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Standard Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)[1]

This standard is issued under the fixed designation D129; 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 Department of Defense.

1. Scope*

1.1 This test method covers the determination of sulfur in petroleum products, including lubricating oils containing additives, additive concentrates, and lubricating greases that cannot be burned completely in a wick lamp. The test method is applicable to any petroleum product sufficiently low in volatility that it can be weighed accurately in an open sample boat and containing at least 0.1 % sulfur.

NOTE 1—This test method is not applicable to samples containing elements that give residues, other than barium sulfate, which are insoluble in dilute hydrochloric acid and would interfere in the precipitation step. These interfering elements include iron, aluminum, calcium, silicon, and lead which are sometimes present in greases, lube oil additives, or additive oils. Other acid insoluble materials that interfere are silica, molybdenum disulfide, asbestos, mica, and so forth. The test method is not applicable to used oils containing wear metals, and lead or silicates from contamination. Samples that are excluded can be analyzed by Test Method D1552.

1.2 This test method is applicable to samples with the sulfur in the range 0.09 to 5.5 mass %.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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]

D1193 Specification for Reagent Water

D1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)

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

E144 Practice for Safe Use of Oxygen Combustion Bombs

3. Summary of Test Method

3.1 The sample is oxidized by combustion in a high pressure decomposition device containing oxygen under pressure. The sulfur, as sulfate in the high pressure decomposition device washings, is determined gravimetrically as barium sulfate.

3.2 (**Warning—**Strict adherence to all of the provisions prescribed hereafter ensures against explosive rupture of the high pressure decomposition device, or a blow-out, provided the high pressure decomposition device is of proper design and construction and in good mechanical condition. It is desirable, however, that the high pressure decomposition device be enclosed in a shield of steel plate at least 13 mm thick, or equivalent protection be provided against unforeseeable contingencies.)

3.3 (**Warning—**Initial testing and periodic examination of the pressure vessel is essential to ensure its fitness for service. This is particularly important if the pressure vessel has been dropped and has any obvious signs of physical damage.)

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[1] 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.

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This test method was adopted as a joint ASTM-IP standard in 1964.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

[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**

4. Apparatus and Materials

4.1 *High Pressure Decomposition Device (see Note 2),* [3]having a capacity of not less than 300 mL, so constructed that it will not leak during the test and that quantitative recovery of the liquids from the high pressure decomposition device may be achieved readily. The inner surface of the high pressure decomposition device may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the high pressure decomposition device assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the sulfur content of the liquid in the high pressure decomposition device.

NOTE 2—Criteria for judging the acceptability of new and used oxygen combustion high pressure decomposition devices are described in Practice E144.

4.2 *Oxygen Charging Equipment*—The valves, gauges, filling tube, and fittings used in the oxygen charging system shall meet industry safety codes and be rated for use at input pressure up to 20 875 kPa and discharge pressure up to 5575 kPa. Separate gauges shall be provided to show the supply pressure and the pressure vessel pressure. The pressure vessel gauge shall not be less than 75 mm in diameter and preferably graduated from 0 kPa to 5575 kPa in 100 kPa subdivisions. Both gauges shall be absolutely oil-free and shall never be tested in a hydraulic system containing oil. The charging equipment shall include either a pressure reducing valve which will limit the discharge pressure to a maximum of 4055 kPa or a relief valve set to discharge at 4055 kPa in case the pressure vessel should accidentally be overcharged. Means shall also be provided for releasing the residual pressure in the filling tube after the pressure valve has been closed.

4.3 *Sample Cup,* platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.4 *Firing Wire,* platinum, No. 26 B & S gage, 0.41 mm (16 thou), 27 SWG, or equivalent. (**Warning—**The switch in the ignition circuit shall be of a type which remains open, except when held in closed position by the operator.)

4.5 *Ignition Circuit,* capable of supplying sufficient current to ignite the cotton wicking or nylon thread without melting the wire. The current shall be drawn from a step-down transformer or from a suitable battery. The current shall not be drawn from the power line, and the voltage shall not exceed 25 V. The switch in the ignition circuit shall be of a type which remains open, except when held in closed position by the operator.

4.6 *Cotton Wicking or Nylon Sewing Thread,* white.

4.7 *Muffle Furnace.*

4.8 *Filter Paper,* "ashless," 0.01 mass % ash maximum.

5. Reagents and Materials

5.1 *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.[4] 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.

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

5.3 *Barium Chloride Solution* (85 g/L)—Dissolve 100 g of barium chloride dihydrate ($BaCl_2\cdot 2H_2O$) in distilled water and dilute to 1 L.

5.4 *Bromine Water (saturated)* .

5.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

5.6 *Oxygen,* free of combustible material and sulfur compounds, available at a pressure of 41 kgf/cm^2 (40 atm).

5.7 *Sodium Carbonate Solution* (50 g/L)—Dissolve 135 g of sodium carbonate decahydrate ($Na_2CO_3\cdot 10H_2O$) or its equivalent weight in distilled water and dilute to 1 L.

5.8 *White Oil, USP, or Liquid Paraffin,* BP, *or equivalent.*

5.9 *Quality Control (QC) Samples,* preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 10.

6. Procedure

6.1 *Preparation of High Pressure Decomposition Device and Sample*—Cut a piece of firing wire 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert between two loops of the coil a wisp of cotton or nylon thread of such length that one end will extend into the sample cup. Place about 5 mL of Na_2CO_3 solution in the high pressure decomposition device (Note 3) and rotate the high pressure decomposition device in such a manner that the interior surface is moistened by the solution. Introduce into the sample cup the quantities of sample and white oil (Note 4 and Note 5) specified in the following table, weighing the sample to the nearest 0.2 mg (when white oil is used, stir the mixture with a short length of quartz rod and allow the rod to remain in the sample cup during the combustion).

NOTE 3—After repeated use of the high pressure decomposition device for sulfur determinations, a film may be noticed on the inner surface. This dullness can be removed by periodic polishing of the high pressure decomposition device. A satisfactory method for doing this is to rotate the high pressure decomposition device in a lathe at about 300 rpm and polish the inside surface with emery polishing papers Grit No. 2⁄0, or equivalent

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[3] A high pressure decomposition device conforming to the test specifications in IP Standard IP 12 is suitable.

[4] *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.

paper,[5] coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide[6] and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before the high pressure decomposition device is used it shall be washed with soap and water to remove oil or paste left from the polishing operation.

6.1.1 (**Warning—**Do not use more than 1.0 g total of sample and white oil or other low sulfur combustible material or more than 0.8 g if the IP 12 high pressure decomposition device is used.)

Sulfur Content percent	Weight of Sample, g	Weight of White Oil, g
5 or under	0.6 to 0.8	0.0
Over 5	0.3 to 0.4	0.3 to 0.4

NOTE 4—Use of sample weights containing over 20 mg of chlorine may cause corrosion of the high pressure decomposition device. To avoid this, it is recommended that for samples containing over 2 % chlorine, the sample weight be based on the chlorine content as given in the following table:

Chlorine Content percent	Weight of Sample, g	Weight of White Oil, g
2 to 5	0.4	0.4
Over 5 to 10	0.2	0.6
Over 10 to 20	0.1	0.7
Over 20 to 50	0.05	0.7

NOTE 5—If the sample is not readily miscible with white oil, some other low sulfur combustible diluent may be substituted. However, the combined weight of sample and nonvolatile diluent shall not exceed 1.0 g or more than 0.8 g if the IP 12 high pressure decomposition device is used.

6.2 *Addition of Oxygen*—Place the sample cup in position and arrange the cotton wisp or nylon thread so that the end dips into the sample. Assemble the high pressure decomposition device and tighten the cover securely. (**Warning—**Do not add oxygen or ignite the sample if the high pressure decomposition device has been jarred, dropped, or tilted.) Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in the following table:

Capacity of High Pressure Decomposition Device, mL	Minimum Gauge Pressure, [A] kgf/cm^2 (atm)	Maximum Gauge Pressure, [A] kgf/cm^2 (atm)
300 to 350	39 (38)	41 (40)
350 to 400	36 (35)	38 (37)
400 to 450	31 (30)	33 (32)
450 to 500	28 (27)	30 (29)

[A] The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures represent a safety requirement.

6.3 *Combustion*—Immerse the high pressure decomposition device in a cold distilled-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. (**Warning—**Do not go near the high pressure decomposition device until at least 20 s after firing.) Remove the high pressure decomposition device from the bath after immersion for at least 10 min. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the high pressure decomposition device and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination and thoroughly clean the high pressure decomposition device before again putting it in use (Note 3).

6.4 *Collection of Sulfur Solution*— Rinse the interior of the high pressure decomposition device, the oil cup, and the inner surface of the high pressure decomposition device cover with a fine jet of water, and collect the washings in a 600-mL beaker having a mark to indicate 75 mL. Remove any precipitate in the high pressure decomposition device by means of a rubber policeman. Wash the base of the terminals until the washings are neutral to the indicator methyl red. Add 10 mL of saturated bromine water to the washings in the beaker. (The volume of the washings is normally in excess of 300 mL.) Place the sample cup in a 50-mL beaker. Add 5 mL of saturated bromine water, 2 mL of HCl, and enough water just to cover the cup. Heat the contents of the beaker to just below its boiling point for 3 or 4 min and add to the beaker containing the high pressure decomposition device washings. Wash the sample cup and the 50-mL beaker thoroughly with water. Remove any precipitate in the cup by means of a rubber policeman. Add the washings from the cup and the 50-mL beaker, and the precipitate, if any, to the high pressure decomposition device washings in the 600-mL beaker. Do not filter any of the washings, since filtering would remove any sulfur present as insoluble material.

6.5 *Determination of Sulfur*—Evaporate the combined washings to 200 mL on a hot plate or other source of heat. Adjust the heat to maintain slow boiling of the solution and add 10 mL of the $BaCl_2$ solution, either in a fine stream or dropwise. Stir the solution during the addition and for 2 min thereafter. Cover the beaker with a fluted watch glass and continue boiling slowly until the solution has evaporated to a volume approximately 75 mL as indicated by a mark on the beaker. Remove the beaker from the hot plate (or other source of heat) and allow it to cool for 1 h before filtering. Filter the supernatant liquid through an ashless, quantitative filter paper (Note 6). Wash the precipitate with water, first by decantation and then on the filter, until free from chloride. Transfer the paper and precipitate to a weighed crucible and dry (Note 7) at a low heat until the moisture has evaporated. Char the paper completely without igniting it, and finally ignite at a bright red heat until the residue is white in color. After ignition is complete, allow the crucible to cool at room temperature, and weigh.

NOTE 6—A weighed porcelain filter crucible (Selas type) of 5 to 9-µm porosity may be used in place of the filter paper. In this case the precipitate is washed free of chloride and then dried to constant weight at 500 ± 25°C.

NOTE 7—A satisfactory means of drying, charring, and igniting the paper and precipitate is to place the crucible containing the wet filter paper in a cold electric muffle furnace and to turn on the current. Drying, charring, and ignition usually will occur at the desired rate.

6.6 *Blank*—Make a blank determination whenever new reagents, white oil, or other low-sulfur combustible material are used. When running a blank on white oil, use 0.3 to 0.4 g and follow the normal procedure.

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[5] The sole source of supply of the apparatus known to the committee at this time is Emery Polishing Paper Grit No. 2/0, which can be purchased from Norton Co., 2600 10th Ave., Watervliet, NY 12189-1766. 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.

[6] The sole source of supply of the apparatus known to the committee at this time is chromic oxide that may be purchased from J. T. Baker, Phillipsburg, NJ 08865. 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.

7. Calculation

7.1 Calculate the sulfur content of the sample as follows:

$$\text{Sulfur, weight percent} = (P - B)13.73/W \qquad (1)$$

where:

P = grams of $BaSO_4$ obtained from sample,
B = grams of $BaSO_4$ obtained from blank, and
W = grams of sample used.

8. Report

8.1 Report the results of the test to the nearest 0.01 %.

9. Precision and Bias[7]

9.1 The precision of this test is not known to have been obtained in accordance with currently accepted guidelines for example, in Research Report RR:D02-1007.

9.1.1 *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 only in one case in twenty:

9.1.2 *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 only in one case in twenty:

Sulfur, weight percent	Repeatability	Reproducibility
0.1 to 0.5	0.04	0.05
0.5 to 1.0	0.06	0.09
1.0 to 1.5	0.08	0.15
1.5 to 2.0	0.12	0.25
2.0 to 5.0	0.18	0.27

NOTE 8—The precision shown in the above table does not apply to samples containing over 2 % chlorine because an added restriction on the amount of sample which can be ignited is imposed.

NOTE 9—This test method has been cooperatively tested only in the range of 0.1 to 5.0 % sulfur.

NOTE 10—The following information on the precision of this method has been developed by the Energy Institute (formerly known as the Institute of Petroleum):

(*a*) Results of duplicate tests should not differ by more than the following amounts:

Repeatability	Reproducibility
$0.016\ x + 0.06$	$0.037\ x + 0.13$

where x is the mean of duplicate test results.

(*b*) These precision values were obtained in 1960 by statistical examination of interlaboratory test results.[8] No limits have been established for additive concentrates.

9.2 *Bias*—Results obtained in one laboratory by Test Method D129 on NIST Standard Reference Material Nos. 1620A, 1621C, and 1662B were found to be 0.05 mass % higher than the accepted reference values.

10. Quality Control

10.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 5.9).

10.1.1 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.

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

11. Keywords

11.1 high pressure decomposition device; sulfur

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 test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL 7).[9]

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 Practice D6299 and MNL 7). Any out-of-control data should trigger investigation for root cause(s).

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.

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1278.

[8] *IP Standards for Petroleum and Its Products, Part I, Appendix E.* Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.

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

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. See Practice D6299 and 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 (D129 – 11) that may impact the use of this standard.

(1) Added information in sections 1.2, 3.3, 4.2, 4.5, 4.7, and 4.8 in Scope and Apparatus sections to keep consistent with equivalent test method IP 61.

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