Designation: D 4530 – 93 An American National Standard

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

This standard is issued under the fixed designation D 4530; 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 the amount of carbon residue (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 (Test Method D 189).

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 % residue should be distilled to remove 90 % of the flask charge (see Section 9 in Test Method D 189 for details). The 10 % bottoms remaining is then tested for carbon residue by this test method.

1.4 Ash-forming constituents as defined by Test Method D 482, 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 D 4046.

1.6 *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 practices and to determine the applicability of regulatory limitations prior to use.* For specific hazard statements see Note 5, Note 6, Note 7, and Note 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 189 Test Method for Conradson Carbon Residue of Petroleum Products[3]

D 482 Test Method for Ash from Petroleum Products[3]

D 4046 Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry[4]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *carbon residue, n— in petroleum products,* the part remaining after a sample has been subjected to thermal decomposition.

3.1.1.1 *Discussion*—The amount of residue is dependent on the test conditions of evaporation and pyrolysis. The term may be misleading here in that the residue may contain other than carbon decomposition products. However, the term is retained due to its wide common usage.

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)."

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 D 189 to which it is equivalent.

5.3 Up to twelve samples may be run simultaneously including a control sample.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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

[3] *Annual Book of ASTM Standards*, Vol 05.01.

[4] *Annual Book of ASTM Standards,* Volume 05.03.

6. Apparatus

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

6.2 *Eyedropper or Small Rod*, for sample transfer.

6.3 *Coking Oven*[5] with circular heating chamber approximately 85 mm (3-⅜ in.) diameter by 100 mm (4 in.) deep, for top loading, with heating capability of 10 to 40°C/min rate to 500°C, with exhaust port 13 mm (½ 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 condensate trap located at the oven chamber base. A schematic diagram is given in Fig. 1.

6.4 *Sample Vial Holder*—Cylindrical aluminum block approximately 76 mm (3 in.) diameter by 16 mm (⅝ in.) thick with twelve evenly-spaced holes (for vials) each 13 mm (½in.) diameter by 13 mm (½ in.) deep. The holes are arranged in a circular pattern approximately 3 mm (⅛ in.) from the perimeter. The holder has legs 6 mm (¼ 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. 2.

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

6.6 *Analytical Balance*, with ±0.1 mg sensitivity to 20 g minimum weighing capacity.

6.7 *Cylinder of Zero Grade Nitrogen (Industrial)*, with 2-stage regulator, for delivery pressure of 0 to 200 kPa (0 to 30 psig).

7. Procedure

7.1 *Sample Preparation*:

7.1.1 Obtain weights of clean sample vials (1 to 12 per batch), and record the mass to nearest 0.1 mg.

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

7.1.3 It is assumed that a representative sample of the stock or process has been obtained for laboratory use following Practice D 4057 or similar method, and that the laboratory has received a sample of about a gallon or less. Stir the sample to

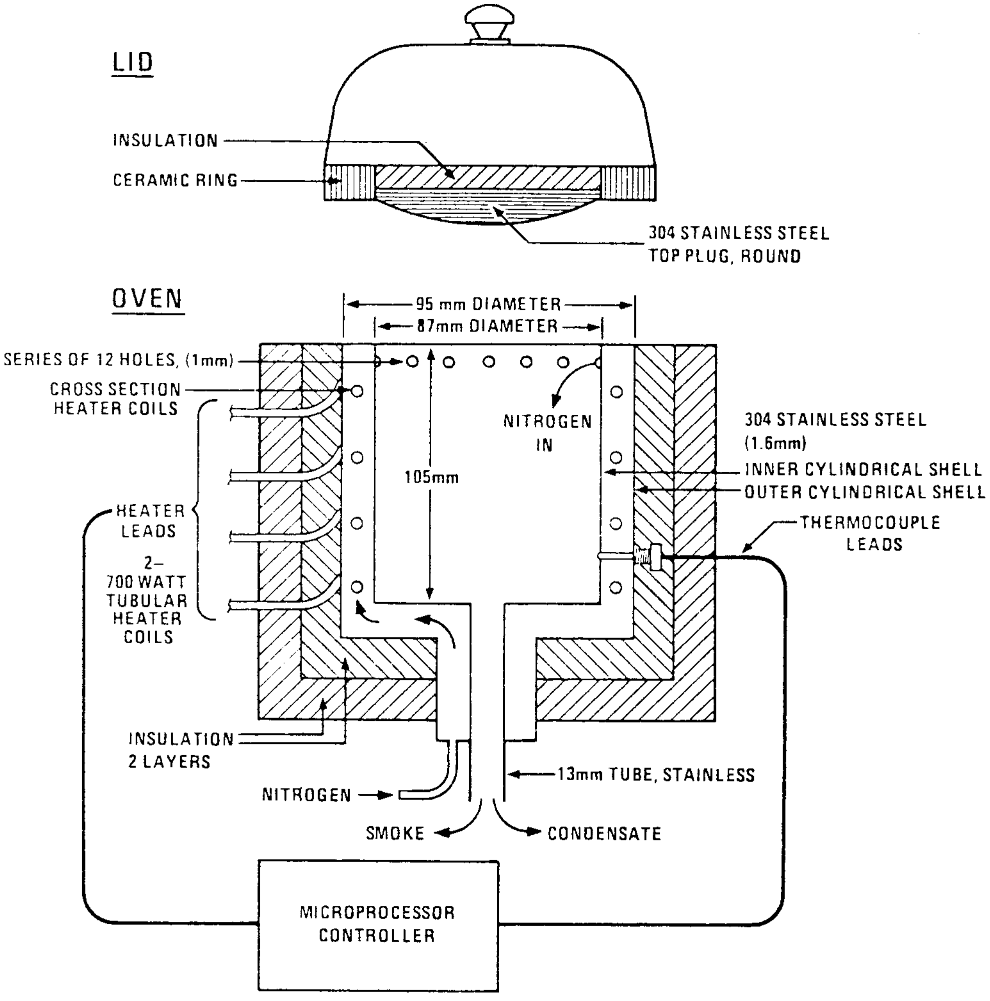

FIG. 1 Coking Oven and Lid

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[5] A satisfactory oven with associated automatic controls that performs this carbon residue test is available from ALCOR, INC., 10130 Jones-Maltsberger Road, San Antonio, TX 78216. This commercial unit is known as the MCRT.

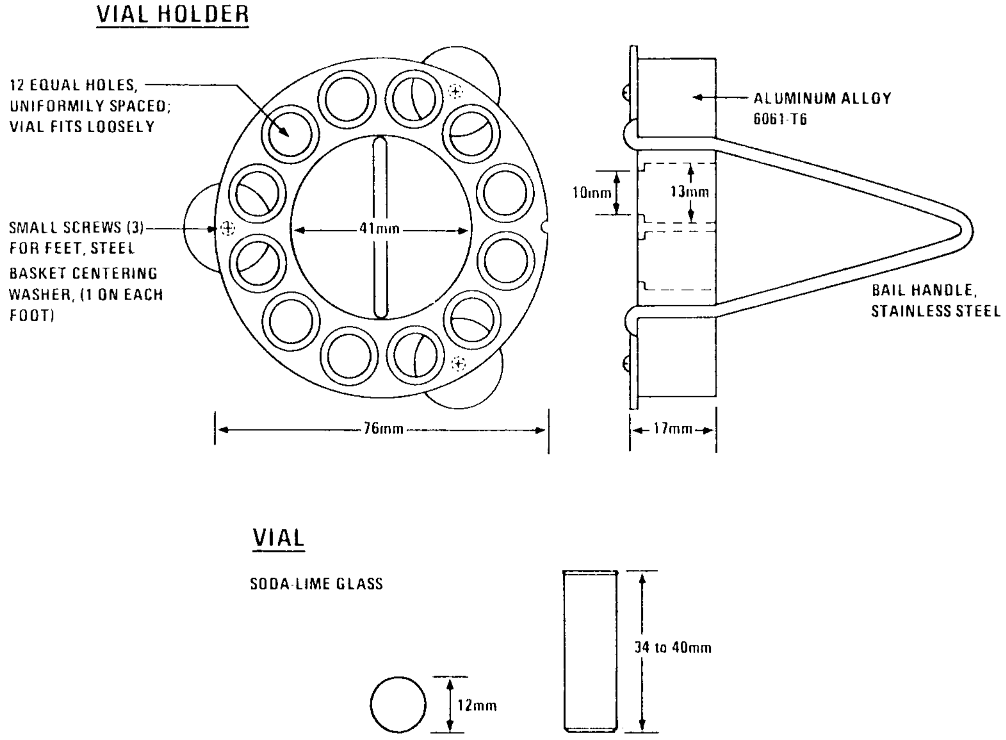

FIG. 2 Sample Vial Holder and Vial

be tested, first warming if necessary to reduce its viscosity. Samples that are homogeneous liquids can be transferred directly to vials using a rod or syringe. Solid materials may also be heated; or frozen with liquid nitrogen, then shattered to provide manageable pieces.

7.1.4 Transfer an appropriate weight of the sample (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 ± three standard deviations. Control results, which are outside these limits, indicate problems with the procedure or the equipment.

7.2 *Processing of Samples*:

7.2.1 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°–15°C/min.

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

TABLE 1 Guide for Sample Size

Sample Description	Expected Carbon Residue, (m/m) %	Recommended Sample Size, g
Black, viscous or solid	>5	0.15 ± 0.05
Brown, viscous	1–5	0.5 ± 0.1
Lube oil consistency and appearance, or 10 % bottoms	<1	1.5 ± 0.5

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.

7.2.3 Hold oven at 500 ± 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.

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.

NOTE 5—**Caution:** 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.

NOTE 6—**Precaution:** 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.

NOTE 7—**Caution:** If a vent line is used, do not connect directly to exhaust chimney to avoid creating negative pressure in the line.

7.3 *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.

7.4 Occasionally examine the condensate trap at the bottom of the oven chamber; empty if necessary and replace.

NOTE 8—**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.

8. Calculation

8.1 Calculate the mass percent carbon residue in the original sample, or in the 10 % distillation bottoms as follows:

8.1.1 Calculate percent residue as follows:

$$\%\text{ carbon residue } = \frac{(A \times 100)}{W} \tag{1}$$

where:
A = carbon residue (7.3.1), g, and
W = sample used (7.1.4), g.

8.1.2 Calculate the percent carbon residue in the original sample, when using 10 % distillation bottoms as follows (see Test Method D 189 for details):

$$\%\text{ residue in original sample} = \left(\frac{A}{C} \times 100\right) \times E \tag{2}$$

where:
A = carbon residue, g
C = 10 % bottoms used, g, and
E = final weight flask charge/original weight flask charge.

9. Report

9.1 Report the value obtained as carbon residue, micro method, to the nearest 0.1 % (m/m).

10. Precision and Bias [6]

10.1 The precision of this test method as determined by (Note 9) statistical examination of interlaboratory results is as follows:

NOTE 9—Precision data and Conradson carbon residue/micro carbon residue correlation data were generated by a task force in 1983. The round robin involved 18 laboratories, six petroleum materials in duplicate analysis for both micro method and Test Method D 189 tests. Range of values for samples was from 0.3 % to 26 %.

10.2 *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 values shown in Fig. 3 only in one case in twenty.

10.3 *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 values shown in Fig. 3 only in one case in twenty.

10.4 *Bias*—The procedure in Test Method D 4530 for measuring carbon residue of petroleum by the carbon residue method has no bias because the mass percent of carbon residue can be defined only in terms of the test method.

11. Keywords

11.1 carbon residue; carbon residue (micro method); diesel fuel; lubricating oil; petroleum products

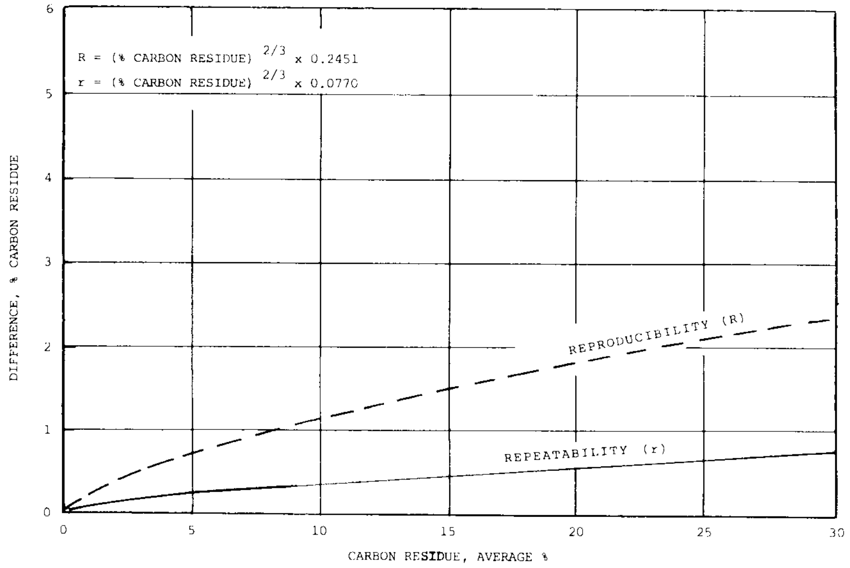

FIG. 3 Carbon Residue (Micro) Precision Data

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[6] Supporting data are available from ASTM Headquarters. Request RR:D02-1192.

APPENDIX

(Nonmandatory Information)

X1. CORRELATION AND OTHER METHODS

X1.1 A correlation (see Fig. X1.1) has been derived between the carbon residue test by the micro method and the Conradson carbon residue test (Test Method D 189) in a cooperative program involving 18 laboratories and six petroleum materials.

X1.2 Statistical analysis using modified Student's t tests and nonparametric analysis show that, considering the precisions of both tests, there is no difference between the two methods. The data generated by the carbon residue test by the micro method are statistically equivalent to the Conradson carbon residue test except for better precision in the micro method residue test.

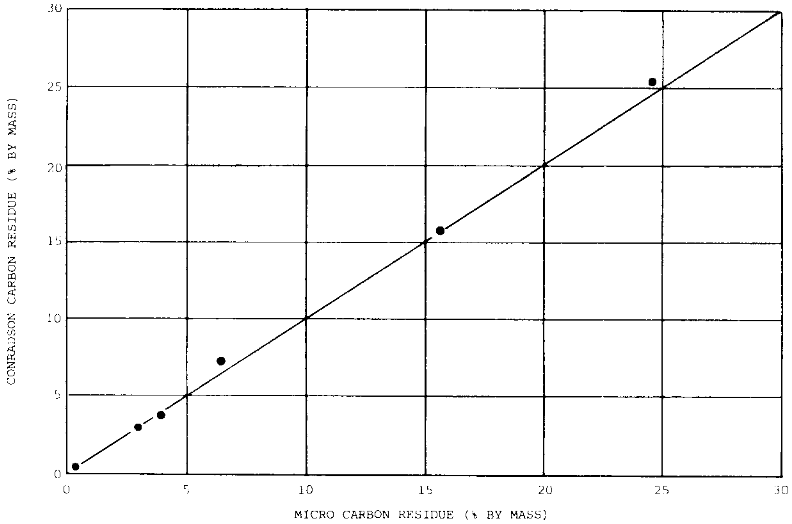

FIG. X1.1 Correlation of Conradson and Carbon Residue (Micro) Tests

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