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An American National Standard

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428

Standard Test Method for Real Density of Calcined Petroleum Coke by Xylene Displacement[1]

This standard is issued under the fixed designation D 5004; 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.

1. Scope

1.1 This test method is intended for the determination of the real density (RD) of calcined petroleum coke. Real density, by definition, is obtained when the particle size of the test specimen is smaller than 75 µm (No. 200 sieve).

1.2 The values stated in SI (metric) units are to be regarded as standard.

1.3 *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.* For specific hazard statements, see Sections 6.1.1, 8, 10, and 11.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Method for Preparing Coal Samples for Analysis[2]

D 2234 Test Methods for Collection of a Gross Sample of Coal[2]

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

D 4292 Test Method for Vibrated Bulk Density of Calcined Petroleum Coke[4]

D 4930 Test Method for Dust Control Material on Calcined Petroleum Coke[5]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

3. Terminology

3.1 *Definitions:*

3.1.1 *calcined coke*—green petroleum coke that has been thermally treated to drive off the volatile matter and to develop crystalline structure.

3.1.2 *petroleum coke*—a solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions or cracked stocks, or both.

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *bulk density*—the mass of the particles divided by the volume they occupy that includes the space between the particles. Refer to Test Method D 4292 for bulk density procedures.

3.2.2 *dedusting material*—see Test Method D 4930.

3.2.3 *real density*—(also referred to as true specific gravity), the mass divided by the volume occupied by the material excluding pores and voids. It is required, therefore, that voids in the coke be eliminated and that pores in the material be filled by the fluid being displaced. This requirement is met for the purposes of this test method by reducing the coke particles to a size smaller than 75 µm.

3.2.3.1 *Discussion*—The density of particles larger than 75 µm up to the largest that can be put into the helium pycnometer can also be determined, but must be designated as particle density (PD). The precision data obtained for RD may not be applicable to PD.

4. Summary of Test Method

4.1 The mass of the sample is determined directly and the volume derived by determining the mass of liquid displaced when the sample is introduced into a pycnometer.

$$RD = M \times D/L \quad (1)$$

where:

M = mass of sample,
D = density of displaced liquid, and
L = mass of displaced liquid.

5. Significance and Use

5.1 The density of petroleum coke directly influences the physical and chemical properties of the manufactured carbon and graphite artifacts for which it is used. Density, therefore, is a major quality specification of calcined petroleum coke and is used as a control in coke calcination.

6. Interferences

6.1 Oil or other material sprayed on calcined petroleum

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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 D02.05.OD on Petroleum Coke Sampling and Procedures.

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[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

coke to control dust will interfere with the determination of real density so the oil must be removed before reducing the sample to 75 µm.

6.1.1 When a petroleum oil was used, it can be removed by flushing with a solvent such as methylene chloride, dichloroethane, or toluene. The solvent must be completely removed before proceeding with the RD determination. Heating to 10°C above the boiling point of the solvent used or application of vacuum is satisfactory for the removal of the dedusting oil.

NOTE 1—**Warning:** Consult the Material Safety Data Sheet (MSDS) for the selected solvent.

6.1.2 An alternative method of oil removal is by heating the calcined coke sample in an oven at 700°C for 1 h.

7. Apparatus

7.1 *Pycnometer*, or specific gravity bottle, 50 mL, with a ground glass stopper with a capillary hole.[7] Bottles with a large neck (12 to 13 mm outside diameter) are preferred.

7.2 *Water Bath*, controlled to a temperature of 25 ± 0.1°C.

NOTE 2—This test method is written to be performed at 25 ± 0.1°C; however, some laboratories may not have the provisions to perform the test at this temperature. It is permissible to perform the test procedure at any temperature between 20 and 40°C providing that the water bath is controlled at ±0.1°C of the chosen temperature and the pycnometers are calibrated at the same temperature that is used to determine the real density of the petroleum coke sample. This is possible due to the fact that the real density of calcined petroleum coke is not affected by temperature changes over a limited temperature range.

7.3 *Analytical Balance*, accurate to ±0.1 mg.

7.4 *Vacuum Desiccator*, with guard, connected to a vacuum source capable of lowering pressure to 75 mm of Hg (10 kPa).

7.5 *Desiccator*, with drying agent. Anhydrous calcium sulphate is satisfactory.

7.6 *Drying Oven*, preferably a vacuum oven, for temperature to 120°C.

7.7 *Lead Weights*, for the pycnometers, to prevent tipping over in the water bath. These can be made by coiling solid wire solder.

7.8 *Wire Sieve*, 75 µm (No. 200 mesh), meeting Specification E 11.

8. Reagents

8.1 *Purity of Water*—References to distilled water shall be understood to mean reagent water as defined by Type III of Specification D 1193.

8.2 Analytical reagent grade solvents are not required but can be used. The technical grade of each of the following is satisfactory:

8.2.1 *Acetone*, *Xylene*, and *Ethyl Alcohol*.

NOTE 3—**Warning:** See 6.1.2

9. Sample Preparation

9.1 For recommended practice for obtaining, handling, and preparing coke samples, refer to Practice D 346, Method D 2013, Test Methods D 2234, and Practice D 4057. See Section 6.

9.2 Crush 50 g of coke so that the entire sample will pass through a 75 µm (No. 200) sieve. Dry the crushed sample in a drying oven at 115± 5°C to constant mass (approximately 8 h). Cool in a desiccator.

NOTE 4—Constant mass is considered to be achieved when change in mass is less than ±0.05 g after a 30 min test drying period.

10. Pycnometer Calibration (Determination of Pycnometer Volume)

NOTE 5—**Caution:** Commercial pycnometers (specific gravity bottles) can either have not been calibrated at 25°C or else not calibrated to the accuracy required for this test method, so it is necessary that the pycnometer volume be determined.

10.1 Clean the pycnometer and its stopper with detergent, rinse thoroughly with water then with acetone. Place in a desiccator to dry, then weigh the empty pycnometer together with its stopper to 0.1 mg (mass W_o). The temperature of the pycnometer is to be close to room temperature when its weight is determined.

NOTE 6—**Precaution:** Do not handle the pycnometer with bare fingers. Finger cots or surgical gloves can be worn, or tongs can be used, when handling the pycnometer to prevent moisture from fingers influencing the weight.

10.2 Fill the pycnometer with freshly boiled (to remove air) and cooled distilled water, and replace the stopper. Immerse the pycnometer up to the neck in the 25° ± 0.1°C water bath for 1 h. Use the lead weights to prevent tipping. Replace water that leaves the capillary during this period. A syringe is convenient for this purpose.

10.3 At the end of the temperature stabilization period, check the capillary to be certain it is completely filled. Remove excess water on the stopper by dabbing with filter paper. If water is inadvertently removed from the capillary it must be replaced. Remove the pycnometer from the 25°C bath, rinse immediately with acetone, dry, and weigh to 0.1 mg (mass W_3).

NOTE 7—**Caution:** Avoid any heating after the pycnometer is removed from the 25°C bath. Heating will expand the water and cause loss from the capillary. Water is not to be added to the capillary after the pycnometer is removed from the 25°C bath. The purpose for the immediate acetone rinse is to contract the contents so it will recede in the capillary. Ethyl alcohol can be used in place of acetone. If laboratory temperature is 25°C or above, a water bath maintained at about 20°C should be provided to cool the pycnometer for about 1 min then dry and weigh. Do not chill the pycnometers so cold that moisture from the atmosphere will condense on them and make accurate weighing impossible.

10.4 Calculate the volume, v, of the pycnometer in cubic centimetres using Eq 2. Round off to 0.001 cm^3.

$$v = \frac{W_3 - W_o}{\rho w} \quad (2)$$

where:

W_o = mass of the empty pycnometer, g,
W_3 = mass of the water filled pycnometer, g, and
ρ_w = density of water at 25°C = 0.9970 g/cm^3.

NOTE 8—**Caution:** If this test method is performed at a temperature other than 25± 0.1°C as stated in Note 2, then ρ_w is the density of water at the temperature chosen for the measurement. The density of water at temperatures other than 25°C is available in numerous standard reference journals.

[7] A Gay-Lussac pycnometer has been found suitable for this purpose.

10.5 Repeat 10.1-10.4 seven times over a two to three day period. Individual values should not deviate from the mean by more than ±0.0015 cm^3. Use the mean value in all calculations using Eq 3. Re-determine the pycnometer volume every three months. The mass, W_o, should remain constant to within ±0.001 g.

11. Determination of the Density of Xylene

11.1 Follow the procedure in 10.1-10.3, but use xylene instead of water. Calculate the density, ρ_x, of xylene at 25°C in g/cm^3 using Eq 3. Round off to 0.0001 g/cm^3.

NOTE 9—**Caution:** Avoid any heating after the pycnometer is removed from the 25°C bath. Heating will expand the xylene and cause loss from the capillary. Xylene is not to be added to the capillary after the pycnometer is removed from the 25°C bath.

$$\rho_x = \frac{W_2 - W_o}{v} \tag{3}$$

where:
W_o = mass of the empty pycnometer, g,
W_2 = mass of the xylene-filled pycnometer, g, and
v = pycnometer volume, cm^3.

12. Procedure

12.1 Clean the pycnometer and its stopper with detergent and rinse thoroughly with water then with acetone and dry in a desiccator.

12.2 Weigh the pycnometer with its stopper to 0.1 mg (mass W_o). The temperature of the pycnometer is to be close to ambient room temperature. (See Note 6.)

12.3 Introduce approximately 10 g of the dried and cooled analysis sample into the clean, dry, pycnometer. Less sample can be used but should not be less than 5 g.

12.4 Replace the stopper, remove any coke adhering to the outer pycnometer surface, and re-weigh. The difference between this mass and W_o is the sample mass (mass W_s).

12.5 Fill the pycnometer with enough xylene to wet and cover the sample and swirl gently to aid wetting and to displace air. Add additional xylene until the pycnometer is about two-thirds full and place it, without stopper, in the vacuum desiccator at as low an absolute pressure (or high a vacuum) as possible to remove air from the coke but to avoid excessive evaporation of the xylene. If a means is available, vibrate the pycnometer gently and intermittently while in the desiccator to assist in the elimination of air. Leave under vacuum until all bubbling stops. It is recommended that time under vacuum be at least 30 min.

12.6 Remove the pycnometer from the desiccator, fill it with xylene, and place it in the 25 ± 0.1°C bath with stopper in place. Immerse the pycnometer up to the neck in the water bath for 1 h. Use the lead weights to prevent tipping. Replace xylene that leaves the capillary during this period. A syringe is convenient for this purpose.

12.7 At the end of the temperature stabilization period, check the capillary to be certain it is completely filled. Remove excess xylene on the stopper by dabbing with filter paper. If xylene is inadvertently removed from the capillary, it must be replaced. Remove the pycnometer from the 25°C bath, rinse immediately with acetone, dry, and weigh to 0.1 mg (mass W_1).

12.8 Upon completion of the test procedure, clean and dry the pycnometers. To facilitate cleaning of the pycnometers, remove a portion of the xylene and replace with acetone. Then shake this xylene/acetone mixture and facilitate removal of the petroleum coke from the pycnometers. Clean the pycnometers as specified in 10.1 before reuse.

13. Calculation

13.1 Determine the density of the sample in g/cm^3 from Eq 4 as follows:

$$\text{density} = W_s\left(\frac{\rho_x}{W_s - (W_1 - W_2)}\right) \tag{4}$$

where:
W_s = mass of sample, g,
ρ_x = density of xylene at 25°C, g/cm^3,
W_1 = mass of the pycnometer filled with sample and xylene, g,
W_2 = mass of the pycnometer filled with xylene alone, g,
$W_s - (W_1 - W_2)$ = mass of xylene displaced by coke, g, and
$\frac{\rho_x}{W_s - (W_1 - W_2)}$ = volume of xylene displaced by coke, cm^3.

14. Report

14.1 Report to the third decimal place the average of duplicate determinations that agree within 0.007 g/cm^3. When this agreement is not met, the values are considered suspect and another duplicate set shall be run. Report the average of all results agreeing within 0.007 g/cm^3. If the second set also fails to agree within 0.007 g/cm^3, report the average of all four values. The operator shall also report if the second set of duplicate determinations fail to agree within 0.007 g/cm^3.

15. Precision and Bias [8]

15.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between successive results by the same operator using the same apparatus under constant operating conditions on identical test materials, will in the long run, in normal and correct operation of the test method, exceed the following values only in one case in twenty: repeatability = 0.0067.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials, will in the long run, in normal and correct operation of the test method, exceed the following values only in one case in twenty: reproducibility = 0.0156.

15.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring the real density of calcined petroleum coke, no statement on bias is being made.

16. Keywords

16.1 calcined petroleum coke; petroleum coke; pycnometer;

[8] The values in the statements were determined in a cooperative program following Research Report RR:D02-1007, available from ASTM Headquarters.

real density; xylene displacement