



Standard Test Method for Determination of Total Sulfur in Iron Ores and Related Materials by Combustion-Iodate Titration¹

This standard is issued under the fixed designation E 395; 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 total sulfur in iron ores, concentrates, agglomerates, and related materials in the concentration range from 0.007 to 0.50 %.

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:

D 1193 Specification for Reagent Water²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁴

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁴

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁵

E 877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials⁶

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁶

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method⁶

3. Terminology

3.1 *Definitions*—For definitions of terms used in this Test Method, refer to Terminology E 135.

4. Summary of Test Method

4.1 The sulfur in the test sample is converted to sulfur dioxide by combustion in a stream of oxygen. The sulfur dioxide is absorbed in an acidified starch-iodide solution and titrated with potassium iodate solution. The potassium iodate solution is standardized against a similar type ore of known sulfur content since the percentage of sulfur evolved as sulfur dioxide varies with different materials.

5. Significance and Use

5.1 This test method is intended to be used for compliance with compositional specifications for sulfur content. It is assumed that all who use these procedures 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 and that proper quality control procedures will be followed, such as those described in Guide E 882.

6. Interferences

6.1 Halogens interfere with this test method.

7. Apparatus

7.1 *Induction Heating Apparatus* for determination of sulfur by direct combustion.

7.1.1 The apparatus must be suitable for the combustion of the sample in oxygen to form sulfur dioxide (SO_2) and must provide an absorption vessel in which the SO_2 is titrated. A typical arrangement is shown in Fig. 1.

7.1.2 *Oxygen Purifiers*—The regular commercial tank oxygen is satisfactory. It must be passed through two pressure reduction valves (approximately 207 kPa (30 psig) and 14 to 28 kPa (2 to 4 psig), respectively) or a suitable two-stage reduction valve to provide an even and adequate flow of oxygen through a tower containing H_2SO_4 and through an absorption tower containing 20 to 30-mesh inert base impregnated with NaOH and anhydrous magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$). A flowmeter and quick-acting shut-off valve for use during preheating periods must precede the resistance furnace assembly. A flowmeter must also precede the induction furnace assembly.

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 E01.02 on Ores, Concentrated, and Related Metallurgical Materials.

Current edition approved March 10, 2002. Published May 2002. Originally published as E 395 – 70. Last previous edition E 395 – 95a.

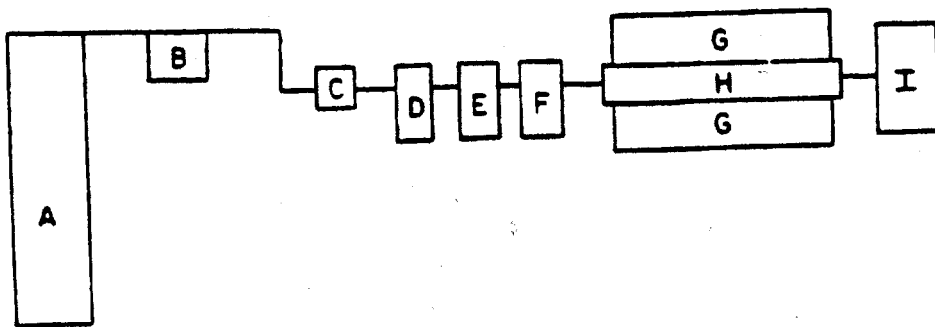
² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

⁵ Discontinued; see 1997 *Annual Book of ASTM Standards*, Vol 03.05.

⁶ *Annual Book of ASTM Standards*, Vol 03.06.



- A—Oxygen Tank
- B—Reduction valve
- C—Quick-acting shut-off valve
- D—Tower containing H_2SO_4
- E—Tower containing CO_2 absorber and anhydrous $Mg(ClO_4)_2$
- F—Flowmeter
- G—Furnace, induction
- H—Combustion tube
- I—Absorption and titration assembly

FIG. 1 Typical Arrangement for Determination of Sulfur by the Direct-Combustion Method

7.1.3 *Combustion Furnace*—Induction Heating: The combustion is accomplished by induction heating. A rheostat to control the power input to the induction coil is required to avoid heating some types of samples too rapidly during the early stages of combustion. The combustion zone of the induction furnace must amply provide for adequate heating of the sample.

7.1.4 *Combustion Tube*—The tube must be of a suitable size to fit the particular furnace used and have an inside diameter large enough to accommodate the crucible and cover. A tapered-end tube is recommended.

7.1.5 *Combustion Crucibles*—The crucibles for use with the furnace must be of adequate thickness to retain the molten slag and have a blank as low and consistent as possible. The crucibles must have adequate capacity and may be provided with suitable covers. The blank requirements that apply to the crucibles also apply to their covers. Prior to use, crucibles and covers must be pre-fired at least 15 min at $1100^\circ C$ and then stored in a desiccator.

7.1.6 *Filter*—Suitable precautions must be taken to prevent metallic oxides from entering the titration vessel.

7.1.7 *Connections*—Connection between the outlet end of the combustion tube and the absorption and titration assembly must be as short and free of bends as possible, with glass connections butted to minimize areas of rubber tubing exposed to gases. All rubber tubing must be essentially free of sulfur.

7.1.8 *Absorption and Titration Apparatus*—The apparatus should consist of an absorption and titration vessel of appropriate volume and containing an inlet bubbler tube for the sulfur gases with a float valve to prevent back flow of liquid when the sample is starting to consume oxygen. The vessel must be shaped to effect complete absorption of SO_2 in a small volume of solution. The buret should be approximately 10 mL in capacity. Automatic titrations which utilize a photoelectric cell to activate a solution inlet valve are commercially available and may be used.

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.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

8.3 *Copper (Low-Sulfur) Accelerator*, chips or rings.

8.4 *Hydrochloric Acid (3+97)*—Add 3 volumes of concentrated hydrochloric acid (HCl) (sp gr 1.19) with 97 volumes of water.

8.5 *Iron (Low-Sulfur) Accelerator*, chips or powder.

8.6 *Potassium Iodate, Standard Solution* (1 mL = 0.1 mg S)—Dissolve 0.2225 g of potassium iodate (KIO_3) in 900 mL of water and dilute to 1 L.

NOTE 1—The sulfur equivalent is based on the complete conversion of sulfur to sulfur dioxide. The recovery of sulfur as the dioxide is less than 100 %, but is consistent when the temperature and the rate of oxygen flow are maintained constant. An empirical factor must be determined by an analysis of a standard sample.

8.7 *Starch-Iodide Solution*—Transfer 1 g of soluble or arrowroot starch to a small beaker, add 2 mL of water, and stir until a smooth paste is obtained. Pour the mixture into 50 mL of boiling water. Cool, add 1.5 g of potassium iodide (KI), stir until dissolved, and dilute to 100 mL.

⁷ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

NOTE 2—This solution shall be prepared daily.

8.8 *Tin (Low-Sulfur) Accelerator*, granules.

9. Hazards

9.1 For precautions to be observed in this Test Method, refer to Practices E 50. Use care when handling crucibles and when operating furnaces to avoid personal injuries such as burn or electrical shock.

10. Sampling and Sample Preparation

10.1 The gross sample shall be collected and prepared in accordance with Practice E 877.

10.2 The laboratory sample shall be pulverized to pass a No. 100 (150- μ m) sieve.

10.3 Weigh to ± 25 mg an amount of prepared sample specified as follows:

Content of Sulfur, %	Weight of Sample, g
0.005 to 0.025	2.0
0.020 to 0.10	1.0
0.10 to 0.25	0.5
0.25 to 0.50	0.2

11. Procedure

11.1 Transfer the test sample to a small, dry weighing bottle and place in a drying oven. After drying at 105 to 110°C for 1 h, cap the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize pressure and weigh the capped bottle to the nearest 0.001 g. Repeat the drying and weighing until there is no further weight loss. Transfer the test sample to a pre-ignited crucible and reweigh the capped bottle to the nearest 0.001 g. The difference between the two weights is the weight of the test sample.

11.2 To the crucible add 1 g of iron, 0.9 g of tin, and 1 copper ring or 0.6 g of copper chips and cover.

11.3 Select a standard sample ore, similar in type and sulfur content to the test sample. Weigh, dry, transfer to a pre-ignited crucible, and add the accelerators as in 11.1 and 11.2.

11.4 Turn on the power of the induction furnace and allow the unit to warm up. With oxygen bubbling through the absorption vessel, fill it to a pre-determined point with HCl (3+97) (Note 3). Add 2 mL of starch solution to the vessel. With the oxygen flow adjusted to 1.0 to 1.5 L/min (Note 4), add KIO₃ solution until the intensity of the blue color is that which is to be taken as the end-point. Refill the buret.

NOTE 3—Always fill the titration vessel to the same point.

NOTE 4—The oxygen flow rate may be adjusted to meet the requirements of individual operators or equipment; however, the flow rate must be the same for the test samples and the standard samples.

11.5 After the unit has warmed up for at least 45 s, place the covered crucible containing the standard sample and accelerators on the pedestal. With the oxygen flow adjusted, raise the crucible, close the furnace, and turn on the power. Burn the sample for 8 to 10 min. Titrate continuously with the KIO₃ solution at such a rate as to maintain as nearly as possible the original intensity of the blue color. The end point is reached when the original blue color is stable for 1 min without further addition of KIO₃ solution. Record the final buret reading and drain the titration vessel through the exhaust stopcock.

NOTE 5—If the blue color in the cell disappears or white fumes escape the surface of the cell, low bias may result.

11.6 Refill the titration vessel with the HCl (3+97), add 2 mL of the starch solution, and titrate with the KIO₃ solution to the pre-selected end-point color. Refill the buret, place the covered crucible containing the test sample and accelerators on the pedestal of the furnace, and proceed as in 11.5.

12. Blank

12.1 Determine the blank by placing the same amount of accelerators used in the test sample in a pre-ignited crucible. Cover and proceed as in 11.5.

13. Calculation

13.1 Calculate the sulfur factor of the potassium iodate as follows:

$$\text{Sulfur factor, g/unit volume } F = (A \times B) / [(C - D) \times 100] \quad (1)$$

where:

A = standard sample used, g,

B = sulfur in the standard sample, %,

C = KIO₃ solution required for titration of the standard sample (Note 6), mL, and

D = KIO₃ solution required for titration of the blank (Note 6) mL.

NOTE 6—Or apparent percentage of sulfur for “direct-reading” burets.

13.2 Calculate the percentage of sulfur in the test sample as follows:

$$\text{Sulfur, \%} = [(E - D)F/G] \times 100 \quad (2)$$

where:

E = KIO₃ solution required for titration of the test sample (Note 5),

D = millilitres of KIO₃ solution required for titration of the blank,

F = sulfur factor of the KIO₃ solution in g/unit volume, and

G = grams of test sample used.

14. Report

14.1 Round the test results that are less than 0.01 % to the nearest 0.001 % in accordance with Practice E 29.

14.2 Report results below the lower scope limit as approximate, for example: ~ 0.000 , ~ 0.001 , ... ~ 0.006 .

14.3 Round test results in the range of 0.01 to 0.50 % to the nearest 0.01 % in accordance to Practice E 29, rounding method.

14.4 Report results greater than 0.5 % as >0.5 %.

15. Precision and Bias

15.1 *Precision*—Nine laboratories cooperated in obtaining the data summarized in Table 1.

15.2 *Bias*—No information on the bias of this test method is known. Accepted reference materials were not included in the materials used in the interlaboratory study. Users of the test method are encouraged to employ accepted reference materials, if available, and to judge the bias of the method from the difference between the accepted value for the sulfur concentration and the mean value from interlaboratory testing of the reference material.

16. Keywords

16.1 agglomerates; concentrates; iron ores; sulfur content

TABLE 1 Statistical Information

Average Sulfur Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
0.004	0.0016	0.0033
0.054	0.0033	0.0147
0.15	0.010	0.022
0.25	0.012	0.029
0.45	0.023	0.024

NOTE 1—For methods tested according to Practice E 173, the reproducibility, R_2 , of Practice E 173 corresponds to the reproducibility index, R , of Practice E 1601. The repeatability, R_1 , of Practice E 173 corresponds to the repeatability index, r , of Practice E 1601.

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).