Designation: D4464 – 15

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

This standard is issued under the fixed designation D4464; 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, catalyst carrier, and catalytic raw material particles and is one of several found valuable for the measurement of particle size. The range of average particle sizes investigated was from 1 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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]

D3766 Terminology Relating to Catalysts and Catalysis
E105 Practice for Probability Sampling of Materials
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1617 Practice for Reporting Particle Size Characterization Data

3. Terminology

3.1 Definitions and recommended nomenclature pertaining to catalysts and to materials used in their manufacture can be found in Terminology D3766.

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 applied when the sample includes 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

---

[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.

Current edition approved April 1, 2015. Published May 2015. Originally approved in 1985. Last previous edition approved in 2010 as D4464 – 10. DOI: 10.1520/D4464-15.

[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 by other methods. Particularly for fine materials (that is, average particle size < 20 µm), significant differences are often observed for laser light scattering instruments of different manufacturers. These differences include lasers of different wavelengths, detector configuration, and the algorithms used to convert scattering to particle size distribution. Therefore, comparison of results from different instruments may be misleading.[3]

5.2 Light scattering theories (Fraunhofer Diffraction[4] and Mie Scattering[5]) that are used for determination of particle size have 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 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, supports, and catalytic raw materials for specifications, manufacturing control, and research and development work.

5.4 For fine materials (that is, average particle size < 20 µm), it is critical that Mie Scattering Theory be applied. This involves entering an "optical model" consisting of the "real" and "imaginary" refractive indices of the solid at the wavelength of the laser. The "imaginary" refractive index is also referred to as the "absorbance," as it has a value of zero for transparent materials such as glass beads. For common materials and naturally occurring minerals (for example, kaolin), these values are known and published, and usually included in the manufacturer's instrument manual (for example, as an appendix). For example, kaolinite measured at 589.3 nm has a "real" refractive index of 1.55. The absorbance (imaginary component) for minerals and metal oxides is normally taken as 0.001, 0.01 or 0.1. Many of the published values were measured at 589.3 nm (sodium light) but often values at other wavelengths are also given. Extrapolation, interpolation, or estimation to the wavelength of the laser being used can therefore be made.[6]

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 such that 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[7] 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 E105. The test portion shall be extracted from the

---

[3] Jillavenkatesa, A., et al., *Particle Size Characterization*, NIST Recommended Practice Guide SP 960-1, 2001.

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

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

[6] Xu, R., *Particle Characterization: Light Scattering Methods*, Chapter 3, Kluwer Academic Publishers, 2000.

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

test sample using a micro sample splitter according to MNL 32.[7] 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 RR:D32-1013.[8]

12. Procedure

12.1 Before analysis of each sample, ensure that the measuring cell is clean per manufacturer's instructions.

12.2 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.

12.3 Obtain representative sample according to Section 9.

12.4 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.

NOTE 2—A duplicate run of the sample is highly recommended as this will allow detection of anomalous artifacts in any single run.

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

12.6 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.

NOTE 3—Determine that the sample is not settling out in the circulation system. This can be checked by repeated runs at higher circulation rates.

NOTE 4—Although this standard does not explicitly address the use of dispersion agents or ultrasound as aids in dispersion, the user should be aware that both are often necessary and utilized to ensure dispersion.[9]

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

12.8 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.

12.9 It is important to repeat 12.2 before the analysis of each sample.

13. Report

13.1 Information shall be reported as agreed between supplier and user, in accordance with Practice E1617. 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.

13.2 When reporting particle size data obtained by laser light scattering, one should ensure that the make and model of the instrument are indicated, together with the refractive index value(s) used (that is, the 'optical model'). If Fraunhofer theory is employed (that is, no optical model), then 'Fraunhofer' should be indicated in place of the refractive index values.

14. Precision and Bias[10]

14.1 *Test Program*—The previous interlaboratory study (1995) was conducted in which particle size was measured as three points in seven separate laboratories on three materials. Each laboratory conducted multiple determinations on each of three samples. Practice E691, modified for nonuniform data sets, was followed for the data reduction.

NOTE 5—Use of the terms repeatability, reproducibility, precision and bias is in accordance with Terminology E456 and Practice E177.

14.1.1 An ILS of D4464, Standard Test Method for Particle Size Distribution of Catalytic Material by Laser Light Scattering, was conducted in 2009. The purpose of the second ILS was to generate inter-lab precision for a second set of samples, which included fine samples and to demonstrate the typical precision obtained for samples with average particle size (APS) of <10 µm. With these samples the refractive index difference between the carrier fluid and the particles is significant and most instruments allow entering particle and solvent refractive index values (that is, the use of Mie Theory). Significant differences are regularly obtained for the same fine particle sample using different laser light scattering instruments.

14.1.2 Eight data sets from six different organizations were obtained, testing six different materials at three selected points on the cumulative particle size distribution. One of the six organizations participated as three laboratories by analyzing the six materials at different times with different analysts. As a

---

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1013.

[9] Nelson, R. D., *Dispersing Powders in Liquids*, Elsevier, New York, 1988.

[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1041.

result, the reproducibility reported here may not represent the reproducibility that would be obtained by eight different laboratory locations. Each lab was asked to report three replicate test results for every material. Except for the use of data from only six reporting laboratories (representing eight 'participating laboratories'), Practice E691 was followed for the design and analysis of data.

14.2 *Precision*—For both interlaboratory studies, 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 (also referred to as the 'critical difference' and abbreviated 'r' or 'R'), 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 micrometers as Fraction Smaller Than (FST). Repeatability is the within laboratory agreement and reproducibility is the agreement between laboratories, expressed both in micrometres and agreement between laboratories (see Tables 1-3). The precision of this test method is based on an interlaboratory study of D4464, Standard Test Method for Particle Size Distribution of Catalytic Material by Laser Light Scattering, conducted in 2009. Analytical results in this study were obtained from eight laboratories, testing six different materials at three selected points on the cumulative particle size distribution. Every "test result" reported represents an individual determination. Each participating laboratory was asked to report three replicate test results for each material. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D32-1041.[10]

14.3.1 *Repeatability Limit, (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "r" value for that material; "r" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

14.3.1.1 Repeatability limits are listed in Tables 1-3.

14.3.2 *Reproducibility Limit, (R)*—Two test results shall be judged not equivalent if they differ by more than the "R" value for that material; "R" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

14.3.2.1 Reproducibility limits are listed in Tables 1-3.

14.3.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

14.3.4 Any judgment in accordance with statements in 14.3.1 and 14.3.2 would normally have an approximate 95% probability of being correct, however, since all requested replicates were not consistently reported, there may be times when differences greater than predicted by the ILS results arise, sometimes with considerably greater or smaller frequency that the 95% probability limit would imply.

14.3.4.1 The ratio of the reproducibility to repeatability (R/r) is reported. As this ratio increases it indicates that while the intralaboratory precision may be very good, the agreement among laboratories decreases. High ratios can indicate sensitivity of precision to different instruments and software, as well as any other procedural differences among different laboratories. The data show that higher ratio values generally occur for the fine samples (C, D, E, F). As expected, differences among instruments are emphasized at smaller particle sizes.

14.4 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method; therefore, no statement on bias is being made.

14.5 The precision statement was determined through statistical examination of 378 results, from eight data sets from six different organizations. The six materials tested were identified as the following:

Material A: FCC Catalyst: X-5388
Material B: FCC Catalyst: X-6705
Material C: Alumina Calcined: 5126
Material D: Alumina Calcined: 6027
Material E: Hydrous Kaolin: Ansilex-93
Material F: Hydrous Kaolin: Lustra

15. Keywords

15.1 catalyst; catalyst carrier; Fraunhofer Diffraction; laser light scattering; Mie Scattering; particle size distribution

TABLE 1 Fraction Smaller than 10 volume %

Material	Average Diameter[A] (µm) $\bar{x}$	Repeatability, Standard Deviation s_r	Reproducibility, Standard Deviation SR	Repeatability Limit r	Reproducibility Limit R	Precision Sensitivity R/r
A	25.8	0.511	1.59	1.43	4.46	3.11
B	39.6	2.70	5.06	7.57	14.2	1.87
C	3.39	0.053	2.00	0.149	5.59	37.5
D	2.27	0.073	1.26	0.205	3.52	17.2
E	1.36	0.122	0.678	0.341	1.90	5.57
F	1.39	0.033	0.975	0.093	2.73	29.4

[A] The average of the laboratories' calculated averages.

TABLE 2 Fraction Smaller than 50 volume %

Material	Average Diameter[A] (µm) $\bar{x}$	Repeatability, Standard Deviation s_r	Reproducibility, Standard Deviation SR	Repeatability Limit r	Reproducibility Limit R	Precision Sensitivity R/r
A	50.1	1.61	2.02	4.52	5.64	1.25
B	81.6	0.639	4.43	1.79	12.4	6.92
C	9.4	0.108	1.84	0.301	5.16	17.1
D	7.00	0.113	0.955	0.316	2.67	8.46
E	3.12	0.064	0.813	0.179	2.28	12.7
F	5.72	0.247	3.75	0.690	10.5	15.2

[A] The average of the laboratories' calculated averages.

TABLE 3 Fraction Smaller than 90 volume %

Material	Average Diameter[A] (µm) $\bar{x}$	Repeatability, Standard Deviation s_r	Reproducibility, Standard Deviation SR	Repeatability Limit r	Reproducibility Limit R	Precision Sensitivity R/r
A	91.0	3.86	4.30	10.8	12.0	1.11
B	136	1.10	10.7	3.07	30.1	9.79
C	18.9	0.268	4.17	0.752	11.7	15.5
D	20.63	1.98	7.40	5.53	20.7	3.75
E	9.65	0.253	3.77	0.709	10.6	14.9
F	26.4	2.35	14.2	6.57	39.8	6.06

[A] The average of the laboratories' calculated averages.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/