



## Standard Test Method for Volatile Matter in Petroleum Coke<sup>1</sup>

This standard is issued under the fixed designation D 4421; 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 approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method determines the volatile matter produced by pyrolysis or evolved when petroleum coke, or both, is subjected to the specific conditions of the test. Samples having a thermal history above 600°C are excluded.

1.2 This test method is empirical and requires the entire test procedure to be closely followed to ensure results from different laboratories to be comparable.

1.3 This test method is not satisfactory for dedusting material content.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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.* Specific precautionary statements are given in Section 8.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

E 11 Specification for Wire-Cloth Sieves for Testing Purposes<sup>2</sup>

E 220 Test Method for Calibration of Thermocouples by Comparison Techniques<sup>3</sup>

### 3. Terminology

#### 3.1 Descriptions of Terms Specific to This Standard:

3.1.1 *analysis sample*—the reduced and divided representative portion of a bulk sample, prepared for use in the laboratory.

3.1.2 *bulk sample*—the reduced and divided representative portion of a gross sample as prepared for shipment to and received by a laboratory, to be prepared for analysis.

3.1.3 *gross sample*—the original, uncrushed, representative portion taken from a shipment or lot of coke.

3.1.4 *petroleum coke*—a solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions and cracked stocks.

3.1.5 *test sample*—the weighed portion of the analysis sample actually used in a test.

3.1.6 *volatile matter*—an empirical value equal to the mass loss on heating expressed as a percent of the moisture free sample used. It is determined only by this ASTM standard for petroleum coke.

### 4. Summary of Test Method

4.1 Volatile matter of a moisture free petroleum coke is determined by measuring the mass loss of the coke when heated under the exact conditions of this procedure.

### 5. Significance and Use

5.1 The volatile matter of petroleum coke affects the density of coke particles and can affect artifacts produced from further processing of the coke.

5.2 The volatile matter can be used in estimating the calorific value of coke.

### 6. Interferences

6.1 Moisture has a double effect. The mass loss is increased and the moisture free sample weight is decreased by the amount of moisture actually present in the test sample.

#### 6.2 Particle Size Effect:

6.2.1 The particle size range of the analysis sample affects the volatile matter. The coarser the analysis sample, the lower the volatile matter will be. The analysis sample (see Annex A1) is crushed to pass a No. 60 sieve (0.250-mm opening) but is not overcrushed. A No. 120 sieve (0.125-mm opening) should retain 40 to 55 % of the sample. The analysis sample is not to be obtained by scalping and discarding a portion of the sample.

6.2.2 Any segregation of particle sizes within the analysis sample shall be corrected by reblending the sample just prior to weighing the test sample.

6.3 Downward drift of furnace temperature caused by an increase in the millivolts per degrees Celsius generated by an aging type K thermocouple produces a lower volatile matter value (Test Method E 220).

<sup>1</sup> 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 on Properties of Fuels, Petroleum Coke, and Oil Shale.

Current edition approved Sept. 15, 1994. Published November 1994. Originally published as D 4421 – 84. Last previous edition D 4421 – 89.

<sup>2</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.03.

6.4 Diffusion of air into the crucible caused by a poor fit between the crucible and its cover or by any other source of available oxygen causes high and erratic volatile matter values.

6.5 Free or tramp iron or mill scale in the coke coats the surface of the platinum crucible and decreases its life. The coating tends to form an oxide film during the preburning step (10.1). The oxide film provides a source of excess weight loss equal to almost twice the oxygen weight gained. Clean the crucible and buff with sand. Buffing will restore luster to the surface of the crucible.

## 7. Apparatus

7.1 *Furnace*, Fieldner, electric, ASTM, calibrated (Test Method E 220) and regulated to maintain a temperature of 950°C (1742°F) ± 15°C as measured by a thermocouple mounted inside the furnace.

7.2 *Nickel Chromium Crucible Support* for the platinum crucible.

7.3 *Platinum 90 % – Rhodium 10 % Crucible*, volatile matter form, reinforced top and bottom, capacity 15 mL; height 33 mm; top diameter 29 mm; fitted with a capsule-type cover 10 mm high. The cover is to have a 0.5-mm diameter hole drilled through the center. The total weight, crucible and cover, approximately 20 g.

7.4 *Reshapers* for the platinum crucible and cover.

7.5 *Rifflers*, with hoppers and closures.

7.6 *Jaw Crusher and Roll Crusher*—Other style crushers which allow control over particle size without contamination are acceptable. (See Annex A1.)

7.7 *Sieves*, as required (Specification E 11).

7.8 *Timers*, stopwatch or second-timer accurate to ±1 s.

## 8. Precautions

8.1 Effusion of gaseous products, including soot and various hydrocarbons and the increase of heat associated with the test can make use of a hood desirable.

## 9. Preparation of Furnace

9.1 If desired, the radiant heat loss to the room from the outside metal cylinder can be reduced by insulating the furnace with a thick layer of insulation and glass wool.

9.2 Fit a thermocouple into the bottom of the furnace. Use borosilicate glass wool to close the opening around the thermocouple. Adjust the thermocoupled position so it rests 2 to 3 mm below the bottom of the platinum crucible with the platinum crucible positioned in the crucible support and the support resting on the top of the furnace.

9.3 Hang a 100 to 150-mm (4 to 6-in.) mirror above the furnace, positioned to allow the operator to observe the platinum crucible during the time it is positioned in the furnace.

## 10. Procedure

10.1 Ignite a platinum crucible and cover at 950°C for 5-min periods to constant mass (±0.5 mg). A burner or any furnace is to be used but the crucible can be set in a nichrome wire support regardless of the style of furnace used. The cover shall not seal the crucible at this time; so that the carbon will burn off. Cool to room temperature in a desiccator before

weighing the crucible and cover. Do not keep the crucible at room temperature more than 20 min before it is weighed. Record all masses to 0.1 mg.

10.2 Avoiding segregation of particles, transfer 1 g (±1 mg) of the analysis sample (Annex A1) to the crucible and weigh the crucible with its content and cover to the nearest 0.1 mg. Fit the cover on the crucible and press it gently into position. Avoid physical distortion of the crucible and cover.

### 10.3 *Manual Method*:

10.3.1 Set the crucible vertically in the holder and center it over the furnace opening with the bottom of the crucible in line with the top surface of the transite furnace cover (Note 1). Be sure neither the crucible nor the holder touch the wall of the furnace. Start the timer.

NOTE 1—There are some coke-VM relationships which require the crucible bottom to be 6 mm (¼ in.) above the top surface of the transite-cover in the initial position. These relationships prevent control of sparks or flames, or both.

10.3.2 After 60 s (±5 s), lower the holder approximately 8.5 mm (⅓ in.) into the furnace. The holder is lowered another 8.5 mm (⅓ in.) after each total elapsed time of 120, 180, 240, 300, and 360 s (each ± 5 s). After the move at 360 s, the top of the crucible should be 19 mm (¾ in.) below the top surface of the transite cover. DO NOT position the bottom of the crucible more than 57 mm (2¼ in.) below the top surface of the transite cover at this time (Note 2).

NOTE 2—The heating rate is extremely important since the test is empirical and equilibrium is not achieved. The heating rate is controlled by the rate of lowering the crucible into the furnace. Once the holder is positioned immediately over the furnace the time schedule must be observed. The crucible shall not be removed, or raised and relowered, without verifying the test.

10.3.3 If at any time during the test, sparking occurs such that the sparks are seen to be above the height of the crucible cover or if a flame or flames occur such that the sum of all visible simultaneous flames extend above the height of the crucible cover, the test must be repeated with slight variations during the first 600 s. These variations are to be made with respect to the position when the sparks or flames occur. A more severe heatup rate (more rapidly lowering) will result in less sparking or flaming subsequently but can result in sparking or flaming earlier in the test. Discretion is necessary. A maximum furnace depth for the bottom of the crucible of 57 mm (2¼ in.) is to be maintained during the first 600 s.

10.3.4 After 600 s (±5 s) total elapsed time, lower the holder so the brass ring of the holder rests directly upon the transite furnace cover (maximum depth in furnace).

10.3.5 After 960 s (±5 s) total elapsed time, raise the holder and crucible out of the furnace and immediately place the crucible in a desiccator.

10.3.6 Weigh the crucible after it has cooled to room temperature and before it has been at room temperature for longer than 20 min.

### 10.4 *Automatic Method* (See Annex A2):

10.4.1 Equipment for automatically lowering the crucibles into the furnace can be built. This equipment permits one or more samples to be run simultaneously with minimal operator