Designation: E1941 – 10 (Reapproved 2016)

Standard Test Method for Determination of Carbon in Refractory and Reactive Metals and Their Alloys by Combustion Analysis[1]

This standard is issued under the fixed designation E1941; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method applies to the determination of carbon in refractory and reactive metals and their alloys in quantities from 20 µg to 500 µg. This corresponds to mass fractions ranging from 0.004 wt % to 0.100 wt % for a 0.5 g sample (see Note 1).

NOTE 1—Actual quantitative range might vary from manufacturer to manufacturer and according to sample mass. Samples of higher mass may allow for proportionally lower detection limits provided complete combustion of the sample is assured.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Terminology E135.

4. Summary of Test Method

4.1 The metal specimen, contained in a single-use ceramic crucible, is ignited (combusted) in an oxygen atmosphere in an induction furnace. The carbon in the specimen is oxidized to carbon dioxide or carbon monoxide, or both, and is eventually carried to the analyzer/detector. The amount of carbon present is electronically processed and is displayed by the analyzer readout.

4.2 This test method is written for use with commercially available analyzers equipped to carry out the above operations and calibrated using commercially available reference materials of known carbon content.

5. Significance and Use

5.1 This test method is intended to test for compliance with compositional specifications. It is assumed that all who use this method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory.

6. Interferences

6.1 The elements ordinarily present in these alloys do not interfere. Halides that are present in some sponge type samples will cause low carbon recovery.

7. Apparatus

7.1 *Combustion Furnace and Measurement Apparatus,* automatic carbon determinator, consisting of an induction furnace; a dust/debris removal trap; an analytical gas stream purification system; an infrared detection system; and an automatic readout (see Note 2).

NOTE 2—Several models of commercial carbon determinators are available and presently in use in industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's instruction manuals for operational details.

7.2 *Oxygen Tank and Regulator.*

7.3 *Ceramic Crucibles and Lids,* that meet or exceed the instrument manufacturer's specifications. Use of lids is optional. If they are used, they should have holes in them.

7.4 *Crucible Tongs,* capable of handling recommended crucibles.

7.5 *Balance,* capable of weighing to the nearest milligram.

7.6 *Furnace,* capable of reaching and sustaining a temperature of at least 700 °C.

---

[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf, Re.

Current edition approved Dec. 1, 2016. Published December 2016. Originally approved in 1998. Last previous edition approved in 2010 as E1941 – 10. DOI: 10.1520/E1941-10R16.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

8. Reagents

8.1 *Acetone (A.C.S. Reagent,* or other suitable, degreasing reagents).

8.2 *Copper Accelerator,* low carbon (see Note 3).

8.3 *High Purity Iron Chip Accelerator,* low carbon (see Note 3).

8.4 *Magnesium Perchlorate (Anhydrone),* purity as specified by equipment manufacturer.

8.5 *Oxygen,* high purity (as specified by equipment manufacturer).

8.6 *Tin Accelerator,* low carbon (see Note 3).

8.7 *Tungsten Accelerator,* low carbon (see Note 3).

8.8 *Sodium Hydroxide on Clay Base,* commonly known as Ascarite III (purity as specified by equipment manufacturer).

8.9 *Reference Materials,* with known carbon content.

NOTE 3—The total carbon content of all accelerators used must be sufficiently low to allow for blanking as described in Section 12.

9. Hazards

9.1 For hazards to be observed in the use of certain reagents and equipment in this test method, refer to Practices E50.

9.2 Use care when handling hot crucibles and operating furnaces to avoid personal injury by either burn or electrical shock.

10. Preparation of Apparatus

10.1 Make a minimum of two determinations to condition the instrument as directed in Section 12 before attempting to calibrate the system or determine the blank.

10.2 *Crucible and Lid Preparation*—Commercially available crucibles and lids (Note 4) often contain levels of carbon sufficient to adversely affect results. To minimize this problem, crucibles and lids may be heat treated prior to use to remove contamination. Heating to 700 °C to 800 °C for at least 2 h or to 900 °C to 1000 °C for at least 1 h. has been determined to be effective. Other heating conditions may be specified if there is data supporting the effectiveness of the time and temperature used on removing contaminants. Remove the crucibles and lids from the furnace and allow them to cool (see Note 5). Use of a desiccator or other covered container for storage is recommended to minimize the potential for contamination. Handle prepared crucibles only with clean crucible tongs.

NOTE 4—The use of lids is optional. If they are used, they should be prepared and stored in the same manner as the crucibles. If they are not used, references to them in this standard may be ignored.

NOTE 5—Crucibles and lids must be used within a specified time period of being removed from the furnace. Four hours has been found to be an acceptable period, but a longer time may be specified by the test facility if supporting data are kept on file. If crucibles or lids, or both, are not used within the specified time period after removing them from the furnace, they shall be reheated as described in 10.2.

11. Sample Preparation

11.1 The sample selected shall be representative of the material to be analyzed.

11.2 Nibble, drill, shear, or machine a clean sample so that pieces are uniform in size and will fit into the ceramic crucible without extending over the rim.

11.3 If necessary, wash the pieces in acetone or other solvents (Note 6) to remove any oil, grease, or cutting fluid contamination. For heavier contamination, the sample may be washed in a soap solution or in a sonic cleaner, or both, and rinsed with a solvent. Decant the solvent and dry the sample. Care should be taken to ensure complete removal of solvents or cleaners, especially from porous samples, which may trap cleaning liquids, biasing results. Store the clean dried samples in a manner that minimizes the potential for contamination.

NOTE 6—Other solvents may be alternative organic solvents, inorganic solvents or inorganic acids that are capable of removing oil, grease or machining fluids.

12. Calibration

12.1 *Calibration Reference Materials*—The calibration reference materials (RMs) will consist of one or more commercial RMs of known carbon content (the high RM value should slightly exceed that of the unknown). Use appropriate accelerators, for example one scoop (approximately 1 g) of iron chip accelerator and one scoop (approximately 1.5 g) of copper accelerator (Note 7) in a prepared crucible, plus a prepared crucible lid.

NOTE 7—Users of simultaneous carbon-sulfur determinators should be aware that copper accelerator will have a negative effect on the sulfur result caused by the formation of copper sulfide. Other accelerator combinations that allow for complete combustion without the use of copper may be used if data supporting the effectiveness of the alternate accelerators is available. The combination of 3 parts iron, 3 parts tungsten, and 2 parts tin has been found effective for carbon and sulfur.

12.2 *Crucible Blank*—The crucible blank will consist of a crucible and lid prepared the same way as those used for samples, containing the same accelerator as that used for samples.

12.2.1 Prepare four crucible blanks as described in 12.2.

12.2.2 Follow the blank calibration procedure as detailed in the manufacturer's instruction manual, using at least 3 blanks.

12.2.3 Analyze one additional blank to verify the blank calibration. The blank value should be within 5 µg of the adjusted zero.

12.2.4 Prepare at least three specimens of a reference material for each calibration point as directed in Section 11 and 12.1. Calibrate the instrument in a manner consistent with the instructions in the manufacturer's operating manual.

12.2.5 Prepare at least one additional RM specimen to validate the calibration. The obtained value shall agree with the certificate value within the range given by the published uncertainty or it shall agree within the limits of a prediction interval calculated using Eq 1. The prediction interval is defined as the range of values bounded by the analysis value $-p$ and the analysis value $+p$. If the prediction interval does not encompass the certified value, determine and correct the cause, and repeat calibration (Note 8). Either acceptance limit criterion is acceptable for routine operation.

NOTE 8—See the instrument manufacturer's instructions concerning the troubleshooting and correcting of errant calibration.

$$p = t \cdot \left(1 + \frac{1}{\sqrt{n}} \right) \cdot s \tag{1}$$

where:

p = one-half the prediction interval,
n = number of replicates used in 12.2.4,
t = student's t chosen for the 95 % confidence level for n replicate measurements (for example: $t = 4.30$ when $n = 3$, 3.18 when $n = 4$, 2.78 when $n = 5$), and
s = standard deviation of n replicates in 12.2.4 (Note 9).

NOTE 9—Here, s should be comparable to S_m, the repeatability standard deviation, given in Table 1. If $s \gg S_m$, there is evidence that the repeatability of the particular instrument is not acceptable for use with this test method. The user should determine and correct the cause, and repeat 12.2.1 through 12.2.3.

12.2.6 One or more continuing calibration verifications must be performed prior to and upon completion of a period of continuous operation, and throughout this period with a predetermined minimum frequency to be established by each individual test facility. The acceptance range for the verification material may be the limits stated on the certified value for the reference material, or may be calculated using Eq 1 and the s and n values for multiple analyses of the verification material. If a continuing calibration verification indicates an out of calibration condition, stop analysis. Results must be supported by acceptable preceding and subsequent verifications to be reported.

12.2.7 It is the responsibility of the user to document the frequency of blank determination (12.2.2), routine calibration and confirmation (12.2.4) and the conditions under which blank determination and/or recalibration beyond this frequency is required (examples may include changing reagents, beginning use of a new batch of crucibles, changing gas cylinders or a personnel shift change).

13. Procedure

13.1 Make any pre-operational instrument checks as recommended by the instrument manufacturer.

13.2 Set the analyzer to the operate mode.

13.3 Prepare a specimen as directed in Section 11 and place it in a prepared crucible (see 10.2), add accelerator, and cover with an optional prepared lid (see 10.2) (see Note 4).

13.4 Enter the specimen mass as recommended by the manufacturer. If specimen identification feature is provided by manufacturer, enter identification.

13.5 Place the crucible plus specimen on the induction furnace pedestal and close the furnace.

13.6 Start the analysis cycle, referring to the manufacturer's recommended procedure.

14. Calculation

14.1 The carbon reading (result) will be direct if the blank and specimen weight have been correctly entered in the appropriate portion of the analyzer (see Note 10).

NOTE 10—If the analyzer does not offer these functions, calculate the carbon content by Eq 2 for single standard (one reference material and one blank) calibrations, or Eq 3 for linear (two or more reference materials and one blank) calibrations:

$$\text{carbon, mg/kg} = (A - B)/C \tag{2}$$

where:

A = µg of carbon in specimen,
B = µg of carbon in blank, and
C = specimen weight (in g).

$$Y = mX = b \tag{3}$$

where:

Y = measurement response,
m = slope,
X = mass fraction of carbon in the calibration material, and
b = Y intercept.

Calculation of the calibration function shall be done using a linear least squares regression. Some manufacturers recommend the use of a curve weighting factor where the Calibration material value is derived as $1/X$. It is acceptable to use this type of curve weighting.

TABLE 1 Carbon in Refractory and Reactive Metals and Their Alloys

Metal	Identity	Carbon found, ppm	Minimum SD (S_M, Practice E1601)	Reproducibility SD (S_R, Practice E1601)	Reproducibility Index (R, Practice E1601)	$R_{rel\%}$
Zirconium	3500701	24	3	6	17	71
	660b	346	7	15	42	12
	SRM 360a	151	6	10	27	18
Titanium	#1	654	8	32	90	14
	#2	72	3	9	27	37
	SRM 176	132	6	19	52	40
Hafnium	420b	194	12	26	74	38
Niobium	752	19	3	7	19	100
	SP5943	327	4	13	36	11
Molybdenum	5657	22	4	7	20	90
	5654	38	3	10	27	72
Tungsten	C-6	56	3	10	28	50
	C-3	111	3	9	24	21
Tantalum	A	119	3	7	20	17
	B	37	3	8	22	60

Nine laboratories contributed results for all the samples included in this study.

14.2 Since most modern commercially available instruments calculate mass fractions directly, including corrections for blank and sample mass, manual calculations by the analyst are not required. If the analyzer does not compensate for blank and sample mass values, then use the following equation:

$$\text{carbon, \%} = \left[(A - B) \times \frac{C}{D} \right] \tag{4}$$

where:

A = digital volt meter (DVM) reading for specimen,
B = DVM reading for blank,
C = mass compensator setting, and
D = specimen mass, g.

15. Precision and Bias

15.1 *Precision*—Nine laboratories cooperated in testing 15 samples representing 7 different matrices. The data obtained is presented in Table 1. The testing and statistical analysis were performed according to the provision of Practice E1601.

15.2 *Bias*—No information on the accuracy of this test method is available because no suitable certified reference materials were available when the interlaboratory test was performed. The user of this method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

16. Keywords

16.1 carbon content; combustion; reactive metals; refractory metals

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/