Designation: D 4464 – 00

Standard Test Method for Particle Size Distribution of Catalytic Material by Laser Light Scattering[1]

This standard is issued under the fixed designation D 4464; 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 the determination of the particle size distribution of catalyst and catalyst carrier particles and is one of several found valuable for the measurement of particle size. The range of particle sizes investigated was 30 to 300 µm equivalent spherical diameter. The technique is capable of measuring particles above and below this range. The angle and intensity of laser light scattered by the particles are selectively measured to permit calculation of a volume distribution using light-scattering techniques.

1.2 *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:*

D 3766 Terminology Relating to Catalysts and Catalysis[2]

E 105 Practice for Probability Sampling of Materials[3]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 456 Terminology Relating to Quality and Statistics[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

E 1617 Practice for Reporting Particle Size Characterization Data[3]

3. Terminology

3.1 Definitions and recommended nomenclature pertaining to catalysts and to materials used in their manufacture can be found in Terminology D 3766.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *background*—extraneous scattering of light by material present in the dispersion fluid other than the particles to be measured. It includes scattering by contamination in the measurement path.

3.2.2 *Fraunhofer Diffraction*—the optical theory that describes the low-angle scattering of light by particles that are large compared to the wavelength of the incident light.

3.2.3 *Mie Scattering*—the complex electromagnetic theory that describes the scattering of light by spherical particles. It is usually applied to particles with diameters that are close to the wavelength of the incident light. The real and imaginary indices of light refraction of the particles are needed.

3.2.4 *multiple scattering*—the re-scattering of light by a particle in the path of light scattered by another particle. This usually occurs in heavy concentrations of a particle dispersion.

4. Summary of Test Method

4.1 A prepared sample of particulate material is dispersed in water or a compatible organic liquid and is circulated through the path of a laser light beam or some other suitable source of light. The particles pass through the light beam and scatter it. Photodetector arrays collect the scattered light which is converted to electrical signals to be analyzed using Fraunhofer Diffraction, or Mie Scattering, or both. Scattering information, typically, is analyzed assuming a spherical geometry for the particles. Calculated particle sizes are, therefore, presented as equivalent spherical diameters.

5. Significance and Use

5.1 It is important to recognize that the results obtained by this test method or any other method for particle size determination utilizing different physical principles may disagree. The results are strongly influenced by physical principles employed by each method of particle size analysis. The results of any particle sizing method should be used only in a relative sense and should not be regarded as absolute when comparing results obtained by other methods.

5.2 Light scattering theories (Fraunhofer Diffraction[4] and Mie Scattering[5]) that are used for determination of particle size has been available for many years. Several manufacturers of testing equipment now have units based on these principles. Although each type of testing equipment utilizes the same

[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.02 on Physical-Mechanical Properties.

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

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

[4] Born, M., and Wolf, E., *Principles of Optics*, Chptr 8, Pergamon Press, Oxford, 1957.

[5] van Hulst, H.C., *Light Scattering by Small Particles*, Chptr 9, John Wiley & Sons, New York, 1908.

basic principles for light scattering as a function of particle size, different assumptions pertinent to application of the theory and different models for converting light measurements to particle size, may lead to different results for each instrument. Furthermore, any particles which are outside the size measurement range of the instrument will be ignored, causing an increase in the reported percentages within the detectable range. A particle size distribution which ends abruptly at the detection limit of the instrument may indicate that particles outside the range are present. Therefore, use of this test method cannot guarantee directly comparable results from different types of instruments.

5.3 This test method can be used to determine particle size distributions of catalysts and supports for materials specifications, manufacturing control, and research and development work.

6. Interferences

6.1 Air bubbles entrained in the circulating fluid will scatter light and then be reported as particles. Circulating fluids, typically, do not require degassing, but should be bubble-free on visual inspections.

6.2 Contaminants, such as non-aqueous solvents, oil or other organic coatings on the sample may emulsify in an aqueous carrier, scatter light, and be reported as part of the particle size distribution. Samples containing such contaminants may be analyzed in a non-aqueous carrier solvent to dissolve the contaminants or washed free of the contaminant with a compatible aqueous solvent.

6.3 Reagglomeration or settling of particles during analysis will cause erroneous results. Dispersions shall be prepared so a stable dispersion is maintained throughout the analysis.

6.4 Insufficient sample loading may cause electrical noise interference and poor data reproducibility. High sample loading may cause excessive light attenuation and multiple scattering, resulting in erroneous particle size distributions.

7. Apparatus

7.1 *Particle Size Analyzer*, based on Fraunhofer Diffraction or Mie Scattering, or both, light scattering analysis techniques. Ensure that the analyzer system or subsystem is optimum for the range of the powder being tested.

7.2 *Micro Sample Splitter*, used in accordance with MNL 32.[6] to obtain the test portion of sample.

7.3 *Ultrasonic Probe or Bath*, if needed, to ensure dispersion of agglomerates prior to analysis.

8. Reagents and Materials

8.1 The selected liquid carrier shall:

8.1.1 Be compatible with the construction materials of the sample delivery system.

8.1.2 Not cause dissolution or clumping of the particles.

8.1.3 Be sufficiently clean to achieve acceptable background levels.

8.2 The use of surfactant(s) is often recommended by equipment manufacturers. However, agents such as surfactants, antifoams, and viscosity modifiers should be used with caution. An interlaboratory study of this test method showed that the use of different types and concentrations of surfactant can significantly affect the results. In calculating the precision of this test method, results obtained using surfactants were excluded because they contributed disproportionately to the scatter in results. Comparisons between laboratories should be performed with liquid carriers which are identical in all respects.

9. Sampling and Sample Size

9.1 A representative test sample shall be obtained according to Practice E 105. The test portion shall be extracted from the test sample using a micro sample splitter according to Manual 32. Quartering shall not be used.

9.2 Refer to the equipment manufacturer's recommendation to ensure that the amount of the test portion is acceptable to achieve optimum light scattering conditions. A wide range of sample portions is acceptable depending upon median particle size, particle density, and the sample delivery system.

9.3 For liquid dispersed materials, redisperse as necessary to ensure representative samples.

10. Preparation of Apparatus

10.1 Allow the instrument to warm up according to the manufacturer's recommendations.

10.2 Install and fill the desired sample delivery system and select applicable instrument range as indicated by the instrument manufacturer's instructions.

10.3 Establish correct optical alignment and calibration at a frequency in accordance with the manufacturer's requirements.

11. Calibration and Standardization

11.1 Performance of the instrument is defined by the geometry of the optical components. (Refer to the manufacturer's instruction manual.)

11.2 Spherical particle standards are available. Diagnostic powders are available from some equipment manufacturers to ensure consistent instrument function. (Some instruments may permit the use of reticles for calibration.)

NOTE 1—A partial list of standards, powders, and reticles can be found in the D32 research report for this test method.

12. Procedure

12.1 Measure the background in the mode in which the analysis will be carried out. Be sure that the carrier is flowing through the light path while measuring the background. Background values shall not exceed the manufacturer's specifications. If background values exceed manufacturer's recommendations, perform the necessary procedures as specified by the manufacturer to bring the background values within acceptable limits.

12.2 Obtain representative sample according to Section 9.

12.3 Select appropriate run time for the sample. This procedure is very specific to the application and is generally gauged by the run-to-run repeatability.

[6] *ASTM Manual Series: MNL 32*, "Manual on Test Sieving Methods," Pope, L.R. and Ward, C.W., eds., 4th ed, 1998.

12.4 Select the desired output parameters according to the requirements set forth by the instrument manufacturer.

12.5 Transfer a representative aliquot to the sample delivery system and allow it to circulate for at least 20 s or until the solid is uniformly dispersed before measuring. (Determine that the sample is not settling out in the circulation system. This can be checked by repeated runs at higher circulation rates.)

12.6 Perform the sample analysis according to the manufacturer's instructions.

12.7 Drain and fill the sample dispersion system in preparation for the next sample analysis. Drain and clean, as necessary, to avoid contamination of the subsequent sample.

13. Report

13.1 Information shall be reported as agreed between supplier and user, in accordance with Practice E 1617. The basis of the reported results is percent volume distribution calculated as equivalent spherical diameter. If all particles have the same density, this is the same as percent weight distribution.

14. Precision and Bias [7]

14.1 *Test Program*—An interlaboratory study was conducted in which particle size was measured as three points in seven separate laboratories on three materials. Each laboratory conducted a single determination on each of three subsamples of each material. Practice E 691, modified for nonuniform data sets, was followed for the data reduction.

14.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than the 95 % probability interval, which is equal to 2.772*S, where S is the estimate of standard deviation.

14.3 *Summary of Precision Results*—The test results are shown in micrometres as Fraction Smaller Than (FST) at the indicated diameter at three selected points on the cumulative particle size distribution. Repeatability is the within laboratory agreement and reproducibility is the agreement between laboratories, expressed both in micrometres and as percent of consensus mean. See Table 1.

14.4 *Bias*—The test method is without known bias.

15. Keywords

15.1 catalyst; Fraunhofer Diffraction; light scattering; Mie Scattering

[7] Use of the terms repeatability, reproducibility, precision and bias is in accordance with Terminology E 456 and Practice E 177. Supporting data are available from ASTM Headquarters. Request RR: D32-1013.

TABLE 1 Precision

Fraction Smaller Than (FST)	Consensus Median Diameter, μm	Repeatability	Reproducibility
D3295001			
10 volume %	37.11	0.61 (1.65 %)	4.66 (12.5 %)
50 volume %	68.04	1.18 (1.74 %)	2.85 (4.19 %)
90 volume %	120.6	3.59 (2.98 %)	9.66 (8.01 %)
D3291003			
10 volume %	39.71	1.91 (4.81 %)	8.59 (21.6 %)
50 volume %	83.28	3.13 (3.76 %)	7.49 (8.99 %)
90 volume %	153.2	6.82 (4.45 %)	16.31 (10.7 %)
D3295003			
10 volume %	57.78	5.53 (9.57 %)	12.30 (21.3 %)
50 volume %	140.4	9.70 (6.91 %)	16.38 (11.7 %)
90 volume %	254.6	17.53 (6.88 %)	53.82 (21.1 %)