



## 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 reapproval. 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 pro-

duced 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).

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

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

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

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)  $\pm$  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  $\pm$ 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 ( $\pm$ 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 ( $\pm$ 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 ( $\frac{1}{4}$  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 ( $\pm$ 5 s), lower the holder approximately 8.5 mm ( $\frac{1}{3}$  in.) into the furnace. The holder is lowered another 8.5 mm ( $\frac{1}{3}$  in.) after each total elapsed time of 120, 180, 240, 300, and 360 s (each  $\pm$  5 s). After the move at 360 s, the top of the crucible should be 19 mm ( $\frac{3}{4}$  in.) below the top surface of the transite cover. DO NOT position the bottom of the crucible more than 57 mm ( $2\frac{1}{4}$  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 ( $2\frac{1}{4}$  in.) is to be maintained during the first 600 s.

10.3.4 After 600 s ( $\pm$ 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 ( $\pm$ 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 attention. Lack of operator attention to the progress of the test can cause problems with repeatability of analysis (see 10.3.3).

10.4.2 These automatic lowering devices are to be capable of lowering the crucible into the furnace at the rates in the manual method. The lowering of the crucible can be stepwise or at a continuous rate during the initial 600 s. From this point,

the automatic equipment must conform to the manual method, Steps 10.3.4 and 10.3.5.

## 11. Calculations

11.1 Calculate the volatile matter of the moisture free prepared coke as follows:

$$\text{Volatile matter, mass \%} = (A/B) \times 100 \quad (1)$$

where:

$A$  = mass loss of the sample, g, and

$B$  = mass of sample, g.

## 12. Precision and Bias <sup>4</sup>

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

12.1.1 *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:

$$\text{Repeatability} = 0.08 (X) \quad (2)$$

where  $X$  is the average of two results in weight percent.

12.1.2 *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:

$$\text{Reproducibility} = 0.21 (X) \quad (3)$$

where  $X$  = the average of two results in mass percent.

12.1.3 *Bias*—The test is empirical, therefore, the results are dependent on the material, on the particulate composition of the sample and on the manner of the test. Bias is not a definable constituent outside this test. Therefore, no statement of accuracy is possible.

## 13. Keywords

13.1 petroleum coke; volatile matter

<sup>4</sup>Supporting data have been filed at ASTM Headquarters. Request RR: D02-1189.

## ANNEXES

### (Mandatory Information)

#### A1. PREPARATION OF SAMPLES

##### A1.1 Preparation of Bulk Sample:

A1.1.1 The bulk sample is prepared by dividing the gross sample in such a manner as to obtain a representative bulk sample.

A1.1.2 The bulk sample can vary in weight from 22.7 kg (50 lb) to 90.6 kg (200 lb.) and will vary in top particle size from 6 mm (¼ in.) to 38 mm (1½ in.), depending upon the particle size of the gross sample.

A1.1.3 Air dry the bulk sample, if needed, so that it can be properly ground and fed through riffles. Air dry using drying pans 38 mm (1.5 in.) deep made of noncorroding metal and of sufficient size that the sample can be spread to a depth of approximately 25 mm (1.0 in.). The maximum depth of the sample must be no more than twice the diameter of the largest particles. The room shall be free of dust and excessive air currents. Avoid excessive drying time.

A1.1.4 An air drying oven can be used to pass slightly heated air over the sample. The oven is to be capable of maintaining a temperature of 30°C to 40°C. Air changes should be at a rate of 1 to 4/min. Avoid over-heating and excessive drying.

A1.1.5 A drying floor can be used to dry bulk samples. This is a smooth clean floor in a room free from dust and excessive air current.

A1.1.6 Any modification of the above that will not overheat or contaminate the bulk sample is permitted.

A1.1.7 After the bulk samples have been air dried, grind the

entire sample to pass a 6.7 mm sieve using a jaw crusher. Do not overgrind, keep a maximum amount of sample as coarse as possible.

##### A1.2 Preparation of Analysis Sample:

A1.2.1 Using a riffle, split the bulk sample to obtain a 700-g portion.

A1.2.2 Pass the coke through the riffle from a feed scoop, feed bucket, or riffle pan having a lip length or opening equal to the full length of the riffle. When using any of the above containers to feed the riffle, spread the coke evenly in the container, raise the container and hold it with its front edge resting on the top of the feed trough; then slowly tilt it so the coke flows in uniform streams through the hopper straight down the chutes into the pans. Under no circumstances shovel the coke into the riffle or dribble the coke into the riffle from a small mouth container. Make sure the riffle has a chute opening of at least 2 to 2½ times greater than the top size particle of the coke being riffled.

A1.2.3 Grind the subsample to pass a No. 6 sieve (3.35-mm opening) using a roll crusher as follows. Do not overgrind (see Annex A1.6).

A1.2.4 Using a No. 6 sieve, separate the coarse particles to be crushed. This is called scalping.

A1.2.5 Set the rolls far enough apart to crush only the largest particles of the sample. Turn the roll crusher on and pour the coarse portion of the sample very slowly through the rolls. Again scalp off the coarse particles that are to be ground

through the roll crusher again. Close the rolls not more than  $\frac{1}{16}$  in. (1.5 mm) for each pass of the scalped sample. The crushing and scalping of the sample is repeated until all of the material has passed through the No. 6 sieve. Make sure all particles are well blended and none of the sample has been discarded.

A1.2.6 Riffle the sample to obtain two 350-g portions. Do not discard any of the sample.

A1.2.7 Using a procedure analogous to A1.2.3, grind one of the 350-gram of sample, in the roll crusher, to pass a No. 60 sieve (0.250-mm opening). Do not overgrind.

A1.2.8 About one-half of the sample at this point shall be retained on a No. 120 sieve (0.125-mm opening). If this

condition is not met, go back to A1.5 and grind the other 350-g portion. Adjust the roll crusher in smaller increments to increase the amount of sample retained on the No. 120 sieve. Likewise, use larger increments to decrease the amount of sample on the No. 120 sieve.

A1.2.9 Recombine the 350-g sample and dry it to constant weight at 95 to 105°C. This dried sample is now ready for analysis and can be stored in a closed container within a desiccator. Samples shall be redried on the fourth day. Excessive heating can result in higher volatile matter values because of oxidation of some cokes.

## A2. REQUIRED OPERATING FEATURES OF A SUGGESTED VOLATILE MATTER LOWERING DEVICE

### A2.1 Apparatus:

A2.1.1 *Crucible Holder*—Steel ring with a chromel wire sling.<sup>5</sup>

A2.1.2 *Furnace, crucible.*<sup>6</sup>

A2.1.3 *Platinum Crucible*, Bishop Fig. 21, 90% – Pt. 10% – Rh; 15 mL, 33 mm high, top diameter 29 mm; capsule type cover 10 mm high with 0.5-mm diameter hole in center.

### A2.2 Set Up Requirements:

A2.2.1 The crucible holder is mounted so the brass rings and sling are unobstructed and the brass ring can rest freely on the furnace with the sling centered in the muffle furnace. Also, the mounting must be such that the crucible holder is always vertical and self-plumbing. The mounting must allow for freedom of vertical movement of the crucible holder. The weight of the crucible holder must rest fully on the transite cover of the furnace to properly position the crucible within the furnace when the lowering device is in its lowest position. No additional mass or force is applied to the holder or furnace by the lowering device. All crucible holders mounted on the lowering device must meet these conditions.

### A2.3 Timed Operations

A2.3.1 There are two timed operations:

A2.3.2 Preheat period at top of furnace. The holder containing the crucible is to be lowered  $2\frac{1}{4}$  in. (57 mm) in 10 min from the start position. The lowering can be at constant rate or in approximately  $\frac{1}{4}$  in. (6-mm) steps. If the latter is chosen, the travel time is to be included in the time for each hold position.

A2.3.3 *Bottom Hold*—Following the preheat period, the crucible is to be quickly lowered to its lowest position within the furnace. The brass ring should be resting on the top of the transite cover on the furnace, where it stays  $360 \text{ s} \pm 5 \text{ s}$ .

A2.3.4 The elapsed times for each position are listed for:

Positions in. (mm)	Seconds
1 Top	0–60
2 $\frac{1}{4}$ (6 mm)	60–120
3 $\frac{1}{2}$ (13 mm)	120–180
4 $\frac{3}{4}$ (19 mm)	180–240
5 1 (25 mm)	240–300
6 $1\frac{1}{4}$ (32 mm)	300–360
7 $1\frac{1}{2}$ (38 mm)	360–420
8 $1\frac{3}{4}$ (44 mm)	420–480
9 2 (51 mm)	480–540
10 $2\frac{1}{4}$ (57 mm)	540–600
11 Bottom	600–960

A2.3.5 The allowable errors in time for the preheat positions is 1 s/step. The maximum overall error for the first 600 s is  $\pm 5 \text{ s}$ . The maximum error in the bottom position is  $\pm 5 \text{ s}$ . The maximum error in the overall timed procedure is  $\pm 5 \text{ s}$ . Travel times between positions are counted as part of the position.

A2.3.6 Travel to the bottom position from Position 10 should not exceed 10 s. Travel time to lift the crucible from the furnace is not more than 20 s.

<sup>5</sup> Sargent Welch S-20265 Preiser Scientific 90-8510-01 or equivalent has been found to be suitable for this purpose.

<sup>6</sup> Fieldner electric crucible furnace has been found to be suitable for this purpose.

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