Standard Test Method for Determination of Low Levels of Antimony in Carbon and Low-Alloy Steel by Graphite Furnace Atomic Absorption Spectrometry[1]

This standard is issued under the fixed designation E1852; 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 antimony in carbon and low-alloy steel in the 0.0005 % through 0.010 % range.

1.2 If this test method is used to test materials having contents less than 0.001 % antimony, users of different laboratories will experience more than the usual 5 % risk that their results will differ by more than 50 % relative error.

1.3 *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

E1184 Practice for Determination of Elements by Graphite Furnace Atomic Absorption Spectrometry

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1770 Practice for Optimization of Electrothermal Atomic Absorption Spectrometric Equipment

E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

2.2 *ISO Standards:*[3]

ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for a Standard Test Method by Inter-Laboratory Tests

ISO 10698 Steel—Determination of Antimony Content—Electrothermal Atomic Absorption Spectrometric Method

3. Terminology

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

4. Summary of Test Method

4.1 The sample is dissolved in hydrochloric and nitric acids and diluted to volume. An appropriate aliquot is injected into the graphite furnace atomizer of an atomic absorption spectrometer, which is equipped with a background correction. The sample is dried, pyrolized, and atomized. The absorbance of the radiation from the external light source is measured and compared to the absorbance of samples of known composition.

NOTE 1—In general, the deuterium correction system should be able to correct for the broad-band background absorbance up to 0.5 to 0.6 absorbance units. Zeeman systems should compensate for background levels as high as 1.0 to 1.5 absorbance units.

5. Significance and Use

5.1 This test method is utilized for the determination of trace levels of antimony in carbon and low-alloy steel. It is assumed that the procedure will be performed by trained analysts capable of performing common laboratory practices skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory and proper waste disposal procedures will be followed.

6. Hazards

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

---

[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 E01.01 on Iron, Steel, and Ferroalloys.

Current edition approved Nov. 15, 2013. Published January 2014. Originally approved in 1996. Last previous edition approved in 2008 as E1852 – 08. DOI: 10.1520/E1852-13.

[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 American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

7. Apparatus

7.1 *Atomic Absorption Spectrometer with Graphite Furnace Atomizer,* equipped with background corrector and appropriate signal output device, such as video display screen, digital computer, printer or strip chart recorder, and autosampler. It is recommended that the instrument meet the following performance requirements after adjusting the instrument and optimizing the furnace heating program as described in Practice E1770.

7.1.1 The characteristic mass determined in accordance with Practice E1770 for antimony shall be less than 25 pg or within the manufacturer's tolerance.

7.1.2 The precision of the most concentrated blank addition solution shall not exceed 10 % of the mean absorbance of the same solution. The precision of the least concentrated blank addition solution (excluding Solution B_0) shall not exceed 4 % of the mean absorbance of the most concentrated blank addition solution when determined in accordance with Practice E1770.

7.1.3 The limit of detection of antimony as described in Practice E1770 shall be less than 20 pg.

7.1.4 Unless the instrument is provided with automatic curve correction circuitry, the graph linearity shall not be less than 0.95 when determined in accordance with Practice E1770.

7.2 *Graphite Tubes,* with pyrolytic coating and grooves for graphite platform, suitable for use with the graphite furnace unit.

7.3 *Graphite Platform,* pyrolytic graphite, L'vov design, to fit graphite tubes specified in 7.2.

7.4 *Labware*—To prevent contamination of the sample(s), all beakers, lids, volumetric flasks, and funnels must be cleaned with hot HNO_3 (1 + 1) before use.

8. Reagents

8.1 *Purity and Concentration of Reagents*—The purity and concentration of common chemical reagents shall conform to Practices E50. It is important that antimony shall not exceed 0.01 µg/mL in each of the reagents and 0.001 µg/mL in the water.

8.2 *Antimony Stock Solution (1 mL = 1 mg Sb)*—Dissolve 0.1000 g ± 0.0001 g high-purity antimony (minimum 99.9 % Sb) in 30 mL HCl + 5 mL HNO_3 in a 100-mL beaker. Boil gently to expel oxides of nitrogen. Cool and transfer the solution into a 100-mL volumetric flask. Dilute to mark with HNO_3 (1 + 1) and mix. Store in polypropylene or high density polyethylene bottle.

8.3 *Antimony Standard Solution (1 mL = 10 µg Sb)*—Transfer 1.0 mL of the antimony stock solution to a 100-mL volumetric flask, dilute to the mark with HNO_3 (1 + 1), and mix. Prepare this solution immediately before use.

9. Sampling and Sample Preparation

9.1 Refer to Practice E1806 for devices and practices to sample liquid and solid steel.

9.2 The sampling procedures shall not involve any steps or operations that can result in the loss of antimony in the sample.

NOTE 2—Arc melting of the sample or induction melting of the sample under vacuum may result in significant loss of several elements that have a low vapor pressure. Arc melting of the sample should be avoided and induction melting should be performed only in an at least partial inert atmosphere.

9.3 The laboratory sample shall be cleaned by first washing in acetone and air drying.

9.4 If brazed alloy tools are used in the preparation of the sample, the sample shall be further cleaned by pickling in diluted nitric acid for a few minutes. The sample shall then be washed several times with water, then several times with acetone and air dried.

10. Procedure

10.1 *Sample Mass*—For samples containing between 0.0005 % and 0.0050 % antimony, the sample mass shall be ≈1.00 g, weighed to the nearest 0.1 mg. For samples containing between 0.0050 % and 0.010 % antimony, the sample shall be ≈0.25 g weighed to the nearest 0.1 mg.

10.2 *Blank*—Simultaneously with the sample, a blank test using the same quantities of all reagents shall be performed. The antimony contents of the blank should be no greater than 10 ng/mL.

10.3 *Test Solution*—Transfer the test portion in accordance with 10.1 into a 250-mL beaker. Add 5 mL HCl and 50 mL HNO_3. Cover the beaker with a watch glass, heat gently until the reaction ceases, and boil for 1 min to remove the oxides of nitrogen.

10.3.1 If sample contains tungsten or niobium, or both, transfer the test portion to a 100-mL beaker and add 1 mL H_3PO_4, 15 mL HCl, and 5 mL HNO_3. Cover beaker with watch glass, and heat gently until reaction ceases. Evaporate the solution to 2 mL to 3 mL; then add 25 mL nitric acid. Boil for 1 min to remove oxides of nitrogen. Conduct a separate blank test corresponding to this procedure.

10.3.2 Allow the solution, which may contain carbides, to cool. Add about 15 mL water, filter through medium texture filter paper, and collect the filtrate in a 200-mL volumetric flask. Wash the filter paper several times with warm water and collect the washings in the flask. Dilute to the mark with water and mix.

10.4 *Test Addition Solutions*—Transfer separate 20.0-mL aliquots of the test solution into a series of five 100-mL volumetric flasks. Using a micropipette, inject the respective volumes of antimony standard solution indicated in Table 1.

TABLE 1 Test Addition Solutions

Name of Solution	Volume of Antimony Standard Solution Added, µL	Concentration of Antimony Added in Test Addition Solutions, ng/mL	Corresponding Mass of Antimony Added, ng	
			Volume Injected, 10 µL	Volume Injected, 50 µL
S_0	0	0	0.0	0.0
S_1	100	10	0.1	0.5
S_2	200	20	0.2	1.0
S_3	400	40	0.4	2.0
S_4	500	50	0.5	2.5

Dilute to the mark with water and mix. These solutions are referred to as S_0, S_1, S_2, S_3, and S_4, respectively.

10.5 *Blank Addition Solutions*—Transfer separate 20.0-mL aliquots of the blank solution into a series of five 100-mL volumetric flasks. Using a micropipette, add the respective volumes of antimony standard solution indicated in Table 2. Dilute to the mark with water and mix. These solutions are referred to as B_0, B_1, B_2, B_3, and B_4, respectively.

10.6 Optical parameters used for the determination of antimony are given in Table 3.

10.7 The atomic absorption spectrometer and the graphite furnace atomizer should be adjusted and optimized as described in Practices E1184 and E1770.

NOTE 3—The volume injected into the atomizer should be between 10 µL and 50 µL, depending on sensitivity, matrix interference, background correction, and range of linearity. The volume 20 µL is usually correct.

10.8 Using the autosampler, inject the predetermined volume of the test solution and blank addition solutions in increasing order into the atomizer. Atomize each solution three times. Record the three peak height readings.

NOTE 4—In most instances, the use of peak area integration is preferable.

10.9 Check the instrument for memory effects, especially at high analyte levels, by running the blank firing program. Reset the baseline to zero if necessary. Record the peak height reading for each determination (see Note 4).

11. Plotting of Additions Graphs

11.1 Calculate the average instrument readings for each of the blank addition solutions of 10.5 "B" against the mass of antimony added, expressed in nanograms, in the blank addition solutions.

11.2 Calculate the average instrument readings for each of the test addition solutions of 10.4 "S" against the mass of antimony added, expressed in nanograms, in the test addition solutions.

NOTE 5—In this test method, any nonspecific absorption effect is eliminated by the background correction of the instrument. Antimony may be present in the reagents. If antimony is present in the reagents, this plot may not pass through the origin.

11.3 The standard additions graphs for the blank and the sample should be parallel.

TABLE 2 Blank Addition Solutions

Name of Solution	Volume of Antimony Standard Solution Added, µL	Concentration of Antimony Added in Blank Addition Solutions, ng/mL	Corresponding Mass of Antimony Added, ng	
			Volume Injected, 10 µL	Volume Injected, 50 µL
B_0	0	0	0.0	0.0
B_1	100	10	0.1	0.5
B_2	200	20	0.2	1.0
B_3	400	40	0.4	2.0
B_4	500	50	0.5	2.5

TABLE 3 Optical Parameters for Antimony Determination

Item	Parameter
Radiation Source	electrodeless discharge lamp (EDL) or hollow cathode lamp
Lamp Current	As recommended by lamp manufacturer
Slit	As recommended by instrument manufacturer
Wavelength	217.6 nm
Background Corrector	yes

12. Calculation

12.1 Most graphite furnace atomizers controlled by computers will calculate the means, establish their own calibration curves, and calculate and display the results. If using instruments not having this capability, prepare the calibrations graphs and perform the calibration in accordance with 12.2 and 12.3.

12.2 Determine the mass of antimony in the test and blank addition solutions, $m_{Sb.1}$ and $m_{Sb.0}$, respectively, expressed in nanograms, as the two intercepts on the mass axis by extrapolating the resulting straight lines in the two additions graphs (see 11.1 and 11.2). The difference ($m_{Sb.1} - m_{Sb.0}$) gives the net mass of antimony, m_{Sb}, in the test solution (Solution S_1).

12.2.1 The net mass of antimony, m_{Sb}, may also be calculated using the least-square-fit method applied to the two straight lines, the blank addition solutions (solutions "B"), and the test addition solutions (solutions "S"). The equation of the straight line relating absorbance to mass is as follows:

$$y = a + bm \tag{1}$$

where:

a and b = constants that correspond respectively to the intercept on the y axis and the slope of the straight line. Calculate b and a using the least-square-fit method as follows:

$$b = \left[n\sum m_i y_i - \sum m_i \sum y_i\right] / \left[n\sum m_i{}^2 \left(\sum m_i\right)^2\right] \tag{2}$$

$$a = (1/n)\left(\sum y_i - b\sum m_i\right)$$

The intercept on the x axis with the straight line of the slope b is ($-a/b$):

$$m_{Sb.1} = (1/nb_1)\left(\sum y_i - b_1\sum m_i\right) \tag{3}$$

$$m_{Sb.0} = (1/nb_0)\left(\sum y_i - b_0\sum m_i\right)$$

$$m_{Sb} = m_{Sb.1} - m_{Sb.0}$$

TABLE 4 Reference Materials Used for Testing the Method

Test Material	Designation of Reference Material	Composition, %				
		Sb	Cr	Ni	Mn	Mo
A	SND 70	0.00025[A]	19.89	24.82	(1.74)	4.52
B	JK 8F	0.0005	16.91	11.01	1.557	7.775
C	JSS.SS	0.0014[A]	16.61	13.45	1.76	2.77
D	SDN 629290	0.0024[A]	...	30.25	...	...
E	ECRM 087-1	0.0046	0.078	0.118	0.671	0.021
F	ECRM 085-1	0.0073	...	...	0.977	...
G	BCS 456	0.0120	...	...	0.20	...

[A] Not certified value.

TABLE 5 Summary of Interlaboratory Testing Results

Test Material	Number of Data Sets Used	Certified Antimony	Antimony Found, % (Material Mean)	Minimum Standard Deviation, S_M (E1601)	Reproducibility Standard Deviation, S_R (E1601)	Reproducibility Index, *R* (E1601)	$R_{rel\ \%}$
A	19	0.00025[A]	0.000299	0.00005668	0.00012919	0.00036174	120.9
B	18	0.0005	0.000534	0.00009188	0.00016342	0.00045757	85.75
C	18	0.0014[A]	0.00135	0.00010526	0.00017933	0.00050212	37.26
D	19	0.0024[A]	0.002331	0.00015778	0.00033219	0.00093012	39.91
E	19	0.0046	0.004389	0.00048664	0.00067564	0.00189179	43.10
F	19	0.0073	0.00715	0.00055260	0.00091573	0.00256406	35.88
G	19	0.0120	0.0126	0.00061124	0.00237178	0.00664100	52.68

[A] Not certified value.

where:

b = coefficient of regression;
n = number of solutions analyzed;
a = intercept on the y axis;
m_i = mass of antimony added in the test or blank addition solutions, ng;
y_i = absorbance corresponding to the test or blank addition solutions;
$m_{Sb.1}$ = mass of the antimony obtained from the test addition solutions, ng;
$m_{Sb.0}$ = mass of the antimony obtained from the blank addition solutions, ng; and
m_{Sb} = mass of antimony in the test addition solution (S_0), ng.

12.3 The antimony content, w_{Sb}, as a percentage by mass is obtained from the equation as follows:

$$w_{Sb} = 100[m_{Sb}(10^5 V_2/V_1)(V_4/V_3)]/10^9\ m \quad (4)$$

$$= 100[m_{Sb}(10^5/V_1)(200/20)]/10^9 m = 0.1\, m_{Sb}/mV_1$$

where:

V_1 = volume injected of a series of test addition solutions and of the blank addition solution (see Table 1 and Table 2), µL;
V_2 = volume of a series of test addition solutions and blank addition solutions (see 10.4 and 10.5), mL;
V_3 = volume of the aliquot of the test and blank solution (see 10.4 and 10.5), mL;
V_4 = volume of the test and blank solutions (see 10.3.2), mL; and
m = mass of the test portion in 10.1, g.

13. Precision and Bias

13.1 *Precision*—Sixteen laboratories cooperated in testing this method and obtained the statistical information summarized in Table 4 and Table 5.

13.2 *Bias*—The accuracy of this test method at certain concentration levels may be judged by comparing the accepted reference values with the arithmetic average obtained by interlaboratory testing (see Table 4 and Table 5).

13.3 *Interlaboratory Studies (ILS)*[4]—This test method was evaluated by a working group within ISO Technical Committee 17 on Iron and Steel (ISO/TC 17SC 1/WG) in accordance with ISO Standard 5725. It was published as ISO 10698. The original ILS data from document ISO/TC 17SC 1 N886 (11/19/1991) was recalculated in accordance with Practice E1601 as summarized in 13.1 and 13.2.

14. Keywords

14.1 antimony; antimony in steel; atomic absorption spectrometry; flameless atomic absorption spectrometry; graphite furnace atomic absorption spectrometry; graphite furnace analysis; trace element determination

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1018.

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 ASTM website (www.astm.org/ COPYRIGHT/).