate national standard for cast irons (see Annex C).

NOTE For cast irons, use drillings with lengths of more than 2 mm. For spheroidal graphite cast irons, use solid portions, approximately 10 mm x 10 mm x 0,3 mm.

8 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.

Take care not to mix methanol with concentrated nitric acid because of the risk of explosion.

8.1 General operating instructions

Purify the oxygen supply (5.2) using tubes packed with the inert ceramic (5.14) impregnated with sodium hydroxide (5.12) and magnesium perchlorate (5.13), and maintain a quiescent flow rate while on standby. Maintain a glass-fibre filter or a stainless steel filter screen 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.

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

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

Select a cast iron certified reference material with a carbon content close to the maximum carbon content in the calibration series, measure the corresponding carbon content in accordance with the manufacturer's instructions and adjust the reading of the instrument to the certified value.

8.2 Test portion

If necessary, degrease the test sample by cleaning in a suitable solvent (5.4). Cautiously evaporate the last traces of the solvent by warming.

Weigh, to the nearest 1 mg, approximately 0,50 g of the test sample.

8.3 Blank test

In parallel with the determination and following the same procedure, carry out two blank tests using the same quantities of all the reagents, including the same quantity of the pure iron (5.3) as used for the test portion (8.2).

Obtain the reading of the blank tests and convert it to milligrams of carbon by means of the calibration curve (see 8.5).

The mean blank value (m_1) is calculated from the two blank values. The mean blank value and the difference between the two blank values shall both not exceed 0,15 mg of carbon. If these values are abnormally high, investigate and eliminate the source of contamination.

8.4 Determination

8.4.1 Dissolution of the test portion

Place the test portion (8.2) in a 250 ml beaker. Add 25 ml of methanol (5.5), 50 ml of water (5.1) and 5 ml of nitric acid (5.9). Immediately cover the beaker with a watch glass and allow to stand for 12 h to 16 h at room temperature.

Add 20 ml of nitric acid (5.9) and allow to stand until further reaction ceases. Place the beaker on a hot plate heated between 50 °C and 60 °C. When vigorous reaction ceases, add 4 drops to 5 drops of hydrofluoric acid (5.10). Continue heating until dissolution is completed. If necessary, add water (5.1) to maintain the original volume.

8.4.2 Filtration of the non-combined carbon

Place two glass-fibre filters (6.1) in a vacuum filtering apparatus (6.2) and moisten with water (5.1). Filter the solution obtained in 8.4.1 with very moderate suction. Transfer the non-combined carbon to the filter and, with a rubber-tipped glass rod detach any particle that may be adhering to the beaker thoroughly. Wash the sides of the funnel to deposit all non-combined carbon on the glass-fibre filter disc.

Wash the filter disc once with hydrochloric acid (5.11), twice with hot water (5.1), three times with hot sodium hydroxide (5.12), twice with hot hydrochloric acid (5.11) and five times with hot water, in the order given. Finally, wash with methanol (5.5) to remove any non-combined carbon from the walls of the funnel.

Stop the suction and remove the top part of the filter assembly. Remove the top filter disc from the filter support by using a small pair of tweezers, fold it in eight parts and place in a ceramic crucible (6.3). Remove the bottom filter disc from the filter support and use it to wipe off any non-combined carbon from the filter apparatus. Fold the filter disc in eight parts and place it in the same crucible.

Dry the crucible containing the filters for 2 h at 105 °C, and store in a desiccator.

8.4.3 Measurements

8.4.3.1 Add 0,500 g of the pure iron (5.3) and the appropriate mass of accelerator to the ceramic crucible containing the dried filters prepared in 8.4.2.

The quantity of accelerator (5.8) will depend on the individual characteristics of the instrument. The amount used should be sufficient for complete combustion.

8.4.3.2 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.

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

8.5 Establishing the calibration curve

8.5.1 Primary product calibration

Weigh, to the nearest 0,1 mg, the masses of barium carbonate (5.6) indicated in Table 1 and transfer to four ceramic crucibles (6.3).

Add two glass-fibre filters (6.1) to the ceramic crucible (6.3) containing the barium carbonate (5.6). Add 0,500 g of the pure iron (5.3) and cover with the same quantity of the accelerator (5.8) as that used in 8.4.3.

Carry out the measurements as specified in 8.4.3.1.

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 the mass of carbon, in milligrams, for each member of the calibration series.

Table 1 — Composition of the calibration with barium carbonate

Mass of barium carbonate (5.6) mg	Corresponding carbon mass mg	Corresponding non-combined carbon content in a 0,5 g test portion % (mass fraction)
0[a]	0	0
82,1	5	1
164,3	10	2
246,4	15	3

[a] Zero member.

8.5.2 Calibration by means of certified reference materials

Select a set of white structure cast iron certified reference materials (5.7) for calibration and verification which, at a minimum, falls at the bottom, top, and quartile points of the operating range.

Weigh, to the nearest 1 mg, approximately 0,50 g of a certified reference material having a carbon content corresponding to the top of the operating range into a crucible (6.3). Add the appropriate amount of accelerator (5.8), two glass-fibre filters (6.1) and combust as in 8.4.3.2 and 8.4.3.3.

Adjust the net instrument reading to correspond to the correct level of carbon in the certified reference material according to the manufacturer's operating instructions. Repeat this measurement twice to check the repeatability of the reading: each result shall be within the range "certified value ±2 σ", where σ is the standard deviation characterizing the certified value.

Check the linearity of the calibration by analysing at least three times two other certified reference materials, one with a content of carbon in the middle and the other at the bottom of the range: the correlation coefficient shall be at least greater than 0,99.

Correct any non-compliant conditions before continuing to the next step.

9 Expression of results

9.1 Primary product calibration

Convert the analyser reading of the test portion to milligrams of carbon (m_0) by means of the calibration curve (8.5.1).

The non-combined carbon content, w_C, expressed as a percentage by mass, is given by Formula (1):

$$w_c = \frac{(m_0 - m_1)}{m \times 10^3} \times 100 = \frac{(m_0 - m_1)}{10m} \quad (1)$$

where

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

m_1 is the mass of carbon in the blank test (8.3), expressed in milligrams;

m is the mass of the test portion (8.2), in grams.

9.2 Calibration by means of certified reference materials

If the instrument has been calibrated to give a read-out directly as a percentage by mass of carbon with automatic compensation for the mass of the test portion, take the average of the set of determinations carried out and report the result.

With some instruments it will be necessary to prepare a calibration curve of instrument reading versus the mass, in micrograms, of carbon in the certified reference materials. Read off the calibration curve the mass of carbon in the test portion in micrograms, correct for the blank and mass of the test portion. Average the determinations carried out and report the result.

10 Precision

A planned trial of this method was carried out by 12 laboratories, using 10 levels of non-combined carbon contents, each laboratory making 3 determinations of non-combined carbon on each level (see Note 1).

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725:1986[1], i.e. one operator, same apparatus, identical operating conditions, same calibration and a minimum period of time.

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

The results obtained were statistically evaluated in accordance with ISO 5725-2 and ISO 5725-3.

NOTE 2 For the preparation of this document the original results were submitted to a new statistical evaluation, based on ISO 5725-2 and ISO 5725-3. This new evaluation led to all the results provided by a laboratory (labelled "USA 1") being discarded, as all the corresponding results showed a systematic low tendency of about 0,2 % for the nine cast iron samples. See Annex B for a comparison between the results of the first and second precision tests.

NOTE 3 The main use of the procedure described in this document deals with the determination of non-combined carbon content in cast irons. Its possible application to steel materials is a border case, as most of these materials do not contain non-combined carbon. For this reason, steel materials were removed from the scope of the method.

The results obtained during the precision test are presented in Table A.1.

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[1] Withdrawn document.

The precision data obtained have no consistent relationship with the related non-combined carbon content mean value, as the correlation coefficients are as follows:

- 0,15 for the logarithmic relation between the repeatability limit (r) and the content mean value;
- 0,43 for the logarithmic relation between the interlaboratory reproducibility limit (R_W) and the content mean value;
- 0,18 for the logarithmic relation between the reproducibility limit (R) and the content mean value.

Therefore, only the experimental data are to be used (see Table A.1).

It has also to be underlined that the experimental reproducibility data for a majority of the samples are above the acceptable limits defined within ISO/TC 17/SC 1, as shown in Table A.2.

11 Notes on the procedure

11.1 Preliminary blank tests

To test water (5.1) and the different reagents, carry out two preliminary blank tests at the same time, following the same procedure and using the same quantities of all the reagents, including the same quantity of the pure iron (5.3) as used for the test portion (8.2).

All the preliminary blank values shall be equal to or less than 0,15 mg of carbon. If they are not, it is necessary to select other reagents and water and to repeat the preliminary blank test.

11.2 Preliminary tests on certified reference materials

After selecting reagents and water, and before carrying out the tests, make preliminary tests using some certified reference materials.

Carry out two determinations under repeatability conditions, following the same procedure and using the same quantities of all the reagents as used for the test portion.

The related mean value should be within the range “certified value ± 2σ” and the difference between the two determinations should be equal to or less than 0,1 %. If they are not, the preliminary test should be repeated until these criteria are met.

12 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 or of the test report;

b) the method used by reference to this document, i.e. ISO/TS 10719;

c) the results and the unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(informative)

Additional information on the international interlaboratory test

Table A.1 summarizes the results of the second international precision test carried out in 1991 on 1 steel sample and 9 cast iron samples in 6 countries involving 12 laboratories (see Note 2 in Clause 10).

The results of the original statistical evaluation of the precision test were reported in document ISO/TC17/SC 1 N 925, February 1992 whereas Table A.1 shows the precision data obtained from their re-evaluation carried out in 2014.

The test samples used are listed in Table A.1 together with the related precision data.

Table A.1 — Test samples used for the precision test and related precision data

Sample	**Total carbon content** % (mass fraction)	**Non-combined carbon content** % (mass fraction)		**Precision data** % (mass fraction)		
		Certified	**Found**	**Repeatability limit** r	**Reproducibility limits**	
					R_W	R
Steel	1,4	0,395[a]	0,397	0,052	0,109	0,142
NIST 342a (Nodular cast iron)	1,9	1,38	1,43	0,077	0,090	0,208
BCS 172/3 (Ni – Cr – Cu – Mo cast iron)	2,2	1,55	1,57	0,065	0,065	0,200
ECRM 483-1 (Cast iron)	2,5	1,65	1,71	0,090	0,125	0,246
CTIF FG20 (Cast iron)	2,5	1,924[a]	1,97	0,079	0,086	0,193
NIST 107c (Ni – Cr – Cu – Mo cast iron)	3,0	1,98	2,15	0,107	0,162	0,374
ECRM 428-1 (Cast iron)	2,8	2,33	2,33	0,111	0,124	0,199
BCS 206/2 (High Si, P cast iron)	2,5	2,4[b]	2,4	0,018	0,045	0,102
NIST 4k (Cast iron)	3,2	2,65	2,67	0,105	0,164	0,264
NIST 122h (Cast iron)	3,5	2,82	2,90	0,168	0,207	0,362

[a] Mean value of a preliminary round robin test (non-certified value).

[b] Non-certified value.

Table A.2 shows the comparison between the experimental reproducibility data, expressed as “variation coefficient”, and the acceptable limits defined within ISO/TC 17/SC 1.

Table A.2 — Comparison between the variation coefficient and the acceptable limits defined within ISO/TC 17/SC 1

Variation coefficient %	Acceptable limits defined within ISO/TC 17/SC 1 %
5,20	2,87
4,54	2,77
5,14	2,70
3,49	2,57
6,21	2,49
1,50	2,39
3,04	2,42
3,54	2,31
4,45	2,24

Annex B
(informative)

Comparison between the results of the first and the second precision tests

Table B.1 — Comparison between the results of the first and the second precision tests

Test sample number	Name of the sample	Non-combined carbon content % (mass fraction)			Precision data % (mass fraction)	
		Certified	Found		Reproducibility limit R	
			1st trial $\left(\frac{\bar{w}_{C,1}+\bar{w}_{C,2}}{2}\right)$	2nd trial	1st trial	2nd trial
20-1	ECRM 430-1	2,338	2,336		0,240	
20-2[a]	Pig iron	0,289	0,519		1,408	
20-3 20-20	Steel	0,395[b]	0,393	0,397	0,191	0,142
20-4	P-405	2,813[b]	2,794		0,330	
20-5 20-17	ECRM 428-1	2,33	2,384	2,330	0,158	0,199
20-6	NIST 5l	1,98	1,991		0,233	
20-7	NIST 8b	2,37	2,361		0,234	
20-8 20-13	ECRM 483-1	1,65	1,688	1,710	0,298	0,246
20-9	CTIF FG 10	1,647[b]	1,694		0,329	
20-10 20-14	CTIF FG 20	1,924[b]	1,907	1,974	0,122	0,193
20-11	NIST 342a	1,38		1,428		0,208
20-12	BCS 172-3	1,55		1,573		0,200
20-15	NIST 107c	1,98		2,148		0,374
20-16	BCS 206-2	2,4[c]		2,422		0,102
20-18	NIST 4k	2,65		2,666		0,264
20-19	NIST 122h	2,82		2,904		0,362

$\bar{w}_{C,1}$: general mean within a day.

$\bar{w}_{C,2}$: general mean between days.

[a] Fine dust sample.

[b] Mean value of a preliminary round robin test (non-certified value).

[c] Non-certified value.

Annex C
(informative)

Effect of fine material in a sample on the determination of non-combined carbon content

C.1 General

During the precision tests carried out by ISO/TC 17/SC 1, the following information was submitted from USA.

C.2 Comments and test results

C.2.1 General

It is possible that the variability in results obtained during these tests might be caused by the presence of fine loose non-combined carbon. The following determinations, which were conducted on 13 samples of NIST 122i (cast iron in chip form) supplied for homogeneity testing for total carbon, tend to support that view.

The samples were taken from large cans of NIST 122i and were identified by a can number, and "T" for samples taken from the top of a can or "B" for samples from the bottom of a can.

C.2.2 Determination of total carbon in separate samples

Each of the 13 samples was run 12 times on a LECO CS-44 instrument using a 0,4 g test portion and 2,2 g of tungsten accelerator. The results are given in Table C.1.

There is a wide range of values for the carbon content, although the mean for the six "T" samples is the same as the mean for the seven "B" samples: 3,494 % (mass fraction) in each case, which is identical to the mean for all 156 determinations.

C.2.3 Determination of total carbon in a composite sample after sieving

A composite sample was prepared by combining 10 g from each of the 13 samples. The 130 g sample was then sieved through a screen (40 mesh) while shaking and tapping for 10 min. Approximately 0,24 g of material passed through the screen.

C.3 Analysis of the composite sample from which the fine material was removed

The results of 13 determinations of the total carbon content in the composite sample described in C.2.3, expressed in % (mass fraction), are shown below:

3,481 - 3,454 - 3,452 - 3,457 - 3,432 - 3,454 - 3,431 - 3,419 - 3,405 - 3,408 - 3,361 - 3,456 - 3,415

The corresponding mean value is 3,433 % (mass fraction), with a standard deviation of 0,031 % (mass fraction) and a coefficient of variation of 0,91 %.

C.4 Analysis of fine material

The total carbon content found in the fine material was 31,8 % (mass fraction).

C.5 Calculated total carbon content of the composite sample before sieving

Mass of carbon in the fine material removed by sieving = 0,24 × 0,318 = 0,076 g.

Contribution to the carbon content of the total 130 g sample = (0,076 × 100)/130 = 0,058 % (mass fraction)

Total carbon content in the composite sample before sieving = 3,433 + 0,058 = 3,491 % (mass fraction).

This correlates very well with the value of 3,494 % (mass fraction) obtained for the mean of 156 determinations of the 13 separate samples.

C.6 Conclusions

This evidence strongly suggests that the presence of excessive non-combined carbon [31,8 % (mass fraction) in this case] in the fine material affects the total carbon homogeneity and would similarly affect the non-combined carbon homogeneity, resulting in the wide spread of results obtained during these trials.