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# Standard Test Method for Carbon Black—Void Volume (VV)[1]

This standard is issued under the fixed designation D 6086; 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 covers a procedure to measure a carbon black structure property known as Void Volume. Compressed void volumes are obtained by measuring the compressed volume of a weighed sample as a function of applied pressure in a cylindrical chamber by a movable piston with a displacement transducer on the piston mechanism. A profile of void volume as a function of applied pressure provides a means to assess carbon black structure at varying levels of density and aggregate reduction.

1.2 Void volume is an important carbon black structure property that relates to the compounded physical properties for carbon black-filled elastomers including viscosity, modulus, and die swell.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 1799 Practice for Carbon BlackSampling Packaged Shipments
D 1900 Practice for Carbon BlackSampling Bulk Shipments
D 2414 Test Method for Carbon BlackOil Absorption Number (OAN)
D 3493 Test Method for Carbon BlackOil Absorption Number of Compressed Sample (COAN)
D 4821 Guide for Carbon BlackValidation of Test Method Precision and Bias

## 3. Terminology

3.1 *Definitions of Terms Specific to This Standard*—Refer to Sections 4 and 9 for a more complete understanding of the use of these terms in this test method.

3.1.1 *compressed volume (carbon black)*, *n*— the measured apparent volume that a specified mass of carbon black occupies when it is contained in a specified cylindrical chamber and subjected to a specified applied pressure by means of a movable piston.

3.1.2 *theoretical volume (carbon black)*, *n*— the volume that a specific mass of carbon black would occupy if there were no void space within the carbon black, and is given by the ratio of mass to skeletal density, where the skeletal density is determined by an accepted test method.

3.1.3 *void volume (carbon black)*, *n*—a measure of the occluded pore volume within the primary structure of carbon black, characterized by the irregularity and non-sphericity of carbon black aggregate particles, and expressed as the difference (compressed volume minus theoretical volume) as a function of applied pressure, and normalized to 100 g mass.

3.1.3.1 *Discussion*—Carbon blacks resist packing, compression, and fracture due to aggregate irregularities and entanglements, size distribution, and aggregate strength or particle-to-particle necks within aggregate branches. Carbon black compressed void volume is also affected by reacting forces to the cylinder wall and the piston tip, which in turn depend on factors including sample shape (that is, the ratio of sample height to cylinder diameter) or interfacial area, which can influence the uniformity of the compaction density. Since the compressed void volumes are specific to the cylinder geometry and possibly to the cylinder wall surface (that is, friction effects), a measured compressed volume is not a true compressed volume unless these factors are corrected or sufficiently minimized.

## 4. Summary of Test Method

4.1 The measured compressed volume (apparent volume) of a weighed dry test sample as a function of applied pressure is

[1] This test method is under the jurisdiction of Committee D24 on Carbon Black and are the direct responsibility of Subcommittee D24.11 on Carbon Black Structure. Current edition approved ~~June 15,~~July 1, 2009. Published July 2009. Originally approved in 1997. Last previous edition approved in ~~2008~~2009 as D 6086 – 0~~8~~9.

[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.

obtained in a void volume instrument appropriately calibrated by the manufacturer or user. From the measured compressed volume, the measured void volume is obtained by subtracting the theoretical volume from the apparent volume then expressing the result normalized to 100 g mass. A true void volume is obtained by correcting the measured void volume for instrument geometry, sample mass, and possible friction effects.

## 5. Significance and Use

5.1 The void volume of a carbon black expressed as a function of applied pressure, VV, is a carbon black structure property. Structure is a generic term that is a function of the shape irregularity and deviation from sphericity of carbon black aggregates. The greater a carbon black resists compression by having substantial aggregate irregularity and non-sphericity, the greater the compressed volume and void volume. Also, the more that a carbon black resists compression, the greater the energy required to compress the sample per unit void volume.

5.2 Structure, traditionally measured by OAN (Test Method D 2414) and COAN (Test Method D 3493), is a property that strongly influences the physical properties developed in carbon black-elastomer compounds for use in tires, mechanical rubber goods, and other manufactured rubber products. Several studies within D24 have demonstrated that void volume data can be used to estimate OAN and COAN numbers of carbon blacks using mathematical models derived from void volume-pressure data and oil absorption data. The models may vary depending on whether dynamic or static void volume measurements are used and the number and types of carbon blacks included within a modeling data set. If necessary, OAN and COAN estimates from void volume models can also be normalized using current SRBs (as practiced in Guide D 4821). Any estimates of OAN or COAN derived from prediction models using void volume-pressure data should be labeled appropriately (that is, Test Method D 6086) to avoid confusion with OAN or COAN data obtained directly from oil absorption methods.

## 6. Apparatus

6.1 *Analytical Balance*, or equivalent, capable of a weighing sensitivity of 0.1 mg.

6.2 *Gravity Convection Drying, Oven*, capable of maintaining 125 ± 5°C.

6.3 *Weighing Dish, Camel Hair or Similar Brush*, to be used for weighing the samples.

6.4 *Void Volume Instrument*, to be used to measure the compressed volume (apparent volume) of carbon blacks as a function of applied pressure from which the void volume is calculated. The void volume instrument or device shall conform to the following generic specifications and be capable of operating as outlined in 6.4.1-6.4.3.

6.4.1 The instrument shall have a rigid framework that contains a cylindrical sample chamber (see an example in Fig. X1.1). Hysteresis in the framework under the range of applied forces should be accounted for in the displacement measurement.

6.4.2 The cylinder shall have a uniform diameter.

6.4.3 By means of a suitable mechanism with sufficient power for the compression forces as required for testing, the piston shall be capable of being moved to compress the sample. A device to record the movement of the piston and measure displacement shall be provided. The compressed volume of any sample is determined by the distance from the end of the piston to the end of the cylinder; this is designated as a "height" in the procedure discussed in Section 9. The sample height and cylinder diameter are used to calculate an apparent sample volume.

6.4.4 A load cell or other suitable force or pressure measurement device is used to measure the pressure applied to the sample.

6.4.5 Two types of void volume instruments are commercially available:

6.4.5.1 A static or equilibrium measurement instrument which is designed to target one or more target pressures; an option to step from one target pressure to another is available allowing the collection of several data points. This type instrument uses an air-powered control cylinder to move the piston and does not control the rate of piston movement. The pressure applied to the sample is not directly measured, but calculated based on air pressure applied to the control cylinder. See Appendix X1 for a brief description of a commercial void volume instrument that meets these specifications.

6.4.5.2 A dynamic void volume instrument is also available which is designed to dynamically scan a pressure range at a controlled rate thereby allowing continuous measurements of apparent volume and pressure at specified data intervals. The dynamic instrument uses an electric motor to operate a linear actuator attached to the piston. The instrument incorporates a load cell to directly measure force or pressure applied to the sample. See Appendix X2 for a brief description of a commercial void volume instrument that meets these specifications.

## 7. Sampling

7.1 Samples of candidate carbon blacks shall be taken in accordance with Practice D 1799 or D 1900.

## 8. Calibration and Normalization

8.1 *Calibration*—Follow the manufacturer's instructions to set up the instrument and to calibrate the measurement systems. The use of a physical standard such as a calibrated steel plug with traceability is recommended to calibrate or verify the height displacement transducer. A reference load cell with traceability is recommended to calibrate or verify the force transducer.

8.2 *Normalization (non-mandatory; user should follow recommendations from manufacturer)*:

8.2.1 Test the 6 current ASTM Standard Reference Blacks (SRBs) four times each to establish the average measured value for each SRB over the range of compression pressures of interest. Additional values are added periodically.

8.2.2 Perform a regression analysis using target SRB values (y value) and the rolling average of the last 4 measured values (x value) across the range of applied pressures specified by the manufacturer. If target SRB curves represent measured void volumes, then the curves are instrument specific and should be obtained from the manufacturer.

NOTE 1—Use only one normalization curve—do not separate the carcass and tread blacks as practiced in Test Method D 2414. The regression model is a straight-line equation or first-order linear model without a fixed or zero intercept from which both a slope and intercept are calculated.

8.2.3 Normalize all test samples as follows:

$$Normalized\ value = (measured\ value \times slope) + y{-}intercept \tag{1}$$

8.2.4 For normalized VV values on the SRBs that are consistently outside the expected measurement range, the test apparatus should be recalibrated in accordance with 8.1.

NOTE 2—The expected measurement range for void volumes at specific applied pressures for an SRB is typically established through round robin testing. In the absence of industry precision data, this information can be established within a laboratory and apparatus through periodic monitoring of the SRBs to determine 3-sigma limits.

8.2.5 When any changes are made to the apparatus such as calibration of the measurement systems or replacement of cylinder or piston tip, a new normalization curve must be generated as described in 8.2.1 and 8.2.2.

## 9. Procedure

9.1 *Method A—Dynamic Void Volume Measurement*:

9.1.1 *Sample Preparation*—Dry an adequate sample of the carbon black for at least 1 h in a gravity-convection oven set at 125 ± 5°C, in an open container of suitable dimensions, so that the depth of black is no more than 10 mm. Cool to room temperature in a desiccator before use.

9.1.2 Weigh a mass of sample specified by the instrument manufacturer.

9.1.3 Define the analysis conditions including a scan rate, ending pressure, and data collection interval.

9.1.4 Initiate the test, and at the appropriate time, transfer the weighed sample to the instrument. Brush the sample pan and funnel to ensure the entire sample is introduced into the cylinder. Proceed with the test.

9.2 *Method B—Equilibrium Void Volume Measurement*:

9.2.1 *Sample Preparation*—See 9.1.1.

9.2.2 Weigh a mass of sample specified by the instrument manufacturer.

9.2.3 Define the analysis conditions including target pressure and, if applicable, any subsequent target pressure(s). Define the initial hold time and, if applicable, any subsequent time intervals.

9.2.4 Transfer the weighed sample to the instrument using a funnel. Brush the sample pan and funnel to insure the entire sample is introduced into the cylinder.

9.2.5 At the end of the test insure residual carbon black has been removed from piston tip.

## 10. Void Volume Calculations

10.1 The measured void volume ($VV_M$) is calculated from the measured apparent compressed volume as follows. The apparent compressed volume of the sample is evaluated by Eq 2.

$$V_A = h \times 3.1416\, D^2 \sout{/4000}\, \underline{/4} \tag{2}$$

where:
$V_A$ = the apparent compressed volume of the carbon black sample, $cm^3$,
$h$ = the "height" of the compressed carbon black in the cylinder, ~~mm,~~cm, and
$D$ = the diameter of the cylinder, ~~mm.~~cm.

10.2 The theoretical volume of the carbon black is evaluated by Eq 3.

$$V_T = m/d_{CB} \tag{3}$$

where:
$V_T$ = the theoretical volume of the carbon black sample, $cm^3$,
$d_{CB}$ = accepted true (skeletal) density of the carbon black = 1.90 $g/cm^3$, and
$m$ = mass of the carbon black sample, g.

10.3 The measured void volume of the candidate carbon black per unit mass (100 g) is given by Eq 4.

$$VV_M = \frac{V_A - V_T}{m}(100) \tag{4}$$

where:

$VV_M$ = measured void volume of carbon black sample, $10^{-5} m^3$ /kg ($cm^3$/100 g),
$V_A$ = the apparent compressed volume of the carbon black sample, $cm^3$, (Eq 2), and
$V_T$ = the theoretical volume of the carbon black sample, $cm^3$, (Eq 3).

NOTE 3—Some carbon blacks have reported skeletal densities of 1.8 to 2.0 g/cm $^3$. The accepted skeletal density of rubber carbon black is 1.90 g/cm $^3$.

10.4 The corrected or true void volume ($VV_T$) at an applied pressure is a value that is independent of the sample shape (that is, the sample to height ratio). It can be determined from the measured void volume with a given cylinder at various sample masses, and subsequent extrapolation of a linear line to an infinitely small mass, $VV_T$ is then only a function of the applied pressure. A method of determining a corrected or true void volume from extrapolation is shown as follows:

$$VV_M(D,p) = a(D,p) * m + VV_T(p) \quad (5)$$

where:
$VV_T$ = corrected or true void volume ($cm^3$/100g), at an applied pressure (the intercept of a linear or straight-line fit through $VV_M$ at various masses (m)),
$VV_T(p)$ = the true void volume at an applied pressure, p (the intercept of the linear line with slope at zero mass),
$VV_M(D,p)$ = the measured void volume in a cylinder of diameter D, at an applied pressure p and determined for variable mass m, and
$a(D,p)$ = The slope of the linear line describing $VV_M$ and mass.

## 11. Report

11.1 Report the following information:
11.1.1 Sample identification.
11.1.2 Sample mass to nearest digit specified by the equipment manufacturer.
11.1.3 If measured void volume ($VV_M$) is reported it is necessary to also report the cylinder diameter.
11.1.4 Void volume ($VV_T$) expressed to the nearest $10^{-6} m^3$/kg (0.1 $cm^3$/100 g).
11.1.5 Applied pressure at which the void volume result was obtained.
11.1.6 Method A or Method B.

## 12. Precision and Bias

12.1 A precision and bias statement has not been developed as of this time.

## 13. Keywords

13.1 apparent compressed volume; measured void volume; skeletal density; structure; theoretical volume; true void volume

# APPENDIXES

**(Nonmandatory Information)**

## X1. BRIEF DESCRIPTION OF AN EQUILIBRIUM VOID VOLUME DEVICE

X1.1 An example of an equilibrium void volume instrument or device is shown in Fig. X1.1.[3]

X1.1.1 The VV instrument meets the specifications in accordance with 6.4. It generally consists of the following.

X1.1.2 A rectangular rigid framework with a vertically oriented cylindrical sample chamber. The top plate contains a mechanism for opening and closing the top end or sample port of the chamber with a rigidly held restraining block or gate.

X1.1.3 When open, the sample port allows the loading of a sample of carbon black to be tested. When loaded, a sample rests on the top end of a piston rod that may be propelled upward along the cylindrical sample chamber. The piston is connected to a flat circular end plate (replaceable tip) that may be connected to a pressure transducer and forms the lower end of the sample chamber. The mass of carbon black to be tested rests on top of the piston tip.

## X2. BRIEF DESCRIPTION OF A DYNAMIC VOID VOLUME DEVICE

X2.1 An example of a dynamic void volume instrument or device is shown in Fig. X2.1.[3]

X2.1.1 The VV instrument meets the specifications in accordance with 6.4. It generally consists of the following.

[3] The sole source of supply of the dynamic void volume instrument known to the committee at this time is Micromeritics Instrument Corporation, 4356 Communications Drive, Norcross, GA, http://www.micromeritics.com/. The sole source of supply of the equilibrium void volume instrument known to the committee at this time is Jaron Technologies, LLC, 2338 Duncan, Pampa, TX 79065, http://www.jarontech.com./. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

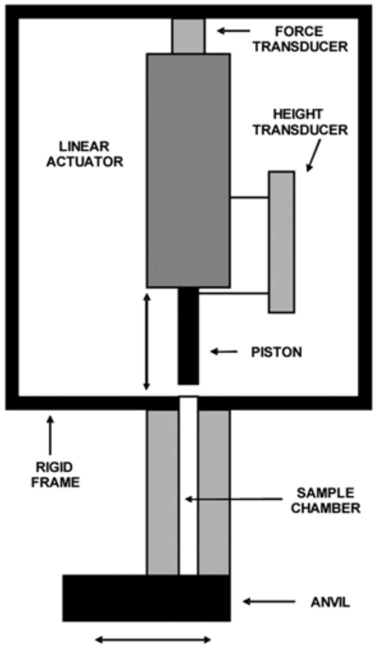
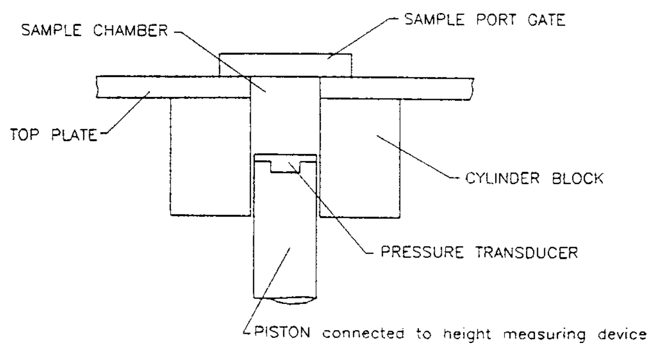



**FIG. X2.1 Schematic Diagram of a Dynamic Void Volume Instrument**




NOTE—This is only an example of a design that could be used to determine Void Volume.

**FIG. X1.1 Schematic Diagram of an Equilibrium Void Volume Instrument**

X2.1.2 A rigid framework with a vertically oriented cylindrical sample cylinder mounted below a linear actuator. The bottom plate contains a mechanism for opening and closing the end of the cylinder with a rigidly held restraining block or gate. A piston is attached to a linear actuator mounted above the sample cylinder. A linear measuring device is attached to the piston. A force transducer is attached to the framework and supports the linear actuator and piston.

X2.1.3 With the bottom plate closed and piston retracted, a sample of carbon black to be tested can be added to the funnel. When loaded, a sample rests in the bottom of the cylinder. The piston is driven at a specified rate into the sample cylinder compressing the carbon black sample.