Designation: E2575 – 08

Standard Test Method for
Determination of Oxygen in Copper and Copper Alloys[1]

This standard is issued under the fixed designation E2575; 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 covers the determination of oxygen in copper and copper alloys in concentrations from 0.0005 to 0.04 %.

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.*

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
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System

2.2 *Material Certificates:*

BCR No. 18 Oxygen in Phosphorus-Deoxidized Copper[3]
BCR No. 22 Oxygen in ETP Copper[3]
BCR No. 58 Oxygen in Continuous Cast Copper Rod[3]
NCS NS 41004 Oxygen in Pure Copper[4]
NIST SRM 885 Refined Copper[5]

3. Terminology

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

4. Summary of Test Method

4.1 This test method is intended for use with commercially available inert gas fusion determinators.

4.2 The test specimen is fused in a graphite crucible under a flowing inert gas stream (argon (Ar), helium (He), or nitrogen (N_2)) at a temperature sufficient to release oxygen. Oxygen from the specimen combines with carbon from the crucible to form carbon monoxide (CO). The detector output is converted to the mass fraction of oxygen in the specimen using a previously establish calibration. Depending on the instrument design, CO is oxidized to carbon dioxide (CO_2) or left as CO and swept by the inert gas stream into an infrared detector.

4.3 In a typical instrument based on infrared detection the evolved gases are swept into an infrared cell through which infrared energy is transmitted. The CO in the gas stream absorbs some of the transmitted infrared energy and the decrease in the energy reaching the detector is processed and displayed directly as percent oxygen. Some instruments oxidize the CO to CO_2, which is subsequently measured by an infrared cell designed to measure CO_2.

5. Significance and Use

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

6. Interferences

6.1 The elements usually present in copper and its alloys do not interfere.

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[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 E01.05 on Cu, Pb, Zn, Cd, Sn, Be, their Alloys, and Related Metals.

Current edition approved March 1, 2008. Published April 2008. DOI: 10.1520/E2575-08.

[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.

[3] Available from European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, B-2440 Geel, Belgium, http://irmm.jrc.ec.europa.eu/.

[4] Available from Central Iron and Steel Research Institute (CISRI), No. 76 Xueyan Nanlu, Haidian District, Beijing, China 100081, http://www.cisri.com/.

[5] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.

7. Apparatus

7.1 *Instrument*—Fusion and measurement apparatus consisting of an electrode furnace, provision for scrubbing impurities from analytical gas stream, infrared measurement system, and auxiliary gas purification systems. (See Note 1.)

NOTE 1—The apparatus and analysis systems have been previously described in Test Method E1019. Several models of commercial oxygen determinators are available and presently in use by industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's manual for operational details.

7.2 *Graphite Crucibles*—The crucibles must be made of high-purity graphite as recommended by the instrument manufacturer and be of the dimensions recommended by the instrument manufacturer.

7.3 *Tweezers*—Approximately 6 in. (152 mm), used during the sample preparation process.

7.4 *Balance*—Measurement apparatus with capacity up to 10 g capable of weighing ±0.1 mg accurately or as specified by the instrument manufacturer.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

8.2 *Graphite Powder/Carbon Black*—High-purity graphite powder or carbon black specified by the instrument manufacturer.

8.3 *Inert Gas*—Use the purity and type (Ar, He, or N_2) specified by the instrument manufacturer.

8.4 *Magnesium Perchlorate ($Mg(ClO_4)_2$)—Anhydrous*—Used as a moisture trap. Use purity specified by the instrument manufacturer.

8.5 *Rare Earth/Copper Oxide*—Reagent used in some instruments to oxidize CO to CO_2. Use purity specified by the instrument manufacturer.

8.6 *Sodium Hydroxide Impregnated Clay*—Used to absorb CO_2 in the inert gas stream. Use purity specified by the instrument manufacturer.

8.7 *Methanol*—Used in sample preparation, see Section 10.

8.8 *Copper Pickle Solution*—Prepare a fresh solution of equal parts of concentrated nitric acid (HNO_3), concentrated acetic acid (CH_3OOH), and concentrated phosphoric acid (H_3PO_4). Used in sample preparation, see Section 10.

9. Hazards

9.1 For hazards to be observed in the use of certain reagents in this test method refer to Practice E50.

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

10. Sampling and Sample Preparation

10.1 Use only solid samples to minimize the potential for errors due to surface oxidation. Samples must be of the proper size to permit free introduction into the sample-loading device of the instrument. Sample weight range should be 0.5 to 2.0 g. Refer to instrument manufacturer's recommendations.

10.2 Cut the sample to an appropriate size using a silicon carbide, water-cooled cut-off wheel or by other means that will avoid overheating. Avoid oxide cutting or abrading materials.

10.3 Etch sample with concentrated hydrochloric acid (HCl) at 20°C for 3 minutes.

10.4 Etch sample in a mixture of equal parts of concentrated HNO_3, concentrated CH_3COOH, and concentrated H_3PO_4 at 70°C for one minute.

10.5 Rinse sample in three (3) successive distilled water rinses.

10.6 Rinse sample in three (3) successive methanol rinses.

10.7 Dry in a stream of hot air (hair drier).

10.8 Do not touch sample with fingers during and following the final stages of cleaning. Store the prepared sample in a desiccator. If samples are not analyzed within four hours of preparation, repeat 10.3-10.7 prior to analysis. (See Note 2.)

NOTE 2—Careful adherence to the sample preparation procedure described above is critical to obtaining accurate and precise results. The use of small and irregular shaped samples requires a diligent effort to ensure that all surface contamination has been removed.

11. Preparation of Apparatus

11.1 Assemble the apparatus as recommended by the manufacturer. Make the required power, gas, and water connections. Turn on the instrument and allow sufficient warm up time to stabilize the system.

11.2 Change the chemical reagents and filters as required. Test the furnace and the analyzer to insure the absence of leaks. Make a minimum of two determinations using a sample as directed in Section 13 to condition the instrument before attempting to calibrate the system or to determine the value of the blank.

11.3 Calibrate balance as recommended by the manufacturer using internal or external weights traceable to the SI (see IEEE /ASTM SI 10).

12. Calibration

12.1 *Calibration Reference Materials* (see Note 3)—Use only copper or copper alloy reference materials. Select four reference materials containing approximately 0.0005, 0.01, 0.03, and 0.04 % oxygen and designate them as Calibrants A, B, C, and D respectively.

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[6] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

NOTE 3—The oxygen content of the materials selected must fall within the scope stated by the standard test method, and within the analytical range of the determinator.

12.2 *Measurement System Conditioning*—Using a copper alloy reference material, or Calibrant C (see Note 4), proceed as directed in Section 13. Repeat until the absence of drift is indicated. Continue running a series of samples until the last four readings have a maximum range of 0.001 % oxygen.

NOTE 4—Due to availability and cost issues associated with many certified reference materials, it is acceptable to use more readily available and less expensive samples with known oxygen content of sufficient homogeneity to condition the measurement system. In some cases these copper alloy samples may be plated to prevent oxidation during storage. In this case they can be used without additional surface treatment.

12.3 *Determination of Blank Reading*—Proceed as directed in Section 13 with a graphite crucible containing graphite powder or carbon black (see Note 5) and analyze the graphite crucible with the sample omitted. Use a fresh crucible each time. Determine the average blank of at least three individual runs and enter this value into the appropriate mechanism of the instrument. Refer to the instrument manufacturer's instructions for proper blanking procedures.

NOTE 5—The addition of graphite powder or carbon black (0.05 to 0.5 g depending on crucible size and style) is designed to optimize furnace performance and facilitate the release of oxygen from the test sample. Refer to the instrument manufacturer's instructions for recommended graphite powder additions.

12.4 *Calibration Procedure:*

12.4.1 Prepare a minimum of four appropriate size specimens of Calibrant C as directed in Section 10.

12.4.2 Run a series of at least four samples of Calibrant C. Adjust the instrument calibration to provide a reading within ±0.0005 % of the known value for the Calibrant using the average of the last four readings. Refer to the manufacturer's instructions. Follow the calibration procedure recommended by the manufacturer using Calibrant C to determine the calibration slope. Weigh specimens to the nearest 1 mg. This copper oxygen reference material should have oxygen content greater than or approximately equal to the unknown samples within the scope of this test method (0.0005 and 0.04 %). Treat each specimen as directed in Section 13.

12.4.3 Confirm the calibration by analyzing an additional specimen of Calibrant C after the calibration procedure is completed. The value should agree with the assigned value for Calibrant C within a range of $\pm ts$ (95 % confidence level), where s is the standard deviation of the determinations of Calibrant C and t is the student's variable. If not, repeat the calibration procedure.

12.4.4 Prepare a minimum of four appropriate size specimens of Calibrant D as directed in Section 10.

12.4.5 Treat each specimen as directed in Section 13, before proceeding to the next one.

12.4.6 Record the results and compare them to the assigned value for Calibrant D. The average of the results should agree with the assigned value for Calibrant D within a range of $\pm t\,(s^2 + (U/2)^2)^{0.5}$, where s is the standard deviation of the determinations of Calibrant D and U is the expanded uncertainty (95 % confidence level) of the assigned value for Calibrant D (see Note 6). If not, refer to the instrument manufacturer's instructions for checking linearity of the system.

NOTE 6—The certificate of analysis may provide the value for the expansion factor for U. If it does, substitute that value for 2 in the denominator of the term $U/2$. It is possible that the certificate will give an uncertainty estimate that is not expanded. In that case, the value in the denominator should be 1.

12.4.7 Analyze Calibrants A and B following the same convention as Calibrants C and D in 12.4.1-12.4.6.

13. Procedure

13.1 Assemble apparatus, calibrate, set the blank, and test the performance as directed in Section 12.

13.2 Prepare an appropriate sized specimen, prepared as directed in Section 10, weighed to the nearest 1 mg, and transfer to the instrument sample-loading device. Refer to instrument manufacturer's instructions regarding entry of sample mass.

13.3 Place the crucible with carbon black or graphite powder into the determinator per the instrument manufacturer's instructions and start the crucible outgas cycle (see Note 7).

13.4 After the outgas cycle, transfer the sample to the crucible and start the analysis cycle (see Note 7).

NOTE 7—For some instruments this procedure is automatic.

13.5 Some instrument manufacturers recommend drift correction of the apparatus to accommodate for variances that may change calibration. Please refer to the manufacturers instructions with regards to these procedures.

NOTE 8—The user may drift correct the calibration per the instrument manufacturer's instructions utilizing an in-house or commercially available reference material; provided that it is sufficiently homogeneous and stable. Repeat the calibration when the process is determined to be out of control with the use of a control chart as described in Guide E882.

13.6 *Gas Dosing*—Automated and manual gas dosing (offered by some instrument manufacturers) can be used to check or drift correct the instrument, but instrument response must be confirmed as recommended by the instrument manufacturer. Please refer to the manufacturer's instructions.

14. Calculation

14.1 Follow the manufacturer's directions and related equations to ensure that all essential variables in the calculation of analysis results have been accounted for, including the blank, mass of sample, and calibration data. Because the output of most modern instruments is given directly in percent concentration, post-analysis calculations may not be required.

NOTE 9—If the determinator does not compensate for blank and sample weight values, then use the following equation:

$$\text{Oxygen}\ \% = \left[(A - B) \times C/D\right] \qquad (1)$$

where:

A = DVM reading for test sample,
B = DVM reading for blank,
C = weigh compensator setting,
D = test sample mass in grams, and
DVM = digital volt meter.

TABLE 1 Statistical Information—Oxygen in Copper

Test Material	Test Material	Number of Laboratories	Oxygen Found, %	Minimum SD (s_M, E1601)	Reproducibility (s_R, E1601)	Reproducibility Index (R, E1601)	R_{rel}, %
D	LECO In-House Reference Material[A]	8	0.00020	0.000038	0.000280	0.000785	390.0
A	NCS NS 41004	8	0.00049	0.000063	0.000264	0.000738	150.9
B	BCR No. 18	8	0.00738	0.000136	0.000266	0.000746	10.1
E	BCR No. 22	8	0.01418	0.000137	0.000311	0.000871	6.1
C	BCR No. 58	8	0.03962	0.000630	0.001115	0.003122	7.9
D	LECO In-House Standard[A]	7	0.00011	0.000024	0.000081	0.000228	214.7
A	NCS NS 41004	7	0.00041	0.000064	0.000131	0.000367	90.2

[A] LECO supplied in-house reference material; EXTINCT.

TABLE 2 Statistical Information—Check Standards

Test Material	Test Material	Number of Laboratories	Oxygen Found, %	Reproducibility (s_R, E1601)	Reproducibility Index (R, E1601)	R_{rel}, %
Initial Check	NIST SRM 885	8	0.03106	0.000175	0.000491	1.6
Final Check	NIST SRM 885	8	0.03095	0.000266	0.000743	2.4

TABLE 3 Test Material Information

Test Material	Certified Oxygen, %	B-value,[A] %	Material Identification (Source)	Description
A	0.00046	0.000029	NCS NS 41004	Pure copper
B	0.0070	0.00038	BCR No. 18	Phosphorus-deoxidized copper
C	0.0390	0.00062	BCR No. 58	Continuous cast copper rod
D	...	...	LECO In-House Standard[B]	OFHC copper
E	0.0138	0.00038	BCR No. 22	ETP copper
Check	0.031	...	NIST SRM 885	Refined Copper

[A] B-Value, *n-in statistics*, the difference between the mean of a set of results on a material and its accepted reference value.

[B] LECO supplied in-house reference material; EXTINCT.

TABLE 4 Oxygen Concentration (%)

Material	Average $\bar{x}$	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Index r	Reproducibility Index R
A	0.000489	0.000063	0.000264	0.000176	0.000738
B	0.00738	0.00014	0.00027	0.00038	0.00075
C	0.03962	0.00063	0.00112	0.00176	0.00312
D	0.000201	0.000038	0.000280	0.000105	0.000785
E	0.01418	0.00014	0.00031	0.00038	0.00087
Check	0.03101	N/A	0.00022	N/A	0.00062

15. Precision and Bias[7]

15.1 *Precision*—The accuracy of this test method may be judged by comparing the results obtained from certified reference materials with their certified values. Eight laboratories cooperated in testing samples A through E and an additional check standard. The data obtained are presented in Table 1 for the test materials and Table 2 for the check standard.

NOTE 10—The precision of this test method is based on an interlaboratory study of this test method conducted in 2006. Each of eight laboratories tested five different copper specimens and one standard reference material (as an initial and final check standard). Every “test result” represents an individual determination. All participating laboratories reported triplicate test results (analyzed by one operator) for each specimen type. Table 3 contains test material information.

15.1.1 *Repeatability*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the “*r*” value for that material; *“r”* is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

15.1.2 *Reproducibility*—Two test results shall be judged not equivalent if they differ by more than the “*R*” value for that material; “*R*” is the interval representing the difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1108.

15.1.3 Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

15.2 *Bias*—The analysis of NIST SRM 885 was incorporated into this interlaboratory study. The certified value of oxygen (percent by weight) based on the results of a cooperative program for certification is 0.031, with an uncertainty of 0.002. With eight laboratories each reporting two results for the analysis of NIST SRM 885, the average value reported was 0.031 with a standard deviation of 0.0002, showing no apparent bias.

15.3 The precision statistics were determined through statistical examination of 136 results, from eight laboratories, on six materials. See Table 4 for the summary statistics. The six materials were identified in Table 3. To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

16. Keywords

16.1 copper; copper alloys; inert gas fusion; infrared; oxygen content; thermal conductivity

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