Designation: ~~D5187 – 10 (Reapproved 2015)$^{\varepsilon 1}$~~ D5187 – 21

Standard Test Method for
Determination of Crystallite Size (L_c) of Calcined Petroleum Coke by X-Ray Diffraction[1]

This standard is issued under the fixed designation D5187; 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.

~~ε^1 NOTE—Editorial changes were made throughout in December 2015.~~

1. ~~Scope~~ Scope*

1.1 This test method covers the determination of the mean crystallite thickness of a representative, pulverized sample of calcined petroleum coke by interpretation of a X-ray diffraction pattern produced through conventional X-ray scanning techniques.

1.2 Calcined petroleum coke contains crystallites of different thicknesses. This test method covers the determination of the average thickness of all crystallites in the sample by empirical interpretation of the X-ray diffraction pattern. The crystallite diameter (L_a) is not determined by this test method.

1.3 The values stated in SI (metric) units are to be regarded as the standard. The inch-pound units given in parentheses are provided for information purposes 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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:*[2]

~~D346~~D6969 Practice for ~~Collection and~~ Preparation of Calcined Petroleum Coke Samples for ~~Laboratory~~ Analysis
~~D2013~~D6970 Practice for ~~Preparing Coal~~ Collection of Calcined Petroleum Coke Samples for Analysis
~~D2234/D2234M Practice for Collection of a Gross Sample of Coal~~
~~D4057 Practice for Manual Sampling of Petroleum and Petroleum Products~~
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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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 D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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[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**

3.1.1 *crystallites, n*—stacks of graphitic carbon platelets located parallel to one another.

3.1.2 L_c, *n*—the mean or average thickness of crystallites in a sample. It is expressed as a linear dimension in angstrom units, A° (10^{-1} nm).

3.1.3 *hkl(002), n*—the Miller indices of the crystalline planes of graphite corresponding to a lattice spacing (*d*) of 3.35 Å.

3.1.4 *Theta angle*, Θ, *n*—the glancing angle produced when a parallel beam of uniform X-rays impinges upon a crystalline lattice. This angle is measured by the X-ray goniometer and is usually expressed in degrees TwoTheta ° (2Θ).

4. Summary of Test Method

4.1 A packed sample pulverized to less than 75 µm is subjected to a monochromatic X-ray beam and rotated to produce a diffraction pattern under specific conditions. The location and shape of the peak with $hkl = (002)$ at $d = 3.35\ A^\circ$ is used to calculate the L_c by manual interpretation of the peak or by computer simulation.

5. Significance and Use

5.1 The crystallinity of petroleum coke, as reflected by the L_c value, is a general measure of quality affecting suitability for end use and is a function of the heat treatment.

5.2 The crystallite thickness is used to determine the extent of such heat treatment, for example, during calcination. The value of the L_c determined is not affected by coke microporosity or the presence of foreign, non-crystalline materials such as dedust oil.

6. Apparatus

6.1 *X-Ray Powder Diffractometer,* equipped with an X-ray source, a monochromator or filter for restricting the wavelength range, a sample holder, a radiation detector, a signal processor, and readout (chart or computer memory). The diffractometer must be capable of rate scanning at 1 °2Θ/min or incrementally step scanning at 0.2 °2Θ steps.

6.2 *Sample Holders,* as specified by the manufacturer of the diffractometer that enables packing of a pulverized sample of sufficient thickness to expose a level, smooth surface to the X-ray beam.

6.3 *Briquetting Press,* capable of generating pressures up to 69 MPa (10 000 psi).

6.4 *Compressible Aluminum Caps,* used as a support for producing a briquetted sample.

6.5 *Silicon or Quartz Sample,* available from National Institute of Standards and Technology (NIST).

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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.

7.2 *Acetone.*

7.3 *Polyethylene Glycol,* (approximate molecular weight of 200 AU).

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[3] ~~*“Reagent Chemicals, American Chemical Society Specification.” American Chemical*~~ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, ~~D.C.~~DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*“Analar*~~*Analar Standards for Laboratory* ~~*U.K.*~~*Chemicals,* ~~Chemicals,”~~ BDH Ltd., Poole, Dorset, U.K., and the ~~*“United States Pharamacopeia.”*~~*United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.4 *Binding Agent*—Prepare a 15 % by mass solution of polyethylene glycol and acetone by adding 15 g of polyethylene glycol to 85 g of acetone.

8. Sample Preparation

8.1 For recommended practices for obtaining, handling and preparing coke samples, refer to ~~Test Methods D2013 and D2234/D2234M and~~ Practices ~~D346~~D6969 and ~~D4057~~D6970. The equipment and procedures for crushing and dividing are also described in these ~~test methods.~~practices.

8.2 Reduce and divide the gross sample to obtain a laboratory analysis sample.

8.3 Divide, by riffling, a minimum of 100 g from the laboratory analysis sample.

8.4 Crush 100 g of the test sample such that 98 % will pass through a 75 µm (No. 200) sieve.

8.5 *Techniques*—Any of the following techniques can be used for packing the sample into the X-ray diffractometer specimen holder:

8.5.1 *Back Fill Technique*—Put the window on a glass slide (Slide 1) and transfer sufficient quantities of sample into the window. Work the sample towards the corners of the holder by use of a glass slide or spatula. Press down using a flat glass slide and scrape off any excess material. Place a glass slide (Slide 2) on top of the sample and secure with tape. Remove Slide 1 to expose a flat, smooth surface before inserting into the diffractometer for analysis.

8.5.2 *Front Fill Technique*—Place a confining ring over the round sample holder and fill the holder cavity and ring with sample. The ring will initially overfill the sample holder. Work the sample into the entire cavity and ring. Scrape the excess off with a glass plate or spatula. Press down using a flat glass slide. Remove any excess material on the front face of the holder. Repress the sample with the glass slide while turning clockwise and anti-clockwise. Continue until the sample is level with the holder face. Place the sample in diffractometer holder.

8.5.3 *Side Loading Technique*—Pack the sample following the procedure used by the National Institute of Standards and Technology and the Joint Committee on Powder Diffraction Standards to prepare standard powder diffraction patterns.[4] Clamp a glass slide over the top face to form a temporary cavity wall. With the holder in a vertical position, drift the powdered sample into the end opening. If necessary, use a cardboard pusher cut to fit the cavity to lightly compress the sample so it will remain in the cavity. Return the holder to a horizontal position and carefully remove the glass slide. Place the sample in diffractometer holder.

8.5.4 *Briquetting Technique*—Weigh out 4.0 g of the sample onto a watch glass and pipette exactly 3 mL of the binding agent onto the sample and mix thoroughly with a spatula. Place the sample under an infrared heat lamp and allow the acetone to evaporate. Typically, between 1 min and 2 min will be required to eliminate the acetone odor from sample. Break up the caked sample with a spatula and transfer to an aluminum cap whose diameter is compatible with the sample holder of the diffractometer. Place the cap in a briquetting press and press at 48 MPa (7000 psi). Transfer the pelletized sample to the sample holder and insert into the diffractometer for analysis.

9. Calibration

9.1 Calibration consists of ensuring that the diffractometer is in correct mechanical and optical alignment and intensities have been maximized through the procedures described in the instrument manufacturer's documentation. This is best accomplished by a service engineer or in-house technician who has been well instructed in the correct alignment procedures suggested by the manufacturer.

9.2 Proper angles and intensities are monitored by a reference material such as NIST silicon and corrective actions taken if necessary.

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[4] McMurdie, et al., "Methods of Producing X-Ray Diffraction Powder Diffractions," *Powder Diffraction*, Vol 1, No. 1, March 1986.

10. Procedure

10.1 Prepare and operate the diffractometer in accordance with the manufacturer's instructions. Once established, closely control all instrumental parameters to ensure repeatable analyses.

10.2 Place the packed sample in the instrument's sample holder and energize the X-ray source.

10.3 Obtain a diffraction pattern rate scanned at 1 °2Θ/min or step scanned at 0.2 °2Θ per step over the range of 14 °2Θ to 34 °2Θ. Record the data either on a strip chart recorder scanning at 1 °/min or through computer software designed to read and store the angular and intensity measurements.

10.4 For manual interpretation from a strip chart recording, refer to Fig. 1.

10.4.1 Determine the average low and high background (Points A and B, respectively) on the diffraction scan and connect them with a straight line.

10.4.2 Construct Line CD parallel to AB and going through the apex of the peak at point *G* [(*hkl* = 002 at 3.35 A°)]. Draw the line such that if the peak is irregular it will pass through the average of the irregularities.

10.4.3 Determine the full width half maximum (FWHM) of the peak by measuring the vertical distance between CD and AB. Construct Line EF such that it intersects the peak at half of its maximum value. The points at which EF intersects the peak are $2\Theta_1$ and $2\Theta_2$, respectively.

10.5 For computer simulation based on the intensities recorded at 0.2 °2Θ intervals, produce a mathematical representation of the diffraction curve. Determine the baseline, peak, peak height, and half peak height to produce the half peak height angles, $2\Theta_1$ and $2\Theta_2$, as above.

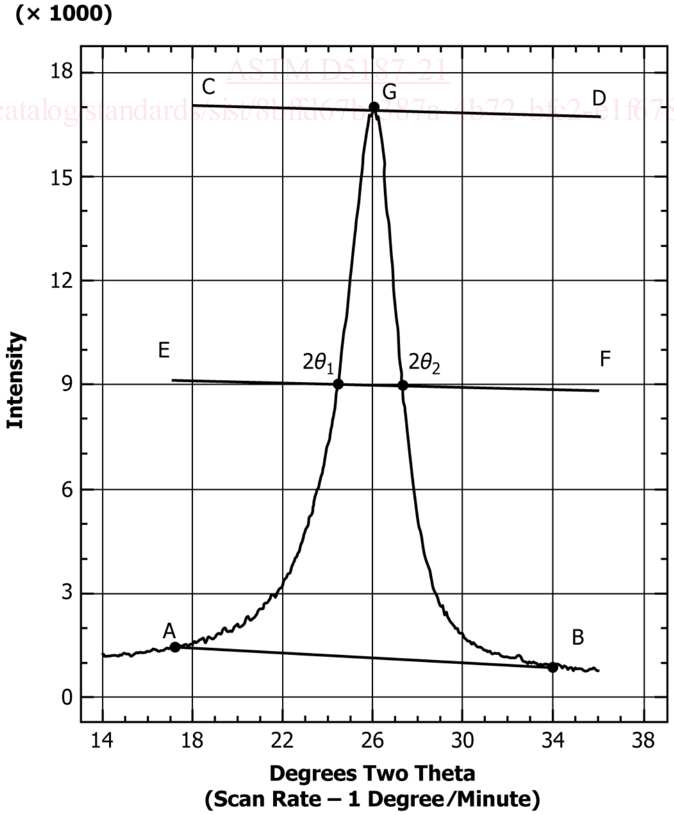

FIG. 1 Typical Diffraction Scan of Petroleum Coke