



Designation: D4530 – 15 (Reapproved 2020)

Standard Test Method for Determination of Carbon Residue (Micro Method)¹

This standard is issued under the fixed designation D4530; 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.

1. Scope

1.1 This test method covers the determination of the amount of carbon residue (see **Note 1**) formed after evaporation and pyrolysis of petroleum materials under certain conditions and is intended to provide some indication of the relative coke forming tendency of such materials.

1.2 The test results are equivalent to the Conradson Carbon Residue test (see Test Method **D189**).

NOTE 1—This procedure is a modification of the original method and apparatus for carbon residue of petroleum materials, where it has been demonstrated that thermogravimetry is another applicable technique.² However, it is the responsibility of the operator to establish operating conditions to obtain equivalent results when using thermogravimetry.

1.3 This test method is applicable to petroleum products that partially decompose on distillation at atmospheric pressure and was tested for carbon residue values of 0.10 % to 30 % (m/m). Samples expected to be below 0.10 weight % (m/m) residue should be distilled to remove 90 % (V/V) of the flask charge (see Section 9). The 10 % bottoms remaining is then tested for carbon residue by this test method.

1.4 Ash-forming constituents, as defined by Test Method **D482**, or non-volatile additives present in the sample will add to the carbon residue value and be included as part of the total carbon residue value reported.

1.5 Also in diesel fuel, the presence of alkyl nitrates, such as amyl nitrate, hexyl nitrate, or octyl nitrate, causes a higher carbon residue value than observed in untreated fuel, which may lead to erroneous conclusions as to the coke-forming propensity of the fuel. The presence of alkyl nitrate in the fuel may be detected by Test Method **D4046**.

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

1.6.1 *Exception*—6.4 and 6.5 include inch-pound units.

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 **D02.06** on Analysis of Liquid Fuels and Lubricants.

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² See *Fuel*, Vol 63, July 1984, pp. 931–934.

1.7 **WARNING**—Mercury has been designated by many regulatory agencies as a hazardous substance that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Use Caution when handling mercury and mercury-containing products. See the applicable product Safety Data Sheet (SDS) for additional information. The potential exists that selling mercury or mercury-containing products, or both, is prohibited by local or national law. Users must determine legality of sales in their location.

1.8 *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, health, and environmental practices and to determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 8.2.3 and 8.4.

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards*:³

D189 Test Method for Conradson Carbon Residue of Petroleum Products

D482 Test Method for Ash from Petroleum Products

D4046 Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry (Withdrawn 2019)⁴

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

E1 Specification for ASTM Liquid-in-Glass Thermometers

E133 Specification for Distillation Equipment

³ 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.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

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

2.2 Energy Institute Standard:
Specification for IP Standard Thermometers⁵

3. Terminology

3.1 Definitions:

3.1.1 carbon residue, *n*—the residue formed by evaporation and thermal degradation of a carbon containing material.

3.1.1.1 Discussion—The residue is not composed entirely of carbon but is a coke that can be further changed by carbon pyrolysis.

4. Summary of Test Method

4.1 A weighed quantity of sample is placed in a glass vial and heated to 500 °C under an inert (nitrogen) atmosphere in a controlled manner for a specific time. The sample undergoes coking reactions, and volatiles formed are swept away by the nitrogen. The carbonaceous-type residue remaining is reported as a percent of the original sample as “carbon residue (micro).”

4.1.1 When the test result is expected to be below 0.10 % (m/m), the sample can be distilled to produce a 10 % (V/V) bottoms, prior to performing the test.

5. Significance and Use

5.1 The carbon residue value of the various petroleum materials serves as an approximation of the tendency of the material to form carbonaceous type deposits under degradation conditions similar to those used in the test method, and can be

useful as a guide in manufacture of certain stocks. However, care needs to be exercised in interpreting the results.

5.2 This test method offers advantages of better control of test conditions, smaller samples, and less operator attention compared to Test Method D189, to which it is equivalent.

5.3 Up to twelve samples may be run simultaneously, including a control sample when the vial holder shown in Fig. 1 is used exclusively for sample analysis.

6. Apparatus

6.1 Glass Sample Vials, 2 mL capacity, 12 mm outside diameter by approximately 35 mm high.

6.2 Larger 4-dram Glass Sample Vials, 15 mL capacity (20.5 mm to 21 mm outside diameter by 70 mm ± 1 mm high), may be used for samples that are expected to yield residues <0.10 % (m/m) so that a more appreciable mass difference can be determined. It should be noted the precision statements for the test method were determined using the 2 mL capacity vials only (with sample residues between 0.3 % and 26 % (m/m) and that the precision associated with using the larger sample vials has not been determined.

6.3 Eyedropper, Syringe, or Small Rod, for sample transfer.

6.4 Coking Oven with circular heating chamber approximately 85 mm (3 3/8 in.) in diameter by 100 mm (4 in.) deep, for top loading, with heating capability from 10 °C/min to 40 °C/min rate to 500 °C, with exhaust port 13 mm (1/2 in.) inside diameter for nitrogen purge of oven chamber (inlet near top, exhaust at bottom center) with thermocouple sensor located in oven chamber next to but not touching sample vials, with lid capable of sealing out air, and with removable

⁵ “Methods for Analysis and Testing,” Institute of Petroleum Standard Methods for Petroleum and Its Products, Part I, Vol 2. Available from Energy Institute, 61 New Cavendish St., London, WIM 8AR, UK.

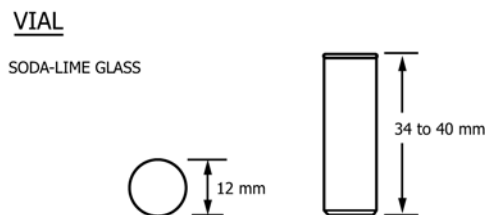
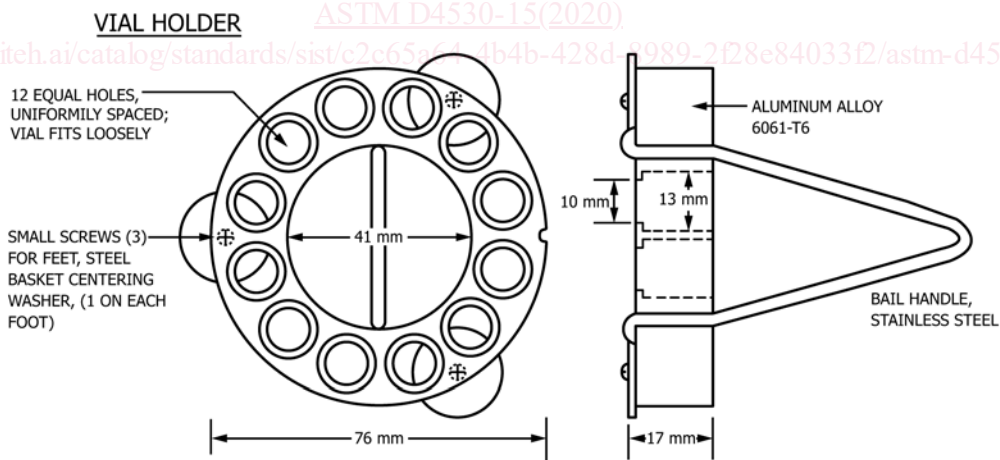


FIG. 1 Sample Vial Holder and Vial

condensate trap located at the oven chamber base. A schematic diagram is given in Fig. 2.

6.5 *Sample Vial Holder*—Cylindrical aluminum block, approximately 76 mm (3 in.) in diameter by 16 mm ($\frac{5}{8}$ in.) thick, with twelve evenly spaced holes (for vials) each 13 mm ($\frac{1}{2}$ in.) in diameter by 13 mm ($\frac{1}{2}$ in.) deep. The holes are arranged in a circular pattern approximately 3 mm ($\frac{1}{8}$ in.) from the perimeter. The holder has legs 6 mm ($\frac{1}{4}$ in.) long, with guides to center in oven chamber, and an index mark on the side to use as position reference. The sample vial holder is shown in Fig. 1.

6.6 A modified version of the standard sample vial holder (see Fig. 1) is required when larger glass sample vials (see 6.2) are used. The modified sample vial holder is similar in nature to the twelve hole vial holder, except that there are six evenly spaced holes (for vials) each 21.2 mm \pm 0.1 mm in diameter by approximately 16 mm deep, arranged in a circular pattern.

6.7 *Thermocouple*, suitable for controller and temperature range of interest, with exterior temperature readout, degrees Celsius.

6.8 *Analytical Balance*, with \pm 0.1 mg sensitivity to 20 g minimum weighing capacity.

6.9 *Nitrogen*, minimum 99.998 % purity with suitable means of delivering a pressure of 0 kPa to 200 kPa (0 psig to 30 psig). Cylinders of zero grade nitrogen have been found suitable to use.

7. Sampling

7.1 Using the practices outlined in Practice D4057 (manual sampling) or Practice D4177 (automatic sampling), ensure that a representative sample of material to be tested is obtained.

8. Procedure

8.1 Sample Preparation:

8.1.1 Determine the mass of each clean sample vial being used in the sample analysis, and record the mass to nearest 0.1 mg.

8.1.2 During weighing and filling, handle vials with forceps to help minimize weighing errors. Discard the sample vials after use.

8.1.3 It is assumed that a representative sample of the stock or process has been obtained for laboratory use following Practice D4057 or similar standard. Stir the sample to be tested, first warming if necessary to reduce its viscosity. Samples that are homogeneous liquids can be transferred directly to vials

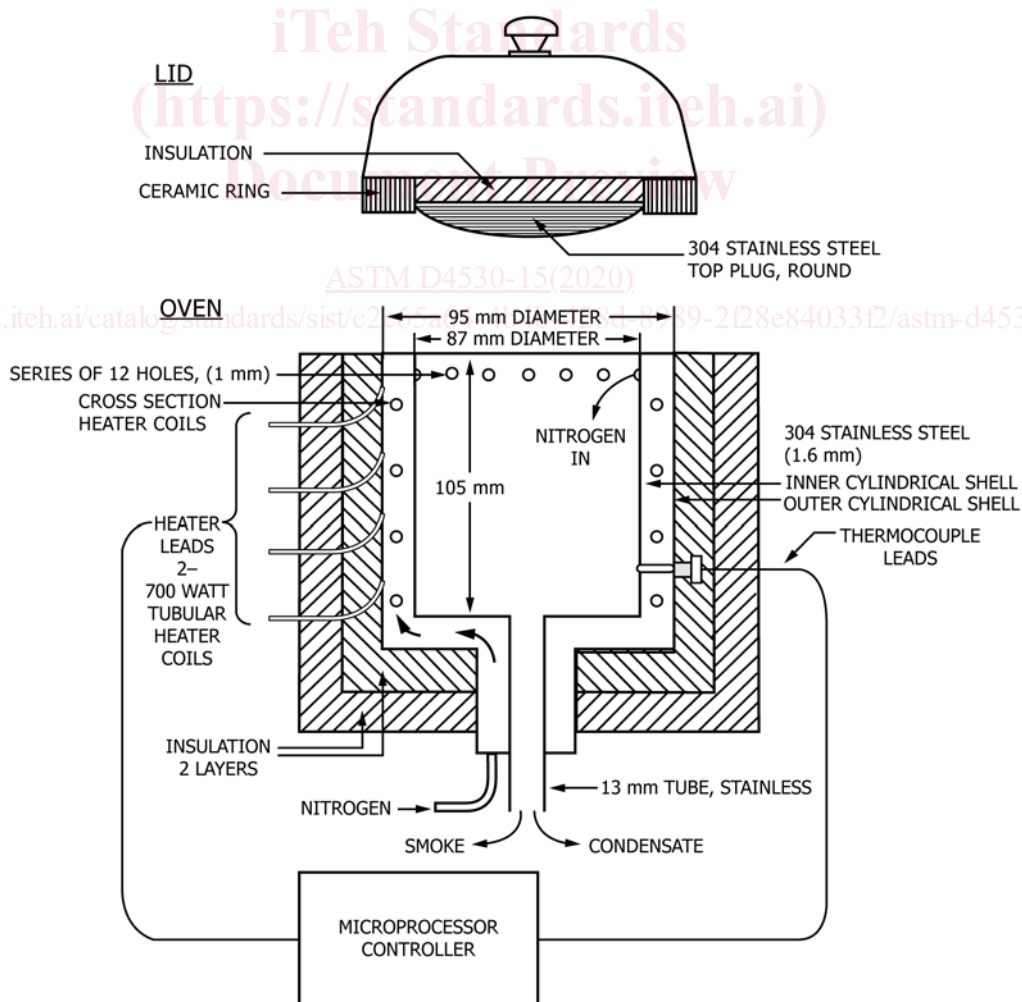


FIG. 2 Coking Oven and Lid

using a rod, syringe, or eyedropper. Solid materials may also be heated; or frozen with liquid nitrogen, and then shattered to provide manageable pieces.

8.1.4 Transfer an appropriate mass of the sample (see [Table 1](#)) into a tared-sample vial, reweigh to nearest 0.1 mg, and record. Place the loaded sample vials into vial holder (up to twelve), noting position of each sample with respect to index mark.

NOTE 2—A control sample can be included in each batch of samples being tested. This control sample should be a typical sample that has been tested at least 20 times in the same equipment in order to define an average percent carbon residue and standard deviation. Results for each batch are deemed acceptable when results for the control sample fall within the average percent carbon residue \pm three standard deviations. Control results that are outside these limits indicate problems with the procedure or the equipment.

8.2 Processing of Samples:

8.2.1 With the oven at less than 100 °C, place the vial holder into the oven chamber and secure lid. Purge with nitrogen for at least 10 min at 600 mL/min. Then decrease the purge to 150 mL/min and heat the oven slowly to 500 °C at 10 °C/min to 15 °C/min.

8.2.2 If the sample foams or spatters, causing loss of sample, discard and repeat the test.

NOTE 3—Spattering may be due to water that can be removed by prior gentle heating in a vacuum, followed by a nitrogen sweep. Alternatively, a smaller sample size can be used.

8.2.3 Hold oven at 500 °C \pm 2 °C for 15 min. Then shut off furnace power and allow oven to cool freely while under nitrogen purge of 600 mL/min. When oven temperature is less than 250 °C, remove the vial holder for further cooling in desiccator. After the samples are removed from the oven, the nitrogen purge may be shut off. (**Warning**—Do not open oven to air at any time during the heating cycle. The introduction of air (oxygen) will likely cause the sample to ignite and spoil the test. (Because of the oven design and materials, such an ignition is normally not a hazard to the operator.) Open the oven only after oven temperature falls below 250 °C during the cooling step. Maintain nitrogen flow until after the vial holder has been removed from the oven.) (**Warning**—Locate the coking oven in laboratory exhaust hood for safe venting of smoke and fumes. Alternatively, install vent line from MCRT oven exhaust to laboratory exhaust system.) (**Warning**—If a vent line is used, do not connect directly to exhaust chimney to avoid creating negative pressure in the line.)

NOTE 4—To reduce oven temperature for the next run, remove the oven lid to allow faster cooling. As required by the procedure, the subsequent test can be started when the oven has been cooled to below 100 °C.

TABLE 1 Guide for Sample Size

Sample Description	Expected Carbon Residue, (m/m) %	Recommended Sample Size, g
Black, viscous or solid	>5	0.15 \pm 0.05
Brown, viscous	1–5	0.5 \pm 0.1
Lube oil consistency and appearance, 10 % bottoms on distillate material	0.1–<1	1.5 \pm 0.5
Large vials only	<0.1	5.0 \pm 1.0
Small vials only	<0.1	1.5 \pm 0.5

8.3 *Final Weighing*—Transfer sample vials (maintained in place in the vial holder) to desiccator and allow vials to cool to room temperature. Weigh the cooled vials to the nearest 0.1 mg and record. Handle the vials with forceps. Discard the used glass sample vials.

8.4 Occasionally examine the condensate trap at the bottom of the oven chamber; empty if necessary and replace. (**Warning**—The condensate trap residue may have some carcinogenic materials present. Avoid contact with the trap residue; dispose of it in accordance with local laboratory practice.)

9. Procedure for Carbon Residue on 10 % (V/V) Distillation Residue

9.1 This procedure is applicable to light distillate materials, such as ASTM No. 1 and No. 2 fuel oil or materials expected to have less than 0.1 % (m/m) carbon residue.

9.2 A distillation analysis using either a 100 mL or 200 mL starting volume is required in order to collect a sufficient amount of the 10 % (V/V) residue needed in this analysis. For a 100 mL distillation, assemble the distillation apparatus described in [Specification E133](#), using flask B (125 mL bulb volume), flask support board with 50 mm diameter opening, and graduated cylinder B (100 mL capacity). For a 200 mL distillation, assemble the distillation apparatus described in [Specification E133](#), using flask D (250 mL bulb volume), flask support board with 50 mm diameter opening, and graduated cylinder C (200 mL capacity). A thermometer is not required, but the use of the ASTM High Distillation Thermometer 8F or 8C, as prescribed in [Specification E1](#), or the IP High Distillation Thermometer 6C, as prescribed in the [Specification for IP Thermometers](#), is recommended.

9.3 Depending upon which distillation flask is used, place either 100 mL or 200 mL of sample (as measured at ambient temperature) into a distillation flask that is held at a temperature between 13 °C and ambient. Maintain the condenser bath temperature between 0 °C and 60 °C so as to provide a sufficient temperature differential for sample condensation, while avoiding any solidification of waxy material in the condenser tube. Use, without cleaning, the cylinder from which the sample was measured as the receiver, and place it so that the tip of the condenser does not touch the wall of the cylinder. The receiver temperature is required to be maintained at the same temperature (within \pm 3 °C) as the sample taken at the start of the test in order to obtain an accurate volume measurement in the receiving flask.

9.4 Apply the heat to the flask at a uniform rate so regulated that the first drop of condensate exits from the condenser between 10 min and 15 min (for 200 mL samples) or between 5 min and 15 min (for 100 mL samples) after initial application of heat. If performing a manual distillation, after the first drop falls, move the receiving cylinder so that the tip of the condenser tube touches the wall of the cylinder. Then regulate the heat so that the distillation proceeds at a uniform rate of 8 mL/min to 10 mL/min (for 200 mL samples) or 4 mL/min to 5 mL/min (for 100 mL samples). For 200 mL samples, continue the distillation until approximately 178 mL of distillate