Designation: D1552 – 16$^{\varepsilon 1}$

Standard Test Method for Sulfur in Petroleum Products by High Temperature Combustion and Infrared (IR) Detection or Thermal Conductivity Detection (TCD)[1]

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 (ε) indicates an editorial change since the last revision or reapproval.

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

ε^1 NOTE—The title was corrected editorially in February 2017.

1. Scope*

1.1 This test method covers 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 a mass fraction of sulfur between 0.22 % and 24.2 %. Other sulfur concentrations may be analyzed, but the precision stated may or may not apply. These procedures use IR detection or TCD following combustion in a furnace.

1.2 Petroleum coke containing a mass fraction of sulfur between 2.53 % to 3.79 % sulfur may be analyzed. Other sulfur concentrations may be analyzed, but the precision stated may or may not apply.

NOTE 1—The D1552–08 (2014) version of this standard contained two other procedures using iodate titrations. Since these procedures are no longer being used in the industry laboratories based on a survey of D02.SC 3 laboratories conducted in September 2014, they are being deleted. For earlier information on the deleted procedures, D1552–08 (2014) may be perused.

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:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

3. Summary of Test Method

3.1 The sample is weighed and placed into a furnace having an oxygen atmosphere sufficient to combust the entire sample and a temperature between 1150 °C and 1450 °C for Procedure A or 1150 °C for Procedure B. Most sulfur present is combusted to SO_2, which is then measured with a detector after moisture and dust are removed by traps. The instrument calculates the mass percent sulfur from the sample mass, the integrated detector signal, and a predetermined calibration factor. The calibration factor is determined using standards approximating the material to be analyzed.

3.1.1 *Procedure A*—After combustion of the sample and subsequent moisture/dust removal, SO_2 is measured using infrared (IR) detection.

3.1.2 *Procedure B*—After combustion of the sample and subsequent moisture/dust removal, SO_2 is measured using

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved July 1, 2016. Published August 2016. Originally approved in 1958. Last previous edition approved in 2015 as D1552 – 15. DOI: 10.1520/D1552-16E01.

[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.

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

thermal conductivity detection. An apparatus utilizing TCD may require the sample gas to pass an oxygen scrubber and adsorption/desorption traps to allow passing of contaminants prior to measuring SO_2.

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. Apparatus

5.1 *Combustion Furnace:*

5.1.1 *Procedure A*—Furnace capable of maintaining a constant temperature (between 1150 °C minimum and 1450 °C maximum) sufficient to ensure quantitative recovery of sulfur as its corresponding gas SO_2.

5.1.2 *Procedure B*—Furnace capable of maintaining a temperature (1150 °C) sufficient to ensure quantitative recovery of sulfur as its corresponding gas SO_2.

5.2 *Combustion and Sulfur Detection System,* comprised of automatic balance, gas flow controls, drying tubes, oxygen scrubber, adsorption/desorption traps as required, combustion furnace, combustion boats or tin (Sn) containers as required and either an IR (Procedure A) or TCD (Procedure B) SO_2 detector.

5.3 *Sieve,* 60 mesh (250 µm).

6. Reagents and Materials

6.1 *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.[3] 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.

6.2 *Combustion Promoter*—Magnesium oxide (MgO), tungsten trioxode (WO_3), or aluminum oxide (Al_2O_3). Alternatively, COM-CAT, a dual promoter that is both a fixing agent and oxidizing agent, may be used.[4]

6.3 *Drying Agent,* Magnesium perchlorate: anhydrone ($Mg(ClO_4)_2$) or phosphorus pentoxide (P_2O_5). (**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.)

6.4 *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.)

6.5 *Inert Gas*—Helium or argon, high purity grade, 99.995 % minimum purity, as required by manufacturer's recommendations.

6.6 *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 11.

7. Sampling

7.1 Take samples in accordance with the instructions in Practice D4057 or D4177.

8. Preparation of Apparatus

8.1 Assemble and adjust apparatus according to manufacturer's instructions. Initialize instrument, check power supplies, set gas pressure and flows, and set furnace temperature.

8.1.1 Condition the instrument with samples that are representative or typical of the sample types to be analyzed. During the interlaboratory study, laboratories analyzed between one and five conditioning samples.

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

9. Standardization

9.1 *Determination of Standardization Factor:*

9.1.1 Because effects such as sample volatility can also affect the relative recovery as SO_2 of the sulfur originally present in the sample, it is necessary to determine a standardization factor. Proceed as described in Sections 9 through 12, using an oil sample of similar type to the unknown sample and of accurately known sulfur content.[5]

9.1.2 Determine the calibration factor for the particular type of sample to be analyzed (lubricating oil, petroleum coke, residual fuel) as recommended by the manufacturer.

9.2 *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.

10. Preparation of Coke

10.1 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.

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[3] *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.

[4] The sole source of supply of COM-CAT known to the committee at this time is LECO Corporation, 3000 Lakeview Ave. St. Joseph, MI 49085 USA. 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,[1] which you may attend.

[5] Residual fuel oil Standard Reference Materials may be obtained from the National Institute of Standards and Technology or other sources.

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

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

11. Analysis of Quality Control Samples

11.1 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 Section 12, depending upon the type of furnace set-up used by the lab.

11.2 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.

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

12. Procedures

12.1 *Procedure A—Combustion with Infrared (IR) Detection:*

12.1.1 Following instrument manufacturer recommendations, allow the system to warm up and the furnace to reach an operating temperature between 1150 °C minimum and 1450 °C maximum.

12.1.2 Mix or swirl the test sample thoroughly to ensure homogeneity. Select the appropriate test specimen size as recommended by the instrument manufacturer. As an example, for liquid samples, take up to 0.13 g for analysis and for solid samples, take up to 0.4 g for analysis.

12.1.3 Determine and store the system blank value.

12.1.4 Weigh solid samples into combustion boats or containers and record the net masses. For liquid samples, follow 12.1.4.1 to 12.1.4.4.

12.1.4.1 Following manufacturer recommendations; add combustion promoter, if used, to combustion boat or container using scoop or spatula. Fill the combustion boat to one-third capacity with evenly spread MgO powder.

12.1.4.2 Place combustion boat or container on the balance and tare.

12.1.4.3 Weigh an appropriate amount of the sample onto the combustion promoter. Record and enter the mass of sample. If using combustion container, seal before recording sample mass.

12.1.4.4 Remove the combustion boat or container from the balance. Additional combustion promoter can be added to open combustion boat after weighing, if recommended by manufacturer's guidance.

12.1.5 Initiate gas flow and load sample into furnace.

12.1.6 When the analysis is complete, read the result from the instrument.

12.1.7 Prepare furnace and instrument for next run according to manufacturer's recommendation. Remove the expended combustion boat from the furnace, if used.

12.1.8 Perform a second determination and average the two values for a single result.

12.2 *Procedure B—Combustion with Thermal Conductivity Detection (TCD):*

12.2.1 Following instrument manufacturer recommendations, allow the system to warm up and the furnace to reach an 1150 °C operating temperature.

12.2.2 Mix or swirl the test sample thoroughly to ensure homogeneity. Select the appropriate test specimen size as recommended by the instrumentmanufacturer. As an example, for liquid samples, take up to 0.13 g for analysis and for solid samples, take up to 0.4 g for analysis.

12.2.3 Determine and store the system blank value.

12.2.4 Weigh solid samples into combustion containers and record the net masses. For liquid samples, follow 12.2.4.1 to 12.2.4.3.

12.2.4.1 Add combustion promoter, if used, to combustion container using scoop or spatula.

12.2.4.2 Place combustion container on the balance and tare.

12.2.4.3 Weigh an appropriate amount of the sample onto the combustion promoter. Seal tin combustion container before recording mass. Record and enter the mass of sample.

12.2.5 Initiate gas flow and load sample into furnace.

12.2.6 When the analysis is complete, read the result from the instrument.

12.2.7 Prepare furnace and instrument for next run according to manufacturer's recommendation.

12.2.8 Perform a second determination and average the two values for a single result.

12.3 In cases of dispute between procedures, Procedure A shall be considered the referee procedure.

13. Calculation

13.1 Report all results using the microprocessor.

13.2 Report the average of two results.

14. Report

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

14.2 Report the following information: Results were obtained according to Test Method D1552, Procedure A or Procedure B.

15. Quality Control

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

15.1.1 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.

15.1.2 When there is no quality control/quality assurance protocol established in the testing facility, Appendix X1 can be used for this purpose.

TABLE 1 Example Precision Calculations, Petroleum Products and Coke, Procedure A

Petroleum Products			Petroleum Coke		
S, % by mass	*r*	*R*	S, % by mass	*r*	*R*
0.25	0.02	0.06	2.55	0.11	0.38
1.00	0.05	0.17	2.75	0.12	0.40
5.00	0.19	0.66	3.00	0.12	0.43
10.0	0.3	1.2	3.25	0.13	0.46
15.0	0.5	1.6	3.50	0.14	0.49
20.0	0.6	2.1	3.75	0.15	0.52

TABLE 2 Example Repeatability Calculations, Petroleum Products and Coke, Procedure B

Petroleum Products		Petroleum Coke	
S, % by mass	*r*	S, % by mass	*r*
0.25	0.03	2.55	0.21
1.00	0.10	2.75	0.22
5.00	0.36	3.00	0.24
10.0	0.6	3.25	0.26
15.0	0.9	3.50	0.27
20.0	1.1	3.75	0.29

16. Precision and Bias[6]

16.1 *For Petroleum Products and Coke by IR Detection, Procedure A*—Each test result is the average of two S determinations (see Section 12).

16.1.1 *Repeatability (r)*—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.

$$r = \% \text{ mass fraction S of } 0.04986 \cdot X^{0.8267} \tag{1}$$

where:

X = the average of the two test results.

16.1.2 *Reproducibility (R)*—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.

$$R = \% \text{ mass fraction S of } 0.1737 \cdot X^{0.8267} \tag{2}$$

where:

X = the average of the two test results.

16.1.3 See Table 1 for example precision calculations for Procedure A.

16.2 *For Petroleum Products and Cokes by TCD Procedure B*—Each test result is the average of two S determinations (see Section 12).

16.2.1 The precision of the test method was determined by statistical examination of interlaboratory (ILS) results. After processing of the data with Practice D6300, analysis showed that the number of labs (three) and reproducibility degrees of freedom were inadequate for the calculation of Procedure B reproducibility. A new round robin will be conducted in order to obtain a full precision statement by 2021 at the latest.

16.2.2 *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:

$$r = \% \text{ mass fraction S of } 0.1 \cdot X^{0.8} \tag{3}$$

where:

X = the average of the two test results.

16.2.3 *Reproducibility*—No reproducibility statement can be presented for Procedure B. A new ILS will be carried out to obtain a full precision statement in the future (see 16.2.1).

16.2.4 See Table 2 for example repeatability calculations for Procedure B.

16.3 *Bias*—The bias of Procedure A and Procedure B in this test method has not been determined. No statement can be made regarding relative bias between Procedure A and Procedure B because this comparison study has not been made.

17. Keywords

17.1 coke; combustion; furnace; high temperature; IR detection; petroleum; resistance furnace; sulfur; thermal conductivity detection

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1838. A 1985 cooperative study may be obtained by requesting RR:D02-1231. The RR:D02-1838 cooperative study involved ten laboratories and eight samples with seven laboratories using IR detection and three laboratories using TCD. The range of measured average sulfur levels was between 0.22 % and 24.2 % for the petroleum products and 2.53 % to 3.79 % for the coke samples.

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*[7]).

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.

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

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[7] *ASTM MNL 7*, "Manual on Presentation of Data Control Chart Analysis," 6th ed., ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.30 has identified the location of selected changes to this standard since the last issue (D1552 – 15) that may impact the use of this standard. (Approved July 1, 2016.)

(1) Title changed to include thermal conductivity detection.
(2) Revised Sections 1 and 3 to include Procedures A and B.
(3) Revised subsections in Sections 5 and 6 to describe Procedure A and B apparatus and reagent requirements.
(4) Updated subsection 7.1 to include automatic sampling practice.
(5) Revised Preparation of Apparatus subsections 8.1 and 8.1.2 to remove archaic language and accommodate Procedure A and B apparatus requirements.
(6) Revised Section 12 title, updated subsection 12.1 and inserted new subsection 12.2 to describe Procedures A and B.
(7) Inserted subsection 14.2 to accommodate form and style procedure identification requirements.
(8) Revised Section 16, Precision and Bias, subsections, tables, and footnotes to reflect interlaboratory study findings.

Subcommittee D02.30 has identified the location of selected changes to this standard since the last issue (D1552 – 08 (2014)$^{\varepsilon 1}$) that may impact the use of this standard. (Approved April 1, 2015.)

(1) Changed the title.
(2) Deleted sections dealing with iodate titration systems throughout the standard, mainly former subsections 3.1, 5, 6.1, 6.3, 7.2, 7.3, 7.5, 7.8 – 7.11, 7.13- 7.16, 9.1, 9.2, 10.1, Tables 1 and 2, 10.1.2.3, 13.1 – 13.3, 14.1 – 14.3, 16.1, Figures 1 and 2, and Footnote 3.
(3) Added new Note 1 and Table 1.
(4) Made appropriate minor verbiage changes throughout the standard.

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