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Titanium and titanium alloys — Determination of carbon — Infrared absorption method after combustion in an induction furnace

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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 sample preparation **2**
8 Procedure **2**
8.1 Test portion 2
8.2 Number of determination 2
8.3 Preparation of the instrument 2
8.4 Blank tests 3
8.5 Calibration 3
8.6 Determination 4
8.7 Calculation 5
9 Precision **5**
10 Test report **6**
Annex A (informative) **Composition of the samples used for the validation precision test** **7**
Annex B (informative) **Graphical representation of the precision data** **8**
Bibliography **9**

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 document 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).

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This document was prepared by Technical Committee ISO/TC 79, *Light metals and their alloys*, Subcommittee SC 11, *Titanium*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Titanium and titanium alloys — Determination of carbon — Infrared absorption method after combustion in an induction furnace

1 Scope

This document specifies an infrared absorption method after combustion in an induction furnace under oxygen atmosphere for the determination of carbon in titanium and titanium alloys.

The method is applicable to carbon contents between 0,003 % (mass fraction) and 0,050 % (mass fraction).

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 terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

A test portion is combusted in presence of an accelerator at a high temperature in a high-frequency induction furnace in a current of pure oxygen.

Carbon is transformed into carbon dioxide and/or carbon monoxide. Measurement is by infrared absorption of the carbon dioxide and/or carbon monoxide carried by a current of oxygen.

5 Reagents

During analysis, unless otherwise stated, use only reagents of recognized analytical grade.

5.1 Magnesium perchlorate, $Mg(ClO_4)_2$ (commercial name: anhydrone), used to absorb moisture. Use purity specified by the manufacturer of the instrument.

5.2 Inert ceramic (attapulgus clay) or silica impregnated with sodium hydroxide or potassium hydroxide, used to absorb carbon dioxide. Use purity specified by the manufacturer of the instrument.

5.3 Accelerator, of tungsten, iron or tin with a particle size above 0,15 mm. Use purity specified by the manufacturer of the equipment.

5.4 Oxygen, with high purity as specified by the manufacturer of the equipment. An oxidation catalyst[copper(ll) oxide or platinum] tube heated to a temperature above 600 °C followed by suitable carbon dioxide and water absorbents shall be used when the presence of organic contaminants is suspected in the oxygen.

5.5 Ethanol or acetone, used to clean the sample from organic contamination. Use purity and type specified by the manufacturer of the instrument.

5.6 Titanium or titanium alloys certified reference materials (CRMs) or reference materials (RMs). Select only titanium or titanium alloy CRMs or RMs. Select CRMs or RMs covering the top, the middle and the bottom of the scope. The accuracy of the present method is largely dependent on the carbon values assigned to the CRMs or RMs and on the homogeneity of these materials.

6 Apparatus

The apparatus required for combustion is a high-frequency induction furnace and an infrared absorption device for the measurement of the evolved carbon dioxide and/or carbon monoxide. These instruments can be obtained commercially from a number of manufacturers.

6.1 Ceramic crucible, high purity crucibles recommended by the manufacturer of the instrument used and capable of withstanding combustion in an induction furnace without evolving carbon-containing chemicals. Ignite the crucibles in an electric furnace at more than 900 °C for at least 1 h. After this treatment, remove the crucibles from the furnace, allow them to cool and store them in a desiccator.

Alternatively, crucibles may not be stored in a desiccator if they are ignited just before a series of analysis.

6.2 Filters for gas cleaning, filters recommended by the manufacturer of the instrument.

7 Sampling and sample preparation

Sampling and sample preparation shall be carried out by normal agreed procedures. The test sample normally is in the form of millings or drillings and no further preparation of the sample is necessary. Millings or drillings shall be uniform in size and do not exceed a length of 5 mm. The test samples shall be dry, free from oil, scale and foreign inclusions.

The test sample shall be cleaned with ethanol or acetone (5.5) and air-dried.

8 Procedure

8.1 Test portion

Weigh to the nearest 1 mg, 200 mg to 600 mg of the test sample.

8.2 Number of determination

The determination shall be carried out at least in duplicate under repeatability conditions.

NOTE For routine purposes and after previous agreement, a single determination can be carried out.

8.3 Preparation of the instrument

a) Assemble the apparatus as recommended by the manufacturer. Make the required power and gas connections.

b) Check the cleanliness of the filters and change them as often as necessary.

c) If the electrical supply has been switched off for a period of time, allow the instrument to stabilize for the time recommended by the manufacturer.

d) Place the ceramic crucible (6.1), which will be subsequently used for analysis, into the furnace; anneal the crucible following the manufacturer's instructions.

Before analysing the samples, as well as after changing filters or reagents, it is necessary to carry out the preparation of the instrument (see 8.3), blank test (see 8.4) and the calibration (see 8.5).

When using computerized instruments, the preparation of the calibration curve, standardization (offset correction, normalization, recalibration) and measurement of the carbon concentration shall be carried out according to the instructions of the manufacturer of the instrument.

8.4 Blank tests

a) Prior to the determination, carry out the following blank test in duplicate.

b) Proceed as described in 8.6, using an annealed ceramic crucible (6.1) and analyse the same quantity of the accelerator (5.3) as that which will be used for the determinations but without any test portion.

c) Obtain the reading of the blank test.

d) The mean value of the blank test shall be equal to or less than 0,001 %.

The difference between two blank values shall be equal to or less than 5 µg.

e) If these requirements are satisfactory, the mean value of the blank obtained shall be recorded in the blank subtraction system of the instrument.

8.5 Calibration

Prior to the determination, carry out the calibration of the instrument as follows:

a) Proceed as directed in 8.6, using titanium or titanium alloys CRMs or RMs (5.6) instead of the test portion.

b) Subtract the mean value of the blank value (see 8.4) from the analyser reading signal.

c) Repeat the above procedure at least three times.

d) Calculate the intermediate equivalence factor (f) and equivalence factor (F), using Formulae (1) and (2):

$$fi = m_0 i / si \quad (1)$$

i = 1 to n

$$F = \frac{\sum_{i=1}^{n} f_i}{n} \quad (2)$$

where

F is the equivalence factor expressed in milligrams of carbon;

f is the intermediate calibration factor expressed in milligrams of carbon, for each reading signal;

m_0 is the mass of carbon in each test portion of titanium or titanium alloys CRMs or RMs [calculated from Formula (3)] expressed in milligrams;

s is the intermediate analyser reading signal after subtraction of the blank mean value;

n is the number of measurements of each titanium or titanium alloys CRM or RM.

The mass of carbon in each test portion of titanium or titanium alloys CRMs or RMs, is given from Formula (3).

$$m_0 = [\ (G \times P\ )\ /\ 100\ ] \times 10^3 \quad (3)$$

where

G is the mass of the test portion of titanium or titanium alloys CRMs or RMs, expressed in milligrams;

P is the content of carbon in titanium or titanium alloys CRMs or RMs, expressed in % by mass.

NOTE Modern equipment calculates the calibration factor automatically.

8.6 Determination

The determination shall be carried out at least in duplicate, under repeatability conditions.

a) Transfer the appropriate mass of accelerators into an annealed ceramic crucible (6.1).

b) Add the test portion (see 8.1) into the crucible.

c) Place the crucible on the furnace pedestal.

d) Operate the instrument by following the instructions of the manufacturer for the combustion of the sample in the oxygen stream, carbon dioxide and/or carbon monoxide extraction and measurement of the infrared absorption.

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

During a series of analysis, analysing titanium or titanium alloys CRMs or RMs at regular intervals is recommended for monitoring the drift and validating the results of the test samples.

Optimum conditions for the type and amount of accelerator depend on the instrument used.

These conditions shall be defined by each laboratory. Typical amounts are:

— tungsten: 1 g,

— iron: about 0,5 g,

— tin: about 0,3 g.

During a series of analysis, analysing titanium or titanium alloys CRMs or RMs at regular intervals is recommended for monitoring the drift and validating the results of the test samples.

8.7 Calculation

Carbon content, W_c, expressed as a % (by mass) is given by Formula (4).

$$W_c = [(A1\text{-}A2) \times F \times 100/m] \times 10^{-3} \quad (4)$$

where

W_c is the carbon content in the test portion, in % by mass;

$A1$ is the analyser reading signal for the sample;

$A2$ is the mean value of the analyser reading for the blank test;

F is the equivalence factor expressed in milligrams of carbon;

m is the mass of the test portion, in grams.

NOTE Modern instruments give directly the carbon content expressed in % (by mass); post-analysis calculations are not required.

9 Precision

Twelve laboratories in four countries participated in an interlaboratory test involving three determinations of carbon at four levels (samples).

Each laboratory carried out two determinations 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. The third determination was carried out at a different time using the same apparatus with a different calibration.

The compositions of the samples used are given in Annex A.

The results obtained were statistically evaluated according to ISO 5725-2 and ISO 5725-3 and are reported in Table 1.

The logarithmic relationships between the carbon content (m) and the precision parameters (r, R_w and R), together with the corresponding correlation coefficients are:

$\lg r = 0{,}480 \lg m - 1{,}921\ 7$ [correlation coefficient = 0,894]

$\lg R_w = 0{,}563 \lg m - 1{,}670\ 1$ [correlation coefficient = 0,981]

$\lg R = 0{,}391 \lg m - 1{,}781\ 8$ [correlation coefficient = 0,988]

The corresponding graphical representation is shown in Annex B.

The smoothed values of the repeatability limit (r) and reproducibility limits (R_w and R) of the test results are summarized in Table 2.

Table 1 — Results obtained from the precision test

SAMPLE	502-876	502-867	Ti64ELI-18	58A SY13001-4
Mean (%)	0,003 24	0,023 6	0,033 6	0,049 4
σ (r), %	0,000 25	0,000 88	0,001 1	0,000 7
σ (R_w), %	0,000 29	0,000 97	0,001 3	0,001 2
σ (R), %	0,000 62	0,001 34	0,001 7	0,001 7
r, %	0,000 70	0,002 5	0,003 0	0,002 0
R_w, %	0,000 82	0,002 7	0,003 7	0,003 3
R, %	0,001 74	0,003 7	0,004 9	0,004 7
CV (R) %	19,2	5,67	5,16	3,42
Aim CV (R) %	10,8	5,41	4,79	4,19
Max CV (R) %	23,7	11,9	10,5	9,21
Assigned content (%)	0,002 7	0,023	0,033	0,049

Table 2 — Smoothed values of the repeatability and reproducibility limits

Carbon content (%)	***r* (%)**	**R_w (%)**	***R* (%)**
0,003	0,000 74	0,000 81	0,001 71
0,005	0,000 94	0,001 09	0,002 08
0,01	0,001 3	0,001 6	0,002 7
0,02	0,001 8	0,002 4	0,003 6
0,05	0,002 8	0,004 0	0,005 1

10 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) a reference to this document, i.e. ISO 13093:2023;

c) the method used by reference to this document;

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

e) any unusual features noted during the determination;

f) any operation not specified in this document or any optional operation which can have influenced the results.

Annex A
(informative)

Composition of the samples used for the validation precision test

The compositions of the samples used for the validation precision test are listed in Tables A.1 and A.2.

Table A.1 — Compositions of the samples used for the validation precision test

Sample	C	Al	V	Fe	Cr	Cu	Mn	Ni
502-876	0,002 7							
502-867	0,023							
Ti64ELI-18	0,033	6,11	4,01	0,167	0,004	0,002	0,001 4	0,003
58A SY13001-4	0,049	6,03		0,187				
58A SY13001-2	0,084	5,10		0,313				

Table A.2 — Compositions of the samples used for the validation precision test

Sample	Si	Sn	Mo	Nb	Zr	O	N	H
502-876						0,304	0,002 5	0,002 8
502-867						0,140	0,012	(0,002 9)[a]
Ti64ELI-18	0,014	0,022				0,118	0,006	0,002 1
58A SY13001-4	0,149		1,02	2,76	1,93			
58A SY13001-2[b]	0,043		0,297	3,63	2,74			

[a] Information value only.

[b] 58A SY13001-2: this sample was used for calibration.