



# Standard Test Method for Sulfur in Petroleum Products (High-Temperature Method)<sup>1</sup>

This standard is issued under the fixed designation D1552; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope\*

1.1 This test method covers three procedures for the determination of total sulfur in petroleum products including lubricating oils containing additives, and in additive concentrates. This test method is applicable to samples boiling above 177°C (350°F) and containing not less than 0.06 mass % sulfur. Two of the three procedures use iodate detection; one employing an induction furnace for pyrolysis, the other a resistance furnace. The third procedure uses IR detection following pyrolysis in a resistance furnace.

1.2 Petroleum coke containing up to 8 mass % sulfur can be analyzed.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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:<sup>2</sup>

D1193 Specification for Reagent Water

D1266 Test Method for Sulfur in Petroleum Products (Lamp Method)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6792 Practice for Quality System in Petroleum Products

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Dec. 1, 2008. Published December 2008. Originally approved in 1958. Last previous edition approved in 2007 as D1552-07. DOI: 10.1520/D1552-08.

<sup>2</sup> 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.

## and Lubricants Testing Laboratories

## 3. Summary of Test Method

3.1 *Iodate Detection System*—The sample is burned in a stream of oxygen at a sufficiently high temperature to convert about 97 % of the sulfur to sulfur dioxide. A standardization factor is employed to obtain accurate results. The combustion products are passed into an absorber containing an acid solution of potassium iodide and starch indicator. A faint blue color is developed in the absorber solution by the addition of standard potassium iodate solution. As combustion proceeds, bleaching the blue color, more iodate is added. The amount of standard iodate consumed during the combustion is a measure of the sulfur content of the sample.

3.2 *IR Detection System*—The sample is weighed into a special ceramic boat which is then placed into a combustion furnace at 1371°C (2500°F) in an oxygen atmosphere. Most sulfur present is combusted to SO<sub>2</sub> which is then measured with an infrared detector after moisture and dust are removed by traps. A microprocessor calculates the mass percent sulfur from the sample weight, the integrated detector signal and a predetermined calibration factor. Both the sample identification number and mass percent sulfur are then printed out. The calibration factor is determined using standards approximating the material to be analyzed.

## 4. Significance and Use

4.1 This test method provides a means of monitoring the sulfur level of various petroleum products and additives. This knowledge can be used to predict performance, handling, or processing properties. In some cases the presence of sulfur compounds is beneficial to the product and monitoring the depletion of sulfur can provide useful information. In other cases the presence of sulfur compounds is detrimental to the processing or use of the product.

## 5. Interferences

5.1 For the iodate systems, chlorine in concentrations less than 1 mass % does not interfere. The IR system can tolerate somewhat higher concentrations. Nitrogen when present in excess of 0.1 mass % may interfere with the iodate systems; the extent of such interference may be dependent on the type of

\*A Summary of Changes section appears at the end of this standard.

nitrogen compound as well as the combustion conditions. Nitrogen does not interfere with the IR system. The alkali and alkaline earth metals, as well as zinc, phosphorus, and lead, do not interfere with either system.

## 6. Apparatus

### 6.1 Combustion and Iodate Detection System:

6.1.1 *Furnaces*—Two major types are available, the primary difference being the manner in which the necessary high temperatures are obtained. These two types are as follows:

6.1.1.1 *Induction Type*, which depends upon the high-frequency electrical induction method of heating. This assembly shall be capable of attaining a temperature of at least 1482°C (2700°F) in the sample combustion zone, under the conditions set forth in 9.1 and shall be equipped with an additional induction coil located above the combustion zone, substantially as shown in Fig. 1.

6.1.1.2 The furnace work coil should have a minimum output of 500 W; the minimum input rating of the furnace must be 1000 W. With the correct amount of iron chips, weighed to  $\pm 0.05$  g, the maximum plate current will be between 350 and 450 mA. (**Warning**—This type of furnace is capable of inflicting high frequency burns and high-voltage shocks. In addition to other precautions, maintain all guards properly.) (**Warning**—Disconnect the furnace from the power line whenever electrical repairs or adjustments are made.)

6.1.1.3 *Resistance Type*, capable of maintaining a temperature of at least 1371°C (2500°F).

6.1.2 *Absorber*, as described in Test Method D1266.

NOTE 1—Also suitable for use with either type of furnace is an automatic titrator, specifically designed for iodometry. This combines the functions of absorption and titration to a predetermined end point.

6.1.3 *Buret*, standard 25-mL or automatic types available from the manufacturers of the specific combustion units, are suitable (Note 1).

6.2 *Combustion and IR Detection System*, comprised of automatic balance, oxygen flow controls, drying tubes, combustion furnace, infrared detector and microprocessor. The furnace shall be capable of maintaining a nominal operating temperature of 1350°C (2460°F).<sup>3</sup>

6.3 *Miscellaneous Apparatus*—Specific combustion assemblies require additional equipment such as crucibles, combustion boats, crucible lids, boat pushers, separator disks, combustion tubes, sample inserters, oxygen flow indicator, and oxygen drying trains. The additional equipment required is dependent on the type of furnace used and is available from the manufacturer of the specific combustion unit. To attain the lower sulfur concentration given in Section 1, the ceramics used with the induction furnace assembly shall be ignited in a muffle furnace at 1371°C (2500°F) for at least 4 h before use.

6.4 *Sieve*, 60-mesh (250- $\mu$ m).

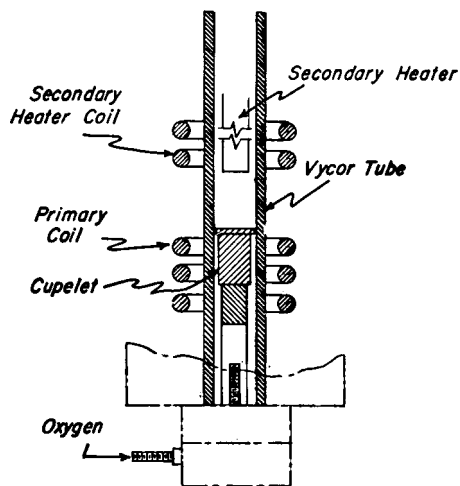


FIG. 1 Combustion Tube

## 7. Reagents and Materials

7.1 *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.<sup>4</sup> 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II or III of Specification D1193.

7.3 *Alundum* ( $\text{Al}_2\text{O}_3$ ) or *Magnesium Oxide* (Com-Aid).

7.4 *Anhydrone* (*Magnesium Perchlorate*). (**Warning**—In addition to other precautions, handle magnesium perchlorate with care. Avoid contacting it with acid and organic materials. Reactions with fuel may be violent.)

7.5 *Hydrochloric Acid* (3 + 197)—Dilute 30 mL of concentrated hydrochloric acid (HCl, relative density 1.19) to 2 L with water. (**Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns.)

7.6 *Oxygen* (*Extra Dry*)—The oxygen shall be at least 99.5 % pure and show no detectable sulfur by blank determination. (**Warning**—Oxygen vigorously accelerates combustion.)

7.7 *Phosphorus Pentoxide*—( $\text{P}_2\text{O}_5$ ).

7.8 *Potassium Alum* (*Aluminum Potassium Sulfate*).

7.9 *Potassium Iodate, Standard Solution* (0.06238 N), 1 mL of this solution is equivalent to 1 mg S—Dissolve 2.225 g of potassium iodate ( $\text{KIO}_3$ ) that has been dried at about 180°C to constant weight, in water and dilute to 1 L. Thoroughly mix the solution.

7.10 *Potassium Iodate, Standard Solution* (0.006238 N), 1 mL of this solution is equivalent to 0.1 mg S—Measure

<sup>3</sup> The sole source of supply of Models SC32 or SC132 known to the committee at this time is LECO Corp., 3800 Lakeview Ave., St. Joseph, MI 49085-2396. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>4</sup> *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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

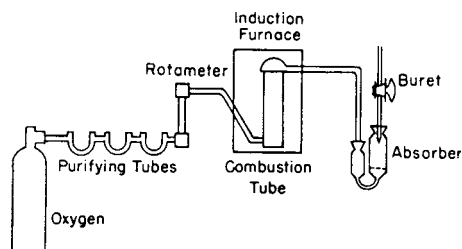


FIG. 2 Schematic Illustration of Induction-Type Furnace

exactly 100 mL of  $\text{KIO}_3$  solution (0.06238 N) into a 1-L volumetric flask, and dilute to volume with water. Thoroughly mix the solution.

7.11 *Potassium Iodate, Standard Solution* (0.01248 N), 1 mL of this solution is equivalent to 0.2 mg S—Measure exactly 200 mL of  $\text{KIO}_3$  solution (0.06238 N) into a 1-L volumetric flask and dilute to volume with water. Thoroughly mix the solution.

7.12 *Ascarite*, 8 to 20 mesh.

7.13 *Special Materials for Induction-Type Furnaces:*

7.13.1 *Tin* (20 to 30-mesh).

7.13.2 *Iron-Chip Accelerator* having a sulfur content of not more than 0.005 mass %.

7.14 *Standard Sample*—Potassium alum ( $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ).

7.15 *Starch-Iodide Solution*—Make a paste by adding 9 g of soluble starch to 15 mL of water. Add this mixture, with stirring, to 500 mL of boiling water. Cool the mixture, add 15 g of potassium iodide (KI), and dilute to 1 L with water.

7.16 *Sulfuric Acid (relative density 1.84)*—Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ). (**Warning**—Poison. Corrosive. Strong oxidizer.)

7.17 *Vanadium Pentoxide*, anhydrous, powdered  $\text{V}_2\text{O}_5$ .

7.18 *Quality Control (QC) Sample(s)*, preferably are portions of one or more petroleum products that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process and performance of the instrument as described in Section 12.

## 8. Sampling

8.1 Take samples in accordance with the instructions in Practice D4057.

## 9. Preparation of Apparatus

9.1 *Induction-Type Furnace*—Assemble the apparatus according to the instructions furnished by the manufacturer. Purify the oxygen by passing it through (1)  $\text{H}_2\text{SO}_4$  (relative density 1.84), (2) Ascarite, and (3) magnesium perchlorate ( $\text{Mg}(\text{ClO}_4)_2$ ) or phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) (**Warning**—see 7.4). Connect a rotameter between the purifying train and the furnace. Insert a small glass-wool plug in the upper end of the glass tubing connecting the furnace with the absorber to catch oxides of tin. Connect the exit end of the combustion tube to the absorber with glass tubing, using gum rubber tubing to make connections. Position the absorber so as to make this delivery line as short as possible. Fig. 2 illustrates schematically the assembled apparatus. Adjust the oxygen flow to  $1 \pm 0.05$  L/min. Add 65 mL of HCl (3 + 197) and 2 mL of

TABLE 1 Sample Weight for Induction Furnace

Sulfur Content, %	Weight of Sample to be Taken, mg	Normality of Standard $\text{KIO}_3$ solution for Titration
0 to 2	90 <sup>A</sup>	0.006238
2 to 4	50 to 90	0.006238
4 to 10	50 to 90	0.01248
Over 10	12.1.1	(Note 2)

<sup>A</sup> Approximate.

starch-iodide solution to the absorber. Add a sufficient amount of the appropriate standard  $\text{KIO}_3$  solution (Table 1) to produce a faint blue color. This color will serve as the end point for the titration. Adjust the buret to zero. Turn on the furnace filament switch and allow at least 1 min warm-up before running samples (**Warning**—see 7.4).

9.2 *Resistance-Type Furnace*—Assemble the apparatus according to the instructions furnished by the manufacturer. Purify the oxygen by passing it through (1)  $\text{H}_2\text{SO}_4$  (relative density 1.84), (2) Ascarite, and (3)  $\text{Mg}(\text{ClO}_4)_2$  or  $\text{P}_2\text{O}_5$  (**Warning**—see 7.4). Connect a rotameter between the purifying train and the furnace. Fig. 3 illustrates schematically the assembled apparatus. Turn on the current and adjust the furnace control to maintain a constant temperature of  $1316 \pm 14^\circ\text{C}$  ( $2400 \pm 25^\circ\text{F}$ ). Adjust the oxygen flow rate to  $2 \pm 0.1$  L/min. Add 65 mL of HCl ( $3 \pm 197$ ) and 2 mL of starch-iodide solution to the absorber. Add a few drops of the appropriate standard  $\text{KIO}_3$  solution (Table 2) to produce a faint blue color. Adjust the buret to zero.

9.3 *Resistance-Type Furnace—IR Detection*—Assemble and adjust apparatus according to manufacturer's instructions. Initialize microprocessor, check power supplies, set oxygen pressure and flows and set furnace temperature to  $1371^\circ\text{C}$  ( $2500^\circ\text{F}$ ).

9.3.1 Condition a fresh anhydrous scrubber with four coal samples when analyzing petroleum coke samples, or with four petroleum product samples that are representative or typical of the sample types to be analyzed.

9.3.2 Calibrate the automatic balance according to manufacturer's instructions.

## 10. Standardization

10.1 *For Iodate Methods:*

10.1.1 *Determination of Alum Factor:*

10.1.1.1 Because these rapid combustion methods involve the reversible reaction  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ , it is not possible to evolve all the sulfur as  $\text{SO}_2$ . The equilibrium of the reaction is temperature dependent and, in an oxygen atmosphere above  $1316^\circ\text{C}$ , about 97 % of the sulfur is present as  $\text{SO}_2$ . To assure that the furnace is in proper adjustment and that its operation produces acceptably high temperature, potassium alum is employed for standardizing the apparatus. Depending on the type of combustion equipment used, proceed as described in Sections 10 to 14 to determine the alum factor. Use 15 mg weighed to  $\pm 0.1$  mg of potassium alum for this determination. Use the same materials in the determination of the alum and standardization factors as for the unknown samples. For example,  $\text{V}_2\text{O}_5$  has a definite effect and should be included if used for unknowns as recommended in the procedure with the resistance-type furnace.

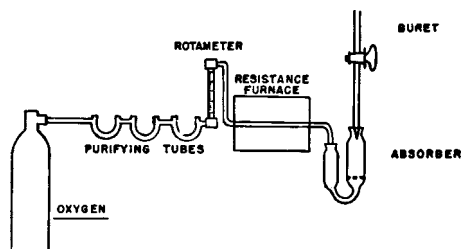


FIG. 3 Schematic Illustration of Resistance-Type Furnace

TABLE 2 Sample Weight for Resistance Furnace

Sulfur Content, %	Weight of Sample to be Taken, mg	Normality of Standard KIO <sub>3</sub> solution for Titration
0 to 2	100 to 200	0.006238
2 to 5	100 to 200	0.01248
5 to 10	100 to 200	0.06238
Over 10	(Note 2)	(Note 2)

10.1.1.2 Calculate the alum factor as follows:

$$\text{Alum factor (AF)} = (S_A \times W_A) / (100(V_a - V_b) \times C_1) \quad (1)$$

where:

- $S_A$  = mass percent sulfur in potassium alum used,
- $W_A$  = milligrams of potassium alum used,
- $V_a$  = millilitres of standard KIO<sub>3</sub> solution used in determining the alum factor,
- $V_b$  = millilitres of standard KIO<sub>3</sub> solution used in the blank determination, and
- $C_1$  = sulfur equivalent of the standard KIO<sub>3</sub> solution used in determining the alum factor, mg/mL.

10.1.1.3 The alum factor should be in the range from 1.02 to 1.08. If values smaller than 1.02 are observed, confirm independently the sulfur content of the alum and the sulfur equivalent of the KIO<sub>3</sub> solution before repeating the alum factor determination. If values larger than 1.08 are observed, make adjustments in the equipment in accordance with the manufacturer's recommendation and repeat the alum factor determination.

10.1.2 Determination of Standardization Factor:

10.1.2.1 Because effects such as sample volatility can also affect the relative recovery as SO<sub>2</sub> of the sulfur originally present in the sample, it is necessary to determine a standardization factor. Proceed as described in Sections 10 through 14, using an oil sample of similar type to the unknown sample and of accurately known sulfur content.<sup>5</sup>

10.1.2.2 For IR detection, determine and load the microprocessor with the calibration factor for the particular type of sample to be analyzed (lubricating oil, petroleum coke, residual fuel) as recommended by the manufacturer.<sup>3</sup>

10.1.2.3 Calculate the standardization factor as follows:

$$\text{Standardization factor (F}_s\text{)} = (S_s \times W_s) / (100 (V_s - V_b) \times C) \quad (2)$$

where:

- $S_s$  = mass percent sulfur in standardization sample used,
- $W_s$  = milligrams of standardization sample used,

<sup>5</sup> Residual fuel oil Standard Reference Materials may be obtained from the National Institute of Standards and Technology or other sources.

- $V_b$  = millilitres of standard KIO<sub>3</sub> solution used in the blank determination,
- $V_s$  = millilitres of standard KIO<sub>3</sub> solution used in determining the standardization factor, and
- $C$  = sulfur equivalent of the standard KIO<sub>3</sub> solution used in determining the standardization factor, mg/mL.

10.1.3 Quality Control—Run a suitable analytical quality control sample several times daily. When the observed value lies between acceptable limits on a quality control chart, proceed with sample determinations.

## 11. Preparation of Coke

11.1 It is assumed that a representative sample has been received for analysis. If the sample of coke received is not dry, it is recommended that the sample be dried prior to grinding.

11.2 Grind and sieve the sample received so as to pass a 60-mesh (250-µm) sieve.

11.3 Dry the sieved material to constant weight at 105 to 110°C.

## 12. Analysis of Quality Control Samples

12.1 A QC sample shall be analyzed each day samples are analyzed to verify the testing procedure and instrument performance. Additional QC samples may be analyzed. The QC samples shall be treated as outlined in Sections 13, 14, or 15, depending upon the type of furnace set-up used by the lab.

12.2 When QC / Quality Assurance (QA) protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

12.3 When there is no QC / QA protocol established in the testing facility, Appendix X1 can be used as the QC / QA system.

## 13. Procedure with Induction-Type Furnace

13.1 Sample Preparation—Add a 3.2 to 4.8-mm (1/8 to 3/16-in.) layer of alundum or magnesium oxide to a sample crucible. Make a depression in the bed with the end of a stirring rod. Weigh the crucible to 0.1 mg. Weigh into the depression the proper amount of sample according to Table 1 (13.1.1) (Note 2). Cover the sample with a separator disk (Note 3). Place on the separator disk the predetermined amount of iron chips necessary to obtain the required temperature (6.1.1.2). This is usually between 1.2 and 2.0 g, but should be held constant with ±0.05 g. Sprinkle about 0.1 g of tin on the iron. Cover the crucible with a lid and place on the furnace pedestal.

13.1.1 Under no conditions shall an organic sample larger than 100 mg be burned in an induction-type furnace.

NOTE 2—More concentrated KIO<sub>3</sub> solutions, such as the 0.06238 N solution, may be found more convenient for samples containing more than 10 % sulfur. The sample size and KIO<sub>3</sub> concentration should be chosen so that not more than 25 mL of titrant are needed.

NOTE 3—The use of the separator disk is optional.

13.2 Combustion and Titration—Turn on the plate current switch. After about 1 min for warm-up, raise the pedestal and lock into position. The plate current will fluctuate for a few seconds and should gradually rise to a maximum value. Add the appropriate standard KIO<sub>3</sub> solution (Table 1) to the absorber to maintain the blue color. Should the absorber solution



become completely colorless, discard the determination. Make KIO<sub>3</sub> additions as the rate of evolution of SO<sub>2</sub> diminishes such that, when combustion is completed, the intensity of the blue color is the same as the initial intensity. Combustion is complete when this color remains for at least 1 min and the plate current has dropped considerably. Record the volume of KIO<sub>3</sub> solution required to titrate the SO<sub>2</sub> evolved.

13.3 *Blank Determination*—Make a blank determination whenever a new supply of crucibles, materials, or reagents is used. Follow the preceding procedure, but omit the sample.

#### 14. Procedure with Resistance-Type Furnace

14.1 *Sample Preparation*—Weigh into a combustion boat the proper amount of sample according to [Table 2](#). Add 100 ± 5 mg of vanadium pentoxide and completely cover the mixture with Alundum.

14.2 *Combustion and Titration*—Place the boat in the cool portion of the combustion tube, near the entrance. To proceed with the combustion, push the boat containing the sample progressively into the hotter zone of the combustion tube using the equipment provided by the manufacturers. The boat should be advanced as rapidly as possible consistent with the rate of evolution of SO<sub>2</sub>. Add the appropriate standard KIO<sub>3</sub> solution ([Table 2](#)) to the absorber to maintain the blue color. Should the absorber solution become completely colorless, discard the determination. Make KIO<sub>3</sub> additions as the rate of evolution of SO<sub>2</sub> diminishes such that, when combustion is completed, the intensity of the blue color is the same as the initial intensity. Combustion is complete when this color remains for at least 1 min. Record the volume of KIO<sub>3</sub> solution required to titrate the SO<sub>2</sub> evolved.

14.3 *Blank Determination*—Make a blank determination whenever a new supply of combustion boats, materials, or reagents is used. Follow the above procedure, but omit the sample.

#### 15. Procedure with Resistance Furnace—IR Detection

15.1 Allow the system to warm up and the furnace to reach operating temperature.

15.2 After homogeneity of the sample is assured, select the sample size as follows: for liquid samples, take up to 0.13 g for analysis and for solid samples, take up to 0.4 g for analysis. In each case mass percent sulfur times weight of sample must be less than or equal to four in the case of the SC32 instrument, and two in the case of the SC132 instrument. For other instruments, consult the manufacturer's instructions.

15.3 Determine and store the system blank value.

15.4 Weigh solid samples into combustion boats and record the net weights. For liquid samples, follow [15.4.1-15.4.4](#). It is possible to weigh and store several weights in the microprocessor before beginning a series of burns.

15.4.1 Fill the combustion boat to one-third capacity with evenly spread MgO powder.

15.4.2 Form a slight trench in the MgO powder with a scoop.

15.4.3 Place the combustion boat on the balance and weigh an appropriate amount of the sample into the trench in the MgO powder. Record and enter the weight.

15.4.4 Remove the combustion boat from the balance and add MgO powder until the combustion boat is filled to two-thirds capacity. (**Warning**—V<sub>2</sub>O<sub>5</sub> can cause deterioration of the furnace ceramics so use it with care.)

NOTE 4—If unacceptable repeatability is encountered for particular oil samples, combustion promoter such as V<sub>2</sub>O<sub>5</sub> or the LECO product *Com-Aid* can be substituted for the MgO.

15.5 Initiate oxygen flow and load boat into furnace.

15.6 When the analysis is complete, read the result from the microprocessor.

15.7 Remove the expended combustion boat from the furnace.

15.8 Make repeated runs until two results differ by less than the repeatability of the method.

#### 16. Calculation

16.1 *Calculation for Iodate Detection*—Calculate the sulfur content of the sample as follows:

$$\text{Sulfur, mass \%} = (100 (V - V_b) \times F_s \times C) / W \quad (3)$$

where:

$V$  = standard KIO<sub>3</sub> solution, mL, used in the analysis,

$V_b$  = standard KIO<sub>3</sub> solution, mL, used in the blank determination,

$F_s$  = standardization factor (see [10.1.2](#)),

$C$  = sulfur equivalent of the standard KIO<sub>3</sub> solution used in the analysis, mg/mL, and

$W$  = milligrams of sample used in the analysis.

16.2 *Calculation for IR Detection:*

16.2.1 Report all results using the microprocessor.

16.2.2 Report the average of two results.

#### 17. Report

17.1 In the range from 0.05 to 5.00 mass % sulfur, report to the nearest 0.01 mass %. In the range from 5 to 30 mass % sulfur, report to the nearest 0.1 mass %.

#### 18. Quality Control

18.1 Confirm the performance of the test procedure by analyzing a quality control sample that is stable and representative of the sample of interest.

18.1.1 When the quality control/quality assurance protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

18.1.2 When there is no quality control/quality assurance protocol established in the testing facility, [Appendix X1](#) can be used for this purpose.

#### 19. Precision and Bias <sup>6</sup>

19.1 *For Petroleum Products by Iodate and IR Methods*—The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

<sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1231. Precision for the IR detection method was determined in a 1985 cooperative study that involved fourteen laboratories and ten samples. No statistically significant bias between the iodate and IR detector procedures was found.

19.1.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

Sulfur, mass-% Range	Repeatability	IR <sup>8</sup>
	Iodate	
0.0 to 0.5	0.05	0.04
0.5 to 1.0	0.07	0.07
1.0 to 2.0	0.10	0.09
2.0 to 3.0	0.16	0.12
3.0 to 4.0	0.22	0.13
4.0 to 5.0	0.24	0.16

19.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

Sulfur, mass-% Range	Reproducibility	
	Iodate	IR <sup>8</sup>
0.0 to 0.5	0.08	0.13
0.5 to 1.0	0.11	0.21
1.0 to 2.0	0.17	0.27
2.0 to 3.0	0.26	0.38
3.0 to 4.0	0.40	0.44
4.0 to 5.0	0.54	0.49

19.2 *For Petroleum Cokes by Iodate and IR Methods*—The precision of the test method as determined by statistical examination of interlaboratory results is as follows:

19.2.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

$$r = 0.05X \quad (4)$$

where  $X$  is the average of the two test results.

19.2.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

$$R = 0.22X \quad (5)$$

where  $X$  is the average of the two test results.

19.3 *Bias*—The bias of the procedure in this test method is being determined.

## 20. Keywords

20.1 furnace; high temperature; induction furnace; iodate titration; IR detection; petroleum; resistance; sulfur; titration

## APPENDIX

### (Nonmandatory Information)

#### X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practices [D6299](#) and [D6792](#) and *ASTM MNL 7*<sup>7</sup>).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practices [D6299](#) and [D6792](#) and *ASTM MNL 7*). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

<sup>7</sup> *ASTM MNL 7*, “Manual on Presentation of Data Control Chart Analysis,” 6th ed., ASTM International, W. Conshohocken, PA.

X1.6 See Practices **D6299** and **D6792** and *ASTM MNL 7* for further guidance on QC and control charting techniques.

### SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D1552–07) that may impact the use of this standard. (Approved Dec. 1, 2008.)

(I) Updated **11.1**, **15.4**, and **15.4.3**.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D1552–03) that may impact the use of this standard. (Approved Dec. 1, 2007.)

(I) Added Practice **D6792** to **X1.2**, **X1.3**, and **X1.6** and to the Referenced Documents.

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