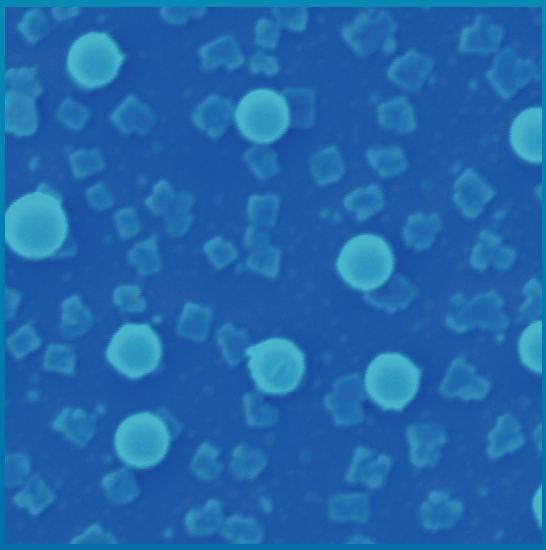
practice guide

NIST recommended

Particle Size Characterization



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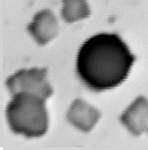

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Particle Size Characterization

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Materials Science and
Engineering Laboratory

January 2001

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PREFACE

Determination of particle size distribution of powders is a critical step in almost all ceramic processing techniques. The consequences of improper size analyses are reflected in poor product quality, high rejection rates and economic losses. Yet, particle size analysis techniques are often applied inappropriately, primarily due to a lack of understanding of the underlying principles of size analysis, or due to confusion arising from claims and counter-claims of the analytical ability of size determination techniques and instruments.

This guide has been written to address some of these issues and concerns in this regard. The guide is by no means an exhaustive and comprehensive text on particle size analysis, but attempts to convey the practical issues that need to be considered when attempting analysis by some of the more commonly used techniques in the ceramics manufacturing community. The document is written to guide persons who are not experts in the field, but have some fundamental knowledge and familiarity of the issues involved. References to pertinent international standards and other comprehensive sources of information have been included. Data and information from studies conducted at the National Institute of Standards and Technology, and experience gained over years of participation in international round robin tests and standards development, have been used in developing the information presented in this text.

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It is our hope that this guide will be added to and revised over the years to come. Please direct your comments and suggestions for future additions and about this text to:

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1. INTRODUCTION TO PARTICLE SIZE CHARACTERIZATION

Knowledge of particle sizes and the size distribution of a powder system is a prerequisite for most production and processing operations. Particle size and size distribution have a significant effect on the mechanical strength, density, electrical and thermal properties of the finished object. Significant production losses can be incurred due to high rejection rates if size and size distribution of powders being used in a process are not adequately controlled. In most instances powder suppliers provide size and size distribution information, but that information needs to be checked for quality control purposes. Also, the validity of the supplied size information needs to be evaluated if the powder batch has been divided into smaller batches based upon the user's requirements. In certain processing operations, powder size and size distribution may have to be monitored at different stages of a processing operation for suitable process control.

Powder size and size distribution can be determined using numerous commercially available instruments, or using instruments designed for operations in very specific environments. Some of these instruments can be used in an on-line mode of operation (i.e., integrated into the manufacturing process) or can be used off-line. The number of instruments that can be used in both modes, with minimal adjustments is steadily increasing. Some manufacturers now provide accessories that enable off-line instruments to be adapted to on-line operations. Most instruments operate in a batch mode of analysis. There are few instruments that can be used in a continuous mode. Instruments can be used for analysis of dry powders and powders dispersed in suspension. Whenever possible, it is desirable to analyze powders dispersed in a state similar to that in which they will be used. Instruments are available that enable analysis over a fairly narrow size distribution or over a very broad size range. The choices available for particle size determination instruments can be quite confusing. Table 1.1 illustrates some of the existing and emerging techniques for size analysis, the physical principle on which the technique is based, and the general sample concentration and size range over which these techniques are applicable.

Factors to be considered before selecting an instrument for size and size distribution analysis include[1], but are not limited to:

1. the amount of sample available;
2. the desired number of points on the size distribution (for data interpretation and/or resolution);
3. number and frequency of analyses required (laboratory, fast-response on on-line methods);

Table 1.1.

Particle Size Analysis Instruments Based on Different Physical Principles

Instrumental Technique	Physical Principle	Volume Fraction Range (%)	Size Range(μm)
Acoustic Attenuation Spectroscopy (N) [Ulltrasonic Attenuation Spectroscopy]	ultrasonics	> 1	0.05 to 10
Centrifugal Sedimentation-Optical (E)	sedimentation	ID	0.01 to 30
Centrifugal Sedimentation-X-Ray (E)	sedimentation	ID	0.01 to 100
Electrical Resistance Zone Sensing (E) [Particle Counting, Coulter Counter]	particle counting	< 0.1	0.4 to 1200
Electroacoustic Spectroscopy (N) [Electrokinetic Sonic Amplitude]	ultrasonics	> 1	0.1 to 10
Gas Absorption Surface Area Analysis (E) [BET Absorption]	surface area analysis	NA	NA
Laser Light Diffraction (E) [Static Light Scattering, Mie Scattering, Elastic Light Scattering]	electromagnetic wave interaction and scattering	0.01 to 5	0.04 to 1000
Light Microscopy (E)	particle counting	NA	> 1.0
Quasi-Elastic Light Scattering (E) [Dynamic Light Scattering, Photon Correlation Spectroscopy, Optical Beating Spectroscopy]		<0.005	0.003 to 6
Scanning Electron Microscopy (E)	particle counting	NA	>0.1
X-Ray Gravitational Sedimentation (E)	sedimentation	ID	0.5 to 100
Colloid Vibration Current (N) [Single Frequency]	ultrasonics	> 1	<10
Electrokinetic Sonic Amplitude (N) [single frequency]	ultrasonics	> 1	<10
Microelectrophoresis (E) [Laser Light Scattering, Quasi-Elastic Light Scattering]	electromagnetic wave interaction and scattering	<0.001	0.1 to 1
Sieving (E)	sieving	NA	5 to 100,000

E: Established Technique **N: Emerging Technique** **ID: Instrument Dependent**

Information compiled by V. A. Hackley, Ceramics Division, NIST

4. extent of human intervention and degree of operator skill required;
5. cost of instrument and other accessories, such as those needed for sample preparation, evaluation of data, etc.;
6. degree of automation required.

It is important to understand that as different instruments are based on different physical principles, there are bound to be differences in the size results obtained from these instruments. Furthermore, even when using instruments based on the same physical principle, manufacturers' use of proprietary algorithms, components and variations in adaptations of the same basic physical principle can give rise to significant variations in the measured size. Thus, comparison of size and size distribution results from different instruments should be conducted with extreme caution. Suitable protocols can be developed for comparison of size results from different instruments. The development of such protocols would require extensive analysis of standard, well characterized powders similar to that of interest. The analysis would have to be conducted over a broad size range on all the instruments to be used, and under conditions similar to those under which the powder of interest would be analyzed. Statistical considerations for deviations in particle shape would have to be factored into the development of such protocols.

Given these considerations, numerous users prefer to consider particle size and size distribution results as relative measurements, where results from one run can be compared with those from another, obtained on the same instrument under similar conditions. The use of particle size and size distribution data as relative measurements is very significant when monitoring size distribution as a process control indicator. In such instances the magnitude and/or direction of change is indicative of changes in the manufacturing process, which can significantly impact on the quality of the product. Often, users define acceptable limits for these fluctuations and monitor size and/or size distribution data to ensure that it lies within these limits. In these applications the precision of the measurement is of far greater interest than the accuracy. Absolute measurements can be conducted with some degree of reliability when using techniques such as microscopy-based analysis. In these cases, the particles being counted for size analysis can be visually examined. However, in such a case the reliability of the absolute measurement can be affected by the number of particles that are counted, the representative nature of the particles included in the analysis, the shape of the particles, the state of dispersion and the specimen preparation technique followed.

The use of primary and secondary standards for calibration can significantly improve the reliability of analysis. Standards for calibration can also be developed from products used by the analyst on a regular basis. In these instances it is critical to compare the material used as the standard against

a primary standard to ensure tractability. The development of protocols for sample preparation, analysis and data interpretation particular to the material system and/or the instrument is a good practice. Reliable and reproducible size analysis can be conducted by thoroughly understanding the instrument manufacturer's instructions for instrument operation. However, the experience gained by the operator through experimentation with different material systems and analysis under different operating conditions is invaluable in understanding the limitations and capabilities of the instrument. A schematic flowchart of the various stages involved in size analysis is illustrated in Figure 1.1.

Effective communication between powder manufacturers/suppliers and customers is a very critical factor in the development of robust size measurement procedures and protocols. This communication includes information about the raw material used for powder manufacture, procedures used for powder production, instruments and instrumental parameters used for analysis, information about sample preparation and powder characteristics. Establishing mutually acceptable protocols and procedures engenders a level of trust that can drastically reduce the amount of time and resources that needs to be devoted for analysis of each powder lot. Incorporating appropriate audits also enable tracking performance and conformity to the agreed upon protocols. Such procedures are now also required for ISO 9000 certification.

This guide is designed to provide a general user, not very familiar with issues related to particle size characterization, guidelines on various aspects of particle size and size distribution analysis. While by no means an exhaustive resource, this guide concentrates on some techniques commonly used in the ceramic manufacturing industry. The techniques examined in this guide include sieving, gravitational sedimentation, laser light diffraction, and microscopy-based methods. The capabilities and limitations of these techniques are examined, together with discussions of the general principles on which these techniques are based. Procedures and precautions generally followed for sample preparation and analysis are presented, and sources of error bias and other variations are identified. A chapter on sampling of materials discusses some fundamental issues concerning representative sampling applicable to techniques described herein. The reader should note that this guide is applicable to size and size distribution analysis of particles rather than crystallites. This note of caution is mentioned as often particle size and crystallite sizes can be very similar. This is encountered when Bayer derived calcined alumina powders are fully ground to their ultimate crystallite size[2]. The same powders when tested in a partially ground or unground state indicate significant difference between the particle size and the crystallite size.

All data reported in this guide have uncertainties that are estimated as ± one standard deviation, unless otherwise specified.

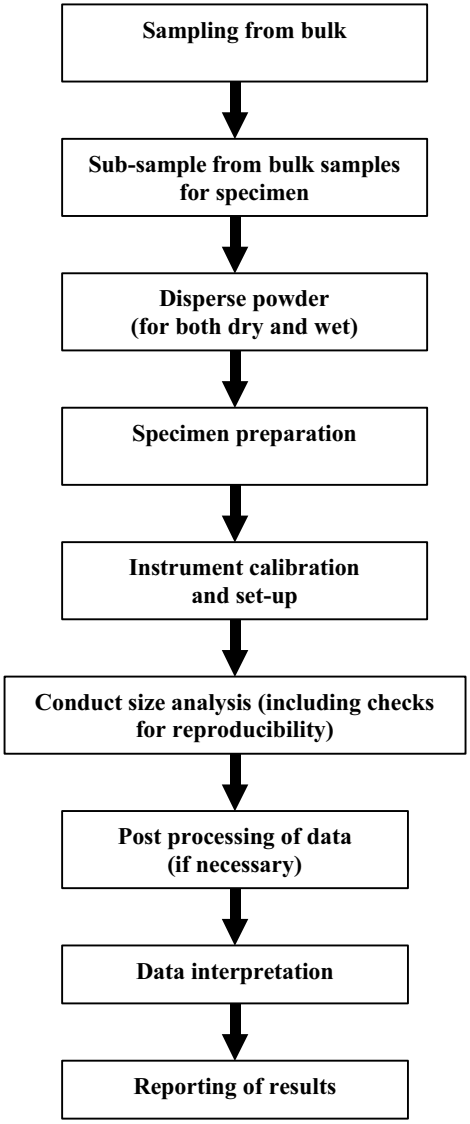

Figure 1.1.

Flowchart of General Procedures Followed for Particle Size and Size Distribution Analysis

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1. L. Svarovsky, Characterization of Powders, in Principles of Powder Technology, M. Rhodes, ed., John Wiley and Sons, Chichester, UK (1990) p. 35.

2. E. Anderson, *Personal Communications* (2000).

2. POWDER SAMPLING

1. Introduction
2. Techniques of Bulk Sampling
   2.1 Large containers sampling
   2.2 Bag sampling
   2.3 Heap sampling
3. Sample Sub-division
   3.1 Cone and quartering
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1. Introduction

Reliable powder sampling constitutes the first step of most powder characterization and processing procedures. The goal of powder sampling is to collect a small amount of powder from the bulk quantity, such that this smaller fraction best represents the physical and chemical characteristics of the entire bulk. Thus, the samples necessarily need to be representative of the bulk. The consequences of incorrect and/or non-representative sampling can be significant and result in poor characterization, systems/process failure, large fraction of defective parts, high rejection rates, and customer dissatisfaction. It is critical to spend the required amount of time, effort and resources in developing sampling procedures that are robust and reliable. It is just as important to recognize that a sampling procedure that works well for one material system may perform inadequately for another material system. The sampling procedure should be developed or adapted considering the following issues:

(a) quantity of powder from which samples are being obtained,

(b) amount of sample required,

(c) powder characteristics, including but not limited to flow characteristics of the powder, shape of the powder particles, size of the powder particles, tendency to segregate, surface chemistry that may cause the powder to be hygroscopic, etc.,

(d) mechanical strength of the powders, i.e., are the particles friable and thus, likely to fracture during transport or during sampling,

(e) mode by which powders are transported,

(f) possibility of powder contamination, and acceptable limits of contamination,

(g) duration of time needed to conduct the sampling procedure (this factor requires careful consideration, as sampling procedures can be cumbersome and time-consuming; the desire to save time and money should be balanced with the need for a high level of certainty about the representative nature of the samples), and

(h) skill and knowledge of operators conducting the sampling process.

The following basic guidelines can be followed to aid obtaining representative samples. These are colloquially known as the "golden rules of sampling"[1].

1. A powder should be sampled when in motion.

2. The whole stream of powder should be taken for many short increments of time in preference to part of the stream being taken for the whole of the time.

It is also important to note that the entire quantity of the sample powder should pass through the device used for sampling. Sampling procedures can be supplemented by the use of established and proven mathematical techniques. Such techniques of "statistical sampling" require the inspection of only a fraction of the bulk and thus greatly reduce the amount of time and effort spent in sampling. They also provide the advantage of calculating the level of certainty of detecting mistakes, upon applying a particular level of inspection[15].

A typical example of the need for sampling is illustrated where a process engineer may be asked to measure the particle size distribution (PSD) of a powder before and after processing operations. A starting batch of 500 kg (bulk) of powder may be contained in several bags, but the test specimen required for analysis is only 2 g. The issue to be addressed would be what sampling processes can be developed or followed to derive from the 500 kg lot test samples of 2 g, such that these samples are representative of the larger lot? Considering the issues mentioned above, it may be decided that powder samples would have to be withdrawn from different regions of different bags (seemingly contradictory to the first golden rule, the application of which would be impractical here), blended to homogenize the powders, and then reduced into smaller sub-samples. Using a randomization technique, some of these sub-samples would be selected, blended again and checked for homogeneity. Using an iterative process of random sub-sample selection and blending, the quantity of the sub-sample lot would finally be reduced to the desired amount.

This process, though time consuming, would best ensure the development of a representative sub-sample.

As powder batches can vary from a few grams to several tons, there are various devices and techniques that have been developed to aid in representative sampling of powders. The design of these incorporate the "golden rules" to the greatest possible extent. Together with statistical sampling procedures, these can provide a high degree of reliability and homogeneity in the samples produced. Some of these techniques are fairly independent of the operator, while others are strongly influenced by human factors. It is thus necessary to develop and implement practices and controls in these procedures that document and track any error or variation that may be introduced by human factors.

2. Techniques of Bulk Sampling

Issues of bulk sampling arise when dealing with powder quantities larger than about 25 kg. Powders in bulk quantities can be shipped in containers of various sizes and shapes, including bags, drums, carboys, hopper cars, etc. Due to the large quantity of powder involved, generating a small amount that is representative of the bulk can be extremely challenging. Often, the techniques used for sampling combine experience, gained over the years dealing with material systems, with simple sampling devices and mathematical procedures. This section describes some of the issues associated with bulk sampling[1-3].

2.1 Large Container Sampling

Powder sampling from large containers (ranging from a hundred kilograms to hundreds of kilograms) is typically encountered when manufacturers receive powders from raw material suppliers, or powder manufacturers ship out powders in bulk quantities to customers. Typical examples would include manufacturers of paints and pigments, certain segments of ceramic component and whitewares manufacturing industries, etc. Due to the large quantities of powder involved, sampling at this stage is mostly to answer questions of a "go – no go" nature, i.e., does the powder batch meet the customer's minimal size requirements such that the lot is acceptable or not?

The ideal location for sampling would be from the moving stream of powder when filling the container. However, as this may not be practical or feasible for the customer, a mutually agreed upon procedure developed by the customer and the supplier may have to be used by the supplier. This requires significant trust between the participants and a proven track record for the supplier. Regular audits need to be conducted to ensure that the sampling procedures meet the agreed upon requirements. In a similar manner, it is just as practical to

sample the powder from a moving stream upon unloading from the container. This would require that the entire container be discharged, and the powder stored.

Samples can also be obtained through a static sampling procedure. A static sampling procedure refers to sampling from powder loads at rest. This requires the use of a sample thief. A sample thief is a long rod with a sampling chamber at the end of the rod. The sample chamber can be opened and closed with controls at the operator's end of the rod. The sample thief is placed at several specifically selected areas. With the chamber closed, the thief is inserted into the selected area. The thief is opened and filled with the powder. The chamber is closed and then removed from the area. This procedure is repeated until all the selected sites are sampled. This sampling method is based upon subjective decisions as to the best areas for removal of the sample. Sampling should be done at several sites throughout the container. The choice of sites to be sampled is dictated by understanding of factors such as possible powder flow and segregation during transport. Sampling of fine powder less than about 2 μm by a sample thief may not be suitable as these powders do not flow well into the thief and the use of these often leads to cross contamination. For powders having a large particle size distribution, fine powders will tend to segregate into the interstitial spaces between large particles, causing the large particles to rise to the top of the container. Heterogeneous packing of powders may occur due to irregular motion during transport. Once all the samples have been obtained, the selected samples may be combined into one bulk sample. This bulk sample can then be divided using a spinning riffler or other sub-sample dividing processes to obtain the necessary smaller laboratory sample. Allen[1] provides some guidelines for sampling from wagons and containers encountered in bulk shipments.

2.2 Bag Sampling

When sampling powders that are shipped in bags, it is best to obtain a representative sample while the powder is in motion. This can be done while the powder is being poured out of the bag. If obtaining samples when the powder is in motion is not possible, a static process as described previously can be used. Using a sampling probe, samples are taken from several specific spots within each bag. Powder samples should be obtained from the bottom, center and top of the bags to account for any sample segregation. Powders should also be sampled from the front and the rear of the bags, depending on how the bags were stacked during transport. Particular attention should be given to the corners of the bags as these tend to trap powder particles in a disproportionate manner. Variations may occur between the bags. To reduce this variability, powder samples should be taken from different bags with the help of a random

number selection process. This process involves assigning a number to each sampling spot, and sampling from some or all of these spots in a random order. The random order to be followed can be created by any simple random number generator. The advantage of following such a process is to minimize any operator bias during the sampling process. After all the samples have been selected, the powders are blended to produce a combined sample. This leads to a powder sample that is a more reliable representation of the entire batch of powders in all the bags. This sampling procedure is based on the assumption that the powders in all the bags will be blended together prior to their use in subsequent processing.

2.3 Heap Sampling

Ensuring representative sampling from a heap is one of the hardest tasks in practical sampling. Segregation of the powders is very prevalent when forming the heap. Segregation occurs due to differences in flow characteristics of powders and their differences in particle motion due to size. The fine particles tend to stay close to the center of the heap while the coarse particles segregate to the peripheral regions of the heap. This segregation is a problem from a sampling point of view. To reduce the extent of segregation, the material should by thoroughly mixed with a scoop by turning the heap over several times. With the last turn, the heap should be formed into a conical pile by placing each scoop of material on top of the previous one. Bias in sampling can be minimized by sampling while pouring the powder to form the heap. Thus, samples may be obtained when the material is being poured out from a container to form the heap.

3. Sample Sub-Division

After samples have been obtained from the bulk, they still need to be further sub-divided in order to reduce the sample size to a manageable quantity. In the following sub-sections, some of the common sampling devices used for dividing bulk samples into laboratory samples are discussed[1,4]. The cone and quartering, and scoop sampling methods are relatively simple methods of dividing the material using very simple tools. These are very widely used techniques; however, both methods are significantly influenced by operator error, and should be used only if application of other techniques of sample subdivision is not practical. Both methods require that the material be formed into a heap before sampling. Segregation of the material may contribute to errors in obtaining a representative sample. Table sampler, chute splitter, and spinning riffler are more efficient sampling devices. Kaye[4] describes studies performed to determine the efficiencies of scoop sampling, cone and quartering, the chute riffler and the spinning riffler methods. The spinning riffler was the most efficient of the methods studied.

3.1 Cone and Quartering

The cone and quartering method requires that the powder be poured into a cone shaped heap on a flat surface. The heap is flattened by a spatula and divided into four identical volumes. One of these smaller volumes is taken and the procedure repeated to produce 1/16 of the original material. This process is repeated until the specimen size desired for conducting the measurement is obtained. This sampling technique is best for powders that have poor flow characteristics and thus, minimal segregation. This technique is strongly operator-dependent. Errors can occur due to differences in the manner the heap is formed and sub-divided. An improperly formed heap will lead to the propagation of the error introduced initially, with every further round of sample sub-division.

3.2 Scoop Sampling

The scoop sampling technique is a widely used, simple technique for sample division. An operator, using a scoop, extracts the laboratory sample from some portion of the bulk sample. This technique is only appropriate for materials that are homogenous and exhibit poor flow characteristics. One of the drawbacks of this technique is that all the bulk material does not go through the sampling process. The other drawback is the dependency on the operator to decide where to scoop the material and what quantity of the sample to extract. If the sample material is taken from the surface, the sampling is more likely to be atypical due to segregation of the material. To eliminate the segregation, the material should be shaken in a container before pouring into a heap and the scooping the sample. Allen and Kaye[1,4] describe this shaking method.

3.3 Table Sampling

Table sampling involves powder flow along an inclined table with obstacles to divert and control the powder flow. The sample is introduced through a feeder at the top of an inclined plane from where the powder travels downward on the table plane. A series of holes is drilled into the table surface, to allow the powder to fall through. Guides in the shape of triangular prisms are placed in rows perpendicular to the direction of powder flow. These prisms serve to divide and guide the powder moving along the table. The interaction of the powder with these guides causes the stream of powder to be divided into different fractions. Some of the powder quantity falls through the holes. The remaining powder passes on to the next series of prisms and holes where more of the powder is removed. The procedure is continued until the remaining powder reaches the bottom of the plane. The powder that is collected at the end of the table is the sample. A table sampling device is shown in Figure 2.1.

In this table sampler, there are four prisms in the front, two in the center and one at the end. Errors can result from variations in the initial feed of the material at the top of the table. The initial feed also needs to be mixed thoroughly such that there is no segregation of the material that is present in the feed. After powder separation, it is critical to blend.

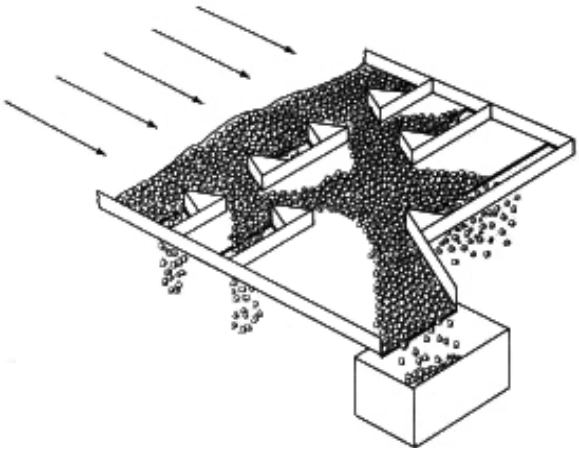

Figure 2.1.

A Schematic Diagram of a Table Sampler[1]
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3.4 Chute Splitting

In the chute splitter device, the sample powder is introduced in a V-shaped trough with two powder collecting trays placed on either side of the trough. Upon introduction, the sample powder flows through a series of chutes feeding into the two collection trays. This process is repeated with powder from one of the trays until the desired amount of sample is obtained. An example of a chute splitter is shown in Figure 2.2. This splitter contains twelve chutes that feed into two trays. Each time the material goes through the splitter, the initial sample is reduced in half. In order to obtain a good representative sample, precautions should be in place to ensure sample loading into the trough without causing powder segregation. Operator bias can affect the results through unequal splitting of the sample by the method of feeding the material.

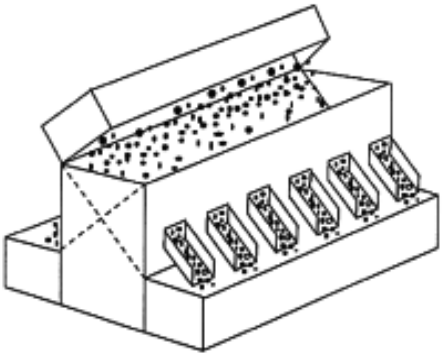

Figure 2.2.

Chute Splitter (Figure from presentation by M. Kahili, Sampling Particulate Materials)

3.5 Spin Riffling

A spinning riffler (see Figure 2.3) causes division of the sample powders into a series of containers mounted on a circular holder. The sample is introduced into the mass flow hopper while ensuring that the powder does not form a heap. The material flows from the hopper to a vibratory chute. The powder travels along the chute to the receivers (glass containers), which are rotating in a circular motion at a constant speed. This causes the containers to be filled uniformly. The operator can control the velocity of the circular motion and also the amplitude of the vibratory motion of the feeder. Thus, different powders with varying flow characteristics can be sub-divided using the same device. The vibratory motion of the feeder causes the powders to flow into the receivers at a uniform controlled rate. The spinning riffler is ideal for sub-division of free flowing powder. The quantity of powders that can be obtained as samples depends on the volume of the glass containers that can be accommodated on the riffler. Spinning rifflers are available in different sizes, enabling sub-division of powders from a few milligrams to grams. A drawback of this technique is that the number of sample containers that can be filled at one time is often small. The maximum number of containers that can be filled in one cycle is dictated by the number that can be accommodated on the circular holder.

3.6 Comparison of Different Sampling Techniques

Allen and Khan[5] conducted a study to determine the reliability of sampling devices. The material tested was a mixture having a volume fraction of 60 % coarse sand and 40 % fine sand. The coarse and fine binary mixtures were

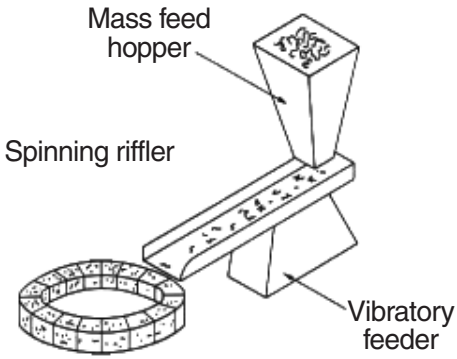

Figure 2.3.

A Schematic Diagram of a Spinning Riffler[1]
(Reproduced with permission from Kluwer Academic Publishers)

prepared by sieving and blending. The coarse grade was composed of 420 µm to 500 µm size sand and the fine grade was composed of 120 µm to 250 µm size sand. It was determined that the spinning riffler was the most reproducible technique for sample sub-division, while the cone and quartering method was the least. Reproducibility of the technique is based on the standard deviation in size distribution observed between different sub-samples generated from the same primary sample. The ability of the spinning riffler to divide the mixture uniformly was far superior to the other methods. Different sampling methods with associated relative standard deviations are shown in Table 2.1. It is obvious from the table that sub-samples produced by spin riffling had the least standard deviation in size distribution between different sub-samples of the same powder lot. Allen[1] discussed other studies that also show spin riffling to be the most reliable technique. Table 2.2 shows a summary of the advantages and disadvantages for each of the sampling devices.

Table 2.1.

Relative Reliability of Sampling Devices

Method	Relative Standard Deviation (%)
Cone & Quartering	6.81
Scoop Sampling	5.14
Table Sampling	2.09
Chute Riffling	1.01
Spin Riffling	0.125

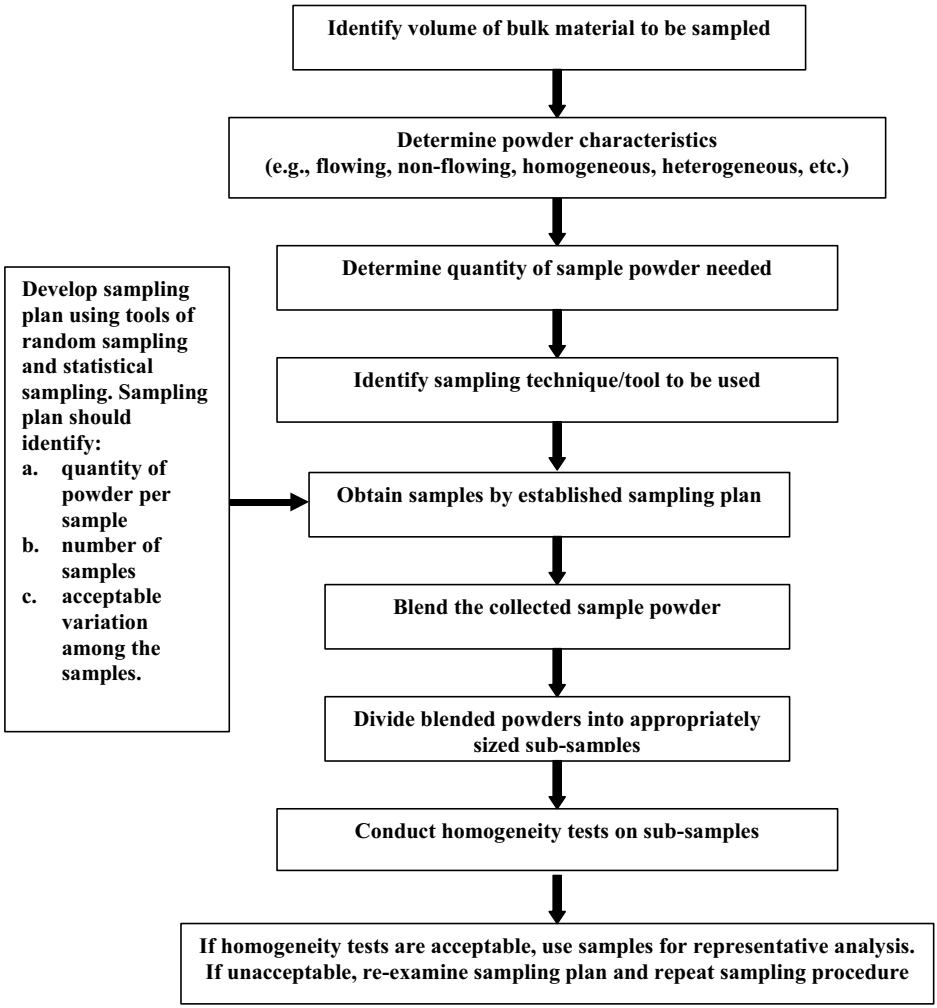

Figure 2.4.

Flowchart Indicating Steps in a Typical Sampling Procedure

Table 2.2.

Comparison of Sampling Devices

Sampling Device	Advantages	Disadvantages
Cone & Quartering	Good for powders with poor flow characteristics	Operator-dependent
Scoop	Reliable for homogeneous and non-flowing powder	Particle segregation
Table	Ability to separate large quantity of material	Dependent on the initial feed
Chute	Ability to reduce powder samples in half after one pass	Operator bias
Spinning riffler	Reliable for free flowing powder	Inability to do large quantity of powder efficiently

3.7 General Procedure

A general sampling procedure involves identification of certain critical parameters such as the size of the bulk sample, the size of each laboratory sample, the number of laboratory samples, powder characteristics, available tools, and development and selection of procedures that work best for the given powder system. Homogeneity testing is a critical component of any sampling procedure as it identifies inconsistencies between sub-samples and thus helps to ensure that the sub-samples are representative of the bulk sample. It is necessary to establish practical limits for acceptable results in homogeneity testing. The use of random sampling and statistical sampling tools can greatly aid in the sampling process, by reducing the number of sub-samples needed, while enhancing the reliability of the homogeneity tests. Figure 2.4 shows the steps that are involved in the design of a typical sampling process for dry powders.

4. Practical Application

Various techniques for sampling have been described previously. A practical example of a sampling procedure used in the production of a NIST Standard Reference Material (SRM®) is discussed here. This example will provide an illustration of the sample division process and the homogeneity study associated with the SRM certification. The homogeneity test measurements were conducted to detect any significant differences in the properties of the selected samples. Any significant differences are an indication that the various sub-samples are not similar to each other and cannot be considered to be representative of the bulk material. Each of the samples tested was randomly selected. Randomly selected samples are important as they minimize operator

bias in selecting samples for testing. The number of randomly selected samples depends on the total number of samples in the lot and the type of measurement test conducted.

The study presented here involves the development of SRM 1982: Thermal Spray Zirconia Powder-Particle Size Distribution[13,14]. The size range of the powder system used in SRM 1982 is from 10 µm to 150 µm. Certification was conducted by scanning electron microscopy, laser light scattering, and sieving methods.

In 1992, at a NIST-sponsored Thermal Spray Workshop, powder characterization and quality control were identified as critical areas for producing cost-effective thermal spray coatings. Thus, the production of a Particle Size Distribution (PSD) Standard Reference Material was initiated and completed in 1996 to provide a reliable and accessible PSD reference material for a thermal-sprayed yittria stabilized zirconia (YSZ) powder.

Different processes can be used for the production of YSZ powder, including sol-gel precipitation and sintering; spray drying and sintering or plasma densification; fusion and crushing or agglomeration and sintering. Powder samples by each of these manufacturing processes were obtained for evaluation as a suitable candidate for SRM production and certification. The desired properties of the YSZ powder for SRM production were identified to be (a) well defined PSD, (b) particles of spherical shape, (c) absence of extensive agglomeration, and (d) high mechanical strength and low friability. After a thorough evaluation of YSZ powders for the properties listed above, a candidate material was chosen. It was a powder produced by a spray drying and sintering process.

The particle shape and degree of agglomeration of the candidate powder determined by SEM imaging at different magnifications is shown in Figure 2.5. The low friability of the powder was demonstrated by comparing the PSD of the powder before and after ultrasonication with a high wattage sonic horn. Figure 2.6 shows the size distribution curve of the powder determined by laser light scattering before and after ultrasonication. The very minimal change in the shape and position of the distribution curve is indicative of the absence of significant fracture (and thus, size reduction) during ultrasonication. The powders were thus considered to possess an adequate mechanical strength such that the particles would not fracture during normal handling and transportation.

A 9.08 kg batch of powder was first split into 16 sub-samples using a spinning riffler. These sub-samples were designated A to P. Each was further riffled to produce 16 smaller bottles, designated A-1 to A-16. The contents of five of the smaller bottles (A-1 to A-16) were combined and riffled for the third time into

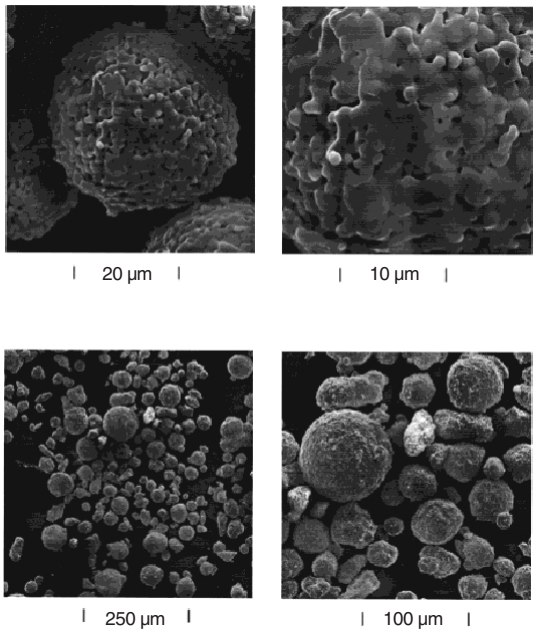

Figure 2.5.

SEM Micrographs of YSZ Powder at Different Magnifications to Illustrate Powder and Particle Morphology[13]

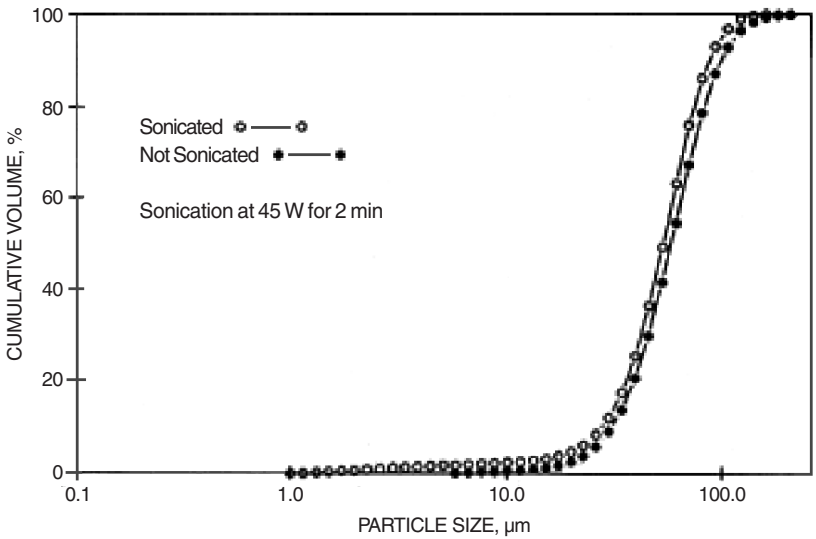

Figure 2.6.

Changes in PSD of YSZ Powder Upon Ultrasonication[13]

16 containers. Each container was weighed to ensure evenness of splitting. It was determined that each sample bottle should have 11 ± 0.5 g. The containers were numbered consecutively from #1. This packaging scheme is summarized in Table 2.3. A randomized set of 100 bottles from the last stage was selected for sample homogeneity testing and PSD certification analyses.

Table 2.3.

Packaging Scheme for SRM 1982

Stage 1	9.08 kg of Zirconia Powder (starting powder) ↓
Stage 2	16 sub-samples of powder (label A to P) ↓
Stage 3	Each stage 2 sub-samples (A) split into 16 smaller containers (label A-1 to A-16) ↓
Stage 4	Five smaller containers (A-1 to A-16) were recombined and split into 16 bottles

The PSD of 15 stage 4 samples from the randomized set were determined in triplicate and in a random sequence using a laser light scattering instrument. The same specified specimen preparation procedure was used for each specimen. The applied instrument and specimen related parameters were (a) sample size for each analysis of 0.2 g, and (b) relative refractive index of 1.8 with respect to water (refractive index of water was 1.33 with zero imaginary component of refractive index). The particle size data were calculated on a volume basis assuming a normal distribution.

Although the laser light instrument produces a continuous plot of weight percentage finer than a given diameter, five cumulative percentiles (10 %, 25 %, 50 %, 75 %, and 90 %) were selected as a representative data set. The homogeneity data were statistically analyzed and are shown in Figure 2.7.

After certification analyses, SRM 1982 was accepted and made available to the public.

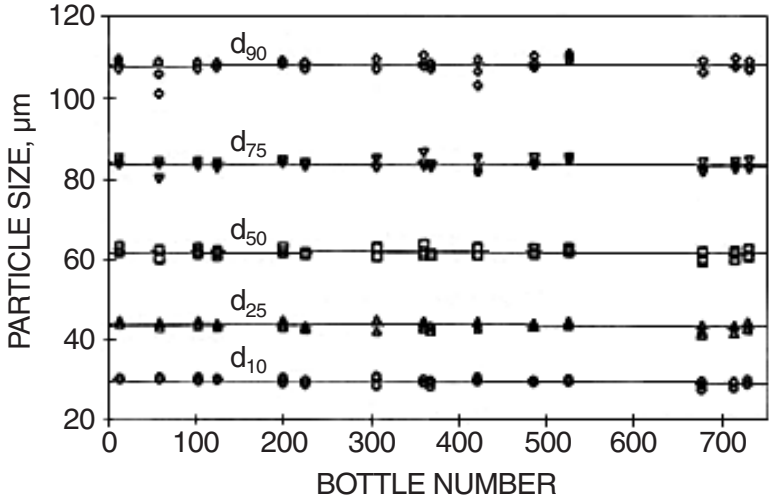

Figure 2.7.

Measure of Variability Between Bottles by a Laser Light Instrument [13]

5. Relevant Standards

Numerous American Society for Testing and Materials (ASTM) standards have been developed for sampling processes. Many of the standards discussed here are not written specifically for ceramic powders. However, they can be used for guidance in sampling bulk shipments or dividing bulk materials into smaller samples.

ASTM C322 Standard Practice for Sampling Ceramic Whiteware Clays[6] is designed for sampling of bulk and bagged shipments of ceramic whiteware clays. This standard provides a detailed sampling procedure for bulk shipments (e.g. obtaining samples of 4.5 kg from containers that can hold upto 30 tons of bulk material). The standard, however, does not describe any procedure for further sample sub-division, and such a procedure is needed as 4.5 kg is too large a quantity for most laboratory analyses.

ASTM D1900 Standard Practice for Carbon Black—Sampling Bulk Shipments[7] shows examples of how to obtain samples from hopper cars with a sample thief. The standard provides general procedures for sampling in three possible scenarios: (a) sampling from the top ports of a hopper car, (b) sampling a hopper car during loading, and (c) sampling from the hopper car while unloading.

Techniques for reduction of large samples to sizes more appropriate for testing are covered in ASTM C702 Standard Practice for Reducing Samples of

Aggregate to Testing Size[8]. The standard describes three methods, namely, (a) using a mechanical splitter, (b) quartering, and (c) miniature stockpile sampling (for damp fine aggregate only). The apparatus for each technique is described along with the procedures to be followed. Guidelines for choosing which method depend on the nature of the sample. Aggregate material can be either fine, coarse or mixtures of coarse and fine aggregates. The mechanical splitter is similar to a chute riffler. The procedure describes how the aggregate samples can be introduced into the chute. A procedure for further reduction of the sample for sizes suitable for testing is described. The quartering method has two procedures where either one or a combination of both may be used. The first technique is a simple cone and quartering method. The second method uses a canvas blanket to roll the material for better mixing and then follows the cone and quartering procedure to divide the sample. A procedure for dividing the sample is described if the surface beneath the canvas blanket is uneven. The latter method is used specifically for damp fine aggregates.

ASTM D75 Standard Practice for Sampling Aggregates[9] is designed for sampling of coarse and fine aggregates from different sources. This standard provides procedures for sampling materials from a flowing aggregate stream (bins or belt charge). Procedures are also presented for sampling materials from conveyor belts, stockpiles, transportation units, and roadways. The minimum mass of field sample that is required for analysis depends on the maximum nominal size of the aggregates. This standard includes a table showing this relationship.

ASTM B215-96 Standard Practices for Sampling Finished Lots of Metal Powders[10] is written for selecting representative samples of metal powders. Two different practices are described in this standard. The first practice is for powders that are in the process of being packaged from blenders or storage tanks using an apparatus similar to a chute splitter. The second practice is for powders already packaged in containers using a keystone sampler that is similar to a sample thief. This standard provides operating procedures for both samplers. The number of containers to be sampled is dependent on the total number of containers in the lot. A table showing this relationship is included in the standard.

A very comprehensive standard for sampling is the British Standard BS 3406: Part 1, Determination of Particle Size Distribution: Part 1. Guide to powder sampling[11]. The standard includes descriptions of different sampling devices for the sub-division of the laboratory sample; it describes each sampling device and presents a simple operating procedure. The standard has a section on the suggested sampling devices for different types of powder: free-flowing powders, non-free flowing powders and non-flowing powders. Flow characteristics of powders are determined by their flow through a

60° funnel with a 10 mm diameter orifice. Non-free flowing powders do not flow readily through the funnel unless assisted, or may flow slowly but leave a residue sticking to the sides of the funnel. A non-flowing powder does not flow from the funnel. A section on the methods for preparation of very small test portions is included. This section describes how to sample from suspensions and pastes. A comparison of the dry powder sampling and wet powder sampling techniques is included in this standard.

A draft standard, ISO/WD 14888: Sample Splitting of Powders for Particle Size Characterization[12] is currently being prepared by the International Organization for Standardization (ISO). This draft describes methods to obtain test samples from bulk material for measurement of size and size distribution. It contains statistical background on sampling and calculation of sampling sequence variances. General procedures for sampling and recommended sampling sequence practices are included. Detailed statistical sampling information pertaining to the spinning riffler and cone and quartering methods is given. A section on suspension sampling is also included.

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3. SIZE CHARACTERIZATION BY SIEVING TECHNIQUES

1. Introduction
2. General Procedures
3. Reporting of Size Data
4. Sources of Error and Variation
5. Practical Concerns
6. Calibration
7. Relevant Standards

1. Introduction

Sieving is one of the oldest techniques of powder classification (i.e., separation based on size or some other physical characteristic) that is still in use today. It is among the most widely used and least expensive techniques for determination of particle size distribution over a broad size range. The preponderance of applications using this technique can be attributed to the relative simplicity of the technique, low capital investment, high reliability, and low level of technical expertise required in its application, characteristics not often associated with other techniques of size analysis. Sieving can be used over a very broad size range, from just over 100 mm to about 20 µm[1]. A test sieve is a measuring device designed to retain particles larger than a designated size, while allowing smaller particles to pass through the device[2].

Size determination by sieving is applicable to free flowing dry powders, and some carefully prepared slurries. The method, in the most general sense, consists of shaking (agitating) the sample through a stacked series of sieves with decreasing mesh size. The mesh with the largest aperture is at the top, and that with the smallest aperture is at the bottom of the stack. Size distribution is reported as the mass of the material retained on a mesh of given size, but may also be reported as the cumulative mass retained on all sieves above a mesh size or as the cumulative mass fraction above a given mesh size. Sieves are typically classified as coarse, medium, or fine, based upon the size of the aperture openings[3]. Coarse sieves have aperture openings in the size range of 100 mm to 4 mm, medium sieves range from 4 mm to 200 µm, and fine sieves extend below 200 µm. Numerous standards define the size of aperture openings in sieves. Three ASTM standards, E 11-95[1], E 161-96[4] and E 323-80[5], define specifications for various types of sieves. E 11-95 addresses requirements and specifications for sieves made by weaving of wire cloth to form sieve openings. E 161 defines specifications for electroformed sieves, while E 323 defines the specifications for perforated plate sieves.

Perforated plate sieves are primarily used for coarse powders and have aperture sizes ranging from 125 mm to 1 mm. The size of the aperture openings in consecutive sieves progress by about $\sqrt[4]{2}$ larger than the previous sieve. The apertures (or perforations) are either circular or square in shape. The circular apertures are patterned in a staggered manner, while square apertures can be arranged in either a staggered manner or rectilinear manner where the perforations line up in both planar dimensions. Perforated sieves are typically formed by punching rigid metal sheets that have not been coated with any material. Woven wire sieves are formed by weaving wire of material, such as stainless steel, brass or bronze to form square shaped openings. The resulting "cloth" is then clamped into a hollow cylinder. The aperture openings in woven wire sieves follow the same ratio of about $\sqrt[4]{2}$ to 1. Table 3.1 lists the American Standard Sieve size descriptors and the nominal corresponding opening sizes which allow the passage of a particle of that size or smaller. Identification of sieves by their sieve number refers to the number of wires per linear inch forming that sieve. The requirement of uncoated wires to be used for weaving the sieve cloth holds true here. The use of uncoated material forming the sieve is to avoid any possible contamination of the sample by wear debris abraded from the sieve material. Electroformed sieves are manufactured by a technique involving the deposition of a photosensitive layer on to a metal surface. The photosensitive layer is then exposed to the image of the sieve pattern, and the photosensitive material and underlying substrate are selectively etched, so that only the area of the metal corresponding to the apertures is dissolved away. As aperture sizes get smaller than 1 mm, the electroformed sieves often exhibit improved precision (with respect to aperture size, separation of aperture centers, and shape of apertures) than woven wire or perforated sieves. This fact is magnified as the aperture sizes get into the tens of micrometers size range. However, it is important to note that as the ability to reproduce aperture openings on different sieves with the same nominal aperture size is limited, reproducing the results of analysis on different sieves with the same aperture size may not be easy. It has been observed that the coefficient of variance may vary between 10 % for sieves with small aperture widths and 5 % for sieves with larger aperture widths[6].

Some other pertinent international standards relating to specification of sieves are the ISO R-565-1972(E): Woven wire and perforated plate test sieves, and the BS 410: Woven wire test sieves.

Sieving Techniques:
General Information and Capabilities

Size Range: From about 125 mm to 20 µm (see text for size categories).

Specimen Type: Dry, free-flowing powders. Some instruments are designed for analysis of slurries.

Operating Mode: Mostly off-line in batch mode. Some automated systems have been designed for on-line process and quality control monitoring.

Ease of operation: Relatively simple. Usually minimal sample preparation required.

Sources of Error and Variations: Can arise during the sieving process (blinding of sieves), due to inadequate and/or improper maintenance of sieves, during/due to material transfer to and from sieves.

Powder characteristics may cause particles to agglomerate or fracture during analysis.

Significant bias may be introduced during analysis of acicular particles.

See Ishikawa diagram (Figure 3.3).

Strengths: Applicable over a broad size range.

Based on simple principles, and thus does not require highly skilled operators.

Low capital investment.

Minimal sample preparation.

Limitations: Requires long analysis times. Analysis times get longer as sieves with finer aperture openings are used.

Extent of automation and computerization is relatively limited.

Mechanical motion during sieving affects repeatability and reproducibility of results.

When particles have high aspect ratios (e.g., needle shaped particles), PSDs are susceptible to large uncertainties due to measurement of smallest diameter by this method.

Table 3.1.

ASTM Sieve Designation and Corresponding Nominal Aperture Openings

ASTM Sieve Designation					
Aperture Opening	**Designation**	**Aperture Opening**	**Designation**	**Aperture Opening**	**Designation**
125 mm	5 in.	9.5 mm	3/8 in.	425 µm	No. 40
106 mm	4.24 in.	8.0 mm	5/16 in.	355 µm	No. 45
100 mm	4 in.	6.7 mm	0.265 in.	300 µm	No. 50
90 mm	3½ in.	6.3 mm	¼ in.	250 µm	No. 60
75 mm	3 in.	5.6 mm	No. 3 ½	212 µm	No. 70
63 mm	2½ in.	4.75 mm	No. 4	180 µm	No. 80
53 mm	2.12 in.	4.00 mm	No. 5	150 µm	No. 100
50 mm	2 in.	3.35 mm	No. 6	125 µm	No. 120
45 mm	1¾ in.	2.80 mm	No. 7	106 µm	No. 140
37.5 mm	1½ in.	2.36 mm	No. 8	90 µm	No. 170
31.5 mm	1¼ in.	2.00 mm	No. 10	75 µm	No. 200
26.5 mm	1.06 in.	1.7 mm	No. 12	63 µm	No. 230
25.0 mm	1.00 in.	1.4 mm	No. 14	53 µm	No. 270
22.4 mm	7/8 in.	1.18 mm	No. 16	45 µm	No. 325
19.0 mm	¾ in.	1.00 mm	No. 18	38 µm	No. 400
16.0 mm	5/8 in.	850 µm	No. 20	32 µm	No. 450
13.2 mm	0.53 in.	710 µm	No. 25	25 µm	No. 500
12.5 mm	½ in.	600 µm	No. 30	20 µm	No. 635
11.2 mm	7/16 in.	500 µm	No. 35		

(Adapted in part from ASTM E11-95)

2. General Procedures

Sieving instruments have evolved with various modifications, but continue to be based upon the same general principle. The goal during modification has been to make the sieving process more efficient and minimize errors and variations arising during sieving. Examples of these modifications include automation of the sieving process to eliminate human error arising due to operator variability, fatigue, etc., application of force by either mechanical or pneumatic means to enable passage of particles through the sieves while minimizing blinding of the sieves, creation of fluidized beds by application of an upward air draft (air-jet sieving) to enable better particle separation on the sieve and consequently, improved passage through the sieve openings.

Sieving processes can be generally categorized as dry sieving or wet sieving processes. Typically wet sieving is conducted for analysis of particles finer than about 200 mesh (75 µm), where powder surfaces develop enough of a surface charge and show an enhanced tendency to agglomerate[6]. Wet sieve analysis of particles even about 10 µm is conducted very routinely. Dry sieving analyses are to an extent still conducted by hand. However, analysis of large quantities of material, or analysis on a frequent basis, requires some degree of automation. Most modern sieving instruments have automated the gyratory/

oscillatory motion of the sieve stacks. The vibratory motion produced by gyrations or oscillation of the sieve stack can be further enhanced by a tapping motion applied to the top of the nest of sieves. The Tyler Ro-tap incorporates the combination of the forces generated by the two actions. Air-jet sieving is another technique utilizing a combination of negative air pressure and pneumatic updrafts to create a fluidized bed of particles above the sieve. Instruments based on this technique combine an upward air draft through a sieve with a simultaneous negative pressure below the sieve, to enable the fine particles to pass through the sieve, while preventing blinding of the sieve by coarser particles. An added advantage of this technique is the prevention of segregation of particles on the sieve that can hamper the smooth flow of undersize particles through the sieve. This technique has been promoted for brittle and friable particles that would otherwise fracture under the action of strong forces. An instrument that combines the pneumatic action with the mechanical vibratory motion is the Allen-Bradley (ATM) sonic sifter. The pneumatic column passing through the sieves raises the particles over the screen, while the mechanical motion shakes and separates the particles, allowing free passage of the fines through the sieve. Such a motion also helps reduce the amount of sieving time. The pneumatic pulse is applied as an oscillatory pulse in the vertical direction. The combination of these two forces also helps prevent blinding of sieves. Some instruments are designed to be vibrated using an electromagnetic coupling system.

Wet sieving techniques follow the same general principle of application of suitable force to enable the flow of fluid and dispersed powders through the aperture openings. Some of the errors and sources of variation associated with this action are discussed later in this chapter. Important facts to be considered while using this technique are controlling the state of dispersion of particles in the fluid to prevent agglomeration, control of the viscosity and surface tension of the fluid to allow smooth flow through the apertures and regular care and maintenance of the screens to prevent wear, corrosion or other damage to the sieves. Wet sieving techniques are often aided by the use of ultrasonic agitation or light vacuum to aid the flow of the fluid through the screens. Extreme caution should be exercised while applying these forces, and the sieves should be examined for damage immediately after the use of such techniques. Most automatic sieving machines are designed for operation in a wet sieving mode. Automatic machines are most commonly used in industrial settings, and the preference for wet sieving is due to the ability to rapidly transport the powder and weigh the amount of powder retained on each screen.

Some recommendations made by Allen[3] for preparing powders for sieving and for the analysis technique itself, include:

- Reducing the charge load (i.e., the amount of sample added to the top sieve) to reduce the time required for analysis. However, the load should be

maintained at a level that ensures adequate accuracy during weighing of the different fractions, so as not to be affected by the amount of powder loss during sieving.

- Removal of the fine fraction by pre-sieving using the screen with the smallest aperture opening. This helps reduce excessive powder loss during sieving, and also the amount of time for sieving.
- Incorporating motion that minimizes the blocking of sieve openings by entrapped particles (blinding). This can be achieved by a jolting action to dislodge particles wedged in the apertures, or by vertical air flow upwards through the sieves.
- Materials that may agglomerate should be pretreated to prevent agglomeration prior to sieving.
- Friable and brittle powders should preferably be sieved in an instrument without jarring forces as may be encountered in sieves incorporating oscillating and/or jolting motion. Air jet sieving or sieving by a sonic sifter provide a relatively gentle sieving action.

A general procedure to conduct dry sieve analysis of a powder system would include the following steps:

1. Classify the powder by sieving through single-screens to limit particle size distribution over a series of four to six consecutive mesh sizes. Such an action might result in numerous fractions of finite size distribution, where each fraction will have to be analyzed separately.
2. Select for each fraction of interest, sieves covering that size range in order to have a nest of five or six sieves.
3. Examine each sieve for any damage, wear, deformities, etc., to screen. Check to ensure that screen openings are not clogged and that screens fit snugly into sieve housing. Any space between the screen and the cylinder will result in powder loss.
4. Stack sieves such that the screen with coarsest aperture opening is at the top, and the screen with finest aperture opening is at the bottom. Stack the collection pan at the bottom of the nest.
5. Load charge on to the top screen.
6. Sieve according to established protocol, i.e., sieve for a given duration of time, and/or sieve until the quantity passing through the sieve is less than some fraction of the original mass in a given period of time (e.g., sieving until the quantity passing through sieve is less than 0.5 % of the total mass (ASTM D452[28]). While developing a sieving protocol for a material system

that would be analyzed often, it is useful to sieve a given quantity of sample for varying amounts of time, e.g., 10 min to 30 min at 5 min intervals. Sieving time is selected based on the time period after which no significant difference in mass change is observed. This technique of fixing the sieving time has been followed at NIST for the development of Standard Reference Materials (SRMs) for particle size distribution. Experience through studies conducted at NIST has indicated that sieving for a fixed period of time is more convenient than sieving until less than a certain fraction of the total mass passes through the sieve in a given period of time. The time and effort to disassemble and assemble a complete set of sieves to ensure that no powder is lost while weighing can be considerable and is not very efficient when attempting to analyze numerous samples.

7. Separate carefully each sieve and transfer the powder retained on each screen on to a weighing paper. If necessary, lightly brush the underside of the screen to release any particles adhering to the screen. This should be done with extreme caution so as not to damage the wire screens.
8. Weigh each fraction on mass balance with adequate sensitivity. In case total mass after sieving reflects powder loss greater than 0.5 % of the initial charge mass, the test should not be considered. Sieves should be examined for damage or improper fit.
9. Plot results either as a histogram representing percentage mass retained on each screen as a function of aperture opening size, and/or as cumulative mass percentage finer or coarser as a function of aperture opening size.
10. Clean sieves, examine for damage and store in a safe environment.

A quick check to ensure that no powder has been lost during the sieving process, is to compare the mass of the powder retained after sieving with the mass of the original charge. This total mass of powder retained after sieving should be the same or very close to the amount of charge with which the sieve analysis was started. Any significant differences in the two quantities is an indication of loss of powder. Total mass loss over 1 % can introduce significant error in the size distribution results and affect the reproducibility of the results.

The above-mentioned procedure is a general procedure that may have to be modified to suit the material system being examined, and to accommodate any instrument specific requirements. Manufacturers of sieving instruments provide detailed instructions specific to the operation of that instrument. Wet sieving would require the development of a similar procedure. Additional steps that would have to be considered would be the amount of sample and dispersant to be added and the level of dilution that would be required to provide a suitable fluid medium. Most manufacturers specify the level of dilution. If not specified, the level of dilution should be such that no significant increase occurs in the

viscosity of the fluid. The application of agitation, ultrasonic energy, vacuum or control of flow by pumps is specific to the instrument and is specified by the manufacturer.

It is critical to examine sieving procedures to ensure their applicability to different material systems. Factors that are often ignored or deemed insignificant, but that have a marked impact on the results include monitoring and control of humidity, frequency at which sieves are vibrated, force of jolt or impact, etc. It is also important to consider whether a set of procedures that are applicable to one material system can be applied to another material system comprised of particles with a size distribution in the same range. Based on the powder characteristics, there can be significant differences in surface properties leading to formation of aggregates or charging effects that may greatly influence the observed results. A sieving procedure developed for an inter-laboratory round-robin test is given in Table 3.2. Participants in this study were supplied with the candidate material and a procedure for analysis. Figure 3.1 shows the reported results of size distribution of silicon nitride, a candidate material in this study. Results from various laboratories reporting the cumulative mass percentage as a function of the aperture opening size is plotted. With the exception of one laboratory (lab 14), the results from all laboratories were in close agreement. The mean d_{50} for the results from all of

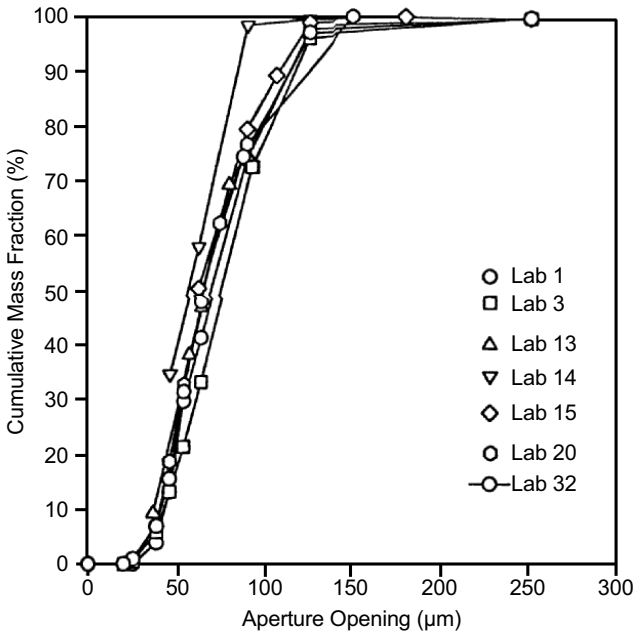

Figure 3.1.

Results of Inter-Laboratory Round-Robin Test on
Particle Size Determination of Silicon Nitride by Sieve Analysis

the laboratories was 66.41 µm with an overall standard deviation of 4.91 µm. Considering that different laboratories used sieving instruments from different manufacturers, the results are in generally good agreement. The variation in the results can be attributed to differences in operational characteristics of instruments, variations due to operators, any possible variations arising from sample handling (samples in different temperature and humidity conditions), differences in accuracy and precision of weighing instruments, differences in conditions of screens, etc.

Table 3.2.

Sieving Procedure Used in Inter-Laboratory Round-Robin Test

1. Weigh each clean sieve.
2. Stack the clean sieves with a collection pan at the bottom and the sieve with the largest opening at the top.
3. Weigh the sample.
4. Place the weighed sample on the top sieve.
5. Cover the sieve and set in the sieving apparatus.
6. Sieve for 30 min,

   OR

   Sieve until the quantity passing through each sieve becomes less than 0.2 % of the mass of the charge in 1 min or less than 10 mg in several minutes.
7. Collect the retained sample on the sieve.
8. Calculate the sample mass on the sieve.
9. Compare the total mass with the starting mass of the powder. The mass loss of the sieving should be within the range of ± 2 %. If the loss is out of this range, the test should be re-examined.
10. Calculate the size distribution.

3. Reporting of Size Data

Results from sieve analysis can be represented as a cumulative graph of mass fraction coarser than or finer than a particular size, or as a histogram of the mass fraction on each screen plotted against the screen size and thus an indication of particle size. Either of these techniques of representation can be used to visualize the particle size distribution. Size data for most powders analyzed by sieving is best reported on a mass basis. This minimizes any errors that may be introduced during transformation from one physical basis to another. However, for material systems comprising of spherical particles that do not change in density with a change in size, the mass basis can readily be converted to a volume basis and represented accordingly. The same conversion

may lead to error if applied to non-spherical particles, due to errors in calculating the correct volume of the particle. An important factor to keep in mind while using histogram based representation is the width of size classes being used in the histogram. The width of the size classes should be the separation of the nominal aperture openings between two consecutive sieves. In case of a very broad class width, there may be significant loss of resolution in the size distribution and finer details, including small changes that

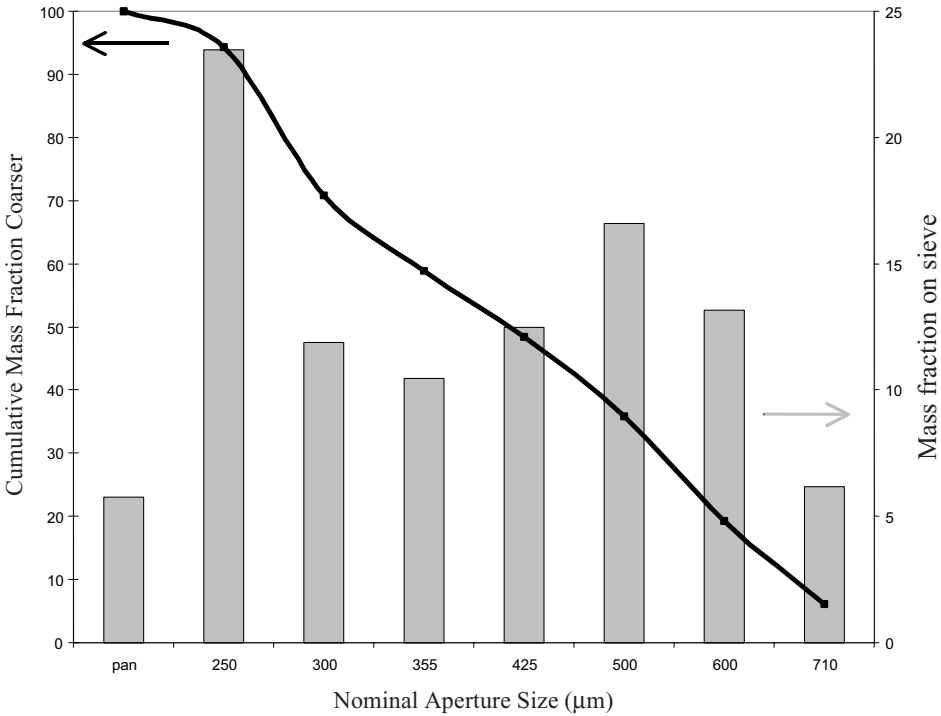

Figure 3.2.

Sieving Data From Sub-Sample Analyzed During Certification of NIST SRM 1018b

may not be observed. Table 3.3 represents one set of data generated during the development of NIST SRM 1018b. The quantity measured after sieve analysis is the mass of glass beads retained on the sieve. This can also be expressed as the fraction of the cumulative mass of glass beads. With these values, it is possible to generate a plot representing the percentage of cumulative mass that is finer or coarser than a particular size. The same data are represented in a graphical format in Figure 3.2, which indicates a histogram representing the mass percentage retained on each sieve and the cumulative mass percent coarser than a particular size.

Table 3.3.

Size Data Obtained by Sieve Analysis of Glass Beads During Development of a NIST Size Standard (Total Mass Sampled = 85.70 g)

US Sieve No	Nominal Size opening (μm)	Mass on sieve (g)	Mass fraction on sieve (%)	Cumulative mass fraction coarser (%)	Cumulative mass fraction finer (%)
25	710	5.28	6.16	6.16	93.84
30	600	11.29	13.17	19.33	80.67
35	500	14.23	16.60	35.93	64.07
40	425	10.7	12.49	48.42	51.58
45	355	8.97	10.47	58.89	41.11
50	300	10.20	11.9	70.79	29.21
60	250	20.11	23.47	94.26	5.74
PAN		4.92	5.74	100	0

More information about representation of size data and some of the issues associated with transformation of data from one basis to another is covered in a later chapter on reporting of size data.

4. Sources of Error and Variation

As in any technique of size analysis, errors and variation can be introduced during the numerous stages involved in the analysis technique. Propagation of errors introduced during the early stages can lead to significant variations in the observed results from the true values. It is very important to recognize the possible sources of error and variation, and the stages at which these can be introduced. Early detection can help prevent and control some of these sources of variation. Operating procedures should be designed keeping in perspective the sources of error, reasons for propagation and means to prevent, control and/or correct for the same. Potential sources of error and variation that can be encountered during sieve analysis are indicated in the Ishikawa diagram[2] in Figure 3.3. An Ishikawa diagram (also known as fish-bone diagram) is a total quality management (TQM) tool that is used to plot all components and sub-processes that constitute a process (e.g., a manufacturing process, or an analysis procedure). By identifying all of the components and steps that are involved in the process, it becomes easier to recognize the various sources of variation associated with each of the steps and thus identify some of the sources of error also. While this diagram considers sources of error and variation arising during the analysis, the probability of introducing variation arises during the sampling process itself. Some commonly encountered sources of error are discussed briefly in the following paragraphs.

1. Sampling and specimen-related sources of error

a. Errors due to non-representative sampling of the bulk material to create test specimens. This source of error can be very significant when sampling from large quantities of bulk (e.g., sampling from box-car loads or other large

containers typically used in shipping where significant segregation of powders occurs during transport and storage).

b. Errors arising from analysis of inadequately prepared powders (e.g., powders containing agglomerates which may not breakup during the sieve analysis, or powders that are very brittle and may fracture into finer fractions during sieve analysis). During wet sieve analysis, it is necessary to ensure that the powders are suitably dispersed in the liquid medium, and do not form agglomerates.

c. During wet sieving, it is critical to control the viscosity and surface tension of the liquid, to ensure adequate and proper flow of the dispersant with the sample through the sieves. Liquids with very high viscosity will not flow through finer apertures. Similarly, inadequate control of the surface tension can cause temporary blinding of the apertures, preventing smooth flow through the sieves.

d. Analysis of powders that develop surface electrical charges during sieving with metallic sieves needs to be avoided. The generation of charges often prevents the passage of particles through aperture openings, where they would otherwise pass through in the absence of these electrical charges.

2. Instrument- and analysis-related sources of error

Potential errors and variations arising during this stage are mapped in the Ishikawa diagram.

a. The selection of the appropriate type of screen and material with which the screen is made is extremely important. Screens used should be properly calibrated and examined to ensure that the screens are in good operational condition. Errors can be introduced due to blinding of screens, corrosion or damage to screens that may have changed the shape and size of the aperture openings. Other factors that can effect the aperture shape and opening size are changes in tension of the wires and wear of the wires. These may occur either as a natural course over a period of time, or may be due to the use of stiff brushes or rough handling of screens during cleaning. While selecting screens to be used in the stack, it is necessary to ensure that the sieves cover the appropriate size range and that they consist of aperture openings with appropriate size separation (i.e., the series of the sieves used should be selected with care).

b. Along with care and attention to the sieves, proper maintenance and operational procedures for the sieve shakers are just as important. Regular maintenance procedures should be developed to ensure that all mechanical moving components are well lubricated, timers are working, any belts or chains are appropriately tensioned. For instruments with air jet or sonic

sifting capabilities, these components should be checked and maintained as per manufacturer's recommendations.

c. Loss of sample during analysis, or during removal for weighing should be avoided at all costs. Loss of sample during analysis can occur due to entrapment of powder between the screen and the frame, or due to spaces between the sieves if stacked incorrectly. While weighing the samples, the balance used should be selected on the basis of desired precision and accuracy. This in turn depends upon the amount of sample charge. The desired resolution of the final result also dictates the type of balance to be used for analysis.

d. Reproducibility of results may be poor when using sieves of different shapes or different sieving techniques due to the nature of vibrations generated in the shakers and transmitted through the screens to the powder in question. Comparison of results from different instruments should be done with extreme caution ensuring that sieving conditions have been reproduced to the greatest extent possible.

5. Practical Concerns

Although sieving is a robust technique and a generally rugged measurement method, sieves do require careful handling during use and regular maintenance. Sieves should be kept clean and dry and stored in containers or cabinets that limit contamination, corrosion and impact by unintended objects. Cleaning can be done by gentle brushing to dislodge adherent particles, but particular care must be taken with mesh sizes greater than 80 (sieves with aperture openings smaller than 150 µm) to prevent damage to delicate woven wires. Low power ultrasonic cleaning in a mild detergent and water solution is often preferred.

Agitation of sieves is a source of variation in measurements of size distribution. Clearly, the energy imparted to the sieve or stack of sieves is the most general description of this procedural step. Duration of agitation is an often measured agitation parameter, whereas amplitude and periodicity are not. Automated mechanical agitation devices, such as sieve shakers, provide more consistent agitation than manual methods. In all cases, duration of agitation should be accurately controlled and recorded.

Measuring a relatively small amount of material which is representative of a larger lot requires care in obtaining samples. Dry powders with a range of sizes can settle during shipment with finer material at the bottom of the container, and other handling can also segregate powders by size. The tendency for powders to separate by size makes sampling a critical step in measuring a useful size distribution. Guidelines recommended by Allen to counteract segregation in a moving stream include sampling a powder when it is in motion

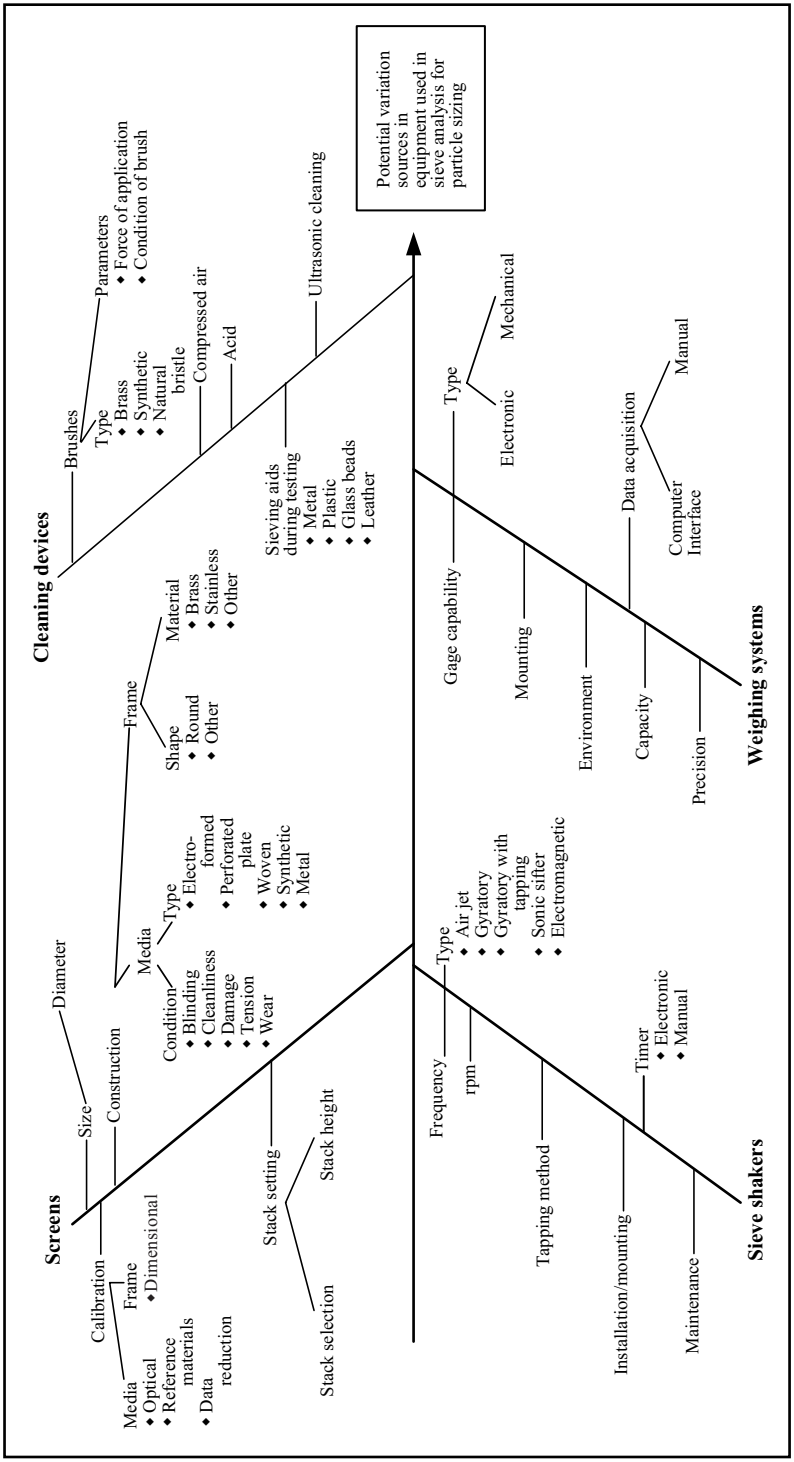

Figure 3.3.

Ishikawa Diagram of Potential Variation Sources in Sieve Analysis[2]

and sampling an entire stream of powder for many short increments of time, rather than sampling a fraction of the stream for all of the time.

The amount of time for analysis can become a major cause for concern if the operational procedure is improperly designed. Considering the fact that as aperture openings become smaller, the amount of time for analysis gets larger, it is necessary to consider the powder size range, the desired size resolution and sizes of sieves in the stack before designing a sieving experiment.

6. Calibration

The measurement of particle size is ultimately based on primary standards of length. The use of light or electron microscopy-based techniques that can be calibrated to standards certified for length serve as the primary particle size measurement methods to which indirect methods, such as sieving, light scattering or other methods are often calibrated.

Sieve calibration is most practically conducted by sieving a material with a known size distribution and determining the similarity of the test results to that of the test material. Standard Reference Materials have been developed for sieve calibration by the National Institute of Standards and Technology. These materials are certified by electron and optical microscopy methods for dimension and are intended for sieve calibration. Table 3.4 lists the appropriate NIST SRMs. A series of publications known as the SP 260 series, sponsored by the NIST SRM[7] program, is available to assist users in the application of SRMs. A more general, but applicable text discussing the general concepts of precision and accuracy as applied to SRMs, and touching upon their impact on quality assurance and measurement processes is available[8]. Another standard, ASTM D1214-89 (Reapproved 1994)[9] can be followed for analysis of glass spheres by sieving techniques. This standard test method is designed specifically for sieve analysis of glass spheres used in reflective road and pavement markings and other industrial uses. A limitation of this standard is its use of non-SI units for reporting of values (i.e., inch-pound units).

Table 3.4.

NIST Standard Reference Materials Designated for Calibration of Sieves

SRM	Material	Particle size diameter, nominal (μm)
1003b	Glass beads	10 to 60 *(600 to 325 mesh)*
1004b	Glass beads	40 to 150 *(270 to 120 mesh)*
1017b	Glass beads	100 to 400 *(140 to 45 mesh)*
1018b	Glass beads	220 to 750 *(60 to 25 mesh)*
1019b	Glass beads	750 to 2450 *(20 to 10 mesh)*

Other proposed techniques for calibration of sieves have included techniques of optical and photometric examination of sieves to record the distribution of aperture sizes in that particular screen. A primary concern with this technique has been the lack of instruments that can examine and record the distribution of aperture openings in a rapid, automated manner[10]. Other techniques of calibration involving the recording of sieve analysis results of a material system with log-normal distribution on a log-probability paper to ensure a straight line fit, and the technique of counting and weighing of undersize fraction passing through a sieve, as suggested by Andreasen and Anderson, have been discussed by Allen[3]. BCR quartz size standards are available from the National Physical Laboratory (NPL), London, for calibration of sieves based on the technique of Andreasen and Anderson.

7. Relevant Standards

There are numerous normative standards pertaining to specifications for sieves, and describing standard techniques for sieving, reflecting the experience gained with this technique over the years that it has been used. Just as interesting is the availability of standards pertaining to sieve analysis of a wide range of materials including ceramic powders, materials for powder metallurgy, soils and fertilizers, industrial chemicals, minerals and other raw materials, spices, green coffee, pigments, porcelains, enamels, clays, concrete, fibers, etc. Standards are typically available defining specifications for sieves that would be used for size analysis or defining standard techniques to be followed for analysis of a particular system. Some standards are also available specifying terminology for use in context of sieving. ISO 2395:1990[11] Test Sieves and Test Sieving-Vocabulary is a standard ISO guide defining terminology used in context of sieving. The ASTM E1638-94[12] is an equivalent Standard Terminology Module Relating to Sieve Analysis, compiled and adopted by the ASTM.

Standards pertaining to specifications for sieves and standard techniques to be followed for sieve analysis of materials are available from every major international standards organization. ASTM E1919-97[13] has a comprehensive listing of the pertinent standards available from ASTM, ISO, BSI, DIN (German standards), AFNOR (French standards) and JSA/JIS (Japanese standards).

There are three ASTM standards defining specifications for different types of sieves:

- ASTM E11-95[1] Standard Specification for Wire Cloth and Sieves for Testing Purposes.
- ASTM E323-80 (Reapproved 1996)[5] Standard Specification for Perforated-Plate Sieves for Testing Purposes.

- ASTM E161-96[4] Standard Specification for Precision Electroformed Sieves.

These standards describe the requirements for sieve construction including details on aperture openings, means to measure the same, wire diameter, frame diameter and techniques for maintenance and cleaning of sieving. ISO standards similar to the above mentioned ASTM standards are also available:

- ISO 3310-1:1990[14] Test Sieves – Technical requirements and testing – Part 1: Test sieves of metal wire cloth.
- ISO 3310-2:1990[15] Test Sieves – Technical requirements and testing – Part 2: Test sieves of perforated metal plate.
- ISO 3310-3:1990[16] Test Sieves – Technical requirements and testing – Part 3: Test sieves of electroformed sheets.

BS 410 (1986) Specification for test sieves was long considered the pertinent British standard and has been withdrawn. However, BS 410-2:2000[17] (ISO 3310-2:1999) Test sieves; Technical requirements and testing: Test sieves of perforated metal plate, is still available from the British Standards Institute.

There are standards available that define standard test methods for characterization of particular class of materials by a particular set of sieves. Some of these standards applicable to ceramics and related material systems adopted by the ASTM are:

- ASTM C136-96a[18] Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates, applicable for the determination of particle size distribution of fine and coarse aggregates by sieve analysis,
- ASTM C285-88 (Reapproved 1994)[19] Standard Test Method for Sieve Analysis of Wet-Milled and Dry-Milled Porcelain Enamel, for determination of the fineness of frit in wet- or dry-milled procelain enamels and other ceramic coatings on metals by use of the No. 200 or No. 325 mesh,
- ASTM C325-81 (Reapproved 1997)[20] Standard Test Method for Sieve Analysis of Ceramic Whiteware Clays, for use in testing shipments of clay and for plant control tests,
- ASTM C925-79 (Reapproved 1995)[21] Standard Test Method for Precision Electroformed Wet Sieve Analysis of Nonplastic Ceramic Powders, for particle size distribution determination of pulverized alumina and quartz for particle sizes from 45 μm to 5 μm by wet sieving,
- ASTM D1921-96[22] Standard Test Method for Particle Size (Sieve Analysis) of Plastic Materials, applicable to particle size determination of

plastic materials in powdered, granular or pelleted forms by dry sieving, with the lower limit of measurement at about 38 μm.

Some pertinent ISO Standards are:

- ISO 2591-1:1988[23] Test Sieving – Part 1: Methods using test sieves of woven wire cloth and perforated metal plate, describing standard techniques of sieving applicable to a broad range of materials,
- ISO 4497:1983[24] Metallic Powders – Determination of particle size by dry sieving,
- ISO 8130-1:1992[25] Coating Powders – Part 1: Determination of particle size distribution by sieving,
- ISO 6274:1982[26] Concrete–Sieve analysis of aggregates.

Another comprehensive source of information on testing techniques and applications of sieve analysis is the ASTM Manual on Testing Sieving Methods[27]. This manual replaces the ASTM STP 447 B edition that has been in circulation and widely used for quite a few years.

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4. SIZE CHARACTERIZATION BY GRAVITATIONAL SEDIMENTATION TECHNIQUES

1. Introduction
2. General Procedures
   2.1 Powder sampling
   2.2 Dispersion
   2.3 Test for dispersion
   2.4 Instrument set-up and analysis
   2.5 Data representation
3. Sources of Error, Variations and Other Concerns
4. Relevant Standards
5. Practical Application: Dispersion Procedure for Silicon Nitride in Aqueous Suspension

1. Introduction

Gravitational sedimentation-based techniques are amongst the most commonly used techniques for particle size and size distribution determination. Instruments based on this type of technique are routinely used in industrial and research applications. Simply put, instruments based on the principle of gravitational sedimentation measure the velocity with which particles in a fluid settle due to the gravitational forces acting on the particle, against the buoyancy of the fluid and other drag forces acting against the settling of particles. This relationship is expressed by Stokes' law, which is valid only for particles settling under conditions of terminal velocity and non-turbulent flow. The terminal velocity can be expressed by the Stokes' equation as:

$$v = \frac{d^2(\rho_P - \rho_L)g}{18\eta_L}$$

where, v is settling velocity of the particles,

d is the particle diameter,

ρ_P and ρ_L are the particle and fluid density respectively,

g is the acceleration due to gravity,

η_L is the viscosity of the fluid.

Thus, time required for the particles to settle in a column of height H can be expressed as:

$$t = \frac{18H\eta_L}{d^2(\rho_P - \rho_L)g}$$

In most instances, the particles upon introduction into the fluid reach terminal velocity very rapidly and in a very short travel distance. Conventional instruments use either a collimated x-ray beam (x-ray gravitational sedimentation) or light beam (photo-gravitational sedimentation) as a probe to determine the concentration of particles at a given depth in the fluid column. In both cases, the attenuation in the intensity of the beam due to either absorption (x-ray) or scattering (light) of the probe signal is used to measure particle concentration at that height. The intensity of the beam after attenuation is compared with the intensity of the beam in the absence of any particles, measured as a baseline signal. Thus, knowing the particle density and by determining the concentration of the particles at various depths, the settling velocities of the particles can be determined and the particle diameter corresponding to that velocity calculated. As settling times increase with decreasing particle sizes, the settling times can be greatly reduced by the application of an external centrifugal force. The settling times can then be expressed as[15]:

$$t = \frac{18\eta \ \ln\left(\frac{r_t}{r_0}\right)}{d^2(\rho_P - \rho_L)\omega^2}$$

where, ω is the angular velocity of the centrifuge,
r_0 and r_t are the radial positions of the particles before and after centrifuging.

The velocity of the particle depends on its position in the suspension as well as its size. The particle velocities increase as the particles move away from the axis of rotation. Allen and others[1-4] have described the different centrifugal sedimentation techniques. Standard test methods of size analyses incorporating this principle are also widely practiced.[5-6]

Some commercial instruments incorporate the centrifugal action with gravitational sedimentation using either a photo or an x-ray probe. These instruments provide the advantage of faster data acquisition times over those without centrifuging capabilities. This is particularly valuable when analyzing powder systems with particles finer than about 1 µm. The use of centrifugal action also enables reliably extending the lower size limit of the instrument to about 50 nm. Claims of lower size limits of 10 nm are influenced by factors such as particle density, solids loading, x-ray mass absorption coefficient and the use of any optical constants.

Gravitational sedimentation techniques are applicable for a wide variety of powder systems. A basic requirement is that all the particles comprising the powder system be of the same density. Under such a condition, the rate at

which different particles settle in the fluid column is influenced only by the particle size. For increased sensitivity, it is necessary that there be an adequate density difference between the density of the particles and the density of the suspension. In some cases, this may require the use of non-aqueous fluids, and thus necessitate knowledge of the fluid's optical properties and specific gravity. Consideration of the fluid surface tension and wetting behavior is critical while choosing the non-aqueous fluid. Furthermore, changing the suspension used in the system would also require calculating the Reynold's number to ensure that all particles settling in the fluid would do so under laminar flow conditions. Jones[7] describes the limitations of the Stokes' Law. Instruments with an x-ray probe exhibit improved sensitivity for materials with high x-ray absorption coefficient. As a general rule, elements with atomic numbers less than 13 do not have high x-ray absorption coefficients, though these increase as the atomic number approaches 20. For instruments equipped with a photo probe (photo-sedimentation-based instruments), knowledge of the materials' refractive index and extinction coefficient values is critical. For powders sizes less than about 2 μm, the use of the imaginary component of the refractive index may be necessary. Incorrect values of real and/or imaginary components of the refractive indices can lead to significant error in the measured size values. Instruments not equipped with centrifugal capabilities are strongly affected by Brownian motion when analyzing particles finer than about 0.5 μm. Depending upon the density and the size of this fine fraction, the random thermal motion can keep the particles from settling, leading to a skewed distribution indicative of a greater fine fraction than is actually present. Keeping the particles well dispersed is just as critical as particle-particle interaction can lead to hindered settling or give rise to significant drag forces which, in turn, affect the settling rate of particles. Centrifugal forces minimize the effects of Brownian motion and drag forces otherwise encountered. Allen[8] describes the limits of the gravitational sedimentation methods relating to concentration limits, upper and lower size limits.

Instruments based on these techniques report the measured size data of powders in terms of the equivalent spherical diameter. This measure represents the diameter of a sphere that would settle at the same terminal velocity as the particle in question, under the same experimental conditions. Though this can be very representative of the particle system being analyzed, if the particles are approximately equi-axed, this measure becomes rather non-representative as the aspect ratio of the particles increases.

Gravitational Sedimentation Instruments: General Information, Capabilities and Limitations

Size Range: Typically about 0.1 μm to 300 μm (lower limit of 0.001 μm and upper limit up to 1000 μm are possible with certain instruments and/or under certain conditions).

Specimen Type: Powders dispersed in suspension. Suspensions can be aqueous or non-aqueous, depending on the desired viscosity and density contrast.

Operating Mode: Off-line or on-line, but only batch mode.

Ease of Operation: Relatively simple, requires a very basic understanding of fundamental principles.

Sources of Error and Variation: Can arise during sample preparation, instrument set-up and operation. Some extent of operator dependence, with possible influence of operator techniques on accuracy.

Strengths: Simple specimen preparation.

Rapid analysis, except below certain size limits.

Robust technique, well suited for industrial environments.

Relatively inexpensive instrumentation.

Does not require highly skilled operators.

Can be used over a broad size range with minimal changes.

Limitations: Cannot be used for analysis of powder batch with particles of different densities.

Analysis times increase with increasing fraction of fine particles (less than about 1 μm, for gravitational sedimentation with centrifugal action).

Sensitivity and accuracy of instruments with x-ray probes is strongly influenced by materials mass absorption coefficient. Sensitivity and accuracy of instruments with photo probes is influenced by the value of optical constants used.

Accuracy of analysis is strongly influenced by physical factors such as solids loading, particle-particle interaction, and in certain size ranges, convection currents and Brownian motion.

Reduced sensitivity, accuracy and resolution for materials with density close to that of the dispersion medium, and under conditions of laminar flow of particles.

Sedimentation techniques for particle size measurements can be classified as either incremental or cumulative measurements. In the incremental method, the solids concentration of the suspension is determined at a given height and time. The rate at which the solids (powder) settle out of the suspension is determined by the cumulative method. Both measurement methods can introduce the powder as a line-start or homogeneous technique. The powder can be introduced as a thin layer on top of a column of liquid (line-start technique) or the powder is uniformly dispersed in liquid (homogeneous technique). Allen and others [1-4] described details of the different sedimentation methods and techniques.

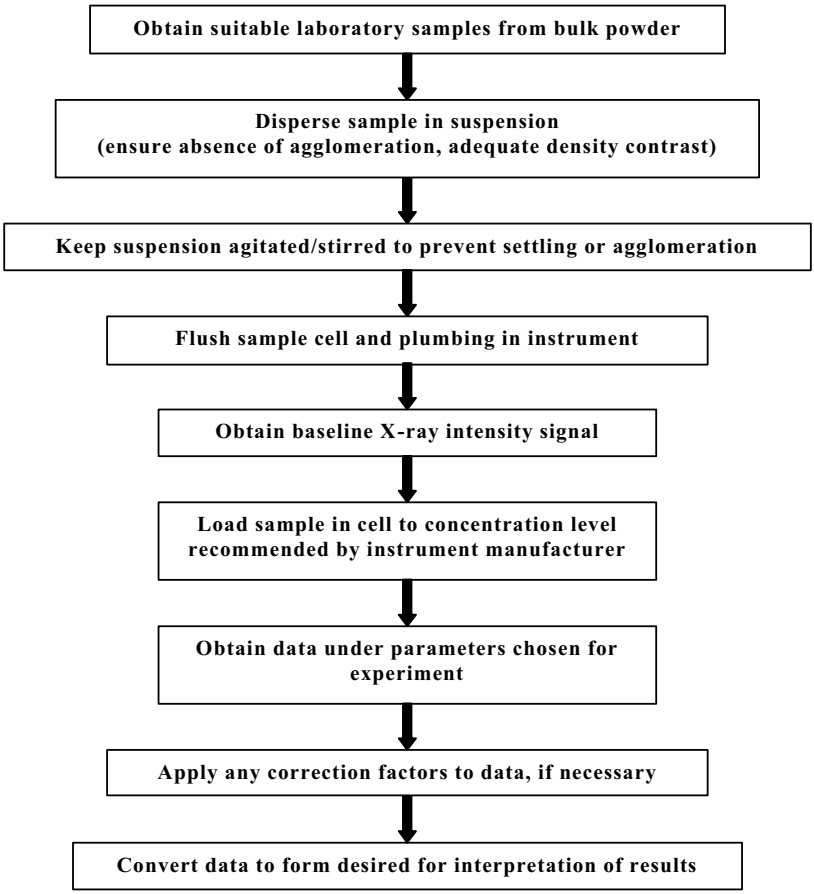

Figure 4.1.

Flowchart Indicating Steps in Size Analysis by X-Ray Gravitational Sedimentation

2. General Procedures

The general procedures required for size analysis by x-ray gravitational sedimentation are illustrated in the flowchart indicated in Figure 4.1. These steps include obtaining a representative sample weighing between a few milligrams and a few grams (dictated by powder density and sample concentration), dispersion and stabilization in a suitable medium, instrument set-up, obtaining data, and post-processing of this data/information to include any necessary corrections and conversion of data to a format suitable for data analysis.

2.1 Powder Sampling

It is critical to ensure that the sample used for testing is representative of the entire batch, and the sampling procedures followed ensure the preservation of that aspect. Specimen preparation is another critical area and a major source of error during analysis. Errors and variations may result due to changes in the nature of the powder during specimen preparation. The nature of the sample may change primarily due to either agglomeration of the powder, or fracture of the particles during attempts to disperse the powder in a suitable dispersion medium. A more detailed discussion on issues of sampling can be referred to in Chapter 2 on Powder Sampling.

2.2 Dispersion

A well-dispersed suspension is a key factor in the reliable and reproducible measurement of particle size and size distribution. Procedures have to be developed for dispersing materials depending upon the physical and chemical characteristics of the powder and the medium in which the powder is to be dispersed. Thus, different material systems will require different dispersion procedures. The selection of the dispersion medium requires consideration of physical properties such as specific gravity of the fluid, viscosity of the fluid and any possible changes in viscosity during fluid flow (e.g., thixotropic or dilatant characteristics). The density of the powder being analyzed should be known, and the dispersion fluid should be so selected that there is adequate density difference between the fluid and the particles, so that the particles will settle in the fluid. The CRC Handbook of Chemistry and Physics, and other similar physical data handbooks are commonly used sources of this information. Usually, the most reliable sources of such information are the manufacturers and suppliers of these materials. The influence of dispersion agents that may be added to the dispersion medium should also be carefully considered.

One of the properties related to the surface chemistry and the electrochemical behavior of the particles is the iso-electric point (i.e.p.). The i.e.p. is the pH

value at which the zeta potential of a system is zero. The zeta potential is the potential at the hydrodynamic slippage plane created in the electrical double-layer surrounding a particle with a charged surface. Expressed simply, at a pH value equal to the i.e.p. of the system the positive and negative charges surrounding the particle surface are balanced (zero net charge). At a suspension pH equal to i.e.p., the particles in suspension will not stay dispersed and will spontaneously agglomerate. The i.e.p. value also provides a range of pH values in which suspensions can be dispersed and it determines whether a material is acidic or basic. As a general rule, the suspension pH should be at least 3 pH units from either side of the i.e.p. in order to aid dispersion. For example, silicon nitride has an i.e.p. of approximately 6 to 7 and thus, suspensions should be stable at around pH 9 to pH 10.

The selection of a dispersing agent is also influenced by the surface chemistry of the material to be dispersed. An acidic polyelectrolyte will work best with a basic solid, while a basic (cationic) polymer is the preferred dispersing agent for an acidic solid. A basic solid is a material that has an iso-electric point greater than pH 7. Similarly, an acidic solid has an i.e.p. below pH 7. For example, alumina with an i.e.p of 9 is a basic solid. The preferred dispersing agent is an acidic polyelectrolyte such as polymethacrylic acid. Low molecular weight polymers (MW 5000 to 10000) are the preferred dispersing agents because of their minimal effect on the solution viscosity.

A study was conducted at NIST to determine the influence of ultrasonication on the state of dispersion of ceramic powders during particle size measurement. The method involves following the change in the particle size distribution as a function of the ultrasonication time used to disperse the powder in dilute suspensions. The ultrasonication energy was kept constant. If agglomerates are broken up due to the energy applied during ultrasonication, then the particle size distribution should shift toward the finer size as the ultrasonication time is increased. The results of this study showed that the measured median diameter of the powder system decreased as the ultrasonication time was increased, within limits. Longer ultrasonication times helps to eliminate the errors associated with dispersion procedures. However, ultrasonication also causes an increase in the temperature of the suspension, and possible evaporation. Figure 4.2 shows that the median diameter of an alumina and silicon nitride powder system decreased as the ultrasonication time was increased, with the ultrasonication energy input kept constant. This trend was observed till a limit of 1 min after which no significant reduction was observed. Increasing the ultrasonication energy input to the suspension also results in a finer median particle size from the deagglomeration of the particles [9].

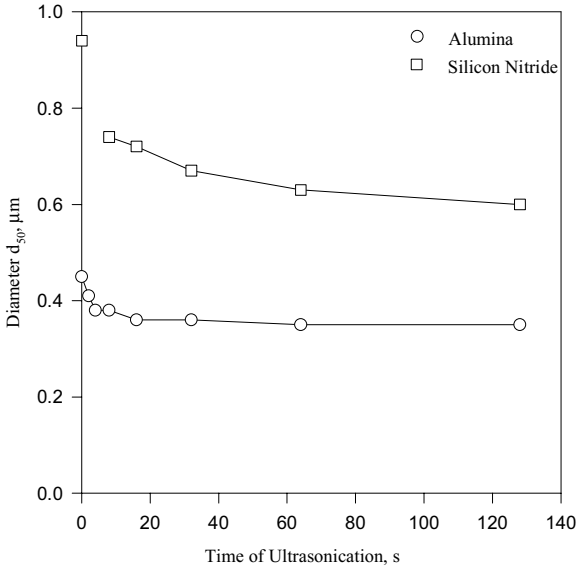

Figure 4.2.

Median Diameter as a Function of Time of Ultrasonication for Alumina and Silicon Nitride Powder

A case study describing studies conducted at NIST involving dispersion of silicon nitride in water is included in Section 5 of this chapter. This example is specific to silicon nitride-water system, and usually dispersion procedures and suspension preparation techniques should be developed specifically for the material system being analyzed.

2.3 Test for Dispersion

After dispersing a sample for testing, it is just as important to ensure that the powders remain well dispersed in suspension prior to analysis. A method that allows a qualitative determination of the state of dispersion involves examining suitable specimens using a microscope. This technique involves placing a glass coupon coated with a thin layer (ideally, monolayer) of a cationic, anionic or non-ionic flocculant depending on the material studied in the suspension of interest. The coupon is kept in the suspension for a period of time, removed and rinsed in distilled water to wash away the suspension fluid. Ideally, those particles in suspension that come in contact with the flocculant surface adhere to the coupon, while the rest of the particles are washed off upon rinsing. Agglomerates that may be present in the suspension will also exhibit a similar behavior and some agglomerates may adhere to the coupon. The slide is then examined under an optical microscope. This technique enables a qualitative judgement only, and works for particles in the 0.5 µm to 50 µm size range.

Particles finer than this size range are too small to be resolved using an optical microscope, while particles larger than this range will spontaneously settle due to the particle mass.

2.4 Instrument Set-up and Analysis

Before attempting any size analysis, it is absolutely essential to ensure that the tubing comprising the plumbing system of the instrument is clear of any powders that may contaminate the sample of interest. Any kinks in the tubing should be cleared, and the tubing around peristaltic pumps checked for wear and tear. Similarly, the sample cell window should be checked to ensure that no powder is adhering on to the window, and that the window is free from scratches. Cell windows get scratched by the abrasive action of powders during fluid flow in the instrument. Scratches on cell windows act as sites for powder adhesion due to the roughened surface, and also cause light to be scattered in instruments that use photo probes.

Instruments should be calibrated as recommended by the instrument manufacturers. The frequency with which these instruments are calibrated depend upon various factors, including how frequently the instrument is used, the nature of application (e.g., quality control, process monitoring or an occasional size analysis requirement). Instruments used for critical applications should be calibrated at least once daily. Some instrument manufacturers supply calibration standards, while others recommend third-party standard materials. In all cases, the standards chosen should be either primary standards or secondary standards traceable to primary standards. Examples of primary standards include SRMs produced by NIST. A discussion of the SRMs is in Section 4 of this chapter. Examples of secondary standards include two garnet material systems with mass median diameters of 3.77 μm and 11 μm produced by Micromeritics Instrument Corp., the manufacturer of the Sedigraph 5100, an x-ray gravitational sedimentation system. One garnet material (3.77 μm) is traceable to NIST SRM 1978.

Prior to actual analysis, the instrument should be setup as per the manufacturer's recommended procedures. Set-up procedures may include establishing powder and suspension medium information, such as powder density, specific gravity and viscosity of suspension, determining the nature of analysis, resolution of analysis, etc. A procedure common to most instruments irrespective of the manufacturer is the establishment of baseline data. A baseline signal for the intensity of the probe transmitted through the suspension fluid in the absence of any sample is first obtained. This signal intensity at different heights of the sample window is compared with the signal intensity that is obtained with the sample powder present in the suspension to determine the settling rates of the powders during analysis.

Samples should be analyzed as soon as possible after preparation. Specimens that have been prepared and allowed to stand may undergo changes in the state of dispersion, and in physical and chemical properties of the powder being analyzed. A global raw material producer aims to analyze samples in less than 20 s after preparation. Powders while in suspension often leach or dissolve on the surface and may indicate non-representative behavior or characteristics upon analysis.

Data obtained from sample analysis may need to be processed further. Processing operations typically include transforming differential distributions to cumulative distributions or *vice versa*. Some instruments might require the application of certain correction factors. Post-processing of data might also include transformation of data from a mass basis to a volume basis or other bases of interest. Most modern instruments come equipped with software that enables such post-processing operations. While using pre-programmed software or transformations, it is a good practice to attempt to understand the nature and design of the algorithms being used. These algorithms are often based on assumptions that may not necessarily be applicable to the material system under study and may lead to significant errors in the observed results.

2.5 Data Representation

The particle size data from the gravitational sedimentation can be presented either in tabular or graphical form. In both forms, the data can be displayed as a plot of the cumulative mass percent finer (or cumulative mass percent coarser) than a particular fraction as a function of the equivalent spherical diameter or as the mass fraction contained in given size intervals expressed as a plot of the mass fraction versus the corresponding size interval. It is good practice to include both cumulative and fractional size distribution data, as such representations allow easy interpretation of whether the powder is of single or multi modal distributions, and also enable judging characteristics such as degree of grinding. Size and size distribution data are always expressed as a function of the equivalent spherical diameter, as the particles settling in the sedimentation column are considered to have a mass equal to that of a sphere settling with the same sedimentation velocity. Thus, for spherical particles, the equivalent spherical diameter is close to that of the particles in question, but, for irregular particles, there will be a significant difference between the two values. As the aspect ratio of the particle increases, the magnitude of this difference also increases correspondingly. Tabulated data are useful in the determination of statistical information about the particle size distribution of the sample and in determining representative size/size distribution measures such as the median diameter (d_{50}), the d_{10} and d_{90} values. The particle size distribution data are expressed on a mass basis. A detailed discussion on

representation of size data is covered in Chapter 7 of this guide. Figure 4.3 shows a graphical representation of particle size data of a silicon nitride powder system plotted as a measure of the cumulative mass percent finer than a given fraction as a function of the equivalent spherical diameter.

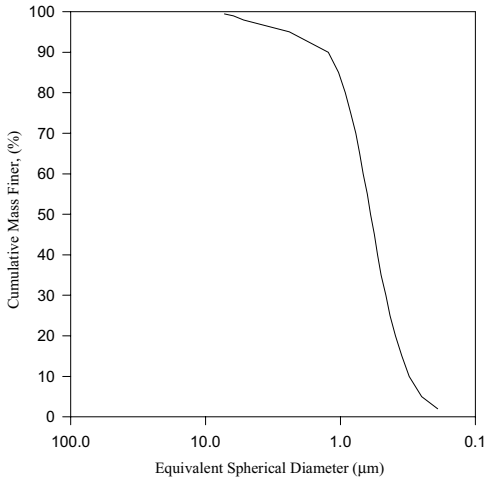

Figure 4.3.

Example of Graphical Representation of
Particle Size Distribution of a Silicon Nitride Powder System

3. Sources of Error, Variations and Other Concerns

Errors and variations in results and analysis may arise at various stages of sample preparation and analysis. These errors and variations can be attributed to various causes including those related to specimen and sample preparation, instruments and equipment, and those due to human factors and intervention. Errors due to human factors are mostly observed during specimen preparation and handling and during instrument setup. These errors can be minimized with the development and adoption of robust operational procedures and techniques. As with any case of classification of errors, those encountered here too can be classified as random or systematic errors. Some commonly encountered sources of error and variation are:

Errors and variation associated with specimen/sample preparation

- Non-representative sampling of powders for specimen preparation is a common source of error. It is important to ensure that samples are obtained from powder lots representative of the entire bulk. This may require that the powder lot be split into smaller batches using some reliable statistical sampling technique.

- Errors often arise during specimen preparation due to inadequate dispersion of powders. Formation of agglomerates during specimen preparation should be avoided, and similarly fracture of particles due to excessive energy input during dispersion should be prevented. Techniques used for dispersing the particles should be reliably tested to ensure that they do not lead to a change in the nature of the powders.
- Contamination of the specimen powder during sample preparation should be carefully avoided. A commonly observed contaminant is wear debris from the ultrasonic probe (typically Ti) over a period of time. Cavitation near the probe tip is a common factor contributing to the rapid degradation of the probe tip.
- Samples should be tested as soon as possible after preparation to minimize the effects of changes in sample properties due to various chemical and surface phenomenon including dissolution, leaching, re-precipitation, etc.
- Errors and variations may also arise due to the concentration effects of the suspension. Particle-to-particle interactions observed at high concentrations give rise to a wide variety of physical effects. Depending upon the surface chemistry of the powder, high solids concentrations can lead to hindered settling of powders, causing a reduction in the settling velocity. This decrease in the particle velocity could shift the particle size distribution lower and produce an effect that indicate a greater concentration of fines than is actually present. Conversely, particle-to-particle interactions at a high concentration may also lead to agglomeration of powders, causing an apparent increase in the coarse fraction. Also, at high concentrations, some fine particles may be entrapped in the wake created by the settling of larger particles, skewing the settling velocity of the finer particles.

Errors and variation associated with instrumentation/equipment

- Improper instrument set-ups due to errors in calibration, lack of calibration, and incorrect baseline signals are factors that contribute to systematic errors in the observed results. Similarly scratches, abrasions or other forms of damage to the sample cell can lead to significant errors in the observed size results. These errors can readily be minimized, if not totally avoided, by following the instrument manufacturer's recommended procedures for instrument set-up and maintenance.
- Analysis of particles finer than about 0.5 μm can be strongly influenced by Brownian motion. For particles of the same size, the influence of Brownian motion is much greater on particles with lower density, rather than those with higher density. The actual size limit at which random thermal motion becomes a significant factor is strongly influenced by particle density, the temperature at which analysis is conducted and fluid specific gravity.

Particles with high density are influenced by Brownian motion at a smaller size limit than particles with low density. Brownian motion interferes with the settling of particles, and increases the settling time of the particles. For very fine particles, Brownian motion may also keep the fines suspended for an indefinite time, grossly skewing the representation of the finer fraction actually present.

- Defective or damaged tubing, forming the plumbing and flow system of an instrument can lead to significant errors in analysis. Two commonly encountered errors that can be directly traced to defective/damaged tubing are air bubbles trapped in the fluid flow system and powder particles trapped or sticking to the walls of the tubing. The latter causes contamination of the sample and may lead to errors in size analysis due to differences in particle density or may cause agglomeration of some of the existing particles. The existence of air bubbles can lead to turbulence in fluid flow and directly interfere with the settling of particles. It is necessary to regularly examine the tubing to ensure no damage or kinks that can trap powder or pinholes that may lead to aspiration of air into the flow system.
- The values of physical properties of the materials being studied should be correctly known as these values are used for calculation of the size results. These include the value of density of powder, specific gravity and viscosity of the suspension medium, temperature of the sample cell, and in some cases, refractive indices of the material and dispersion medium.

The need for correction factors should also be considered. The use of correction factors is most frequently encountered with instruments based on principles of photo-sedimentation. The correction factors would account for scattering of light due to physical phenomenon such as multiple scattering of light. In these techniques, analysis of powders finer than about 2 μm will require a precise knowledge of the real and imaginary component of the refractive index. Determination of the imaginary component of the refractive index for a particular material can be time-consuming and prone to errors. A detailed discussion on issues associated with the role of the imaginary component of the material refractive index and the determination of the same is present in Chapter 6 on Size Determination by Laser Light Diffraction.

The gravitational sedimentation method should not be used as the sole technique to obtain absolute size data, unless the powder contains spherical particles only. The method is very useful for observing the trend of the size distribution when changes are made to the processing parameters. Excessively long sedimentation time, especially in the sub-micron range, can be a source of concern.

4. Relevant Standards

Numerous normative standards and standard materials have been developed for the measurement of particle size and size distribution using gravitational sedimentation techniques.

An ASTM standard test method applicable to ceramic materials is ASTM C958, Test Method for Particle Size Distribution of Alumina or Quartz by X-ray Monitoring of Gravity Sedimentation[10]. This standard is for the determination of particle size distribution of alumina or quartz powders with average particle diameter from 2.5 µm to 10 µm. The dispersion procedure recommends that the powder be suspended in sodium hexametaphosphate and be dispersed in an ultrasonic bath. Our experience with using an ultrasonic bath is that the amount of energy output generated and transferred by the ultrasonic bath is insufficient to break some agglomerates.

ASTM B761, Standard Test Method for Particle Size Distribution of Refractory Metals and Their Compounds by X-ray Monitoring of Gravity Sedimentation[11], has been developed for determination of particle size distributions of refractory metal powders. This standard covers sample preparation and gives a detailed procedure for analysis. Included in this standard is a sample dispersion procedure for refractory metal powders.

Other international agencies for standards have also developed standard test methods for gravitational sedimentation techniques. One of these is the BS 3406, British Standard Method for Determination of Particle Size Distribution – Part 2: Recommendation for Gravitational Liquid Sedimentation Methods for Powders and Suspensions[12]. This is a very comprehensive standard that includes methods for both incremental and cumulative techniques of analysis. The incremental techniques section includes a description of the pipette, photo-sedimentation and x-ray sedimentation methods. Techniques using the sedimentation balances are covered under cumulative methods. The standard includes a brief description of the underlying principles of each method and calculations needed to compute the particle size. It also covers the preparation of a suspension and the dispersion procedure. A table of suitable suspending liquids and dispersing agents for a range of material has been included.

An ISO working draft designated ISO/WD 13317-1, Determination of Particle Size Distribution by Gravitational Liquid Sedimentation Methods – Part 1: General Principles and Guidelines[13] is being compiled for gravitational sedimentation. This draft is applicable to gravitational sedimentation techniques in general, and provides general principles for this method, including an explanation of incremental and cumulative methods using line-start and homogeneous techniques. It discusses the size limitations of these techniques and includes a discussion on how particle size is calculated. A general

discussion on sample dispersion is included. Some general criteria to consider in the selection of the suspension fluid are also discussed. The draft also provides methods to examine the state of the dispersion. A section on the contents of the analysis report is included in this draft.

Another working draft, ISO/WD 13317-3 Determination of Particle Size Distribution by Gravitational Liquid Sedimentation Methods – Part 3: The X-ray Gravitational Technique[14], is being developed specifically for instruments based on the x-ray sedimentation method. This draft includes discussions on the principle of gravitational x-ray method along with a description of the instrument, preparation for analysis and the instrument procedure to be followed.

Similar standard methods developed for sedimentation-based techniques are the German Standard DIN 66 111, Particle Size Analysis: Sedimentation Analysis: Principles; DIN 66 115, Test Method for Particle Size Analysis, Sedimentation Analysis in the Gravitational Field. Standard test methods developed by the French standards institute, AFNOR, include NF X 11-681 Test Method for Particle Size Analysis – Particle Size Analysis by Gravity Sedimentation in a Liquid Medium; and NF X 11-683 Test Method for Particle Size Analysis – Particle Size Analysis of a Powder by Variable Height Gravity Sedimentation in a Liquid-Method Using X-ray Adsorption Measurement. There are also standards developed by the Japanese Standards Institute, JIS Z8820, General Rules for the Determination of Particle Size Distribution by Sedimentation in Liquid.

A list of possible SRMs for calibration of instruments based on gravitational sedimentation is listed in Table 4.1.

Table 4.1.

NIST Standard Reference Materials for Gravity Sedimentation

SRM	Material	Particle Size Diameter (µm)
659	Silicon Nitride	0.2 to 10
1978	Zirconia	0.33 to 2.19

SRM 659 is a silicon nitride powder that has equiaxed primary particles with a minimal amount of large agglomerates. Similarly, SRM 1978 is a zirconium oxide powder comprised of granular, irregular-shaped primary particles consisting of minimal amounts of large agglomerates. These SRMs are specifically certified as standards for particle size determination by gravity sedimentation methods, and can be used to calibrate and evaluate instruments based on these techniques.

5. Practical Application: Dispersion Procedure for Silicon Nitrade in Aqueous Suspension

An example of a dispersion procedure developed for an international inter-laboratory round-robin test is illustrated in Table 4.2. There are many factors to consider when developing a specific procedure. Some of these include concentration of the suspension, the pH of the suspension, the power and duration of the ultrasonication. The volume fraction of the suspension should be dilute (no more than 2 %). Often the optimum volume fraction is determined by trial and error. This optimal value is such that the reduction in intensity of the x-ray beam when it travels through the sample lies within a value recommended by the instrument manufacturer. The pH of the suspension will be different depending on the material being analyzed. Knowledge of the i.e.p. of the specific powder is necessary in developing a stable suspension. Usually, adjusting the pH of the suspension alone will not disperse the material. Energy needs to be applied to break up any agglomerate. The amount of ultrasonication energy may vary depending on the material. The required energy should have the capacity to break soft agglomerates. In this example, a total ultrasonication time of 3 min was used. To prevent overheating of the sample, ultrasonication was done in 3 cycles, with each cycle comprising of power applied for 1 min and shut-off for another minute. The output power of the ultrasonic probe depends on the diameter of the probe used. The temperature of the suspension needs to be monitored. Overheating of the sample can also be minimized by placing the suspension in an ice bath. Each material may need a specific dispersion procedure because the surface chemistry of each material is different. It is preferable to keep the suspension circulating to prevent any settling.

Table 4.2.

Example of a Procedure for Silicon Nitride used for Sample Dispersion in an International Inter-Laboratory Round-Robin Test

Slurry Preparation Procedure for a 4 % Mass Fraction of Solids

- Weigh 4.0 g of silicon nitride powder.
- Dispense 96 g of de-ionized water into a 150 cm^3 beaker.
- Measure the pH and adjust the liquid to a pH of 9, by adding ammonium hydroxide of 1 M concentration.
- Stir for 2 min.
- Measure the pH of the solution and readjust if needed.
- Add silicon nitride powder slowly to the pH-adjusted liquid.
- Stir the slurry while adding the powder so that it does not settle.
- Measure the pH of the slurry and readjust if necessary.
- Stir for 10 min to allow for equilibration.
- Measure the pH of the slurry after stirring and readjust the pH if needed.

Ultrasonication Procedure

The following ultrasonication procedure is recommended for the 100 g slurry in a 150 cm^3 beaker for a 19 mm diameter probe.

- Prepare the ultrasonic probe as per the manufacturer recommendation (including tuning and polishing the tip).
- Rinse the probe well with distilled water.
- Place the probe 20 mm above the bottom of the beaker.
- Adjust the output power to 30 W (use the calibration curve provided by the manufacturer). Note that these power values are approximate since each instrument is not calibrated.
- Apply power for the appropriate period of time.
- Rinse the probe with distilled water after ultrasonication and make sure no powder residue remains on the probe.
- Measure the temperature and the pH of the slurry after ultrasonication.
- Allow the slurry to return to room temperature by stirring. Do not allow the temperature of the slurry to exceed 35 ^{o}C during ultrasonication.

Some instruments require an optimum concentration to enable the instrument to operate efficiently. The user needs to experiment with the mass fraction of the suspension to produce the optimum concentration for the instrument.

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5. SIZE CHARACTERIZATION BY MICROSCOPY-BASED TECHNIQUES

1. Introduction
2. General Procedures
   2.1 Number of particles to count
   2.2 Powder dispersion for specimen preparation
   2.3 Specimen preparation
   2.4 Techniques of size analysis
3. Sources of Error
4. Practical Concerns
5. Relevant Standards

1. Introduction

Microscopy-based techniques for particle size characterization provide a powerful tool for characterization of particle size, size distribution and morphology. They involve direct observation of particles and the consequent determination of size based on a defined measure of diameter (see Chapter 7, Reporting Size Data, Table 7.3). Typically, the calculated sizes are expressed as the diameter of a sphere that has the same projected area as the projected image of the particle. The calculated sizes or size distributions can then be converted to, or expressed in, different measures (area, mass or volume distributions) with suitable precautions. When compared to other techniques of particle size analysis, a significant advantage of microscopy-based techniques lies in the ability to determine the particle shape, in addition to making a direct measurement of size. Numerous commercial instruments and software packages are available for particle size and size distribution analysis. Some commercial instruments are sold as complete packages including the microscope, accessories, dedicated computer systems and software algorithms for analysis. Some packages are available as software add-ons to existing microscopes. Packages with a wide range of functions and levels of complexity are available. While some packages are limited to size determination of well-dispersed particles, other packages have the ability to discern individual particle sizes and shapes from clusters and agglomerates – even the ability to distinguish and determine particles of varying chemical compositions and phases. The analytical capabilities of numerous software packages can be enhanced by the use of additional mathematical algorithms or software systems that can be tailored to meet the needs of individual users.

Microscopy-based techniques can be applied to study a wide range of materials with a broad distribution of powder sizes, ranging from the nanometer to the millimeter scale. Instruments used for microscopy-based techniques have conventionally included optical light microscopes, scanning electron microscopes (SEM) and transmission electron microscopes (TEM). The choice of the instrument to be used is determined by the size range of the powders being studied, magnification, and resolution that is desired. However, the cost of analysis is also observed to generally increase as the size of the powders decreases due to requirements of higher magnification, improved resolution, greater reliability and reproducibility. The cost of size analysis also depends upon the material system being studied, as that dictates the techniques of specimen preparation and image analysis that need to be followed.

Optical microscopes tend to be more affordable, and comparatively easier to operate and maintain than electron microscopes, but are more limited in magnification and resolution. This limits most reproducible analysis by optical microscopy to approximately 1 μm particles[1] with a theoretical resolution limit of about 0.2 μm (dependent upon wavelength of illumination source). However, in practice this limit is not achieved and BS3406[19] recommends sizing by optical microscopy for particles that are a minimum of 10 times larger than the resolution limit of the objective lens present in the microscope. Scanning electron microscopes enable examination of details at higher magnification and resolution, and are thus suitable for particles in the size range of about 0.1 μm to 1000 μm (the lower limit depending upon the quality of the instrument being used). Transmission electron microscopes enable analysis in the size range of 0.01 μm to 10 μm[1], retaining suitable resolution to enable distinguishing surface characteristics. Well-maintained SEMs can regularly be used at resolutions of about 10 nm, while the limit on the resolving power of a TEM is a minimum of 5 nm. In all these cases the magnification and resolving power of the instrument used will be dependent upon the nature of the sample, the instrument operational parameters and the state of technology incorporated in the instrument. The theoretical limit of resolving two discrete points separated by a distance d, can be expressed as:

$$d = \frac{0.61\lambda}{NA}$$

where, λ is the wavelength of the illumination source (expressed in μm) and NA is the numerical aperture. Figure 5.1 illustrates a guideline indicating the relationship between the size of the particle to be determined and the instrument suitable for analysis in that size range.

The skill level required to operate a TEM and to prepare specimens for the instrument is significantly higher than that associated with the use of a SEM.

When comparing these techniques with each other, sample preparation for optical microscopy-based analysis is relatively easy and can be achieved in a short period of time. Sample preparation for SEM analysis requires greater effort and time to ensure suitable mounting of the sample. Samples for TEM techniques are prepared as replicas or thin films, depending on the size of the powders being analyzed. These techniques require the greatest amount of effort and time. However, SEM and TEM techniques offer significant advantages in terms of the greatly enhanced depth of focus that enables viewing of particles with varying sizes in the same field of focus (particles of significantly different sizes can be observed simultaneously without the need to refocus on each particle). Optical microscopes conversely have a very limited depth of focus and thus, require constant correction in the focus field when studying particles of varying height profiles lying on the sample stub. As a general rule, sample preparation for optical microscopy tends to be relatively simple and can be accomplished rapidly, while sample preparation for TEM is far more involved and requires suitable training and a considerable amount of time.

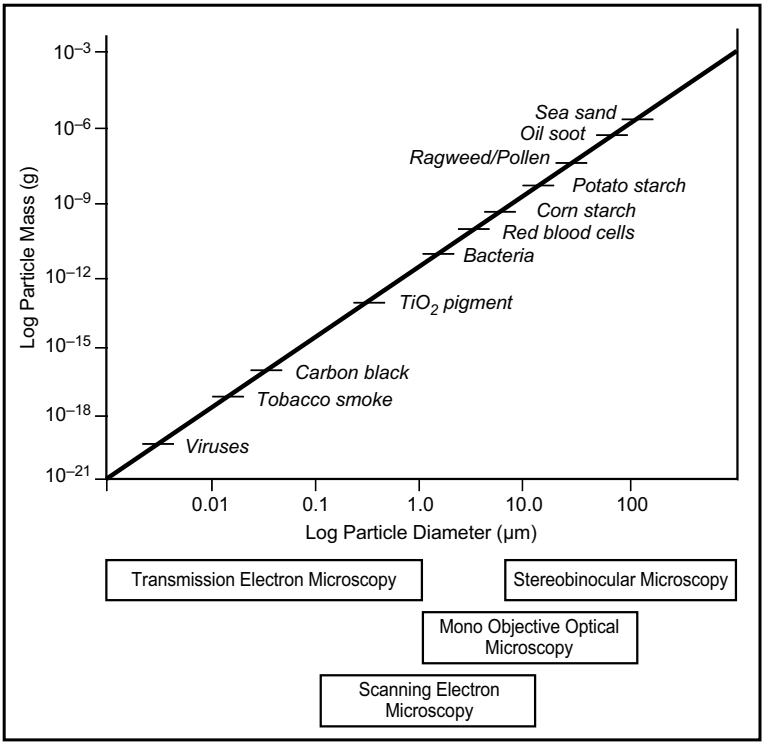


Figure 5.1.

Relationship Between Particle Size and Instrument Suitable for Analysis; based on information in Ref. [2]

2. General Procedures

The general procedures followed during particle size analysis by microscopy-based techniques are illustrated in the flowchart in Figure 5.2. While size analysis by microscopy-based techniques enables direct observation of the powders constituting the material system under study, they can lead to erroneous results if adequate precautions are not taken during sampling and sample preparation. It is absolutely essential that the sample being analyzed is representative of the bulk of the powder. While this is true for any size analysis technique, it has an even greater implication, when sample size gets smaller. Thus, any bias towards either fine particles or coarse particles in the observed field will tend to shift the calculated size and size distribution in that direction. These shifts are not a significant problem, when studying particle systems of relatively uniform sizes. However, this is not true for most real systems, where particles tend to have a broad size distribution. An illustration of this issue can be observed in Figure 5.3. This figure shows the SEM image of a bi-modal mixture of dispersed commercially available silica spheres. This system is a volume fraction mixture of 10 % 1.0 μm (nominal size) and 10 % 0.5 μm (nominal size) silica particles. The number of 0.5 μm (nominal size) particles contained in this volume will be far greater than the number of 1.0 μm (nominal size) particles. In a uniform, well-dispersed system, this ratio will be preserved. The same ratio needs to be maintained if pipetting out a sample to create the microscopy specimen. Often, particle settling or agglomeration may cause particles of a particular size fraction to settle at the bottom, or to be present in a disproportionate amount in the specimen, leading to a bias in the counting and thus a skewed result. The solution to this problem lies in ensuring that (a) the sample is well dispersed, (b) the specimen being studied is representative of the sample, and (c) counting a large number of particles to ensure that statistical errors due to inadequate representation are controlled.

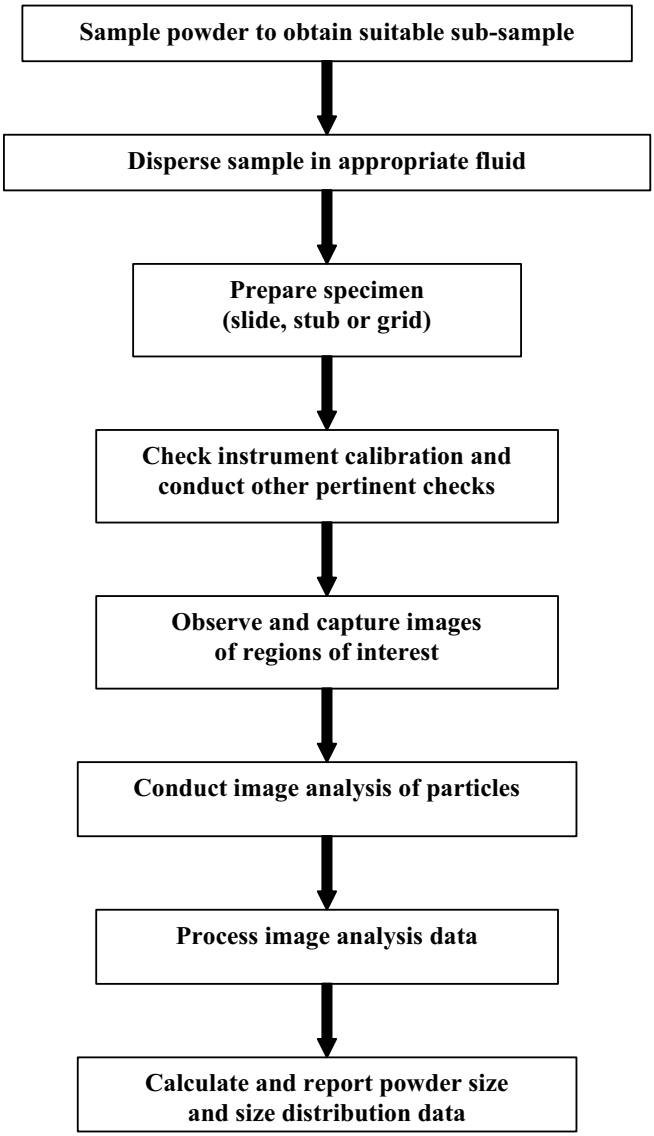


Figure 5.2.

Flowchart Indicating Steps to be Followed in
Particle Size Analysis by Microscopy-based Techniques

2.1 Number of Particles to Count

The statistical errors typically encountered when using microscopy-based techniques are due to counting a disproportionately larger fraction of coarse or fine particles giving rise to a bias towards that fraction, than is actually present in the whole powder. This bias is also enhanced in the calculated standard deviation of the powder size distribution around a central measure. The number of particles to be counted to ensure statistical accuracy depends on whether the distribution is characterized on a number basis or weight basis. Allen[3] states that number-based analyses are simpler than weight-based analyses and that formulae can be used to calculate the number of particles to be sized in order to achieve a given accuracy for both distributions.

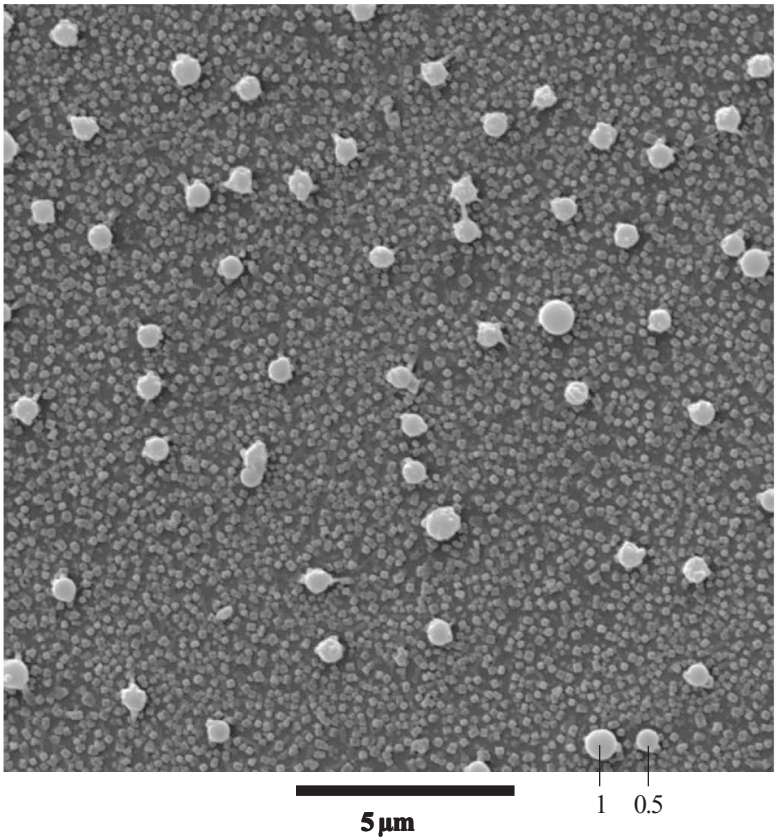


Figure 5.3.

SEM Image of 20 % volume fraction SiO_2 Dispersion Comprised of a Bimodal Mixture of 10 % 1.0 µm (nominal) and 10 % 0.5 µm (nominal) Powders

A more comprehensive mathematical procedure to determine the number of particles to be counted, in order to minimize the error associated with size

determination, has been proposed by Masuda and Iinoya[4]. They have studied the scatter of experimental data due to a particle size distribution. The theory they have put forward has been verified by computational simulation and may be included in the ISO standard on particle size analysis by image analysis methods (currently in draft stage)[14].

From this theory, in order to calculate the number of particles to be counted so as to keep the error within a desired range, the following steps can be followed.

1. Determine the desired range of error, and thus, determine δ.
   For an error of ± 5 %, $\delta = 0.05$; for an error of ± 10 %, $\delta = 0.1$
2. Note the variance of the powder distribution (σ^2).
3. Determine the value of the non-zero exponential constant defining the powder distribution, α.
   The value of this exponent can be found by considering the equation describing the shape of the powder distribution to be $y = K D_p^{\alpha}$.
   Thus, for a log-normal distribution $\alpha = 2$.
4. Determine the basis number for the distribution, β.
   For a powder distribution expressed on a number basis $\beta = 0$, and for a mass basis $\beta = 3$.
5. Calculate the constant c, such that, $c = \beta + \alpha/2$
6. Calculate the value of ω, where $\omega = u^2\alpha^2\sigma^2(2c^2\sigma^2 + 1)$,
   where,

$$u \equiv \frac{\sqrt{n}\delta}{\alpha\sigma\sqrt{2c^2\sigma^2 + 1}}$$

7. The number of particles to be counted (n*) can then be determined by substitution into the following equation:

$$\log n^* = -2 \log \delta + \log \omega$$

(Also see Appendix for further details.)

As an example,

Consider a powder having a log-normal size distribution of variance (σ^2) 0.2209 (such that $\alpha = 2$). If 90 % of the data is desired to be included in the relative error of ± 5 %, then for such a calculation, $\delta = 0.05$ and $P = 0.95$. From equations 1 and 2 (see Appendix), $P = 0.90$ will generate a corresponding value of 1.64 for *u*. As a number count basis corresponds to a β value of 0, thus, in this case $c = 1$.

Substituting these values in equation 5, $\omega = 1.27\ u^2$,

Thus, $\log n^* = -2 \log 0.05 + \log 4.879$

$n^* = 1951.53$

or, approximately 2000 particles need to be analyzed to get the error within the desired range.

If it is desired that 99 % of the data should be included in the relative error of ± 5 %, then P = 0.99. In such a case, using the above described procedure:

$\log n^* = -2 \log 0.05 + \log 8.454$

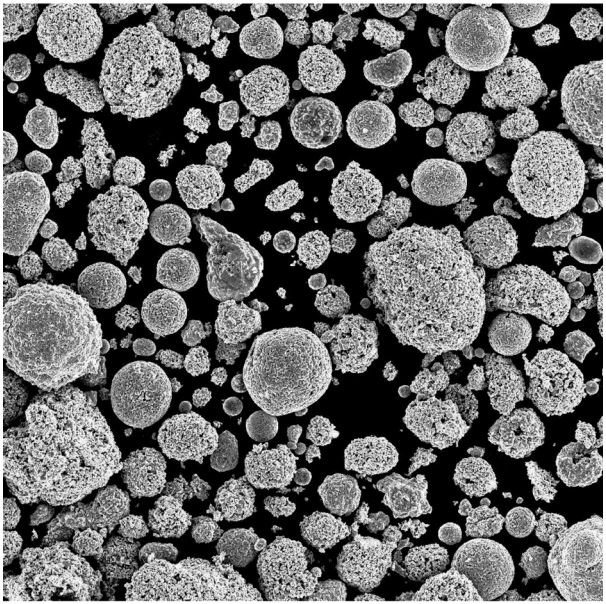
$n^* = 3381.45$

or, approximately 3400 particles need to be analyzed to get the error within the desired range.

The above theory provides some guidelines for estimating the number of particles that need to be analyzed in order to have results with some degree of confidence. However, the assumptions that have been considered in developing this theory do not always hold good for all "real" powder distributions and the user should have a good estimate of the values of terms such as α and σ^2 of the powder distribution.

The development and use of procedures involving large number of particle counts are followed in the development of NIST SRMs. SRM 1004b[5], a particle size distribution standard comprising of glass beads with a size distribution of 40 µm to 150 µm, required the counting and size determination of about 20,000 individual particles to ensure representative sampling. These 20,000 particles were classified into seven size fractions corresponding to seven standard sieve sizes and the results developed into a cumulative distribution curve. Figure 5.4 shows a representative image used for the development of a WC-Co Standard Reference Material (NIST SRM 1985, to be certified for particle size distribution, 20 µm to 50 µm), where a similar procedure involved the counting of a large number of particles, due to the broad size range of the particles present.

Counting such a large number was not necessary in the case of a dispersion comprised of uniformly sized 1.0 µm SiO_2 powders. A typical image obtained from the SEM analysis of this powder system is shown in Figure 5.5(a). Table 5.1 lists the results from image analysis of this powder system. After counting over 3000 particles, the mean and median diameters were computed for 250, 500, 750, 1000, 1500 and 2000 particles selected randomly. It is observed that the calculated sizes and distribution statistics are similar when fewer particles are counted and, also, when large numbers of particles are



20 μm

Figure 5.4.

Representative Image of Particle Size Standard NIST SRM 1985, Comprising Powders with a Broad Size Distribution

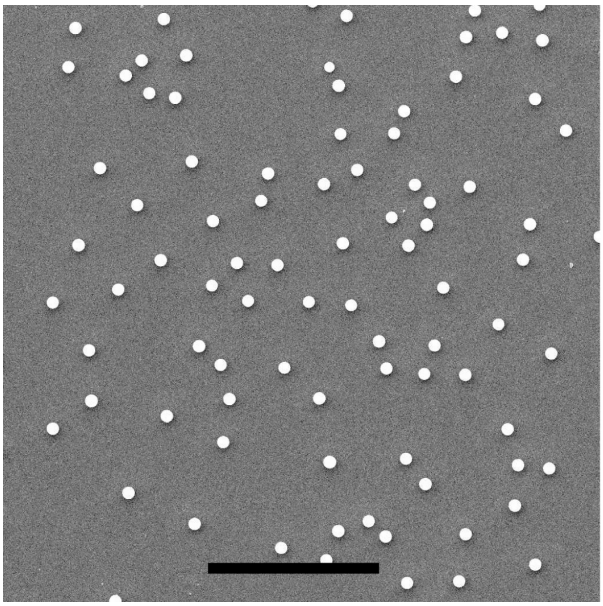
counted. These precautions, incorporated to ensure representative and unbiased sampling, hold true for all microscopy-based techniques. Due to the large number of particles being observed, size analysis would be greatly aided by the use of automated or semi-automated computer systems and algorithms. The use of such systems is gaining increasing acceptance with the falling costs of computer hardware and software.

Table 5.1.

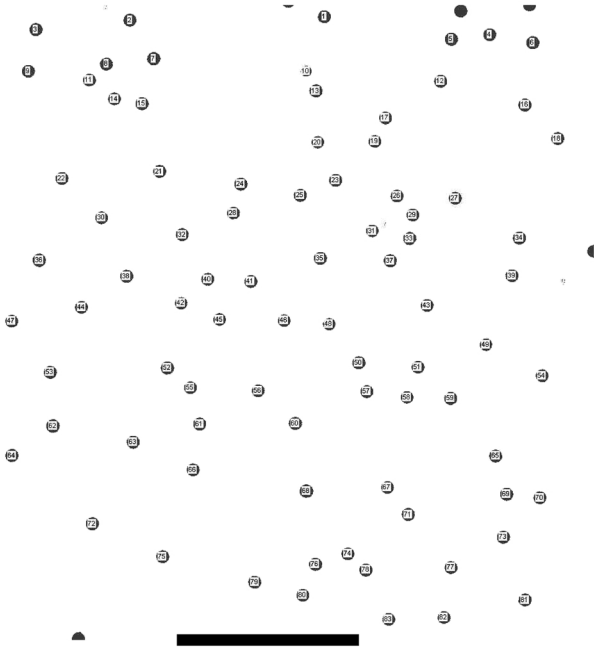
Calculated Diameters of Powder System Comprised of Uniform SiO_2 Particles (Nominal Size of 1.0 μm)

Random Sampling Summary

	Number of Particles Sampled					
	250	**500**	**750**	**1000**	**1500**	**2000**
Mean Dia. (μm)	1.04	1.04	1.04	1.04	1.04	1.04
Median Dia. (μm)	1.03	1.04	1.03	1.04	1.04	1.04
Std. Dev.	0.03	0.04	0.04	0.04	0.04	0.04



(a) 10 μm



(b) 10 μm

Figure 5.5.

(a) Raw Image of Nominally 1.0 μm SiO_2 Particles of Uniform Size Distribution (Table 5.1), (b) Same Image After Processing by NIH Image[6] for Particle Size Analysis and Identification

2.2 Powder Dispersion for Specimen Preparation

In order to ensure that the analysis represents the true picture of the powder size and size distribution, it is necessary that the specimens are prepared from sample powders that are in a physical state similar to that in which they would ultimately be used. Thus, when analyzing powders to be used in slip casting, specimens should ideally be made from the dispersed powders constituting the slip. Similarly, specimens should be ideally made from dry powders when the powders are to be used in such a state (e.g., if powders are to be compacted to form a green body). Irrespective of the physical state of application, the techniques used for specimen preparation should be reproducible and should ensure that the specimens are representative of the sample.

Specimen preparation for any microscopic technique (optical, SEM or TEM) requires that the particles be well dispersed. This is often achieved by dispersing the powders in solution and then preparing the specimens, but often the nature of the sample being studied will require that the sample should not or cannot be dispersed in suspension. Irrespective of whether the powders are sampled in a dry state or when in suspension, the primary goal of specimen preparation should be to produce specimens that are representative of the powder being sampled. The number of particles touching each other or interacting with each other should be minimized, and should be proportional to that which exists in the powder.

It is necessary to ensure that no contaminants are introduced during specimen preparation and storage and that the processes followed during specimen preparation do not lead to fragmentation or segregation of the powders, both of which would lead to erroneous results. The use of ultrasonication devices such as ultrasonic baths and ultrasonic probes are recommended, but with caution, to ensure dispersion of powders. The ultrasonication energy and time should be decided upon with great care to ensure that particle dispersion alone is achieved. Power settings that are too high can cause fragmentation of particles or heating of the fluid constituting the suspension. Also, ultrasonication at too low power may not cause adequate dispersion of the powders. Figure 5.6 indicates the influence of varying ultrasonication duration on the size distribution of a 2 % (by volume) silica suspension. At 0.25 min, the size distribution is extremely large (indicative of possible presence of agglomerates) and after 3 min of ultrasonication, the size distribution does not show any significant changes. The ultrasonic probe transfers 30 W of energy into the suspension. The use of ultrasonic horns and probes to disperse suspensions can lead to the introduction of impurities from the probe/horn during the process of dispersion. This is more of a problem when using a probe that has been in service for a while and starts to exhibit signs of pitting and corrosion due to interaction with abrasive particles and other harsh

environments. The generation of heat during ultrasonication also needs to be controlled by either cycling the operation of the source or by placing the suspension in a controlled temperature bath. Excessive heating can cause irreversible changes in the sample.

The use of ball mills to break up agglomerates present in a powder suspension is a feasible alternative to the use of ultrasonication devices. The obvious advantage to this technique is its applicability to large samples, where the use of ultrasonic horns and probes is impractical due to limitations of sample size and quantity. The limitations of this technique lie in the initial experiments to determine appropriate operational parameters. The speed of the mill and the milling time need to be determined to ensure that no attrition or agglomeration of the sample powder is occurring. Excessive milling would lead to fragmentation and increase the concentration of fines. Possible introduction of contaminants from the milling media and the mill itself is another shortcoming of this technique.

Often agglomeration of powders during specimen preparation occurs when droplets of the medium containing the dispersed powder are allowed to dry on the sample stage. A slow drying process causes the particles to aggregate due to capillary forces pulling the particles together and may lead to errors in discerning naturally occurring agglomerates from those formed during sample preparation. Furthermore, it is good practice to ensure that specimens are labeled with a suitable shelf-life period, after which the dispersion medium holding the particles or the particles themselves may change, and the specimen may not be representative.

Working with powders in a dry state requires greater precautions in order to prevent aggregation and settling of powders in preferred orientations during specimen preparation. Uniform powders that are relatively coarse can be spread out on a glass slide and then picked up on to a tape with an adhesive surface. The powder particles can be spread out by either tapping the slide gently or by spreading them out using a brushing action with light strokes. In some instances, the powders may be spread out directly on to the adhesive surface of the tape itself. These techniques are reliable only if the particles that adhere to the tape are representative of the bulk. Uniform spread of the particles will not easily be attained and may lead to errors if the particles are too fine, or have a marked aspect ratio that leads to settling along preferred orientations. Some of these techniques have been used at NIST in the development of SRMs made up of glass spheres (e.g., SRM 1004b, 1017b, 1018b and 1019b).

Specimens can also be prepared by dispersing a small quantity of the sample powder (typically a few milligrams) in a non-polar liquid, such as isopropanol, ethanol or acetone. A drop of the suspension is then placed on the surface to

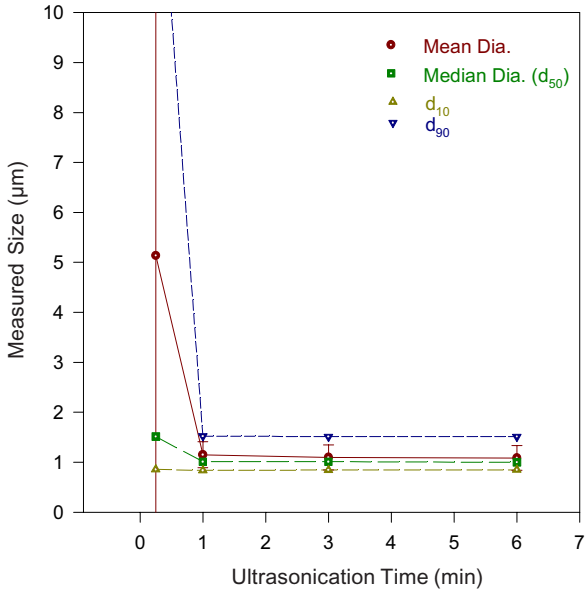


Figure 5.6.

Influence of Ultrasonication Time Upon Particle Size Distribution of a 2 % Volume Fraction SiO_2 Suspension. Ultrasonic Probe Transmitting Approximately 30 W Used

be studied (such as a glass slide, SEM sample stub or mounting tape). Despite the relative ease and simplicity of this technique, there are numerous possible sources of error associated with this. It should be ensured that the small quantity of powder added to the organic dispersant is representative of the bulk quantity of the powder. Dispersing the powders in the fluid may require the use of an ultrasonic bath, and excessive ultrasonication can cause undesirable fragmentation of the powder. The fluid to be used should be selected by judging the nature of the interaction between the powders and the fluid, and the drying rates of the fluid.

In certain instances, specimens can be prepared by filtering the powders through a suitably sized filter. In this technique, the powders are dispersed typically in distilled water and then vacuum filtered, such that the particles are embedded on to the filter. The filter is then suitably mounted on the observation stage and the powders observed accordingly. The important issue to be kept in mind when following this technique of specimen preparation is to ensure that dispersing the powder in water does not change the characteristics of the powder being studied, and thus, does not cause agglomeration of the powder. In order to decide the filter size to be used, it is essential that the operator has some prior knowledge of the powder size distribution, so that there is neither a

loss of the fine fraction nor too slow a filtration rate. This technique requires that the powder concentration being dispersed is dilute enough, such that particle deposition on the filter will not lead to too many particles overlapping each other. Particles with a significant aspect ratio will tend to settle along the long axis of the particle and may cause a significant bias in the observed size distribution. If possible, these particles should be excluded from the count.

2.3 Specimen Preparation

Preparation of specimens for optical microscopy is relatively easy, as, in some instances, the particles may still be dispersed in the fluid medium, when viewed under a microscope. In such a case, the suspension is placed in a groove or depression in the slide and covered with a cover slip through which the specimen is viewed. Such a technique cannot be followed when attempting to prepare specimens for examination by electron microscopy due to the high vacuum conditions maintained in the microscope. Numerous techniques of varying levels of complexity are available for preparation of samples for optical microscopy. Allen describes some of the techniques and their application[7].

Some specimen preparation techniques for examination by TEM use a conducting metallic grid (primarily, copper) on to which the powders are introduced by different techniques[8,9]. In order to hold the powder on the grid, the powder is deposited on a formvar film which is then placed on the grid. Specimens for examination by electron microscopy require that the powders be coated with a conducting film, which prevents electron charge build up at any of the non-conducting surfaces of the specimen. TEM specimens are typically coated with carbon films, while SEM specimens surfaces are coated with Au-Pd, Au or carbon films. The deposited film thickness may vary from about 5 nm to about 20 nm, depending on the material system being studied and the technique used. Other techniques of specimen preparation for examination by electron microscopy-based techniques, are also available[10].

2.4 Techniques of Size Analysis

Manual, semi-automatic or automatic techniques for particle size analysis are all influenced by the skill and procedures used by the operators[11]. Manual techniques of analysis are based on the use of a marking device such as a cross-hair being moved along the particle to obtain a linear dimensional measure of the particle. Other manual techniques involve the use of a graticule with inscribed circles of varying diameters that are used to evaluate the size of the particle, by selecting a circle of suitable diameter that can be circumscribed or inscribed with the particle of interest. Variations to this basic principle have been described by Allen[12].

Semi-automatic techniques of analysis require human intervention but, offer to some degree, the ease of automated analysis. This reduces the tedium and some of the random errors associated with manual counting and analysis. Some of the techniques require the projection of the image of the particles on to a suitable medium[12], where they are compared with spots of known sizes, while others are based on the image shear technique. In the image shear technique two images of the same particle are created by the splitting of the light beam in the microscope. Size analysis is achieved by adjusting the amount of shear to that of the particle diameter, such that the two images only touch each other, without any overlap or marked separation between the two projected images[13]. The shear distances are set for certain values and numerous particles are then examined, enabling particle classification into various sizes.

Other semi-automatic techniques of size analysis include variations to a basic principle of recording the image, converting the image to a gray-scale image, thereby introducing suitable density contrast between the particles of interest and the background. The image is then digitized and the area of the particles then calculated. Figure 5.5 indicates the application of a similar principle to a powder system of silica particles. Figure 5.5(a) shows the raw image obtained using SEM, while 5(b) shows the processed image with the particles identified. In processing the raw image, the software is designed to fit an ellipse to the identified feature, subject to constraints (size, contrast, interior hole-filling) defined by the user. Table 5.2 shows the information that would be obtained and then derived for an image processed in a similar manner. The first column identifies the feature on the processed image, and the second and third columns the dimensions of the major and minor axes of the feature calculated by the software and expressed in terms of pixels. The fourth column represents the area of the feature, also expressed in terms of square pixels. Knowing the calibration factor for the image and the magnification of the image, the area calculated by the software algorithm is expressed as the diameter in microns in the sixth column. From the basic information calculated by the software, other factors of interest such as the aspect ratio can also be calculated. Analysis based on this software has been used in the certification on NIST SRM 1982, a spray-dried zirconia particle size distribution standard (Figure 5.7).

Particles can be counted in semi-automated techniques by a process sometimes called the "Guard Ring Technique." This process involves defining a measurement frame inside the image frame and establishing criteria for particles falling within or intersecting the edges of the measurement frame[14]. Typically, measurement frames are square or rectangular in shape. In some metallurgical applications, circular frames have been used. When using square or rectangular measurement frames, two adjacent edges of the frame can be defined as reject edges, i.e., any particles intersecting these edges get excluded. Any particles within the frame and/or intersecting the other

two adjacent edges are counted for the analysis. Counting can also be accomplished by defining a point in the particle, or along the perimeter of the particle as a feature count point. The same feature count point on every particle in the image field is examined, and particles with that point in the measurement field are included, while those particles that have the feature count point outside the measurement field are excluded. The use of such techniques helps ensure consistency in selection and counting of particles, and are most effective when developed on simple criteria.

Automatic image analysis techniques use a combination of image capture and viewing techniques, followed by image interpretation using algorithms based mostly on Fourier and fractal shape analysis. The strengths of this technique lie in the ability to manipulate the image to enhance certain features, improve contrast and thereby reduce some of the errors that arise due to poor image quality or particle discernment. Similarly, the use of computers and powerful algorithms reduces the amount of time required for analysis, and thereby enable rapid size determination of a large number of particles. The drawbacks of this technique lie in the high cost of equipment and software needed for this analysis. A major drawback to automatic image analysis techniques is the

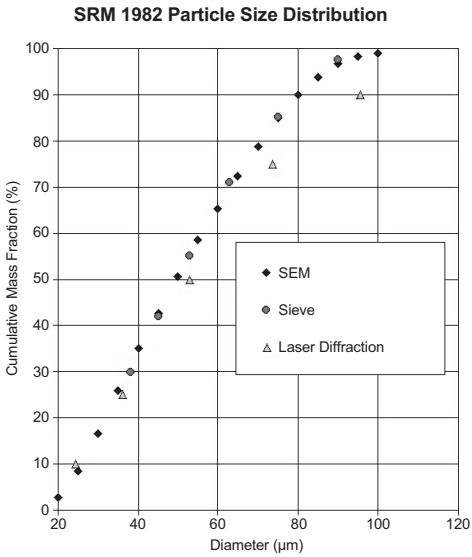


Figure 5.7.

Comparison of Particle Size Distribution for NIST SRM 1982

reduction of operator intervention and decision making. This can often lead to analysis of unwanted features, or analysis using parameters that are inappropriate for that particular system. However, most modern systems do allow some degree of human intervention and control.

Table 5.2.

Table of Data Generated from Semi-Automated Image Analysis System

	Maj.Axis	Min. Axis	Area(pix^2)	Dia. (pix)	Dia. (µm)	Aspec. Rat
1	22.29	21.88	383	22.08	1.09	1.02
2	22.23	21.42	374	21.82	1.08	1.04
3	21.96	21.75	375	21.85	1.08	1.01
4	44.6	21.64	758	31.06	1.53	2.06
5	23.42	22.56	415	22.98	1.13	1.04
6	21.59	20.88	354	21.23	1.05	1.03
7	23.6	22.55	418	23.07	1.14	1.05
8	22.99	22.43	405	22.70	1.12	1.02
9	45.29	22.18	789	31.69	1.56	2.04
10	22.76	22.33	399	22.53	1.11	1.02

3. Sources of Error

Various sources of error, both systematic and random, have been mentioned and discussed in the above sections. A thorough understanding of these is essential in order to be able to identify the occurrence of these and develop procedures to minimize their impact on the final results. It is also necessary to understand that while these errors cannot be eliminated, implementation of standard procedures and protocols can help characterize the errors and the magnitude of their influence on the measured results.

Some of the common sources of errors are summarized below:

Errors associated with specimen/sample preparation

- Non-representative sampling of powders
- Inadequate or improper dispersion of powders during specimen preparation
- Agglomeration or fracture of primary particles during specimen preparation
- Contamination of specimen/introduction of artifacts during specimen preparation/storage
- Specimen degradation during storage.

Errors associated with instrumentation/equipment and image analysis

- Improper calibration of microscope magnification
- Microscope operation under less than ideal parameters (e.g., accelerating potential or condenser lens current set too high or too low, errors due to stigmatism)
- Charging of specimen surface while observing under an electron beam

- Operating microscope in regions of "empty magnification" (i.e., no gain in resolution beyond a certain magnification limit)
- Improper calibration of image analysis hardware/software
- Errors in establishing gray scale threshold in image analysis techniques
- Counting of inadequate number of particles.

Errors due to human and other factors

- Operator fatigue
- Operator skill level and experience (in use of equipment, techniques associated with analysis)
- Lack of understanding of equipment and software/hardware capabilities and limitations
- Errors due to inadequate or incorrect statistical analysis.

The above list identifies some commonly encountered sources of errors. Development of procedures that address the above issues can help alleviate the impact of some of these sources of errors. Successful procedures are those that are simple and lead to reproducible results.

4. Practical Concerns

Some of the practical concerns pertaining to sample and specimen preparation have been discussed in the previous sections. Errors in analysis can be reduced by ensuring that the powders are well dispersed, and do not agglomerate when introduced on to a specimen stage. If agglomeration is observed, such agglomerates should not be included in the analysis. Other important concerns arise when analyzing irregularly shaped particles or particles with a significant aspect ratio. Irregularly-shaped particles may come to rest on the sample stub in a preferred orientation and may thus bias the analysis. Care should be taken to ensure that such orientation of particles is minimized and, if unavoidable, procedures should be designed to factor in such a bias in the results. An extreme example of such preferred orientation may be observed in analyzing fine fibers or fiber-shaped particles. If the system being studied consists primarily of such particles, then the measure used to express the particle size should reflect some information about the particle shape and aspect ratio. When using projected area values of the particles in the image to generate a size distribution curve, anisotropic particles at rest in a preferred orientation can introduce a significant error if that size distribution is expressed on a mass or volume basis.

Other concerns during size analysis by microscopy-based techniques arise due to systematic errors or artifacts associated with the instruments used for observing the particles. The microscopes being used should be adjustable such

that the effects of aberrations, flare, stigmatism, can be eliminated using standard practices (see next section, Relevant Standards) or manufacturer-recommended procedures. Most importantly, the magnification scale of the microscopes should be calibrated. Magnification scales can be calibrated by using size standards pertinent to that range, or magnification standards such as SRM 484g that can be used to calibrate the magnification scale of an SEM in the range of 1000x to 20000x. SRM 2090 (currently in preparation) will be a new magnification standard made of a silicon chip with well-defined line separations. SRM 2069b is a SEM performance standard of graphitized rayon fibers. Optical microscopes can be calibrated using standards such as SRMs 2059, 475 and 476, all of which comprise of opaque lines and clear spaces in a substrate. These standards have varying line widths and pitch values. When calibrating the magnification power, the procedure used should be a standardized technique that takes into account all possible sources of variation, and calibration should be done not just for the magnification power that will be used in the analysis, but for a range of magnification powers.

5. Relevant Standards

Standards covering various aspects of size analysis by microscopy-based techniques have been developed or are under development. A draft standard addressing general issues of size analysis by imaging techniques is ISO/CD 13322, Particle Size Analysis – Image Analysis Methods[14]. This standard defines some terms and symbols that are commonly used and encountered in image analysis. The standard also describes some techniques for sample preparation of both dry powders and powders in suspension. Issues and requirements for recording the image of the specimen and further image analysis are discussed.

ASTM E20 Practice for Particle Size Analysis of Particulate Substances in the Range of 0.5 µm to 75 µm by Optical Microscopy is another general standard, which was discontinued in 1994. Other pertinent ASTM standards include the ASTM E175-82(1995)[15], a standard defining terminology for microscopy-related applications. The definitions in this standard cover a broader range of terms (including instrumentation, errors and units) than the ISO/CD 13322 in its present draft form. ASTM E766-98[16] is a standard practice for calibrating the magnification of a SEM and is particularly useful in ensuring that the instrument is truly observing specimens at the indicated magnification values. As there are numerous factors (SEM accelerating potential, condenser lens current, working distance, etc.) that can lead to discrepancies between the stated magnification and the true value, the use of this standard may help minimize some of these errors.

Other standards pertaining to size analysis by optical microscopy include the French standard, NF X11-661: Test Method for Particle Size Analysis –

Determination of Particle Size of Powders – Optical Microscope[17]. NF X11-696 Test Methods for Particle Size Analysis Through Image Analysis[18] can be applied for general image analysis techniques, and the British Standard, BS 3406: Methods for Determination of Particle Size Distribution, Part 4: Guide to Microscopy and Image Analysis Methods[19] is a very comprehensive and descriptive guide designed for size determination by microscopy-based techniques. This guide describes some standard symbols and terms pertaining to microscopy. Some of the terms and symbols described here are also found with similar notations in the draft ISO/CD 13322. The standard has a section on sample preparation describing some important factors to keep in mind while preparing the samples, to ensure reproducibility and also minimize errors and bias during analysis. It describes the resolution limits of the three microscope systems based on the basic mathematical formulae for resolution. A section on calibration of the microscope system describes means to set up the instrument for analysis. It then describes means to conduct measurements using manual methods with graticules and strip counts, and with image analyzers. Means to calculate the size distribution and assess the accuracy and precision of the calculated values are also described in detail. The guide also has annexes describing the equipment used in these techniques, together with some background information on the techniques, and highlights some issues to be addressed when deciding on the type of image analysis system to be used.

Appendix

From the calculations of Masuda and Iinoya[4,14], if P represents the probability that the experimental data may be in the range of relative error -δ to +δ, then:

$$\frac{1-P}{2} = \Phi(-|u|) \quad \textbf{(1)}$$

where, Φ(-|u|) represents a normal probability distribution function of the form:

$$\Phi(z) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-\frac{z'^2}{2}} dz' \quad \textbf{(2)}$$

and,

$$u \equiv \frac{\sqrt{n}\delta}{\alpha\sigma\sqrt{2c^2\sigma^2+1}} \quad \textbf{(3)}$$

where, n is the size of a random sample,

α is the non-zero exponential constant that defines the powder distribution, i.e., ($y = K D_p^{\alpha}$),

σ^2 is the variance of the distribution, and

c is a constant of the form $c = \beta + \alpha/2$, where β is 0 when computing the population-mean particle diameter on count basis and 3 when computing on mass basis.

Thus, defining n^* as the number of particles that needed to be counted, the following equations can be used to determine n^*:

$$\log n^* = -2 \log \delta + \log \omega \quad \textbf{(4)}$$

where,

$$\omega \equiv u^2\alpha^2\sigma^2 (2c^2\sigma^2 + 1) \quad \textbf{(5)}$$

and, δ is the desired relative error (e.g., if the desired relative error is 5 %, δ is 0.05).

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6. SIZE CHARACTERIZATION BY LASER LIGHT DIFFRACTION TECHNIQUES

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   2.1 Instrumentation
   2.2 Mie scattering
   2.3 Fraunhofer approximation
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3. General Procedures
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1. Introduction

Size determination techniques using a light beam as a probe are broadly classified into imaging and non-imaging types. Some aspects of the imaging-based techniques are discussed in Chapter 5 on Size Characterization by Microscopy-based Techniques. Techniques constituting the non-imaging methods of size determination can further be classified into numerous groups based upon the physical principle describing the interaction between the light beam and the particle and the information that can be deduced from that interaction. Laser diffraction instruments fall within this category of non-imaging type of instruments. Manufacturers produce instruments that are based upon the same general principles of laser diffraction but the use of different components,

configurations, and algorithms gives rise to a broad selection of instruments with analysis capabilities covering a wide range of sizes and size distributions.

The underlying assumption in the design of laser diffraction instruments is that the scattered light pattern formed at the detector is a summation of the scattering pattern produced by each particle that is being sampled. Deconvolution of the resultant pattern can generate information about the scattering pattern produced by each particle and, upon inversion, information about the size of that particle. In order for this to be true, multiple scattering of light should not be permitted. Multiple scattering refers to the phenomenon where light scattered from one particle interacts with another particle and gets scattered again. This places an inherent limitation on the concentration of particles that can be analyzed. The concentration limit is determined by the design of the instrument and varies depending on the nature of the incident light source, optical geometry and light detection system. Laser diffraction instruments can be used for the analysis of dry powders, powders dispersed in aqueous or non-aqueous dispersants, and also finely divided aerosols. These instruments are mostly used for analysis of small sample quantities (typically, a few milligrams to a gram), though some are designed for, or have accessories that enable sampling from a moving stream and are thus, suited for size characterization and process control of an industrial production line.

Instruments are designed with capabilities for applying various optical models for deconvolution of the scattered pattern and size determination. Those using the Fraunhofer model for size analysis have typically a lower size limit of about 2 µm and an upper limit of about 8000 µm. However, it should be kept in mind that the Fraunhofer model is not valid below a size range of about 2 µm to 4 µm. In such instances it is better to use instruments that have capabilities for the Mie optical model. Instruments using this model typically enable analysis to about 0.1 µm, and reliable analysis in even finer size ranges is possible depending upon the configuration of the optical elements and the detector array used in the instrument. The difference between these two models is discussed later in this chapter and refers to the mathematical solutions used to solve the scattering problems.

The interaction of a particle and light incident upon it gives rise to four different but inherently related scattering phenomena, namely, *diffraction, refraction, reflection and absorption* of the incident beam[1]. The magnitude of each phenomenon will vary depending upon the nature and size of the particle and the beam. Size analysis by interpretation of the scattered light patterns formed due to diffraction of the incident light is of primary interest in this chapter.

Diffraction of light occurs at the surface of the particle and can be thought of as the bending of light waves by the surface of the particle. Diffraction arises due to slight differences in the path length of the light waves created upon interaction with the particle surface. These differences in the path length cause

Laser Diffraction Instruments:
General Information, Capabilities and Limitations

***Size Range*:** Typically about 0.04 µm to 8000 µm (limits vary for different instruments).

***Specimen Type*:** Powders dispersed in suspension. Some instruments are designed for dry powder specimens.

***Operating mode*:** Usually off-line, but some instruments have accessories to enable, or are designed for, on-line use.

***Ease of operation*:** Relatively simple. Some understanding of basic principles and algorithm design is required.

***Sources of Error and Variations*:** Can arise during sampling, specimen preparation, instrument set-up and operation, and user dependent.

Significant variations in calculation algorithms.

***Strengths*:** Rapid analysis.

Relatively simple specimen preparation.

Some instruments can be used for both dry powders and powders in suspension.

Some instruments can be used on-line and off-line.

Relatively inexpensive.

Do not require highly skilled operators.

***Limitations*:** Instrument performance and operation is highly dependent on instrument design (e.g., laser sources of different wavelengths, differing number and positions of detectors).

Given the above reason, comparison of results from different instruments may be misleading.

May require a precise knowledge of optical properties of specimen.

Cannot distinguish between dispersed particles and agglomerates.

Significant error and bias may be introduced in the particle size distribution results, if powder particle shapes deviate from spherical configurations.

Instrument design precludes analysis of concentrated suspensions.

constructive and destructive interference between the sinusoidal light waves leading to characteristic diffraction patterns. The diffracted waves are then scattered in different directions. The direction of scatter depends on the size and shape of the particle. Large, spherical particles scatter mostly in the forward direction. As the particle size gets smaller, the scattering occurs over a broader range of angles. This description is a very simplistic perspective. In practice, scattering is significantly more complex and is influenced by the nature of polarization of the incident light, optical properties of the particle and surface roughness of the particle. Numerous texts deal in detail with the underlying mathematics and physics of scattering and diffraction[2-4]. Laser light scattering instruments are often referred to as Fraunhofer diffraction instruments, because instruments based on early designs processed the diffracted light scattered in the forward direction by the particles using the Fraunhofer approximation to deduce particle size from the scattered signal.

The development of instruments based on laser diffraction has been closely related to developments in technology that have enabled the miniaturization of laser light sources and photo-detector arrays and systems. Early particle size analysis instruments based on this principle used simple configurations of optical elements, such that the light scattered only in the forward direction, over a relatively narrow angle from the optic axis, was focussed on the detector system. Detector systems used in these instruments comprised of individual detector elements rather than multi-element arrays and thus, needed to be placed at discrete distances from each other. This also limited the number of detectors that could be placed to receive the scattered signal and so early instruments would process signals from a very narrow segment of the scattering cross-section and were thus limited for size analysis over a range of about 300 μm to 2 μm[5]. Size determination of particles finer and coarser than these limits has been possible due to developments of both suitable hardware and signal processing algorithms. Multi-element detectors and arrays have enabled positioning of more detector elements closer to each other and over a wider scattering angle, contributing to the improved sensitivity and resolution in more recent instruments. The development of better optical configurations and techniques makes possible the analysis of signals scattered over a wider range of angles off the optic axis, and thus the analysis of finer particles. Processing of the signals scattered from the fine particles by algorithms based on the Mie theory provide a more realistic estimation of the size of the fine particles. Instrument resolution and sensitivity for size calculation of the fine particles have been improved by other techniques including the use of 90° scattering configurations (additional detector elements at a 90° angle to the incident beam), and observing the changes in polarization of light after scattering.

Instruments for particle size determination based on closely related principles of light scattering are also available and may be confused with light diffraction

instruments. These instruments include those based on single particle light interaction methods[6], where the interaction of a single particle with the light beam causes a reduction in the intensity of the light beam due to absorption and scattering of light by the particle. The reduction in transmitted light intensity (extinction) is translated into an electrical signal the strength of which correlates to the particle size. By the very nature of this technique, these instruments can be used only on extremely dilute suspensions. Other instruments are based upon the principle of quasi-elastic light scattering (QELS)[7], a generic term encompassing a wide range of specific methods including photon correlation spectroscopy, dynamic light scattering, and heterodyne spectroscopy. These instruments are designed to make use of the Brownian motion of particles in suspension. Consequently, the measurement of variations in the intensity and frequency of the scattered light (incident light is monochromatic in nature) can be correlated to the Brownian motion and other dynamics of the particles that cause the scattering[8]. Because of the dependence on Brownian motion and relaxation time associated with the random motion, these techniques are ideally suited for particles smaller than 1 μm and require very dilute suspensions. Thus, only small quantities of sample powder (order of a few milligrams) are needed.

2. General Principles

Light diffraction instruments are based on three basic assumptions:

(a) The particles scattering the light are spherical in nature,

(b) There is little to no interaction between the light scattered from different particles (i.e., no multiple scattering phenomena), and

(c) The scattering pattern at the detectors is the sum of the individual scattering patterns generated by each particle interacting with the incident beam in the sample volume.

Deviations from these assumptions will introduce some degree of error due to the inability of the mathematical algorithms for the deconvolution and inversion procedures to account for the deviations. The assumption of spherical particle shape is particularly important as most algorithms in commercial instruments use the mathematical solution for Mie, Fraunhofer and Rayleigh scattering from spherical particles. At present even though mathematical solutions for cylindrical systems are available, these solutions have not been incorporated into commercially available programs. However, those interested can attempt to develop such algorithms based on published mathematical solutions[3]. Similarly, the assumption of the lack of multiple scattering is critical due to the nature of the mathematical models which are used to deconvolute the resultant diffraction patterns. Most algorithms and mathematical models do not take into

consideration the effects of multiple scattering on the resultant diffraction patterns and thus are unable to account for such interactions. The need to prevent multiple scattering also places an inherent limitation on the concentration of particles present in the sample volume.

2.1 Instrumentation

Light diffraction instruments comprise of a light source, typically a low power (approximately 10 mW Helium-Neon, in the region of 632 nm wavelength) laser source, optical elements to process the incident beam, a sample cell within which the sample is introduced. Some sample cells have built-in ultrasonicators or agitators to keep the specimen powders dispersed and to prevent agglomeration. Sample cells also possess pumping systems to keep the specimen circulating. Light diffraction instruments lack the ability to distinguish between well-dispersed powders and agglomerates, and thus, prevention of agglomeration is a key factor in ensuring reliability and reproducibility. Light scattered from the sample is then focussed on to a detection system, that can be a multi-element array or numerous detectors placed at discrete locations. The detectors convert the scattered light intensity incident upon them into electrical signals that are then processed to obtain information about the particle size and size distribution. Figure 6.1 is a schematic diagram of the different components. Conversion of a scattering pattern into size distribution information requires the use of optical models and inversion procedures (detailed discussion in the Appendix at the end of this chapter).

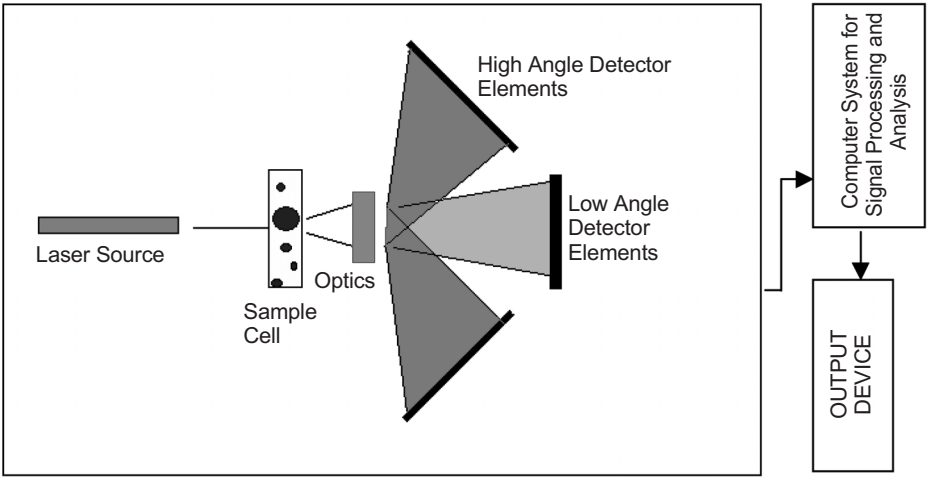

Figure 6.1.

Schematic Diagram of Components in a Typical Laser Diffraction Instrument

The need for optical models arose in order to explain the scattering of light from spherical particles. Gustav Mie published a theoretical analysis for scattering of light from spherical particles in 1908[9]. Lorenz is credited with having derived a solution for the same problem independently in 1890. Solutions to scattering of light by spherical particles of varying sizes can be thought to fit into the following categories:

(i) When the particle diameter (d) >> wavelength of incident light (l), the Fraunhofer model may be used, and this represents one limiting case of the Mie theory.

(ii) When $d << \lambda$, the solutions for scattering are best represented by Rayleigh scattering models.

(iii) When $d < \lambda$, the Rayleigh–Gans optical model best represents the solutions to the scattering of light by the particles.

While the Fraunhofer model is independent of the material properties, the Rayleigh and Rayleigh–Gans models, which can be derived from the Mie scattering theory, are very much dependent on the optical properties, and thus require the use of both the real and imaginary components of the material's refractive index. The value of the real component of the refractive index can be found with relative ease, but determining the value of the imaginary component can be far more difficult.

The above distinctions represent solutions to general scattering problems of light by spheres under varying boundary conditions. Numerous texts[3, 4, 10] detail the mathematical operations involved to obtain these solutions. The following descriptions together with the details presented in the Appendix at the end of this chapter attempt to collect this information and present it in a manner suitable for a brief description of the basic principles and includes references from various texts[3, 4, 10-13].

2.2 Mie Scattering

The Mie scattering theory is a comprehensive mathematical solution to scattering of incident light by spherical particles. The theory can be extended to consider scattering from particles with different shapes and aspect ratios. This theory indicates the necessity for a precise knowledge of the real and imaginary components of the refractive index of the material being analyzed, to determine particle size and size distribution. Most modern instruments based on laser light diffraction for particle size determination utilize this theory (with some proprietary variation) for modeling the diffraction patterns that

are formed. The Mie theory is applicable when the particle size is equal to, or smaller than, the wavelength of the incident light. (*See Appendix at the end of the chapter for more information and theoretical treatment of the Mie scattering theory).*

2.3 Fraunhofer Approximation

The Fraunhofer approximation (also referred to as the Fraunhofer theory) is applicable when the diameter of the particle scattering the incident light is larger than the wavelength of the radiation. The Fraunhofer theory can be derived from the Mie scattering theory, or can be derived independently considering simple diffraction of light from two points giving rise to a phase difference between the two diffracted beams. The resultant diffraction pattern is marked by a series of maxima and minima. The spatial separation between these can be used to calculate the size of the particle. In the case of diffraction from numerous particles, the resultant diffraction pattern is the summation of the intensities of each pattern corresponding to the particle giving rise to that pattern. By its very nature, this model does not need any information about the refractive index of the particle and so is extremely useful for analysis of powders coarser than about 1μm to 2 μm. *(See Appendix at the end of the chapter for derivation of the Fraunhofer approximation, from the Mie theory.)*

2.4 Rayleigh and Rayleigh–Gans Scattering

These two scattering models are based on the Rayleigh scattering model that is applicable when the size of the particle is much smaller than the wavelength of the incident light. The Rayleigh–Gans theory, however, is applicable when the particle diameter is not significantly smaller than the wavelength of the incident light. Like the Mie theory, both these models require the use of both the real and imaginary component of the material's refractive index. *(See appendix at the end of chapter for a brief discussion on the derivation of the Rayleigh and Rayleigh–Gans theory.)*

2.5 Role of Refractive Index

An important point to be made here is the need for a precise knowledge of the optical constants of the material in certain instances. As is observed from equations 10-13, 17 and 19 presented in the Appendix, the solutions by the Mie, Rayleigh and Rayleigh–Gans theories all require the definition of the complex refractive index ($m = n - in'$, where n is the real component of the refractive

index and n´ the imaginary component of the same). However, equation 15, which represents the Fraunhofer solution, does not include the term m, and indicates no dependence and, hence, there is no need for a knowledge of the optical property. It is for this reason that optical models based on the Fraunhofer solution do not require the user to specify the refractive index of the material being studied, but those based on the Mie models do require the user to specify the values of both the real and imaginary components. Thus, the Fraunhofer model is preferred when analyzing powder systems containing mixtures of different materials, or when analyzing particles with inherent heterogeneity in density distribution. However, applicability of this model with the appropriate size criterion also has to be met.

Though there are various sources for obtaining the values of the refractive indices of materials[14-17], caution should be exercised while using them. The wavelength at which these values have been determined and reported may not be the same wavelength at which the instrument is operating and may thus introduce systematic errors. For materials that occur in different stable phases, the value used should correspond to that particular phase. For instance, it has been reported that the real component of the refractive index of α-Al_2O_3, occurring as natural corundum is 1.77, while that γ-Al_2O_3 is 1.70. In most instances, it is relatively easy to find the value of the real component of the refractive index. It is however, far more difficult to obtain the value of the imaginary component of the refractive index of the material. Some tables exist for determination of these values, but often trial and error procedures of size determination using a microscopy-based technique and an instrument using laser diffraction have to be utilized. Such a procedure could introduce significant errors in the value determined and may be biased by the algorithm incorporated in the laser diffraction instrument. Furthermore, the imaginary component is affected by factors such as the surface roughness of the particle, density heterogenities in the particle. To enable repeatability and reproducibility of experiments, it is a good practice to report the wavelength of the incident radiation used when reporting refractive index values or size values based upon the use of the refractive index information of a material.

Figure 6.2 shows the influence of changing the value of the imaginary component of the refractive index (based on Mie models) of a powder system comprised of nominally 1 μm spherical SiO_2 particles, at a fixed value of the real component of refractive index of 1.44 and 1.43 (data generated during studies at NIST). The plots represent the change in the value of the d_{10}, d_{50} and d_{90} size fractions, and thus represent a change in the measured size distribution, as measured by a laser diffraction instrument.

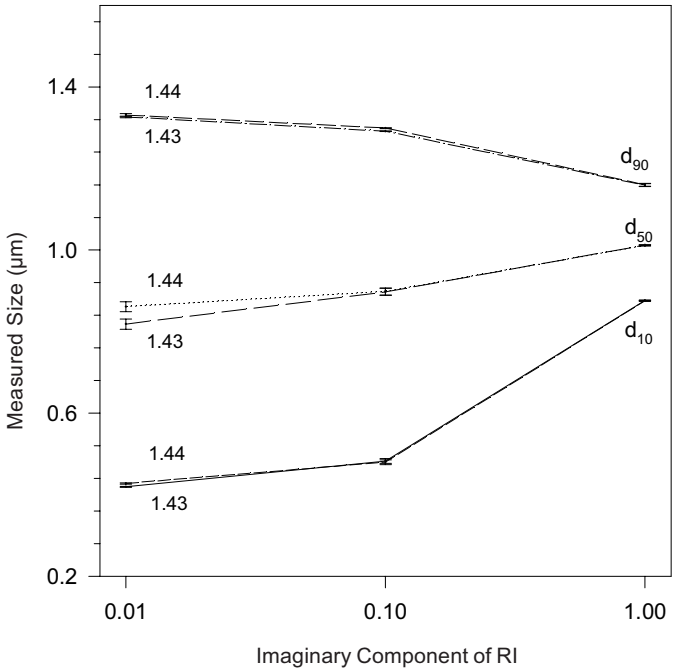

Figure 6.2.

Influence of Imaginary Component of Refractive Index on Size Distribution Measured by a Laser Light Diffraction Instrument (Using Mie Models)

The trends in this plot indicate the importance of using the precise value of the imaginary component of the refractive index. Considering the use of a real component of 1.44, upon changing the imaginary component from 0.01 to 1.0, the width of the distribution between d_{90} and d_{10} changes from about 0.88 µm to approximately 0.4 µm, almost a 50 % decrease. The median value of the powder distribution (d_{50}) increases from about 0.84 µm to almost 1.0 µm. Put together, this shows that the calculated width of the size distribution is much narrower upon using an imaginary component of 1.0, than when using a value of 0.01. Based upon analysis by SEM and optical microscopy, we know that the size distribution of this powder system is very narrow and close to that calculated at an imaginary component of 1.

Huffman has addressed the application of optical constants calculated for bulk materials to small particles. The use of these values is an important issue as the optical properties of the small particles may be significantly different from those of the bulk materials, even without entering the regime where breakdown of optical constants occur. These variations are most pronounced in the

ultraviolet region for metals, and the infrared region for insulators. These deviations are observed to occur in the proximity of frequencies close to the surface mode resonance. The conditions under which optical constants for the bulk can be used for small particles have been identified by Huffman as: (a) the constants are measured with a high degree of accuracy, (b) the particles of interest are of the same homogeneous state as the bulk material, i.e., both particle and bulk are crystalline, or both are amorphous, and (c) the particles are well dispersed such that there is no particle-particle contact or agglomeration. The same holds true also when the particle size is large enough to negate any quantum size effects and the damping of free electron oscillations is not determined by the particle size.

3. General Procedures

Procedures to be followed for particle size determination by laser light diffraction instruments are to a great extent specific to the instrument being used and are usually very well defined by the manufacturer. The procedures are designed to work best with the algorithms used in the instrument and are optimized for the instrument set-up. As a result, these procedures vary from one instrument to another. This also requires a fair amount of work by the user to find the set of parameters (e.g., real and imaginary components of refractive index, solids loading, signal collection time) that appears to work best for that instrument. However, irrespective of the instrument being used there are certain general procedures that can be adopted in order to minimize various systematic errors. Some of these general procedures are discussed in this section. Figure 6.3 shows the general steps involved in the determination of the particle size and size distribution of a powder system by laser light scattering.

3.1 Sampling

Powder sampling is conducted in a manner which ensures that the specimen being examined is representative of the entire batch. Various techniques for sampling are discussed in Chapter 2. While most laser diffraction instruments are set up for batch samples, there are numerous instruments that are set-up for on-line sampling or have accessories that can sample from an on-line stream. An example of an on-line sampling system would be the use of laser diffraction instruments in a cement production plant where tight control of the powder size during grinding operations is desired. In such instances, wherever practical, the guideline of sampling the entire stream for some time, rather than the some of the stream all the time, should be practiced. In case of batch samples, it should be ensured that the specimen is representative of the powder system under study.

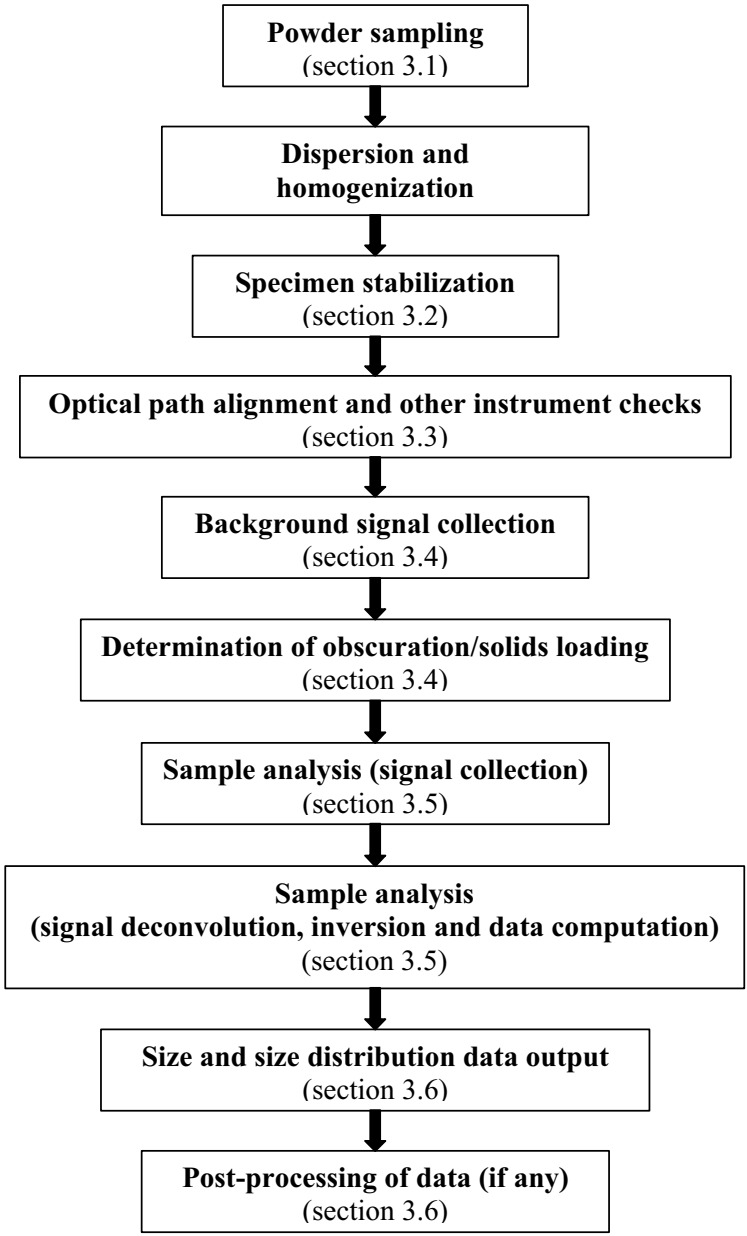

Figure 6.3.

Flowchart Indicating Steps Involved in Particle Size Determination by Laser Light Diffraction Technique

3.2 Dispersion and Homogenization

The state of the powder being sampled also plays a role in deciding the sampling procedure to be used. Flow of dry powders may be significantly different from that of powders dispersed in a liquid. Powders in both cases may segregate in the case of a broad size distribution causing some size fractions to be present in a non-representative manner. Agglomeration of these powders may be observed depending upon the surface characteristics of these powders and the stability of the dispersions. Sampling procedures that are followed should take into account these factors. Development of suitable dispersion procedures during or immediately prior to the analysis helps ensure that powders are well dispersed and agglomeration is minimized. Most instruments are designed for analyzing samples dispersed in fluids such as water or isopropanol or other low hazard fluids. Instruments have special cells designed for flammable liquids or explosive vapors. Accessories may be available from the instrument manufacturer for analysis of powders in a dry state, obviating the need for dispersion in a fluid. While using such an accessory it is still essential to ensure that the powders are not agglomerated and particle-particle bridging is minimized. Procedures recommended by the manufacturer should be followed in such instances. Additional procedures to prevent agglomeration or segregation may be designed and implemented by the user.

Ensuring a good degree of dispersion prior to sample analysis is an important step to ensure reliable and reproducible size analysis. Due to the inability of the instrument to distinguish between agglomerates and primary particles, this process can help reduce some bias and other systematic errors in the calculated powder size distribution. Sample dispersion can be achieved by numerous methods including ultrasonication, milling, pH stabilization, addition of dispersion agents, etc.

Regardless of the technique followed, it is critical to ensure that the process of dispersion does not lead to creation of stable air bubbles, fracture of brittle particles or agglomeration. The occurrence of any of these will lead to skewed particle size distribution results. The use of ultrasonic probes to disperse powders is well suited for this technique due to the small quantities of sample powders needed for analysis. While ultrasonication does lead to dispersion, the specimens may still need to be stabilized in such a state by either controlling the pH of the suspension or adding dispersion agents. After stabilization, it is preferable to keep the suspension agitated to prevent any settling or agglomeration. Instrument manufacturers are making available ultrasonic kits that can be attached to the specimen chamber to ultrasonicate the specimens prior to analysis.

Important factors that are to be considered for determining ultrasonication parameters are the ultrasonication duration, energy, diameter of the probe/horn

and coupling between horn and sample. Time and power output to be used for ultrasonication are dictated by the nature of the material being dispersed. Ultrasonication duration can extend from a few seconds to a few minutes. Ultrasonication should be carried out until no further reduction in particle size distribution is observed. In some instances, this might call for ultrasonication durations of a few minutes. For systems that tend to generate heat upon ultrasonication for such lengths of time, the energy can be applied in fractional duty cycles (e.g., 50 % on and 50 % off during the duty cycle), or the beaker containing the sample being ultrasonicated can be placed in an ice bath. Close attention should be paid to the nature of the coupling observed between the ultrasonic probe and the sample. The nature of the coupling defines the efficiency of power transfer from the probe to the material system. The depth of the probe into the sample influences the coupling. It has been observed that glass beakers provide better reflection of ultrasonic energy and thus lead to better coupling than polystyrene beakers. Determination of ultrasonication parameters is mostly by a trial-and-error process, designed to ensure minimization of the particle size distribution, without causing fracture of the primary particles.

Figures 6.4 and 6.5 (studies at NIST) indicate the need to create and maintain stable dispersions for particle size analysis by laser diffraction. Figure 6.4 shows the influence of the duration of ultrasonication on a suspension of nominally 1 µm spherical SiO_2 powder system. The specimens were ultrasonicated for 15 s, 1 min, 3 min and 6 min and then stabilized at a pH value of 8. The graph represents the observed size distribution (d_{10}, d_{50} or median size and d_{90}) and a measure of the mean size as a function of ultrasonication duration. A significant difference is observed upon increasing the ultrasonication duration from 15 s to 1 min. Ultrasonication for 3 min causes a small reduction in the mean particle size and size distribution. Ultrasonication for 6 min does not produce any significant improvement in the results. However, ultrasonication for 6 min causes significant heating of the suspension. Thus, excessive ultrasonication may cause changes in the physical and chemical state of the powder system being analyzed. From this information, ultrasonication duration of 3 min was chosen to be the desired value for this material system.

Figure 6.5 shows the change in the measured size of a nominally 1 µm spherical SiO_2 powder system that has been ultrasonicated for 3 min. at 30 W and adjusted to different pH levels prior to size analysis by laser diffraction. As this powder system has an i.e.p near 2.5, it is expected that the particles will agglomerate at pH values close to the i.e.p and be well dispersed at pH values further away from the i.e.p. Thus, at low pH values of the dispersion, the measured mean and median sizes are significantly larger than the expected values. At higher pH values this size is closer to the expected value.

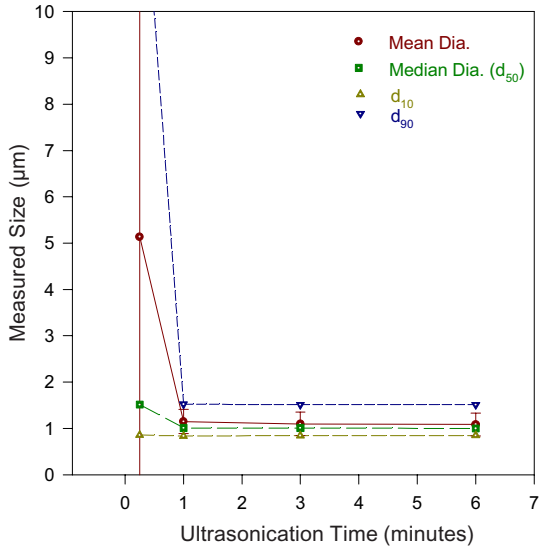

Figure 6.4.

Influence of Ultrasonication Duration Upon Particle Size Distribution, Measured by a Laser Diffraction Instrument

Furthermore, the associated uncertainty in the measured value is significantly higher at lower pH values. Each point represents the average value of 3 sets of measurements.

After dispersing the powders, it is essential to ensure that the dispersions are stabilized in such a state. Stabilization is usually achieved by addition of suitable additives to the dispersion. Controlling pH by addition of a suitable acid or base to keep the pH of the dispersion well away from the i.e.p of the system constitutes a technique of electrostatic stabilization. Addition of suitable deflocculants to physically prevent the coagulation of particles is known as steric stabilization. Some polyelectrolytes often used as deflocculants include sodium polyacrylate, ammonium polyacrylatae, sodium silicate, sodium carbonate, tetrasodium pyrophosphate, sodium polysulfonate and ammonium citrate. For milling techniques of size reduction and dispersion, it is desirable to use polyelectrolytes with short polymeric chains. This prevents damage to the polymeric chains during the milling operations, which would reduce the efficacy of the deflocculant.

3.3 Optical Alignment and Other Instrument Checks

Other general procedures to be followed prior to analysis include ensuring optical alignment and establishing a background or threshold signal level. It is absolutely critical to perform these procedures as any deviations will lead to significant errors in the calculated results. Optical alignment includes

corrections in vertical, horizontal or angular positions of the laser source, the optical elements including lenses and the sample cell and the detector arrays so that the incident beam is aligned with the optic axis of the instrument. Loss of alignment occurs primarily due to ambient vibrations transmitted through the structures such as laboratory benches, tables, etc., and those introduced during the sample pumping process. Alignment procedures are instrument-specific and clearly defined by the instrument manufacturer. In some cases, the alignment procedure may require manual intervention by the operator, or may be conducted electronically with minimal operator intervention.

3.4 Background Signal Collection and Determination of Obscuration Levels

A background signal or threshold should be obtained immediately after optical alignment. By obtaining a background signal the current levels at each detector element in the absence of diffracted light is established. When analyzing a specimen, the current signals at the detector due to diffraction are compared with those determined during the background scan. Furthermore, the intensity of the laser beam in the absence of a specimen is determined during the background scan. By comparing the signal intensity of the laser beam without any sample present to the signal intensity with a specimen loaded in the sample cell, the obscuration level (extent of attenuation of incident beam intensity due to presence of particles) can be calculated.

Obscuration values are required to calculate the sample concentration present in the specimen. Most instruments are designed to operate within a particular obscuration value range. Means to determine whether the sample loading is within this range are specified by the instrument manufacturer. This includes either a number range or a bar graph specific to that instrument. Higher particle concentrations that may cause high levels of obscuration can lead to multiple scattering, while low solids loading corresponding to low levels of obscuration may cause inadequate signal strength at the detector elements. The impact of changes in the obscuration level on the determined particle size distribution is a function of the particle system being studied, the optical model used, and the algorithm used for deconvolution and inversion. Figure 6.6 (studies at NIST) indicates the effect of varying obscuration levels on the calculated particle size distribution of a nominally 1 μm SiO_2 powder system. In the case of the instrument used in this study, the manufacturer recommended range indicates obscuration levels of 7 % to be low and 13 % to be high. An obscuration level of 10 % is in the middle of the range specified for the instrument. As is observed there are small differences in the calculated size distribution at these varying obscuration levels. Though the observed differences are small for the quoted example, these difference can be significant for other material systems.

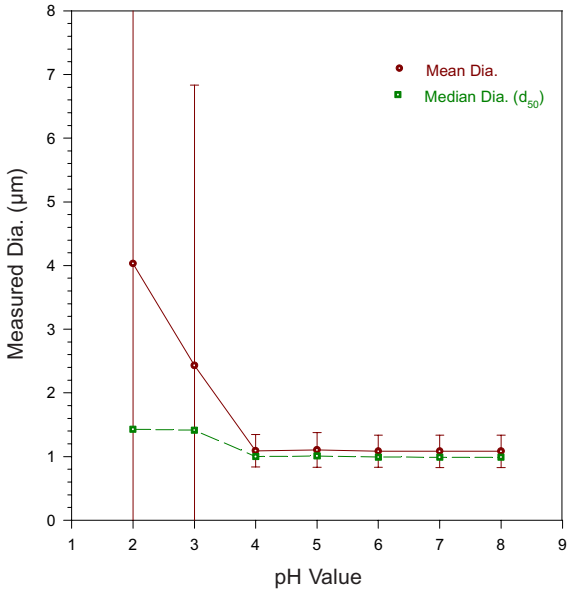

Figure 6.5.

Graph Representing Variation in Measured Size of Nominally 1µm SiO_2 Powder System After Ultrasonication and Stabilization at Varying pH Levels

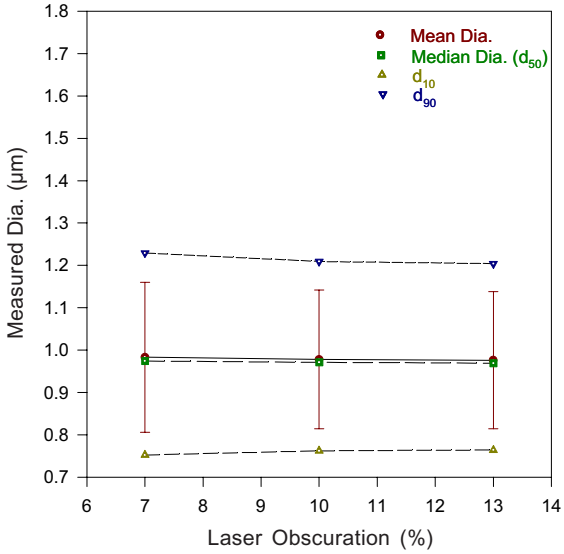

Figure 6.6.

Effect of Varying Obscuration Levels on Calculated Particle Size Distribution of Nominally 1.0 µm SiO_2 Powder System

3.5 Sample Analysis

In numerous cases, the results of the particle size analysis are only as good as the optical model chosen to interpret and convert the diffraction pattern into particle size distributions. Instruments are set up to enable the user to select from a predetermined set of optical models. These optical models are usually a combination of values representing the real and imaginary components of the refractive index of the material being analyzed. In some instruments, the user may be asked to make some selections about the expected shape and width of the size distributions. Some instruments allow the operator to create optical models based on their choice of real and imaginary components of the refractive indices. The importance of knowing the correct values and the associated difficulties have been discussed previously. Instruments that are designed for size analysis of powders coarser than about 2 μm may not have these requirements, as the algorithms in these instruments are based on a Fraunhofer diffraction model and thus totally independent of material properties. Figure 6.7 (studies at NIST) shows how changes in optical models can create significant changes in the calculated particle size distribution. The graphs show the powder size distribution of a hydroxyapatite powder system represented as a differential volume distribution. The five curves represent size distribution results calculated using different optical models including the Fraunhofer model, labeled as such. The remaining four graphs are based on Mie models, and in this case the real component of the refractive index of the powders was reliably determined to be 1.63. However, there was some uncertainty about the correct value for the imaginary component. As is observed, significant differences are observed in both the shape and magnitude of size distribution depending upon the refractive index value chosen. For imaginary values of 0 and 0.01, the lower range of the distribution is calculated to be in the vicinity of 1 μm. For the Fraunhofer model and the Mie models with imaginary components of 0.1 and 1.0, the lower range is found to be smaller than 0.1 μm. The choice of the "correct model" in this case has to be made with the aid of other techniques, such as microscopic determination, that would enable a direct examination of the powder system.

3.6 Data Output and Post-Processing

Particle size distribution results are typically expressed as a function of the equivalent spherical diameter. This is based on the assumption of spherical particles giving rise to the diffraction process. Size distributions are typically expressed on a volume basis. This basis though not always accurate does simplify matters to a great extent. A very precise representation would require the distribution to be expressed on the scattering cross-sectional area basis. If the particles are spherical or are assumed to be so, then the volume

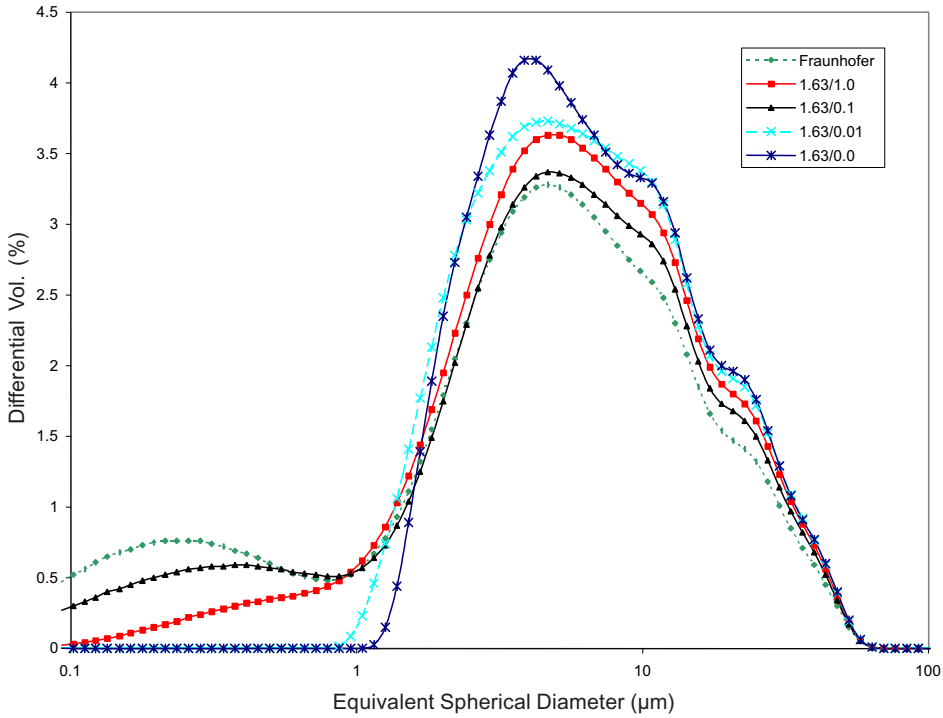

Figure 6.7.

Influence of Optical Model on Calculated Particle Size and Size Distribution

representation can be easily converted to a cross-sectional area, and *vice versa*. Size distributions can also be expressed in terms of a number or surface area basis, but it should be remembered that such expressions are derived from the volume basis. Thus, any deviations from the spherical nature of the powders will introduce significant error and/or bias in the particle size distribution representation. For these very reasons, when reporting size distributions in a quantitative manner (e.g., using the mean value and the d_{10}, d_{50} and d_{90} values), these numbers should be calculated from the volume basis distribution graph.

It is a good practice to represent the results of the particle size distribution as both a cumulative finer than and fraction distribution graph as a function of the observed particle size. This enables the user to observe the nature of the distribution (unimodal, bimodal, etc.) the fraction of the distribution in a particular size range of interest, and be able to determine the size corresponding to a particular fraction (d_{10}, d_{50} or d_{90}, etc.). Availability of this information enables conversion from one format or distribution (e.g., volume based distribution to mass based or number based distribution) to another with relative ease.

4. Sources of Error, Variations and Other Concerns

Errors and variations in the observed results can be introduced in various stages of analysis, right from sampling to data interpretation. Some of these have been discussed in previous sections. Most instrument manufacturers list sources of error particular to the instrument and suggest means and techniques to avoid them. The following discussion lists briefly in a general manner the various stages at which errors and other variations can be introduced in the analysis process.

1. Sampling and specimen preparation related

a. *Errors introduced due to use of non-representative samples,* i.e., errors due to incorrect sampling procedures. This holds true for both dry powders and powders dispersed in suspensions. Proper sampling procedures can ensure that these errors can be minimized, if not eliminated completely.

b. *Analysis of powders finer or coarser than the detection limits* of the instrument being used. Even when analyzing powders with dimensions close to the upper and lower detection limits, it is a good practice to verify the validity of these limits using suitable primary or secondary standards.

c. *Errors introduced upon analysis of non-spherical powders.* Due to the assumptions of particle sphericity, any deviations from this shape will cause bias and errors to be introduced in the particle size and size distribution results. Unless analyzed by appropriate algorithms designed as part of the instrument software, or designed for use on the obtained scattering patterns, it may be expected that the magnitude or error will be magnified as the deviation from spherical shapes is increased.

d. *Errors associated with optical properties of the material.* In most instances it is extremely helpful to know the optical properties and some physical properties such as density of the material being tested. Most instruments require the user to provide this information for calculation of the particle size and size distribution and any errors in these values are reflected in the calculated results.

e. *Reliable procedures for creating and maintaining stable dispersions* of the powders should be developed. The particles should remain dispersed even in the sample cell, as these instruments lack the ability to distinguish between primary particles and agglomerates. These procedures should not cause fragmentation of friable particles or lead to formation of stable bubbles that can interfere with the

measurement and bias the calculated result. Closely related to this is the issue of sample stability, where certain powders may change size over a period of time due to dissolution or precipitation mechanisms. In such cases, samples should be prepared immediately prior to analysis and discarded after analysis.

2. Instrument and procedure related

a. *Errors introduced due to non-aligned or misaligned optics.* The need for ensuring proper alignment has been discussed in detail in the previous sections. Instrument manufacturers specify procedures and checks to ensure proper alignment.

b. *Errors due to lack of background signals or errors in procedures for obtaining background signals.* In this instance, the detector elements use an incorrect background signal to ratio the diffracted signal. Thus, if the dispersion medium has been changed then an incorrect signal will be used leading to errors in the calculated size and size distribution.

c. *Light leakage due to stray or extraneous light* in the instrument will cause additional signals at the detector elements that will be analyzed as diffracted signals from the particles and be included in the size distribution results.

d. *The use of incorrect optical models* will have a significant effect on the calculated size distributions. These effects may be manifest not only in the range of the size distribution, but also in the shape of the distribution. The importance of using the correct optical model has been discussed in detail in the preceding sections. Determining whether the optical model used is appropriate can be quite complex. Some manufacturers are working on software routines that will enable determination of a theoretical scattering pattern from the calculated size distribution and based on the chosen optical model. A comparison of the calculated scattering pattern with the observed scattering pattern can provide a check of the model used. In numerous instances, microscopy-based techniques may have to be used to compare the calculated size distributions. In these cases however, appropriate precautions need to be observed (see Chapter 5).

e. *Software related bias* may cause significant errors in the calculated results. Most errors would arise due to the design of the deconvolution and inversion algorithms that may be based on assumptions not reflected or applicable to the particle system under study. An example of such an error would be the use of a model-dependent inversion procedure (i.e., inversion procedure that assumes a particular shape for the powder distribution) on a multi-modal powder system.

f. Errors due to non-linear detector responses arise when sample loading is either too high or too low. This issue has been discussed in terms of the obscuration of the incident beam and the need to ensure obscuration in the range specified by the manufacturer. Put differently, obscuration levels outside the range specified by the manufacturer correspond to the non-linear response range of the detector elements, and the current signals generated by the diffracted beam are not proportional to the diffracted signal incident on the detector.

Errors and precautions pertaining to representation and interpretation of size data are discussed in greater detail in Chapter 7 on Reporting Size Data.

5. Relevant Standards

ISO 13320-1 Particle Size Analysis – Laser Diffraction Methods – Part 1: General Principles[14], is an international standard covering general principles and procedures pertaining to particle size analysis using laser diffraction techniques. This standard is designed to be in two parts, with Part 2 pertaining to the validation of inversion procedures used for processing the diffracted light signals into particle size and size distribution data. Part 1 defines some terms and symbols used in conjunction with this technique of size analysis. Elements constituting the instrument and their interaction with other components in the system are described in general terms. Descriptions about operational procedures for size analyses include selection criteria for specimen dispersion fluids, some techniques for sample preparation and dispersion and precautions to be observed while following these procedures. Other discussions include procedures and precautions to be observed for the actual measurement, ensuring reproducibility and accuracy, sources of random and systematic errors and means to identify the occurrence of the same, and factors that could affect the resolution of the instrument. It is recommended that reporting of results be along the guidelines set forth in ISO 9276-1[22] (described in the chapter on Reporting Size Data). Attached annexes have concise and useful descriptions of the underlying theory of laser diffraction and the need for different diffraction models, and a useful listing of the refractive indices of different liquids and solids. This listing is a compilation of values from various sources in the literature. The imaginary component of the refractive index of only certain materials is reported in this compilation. However, for most applications, the user will need to determine the appropriate value of the imaginary component of the refractive index. The determination of such a value is not a trivial task and is compounded by the fact the surface roughness of the particles and any heterogeneity in density distribution of the particle will influence the value of the imaginary component.

ASTM B822-97 Standard Test Method for Particle Size Distribution of Metal Powders and Related Compounds by Light Scattering[23] is an ASTM standard test method for size determination of particulate metals and compounds by laser diffraction. The test method is applicable over a size range of 0.1 µm to 1000 µm for both aqueous and non-aqueous dispersions. An important issue stressed in this standard is that even though different instruments are based upon the same basic principle, significant differences are present in the arrangement of the optical components (including the collection lenses and the number and position of detector elements), and the algorithms used to interpret the scattering pattern and convert it to particle size data. These differences may lead to different results from different instruments, and thus, comparison of results from different instruments should be done with caution. Sources of interference that can lead to random and/or systematic errors are identified and information about sampling, calibration and general procedures for measurement are defined.

ASTM E1458-92 Standard Test Method for Calibration Verification of Laser Diffraction Particle Sizing Instruments Using Photomask Reticles[24] is a very useful standard outlining the procedures to be followed to ensure that the laser diffraction instrument is operating within the manufacturer specified tolerance limits. This procedure is based upon the use of a photomask made up of a two-dimensional array of thin, opaque circular discs on a transparent substrate, simulating the cross-section of spherical particles of varying diameters that would diffract the incident light beam. A photomask is used as it is difficult to generate, in a reproducible manner, an aerosol containing a controlled population and distribution of droplets or particles that can be used for calibrating the instrument. This test method can be used to compile calibration data that can be used to check the instrument operation. This standard describes the photomask reticle to be used and the procedures to be followed for the calibration process. The precision and bias that can be expected from this technique of calibration are also described. The occurrence of artifacts and other sources of error that can influence the calibration procedure are explained and discussed.

NIST has developed various size standards, available as SRMs, for calibration and performance evaluation of laser diffraction instruments. SRM 1690, 1691, 1692, 1960, 1961 and 1963 comprise of polystyrene latex spheres dispersed in water and can be selected based on the desired size distribution. In addition to these, SRM 1003b, 1004a, 1017b. 1018b and 1019b comprise of glass beads of varying particle size distributions ranges and sizes. SRM 1982 comprising of zirconia was developed using various laser diffraction instruments in an inter-laboratory round-robin study. Currently various standards are being developed for certification as SRMs. The development of these has been based on measurements using laser diffraction instruments and the standards are made

of WC-Co powders and a zeolite-based system. In addition to the NIST Standard Reference Materials, numerous secondary standards are available from instrument manufacturers and vendors of scientific supplies. These secondary standards are all calibrated against primary standards developed by international standards accreditation agencies.

Appendix

The following sections present a slightly more detailed discussion of the underlying theory of the various scattering processes. The references quoted in these discussions delve into significantly greater detail than what is presented here.

1. Mie Scattering

Derivations of the Mie solutions arise from Maxwell's equations for electromagnetic radiation. Representing the electric and magnetic induction vectors as **E** and **H** respectively, and, μ being the permeability and ε the permittivity, Maxwell's equations can be represented as:

$$\nabla \bullet E = 0 \tag{1}$$

$$\nabla \bullet H = 0 \tag{2}$$

$$\nabla \times E = i\,\omega\,\mu\,H \tag{3}$$

$$\nabla \times H = -i\,\omega\,\varepsilon\,E \tag{4}$$

Assuming, $k^2 \equiv \omega^2 \varepsilon \mu$, then equations 3 and 4 can be rewritten as:

$$\nabla^2 E + k^2 E = 0 \tag{5}$$

$$\nabla^2 H + k^2 H = 0 \tag{6}$$

To solve the above set of equations, separation of variables leads to a general solution of the form[12]:

$$\psi = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} [A_l^m \cos(m\phi) P_l^m \cos(\theta) z_n(kr) + B_l^m \cos(m\phi) P_l^m \cos(\theta) z_n(kr) \tag{7}$$

where, P_l^m (x) are the associated Legendre polynomials and z_n(x) are the spherical Bessel functions, and ψ is a scalar function.

Expressing the boundary conditions of a sphere (representing the particle) and the incident plane wave in vector spherical harmonics, the complex plane wave (E_c) can then be expressed in the form:

$$E_c = \sum_{m=-l}^{l} \sum_{n=0}^{\infty} (B_{mn}^e M_{mn}^e + B_{mn}^o M_{mn}^o + A_{mn}^e N_{mn}^e + A_{mn}^o N_{mn}^o) \tag{8}$$

The above expression can further be simplified under the condition that the incident plane wave is polarized such that m = 1 is the only contributing factor, and so equation 8 now is of the form:

$$E_c = \sum_{n=0}^{\infty} i^n \frac{2n+1}{n(n+1)} \left[M_{1n}^{0(1)} - i N_{1n}^{e(1)} \right] \tag{9}$$

The vector spherical harmonics expressed in equation 9 can be used to arrive at two scalar components, each of which has a spherical Bessel function and this information can be used to calculate the initial electromagnetic field outside the sphere.

Applying the boundary conditions that the transverse components of the total electric and magnetic induction fields at the particle surface are zero enable calculating two components for the internal and the scattered fields, which correlate to the scattered wave outside the sphere and the wave produced inside the sphere itself.

Representing the constants for these solutions as a_n and b_n and $\pi_n(x)$ and $\tau_n(x)$ as supplementary functions, the amplitude functions are expressed as:

$$S_1(\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[a_n \pi_n \cos(\theta) + b_n \tau_n \cos(\theta) \right] \tag{10}$$

and,

$$S_2(\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[b_n \pi_n \cos(\theta) + a_n \tau_n \cos(\theta) \right] \tag{11}$$

The extinction and scattering efficiencies are resolved to have the form:

$$Q_{ext} = \frac{2}{x^2} R \sum_{n=1}^{\infty} (2n+1)(a_n + b_n) \tag{12}$$

and,

$$Q_{sca} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \tag{13}$$

S_1 and S_2 are elements of the amplitude scattering matrix of the form:

$$\begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix}$$

that arise from the linear relationship existing between the scattered and incident amplitudes as per Maxwell's equations[10]:

$$\begin{pmatrix} E^{(l)} \\ E^{(r)} \end{pmatrix} = \left(\frac{2\pi i d}{\lambda_0} \right)^{-1} e^{-2\pi i (d-s)/\lambda_0} \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \begin{pmatrix} E_0^{(l)} \\ E_0^{(r)} \end{pmatrix} \tag{14}$$

$E_0^{(l)}$ and $E_0^{(r)}$, $E^{(l)}$ and $E^{(r)}$ are components of the electric vector for the incident and scattered wave, respectively. The scattered wave is separated from the incident wave by a phase difference of $2\pi i(d-s)/\lambda$. In case of scattering for

homogeneous, spherical scatterers, the elements S_3 and S_4 vanish, and thus only solutions for S_1 and S_2.

Equations 10 to 13 represent the analytical solution as per Mie theory. Thus, for scattering of unpolarized light by a spherical particle, the scattered intensity can be represented by the equation[14]:

$$I(\theta) = \frac{I_0}{2k^2a^2}\left[[S_1(\theta)]^2 + [S_2(\theta)]^2\right] \tag{15}$$

where, I_0 is the intensity of the incident light, k represents the wavenumber $2\pi/\lambda$, and a is the distance from the scatterer to the detector. $S_1(\theta)$ and $S_2(\theta)$ represent the complex functions describing the change in amplitude of the perpendicular and parallel polarized light as a function of the angle θ, measured in the forward direction.

2. Fraunhofer Approximation

When the particle diameter is larger than the wavelength, scattering occurs mostly in the forward direction(i.e., θ is small) and so equation 14 simplifies to:

$$I(\theta) = \frac{I_0}{2k^2a^2}x^4\left[\frac{J_1(x\sin\theta)}{x\sin\theta}\right]^2 \tag{16}$$

$$\text{as, } (S_1)^2 = (S_2)^2 = x^4\left[\frac{J_1(x\sin\theta)}{x\sin\theta}\right]^2 \tag{17}$$

The term x represents a dimensionless size parameter of the form $x = \pi D/\lambda$, (D being the particle diameter) and J_1 is a Bessel function of the order unity. Equation 16 represents the Fraunhofer approximation of the Mie theory.

3. Rayleigh Scattering

When the particle diameter is much smaller than the wavelength of the incident radiation, the solution to the scattering problem is given by Rayleigh's solution[4].

The scattered intensity in this case is the sum of the scattered components $S_1(\theta)$ and $S_2(\theta)$, and thus can be represented as:

$$I(\theta) = |\alpha|^2\left(\frac{2\pi}{\lambda}\right)^4\frac{1}{2a^2} + |\alpha|^2\left(\frac{2\pi}{\lambda}\right)^4\frac{\cos^2\theta}{2a^2} \tag{18}$$

In the above equation, α represents particle polarizability. Furthermore, for homogeneous spheres of volume V and refractive index relative to the surrounding medium of *m*, as m–1 → 0 (i.e., anamolous diffraction model), equation 18 can be simplified as:

$$\alpha = \frac{(m^2 - 1)}{(m^2 + 2)} \frac{3V}{4\pi} \tag{19}$$

$$\alpha = (m^2 - 1)\frac{V}{4} \cong 2(m-1)\frac{V}{4} \tag{20}$$

The value of α from equation 19 can then be substituted into equation 18 to calculate the scattered intensities.

4. Rayleigh–Gans Scattering

In case of Rayleigh–Gans scattering, which may be thought of as a special condition of the Rayleigh scattering, the particle diameter is not significantly smaller than the wavelength of the incident radiation. Under such conditions, the scattered intensity is still a sum of the intensities for the horizontal and vertically polarized components. Thus, equation 18 now has the form:

$$I_\theta = I_0 \left[\frac{k^4 V^2 (m-1)^2}{8\pi^2 r^2} \right] \left[\frac{3}{u^3} (\sin u - u \cos u) \right] \left(1 + \cos^2 \theta\right) \tag{21}$$

In the above equation, u = 2πD/λ(sin(θ/2)) and k = 2π/λ. Equation 21 reduces to equation 18 (the Rayleigh solution) when the term $(3/u^3)(\sin u - u \cos u)$ tends to 1.

5. Inversion Procedures

The calculation of the particle size distribution of the powder system being examined, requires the application of an inversion procedure to the diffraction pattern formed at the detector system in the instrument. The calculated size distribution is very dependent on the nature of the algorithm used for processing the scattering intensity data. The algorithms can be designed to make no assumption about the functional form and shape of the size distribution, in which case the algorithms are said to be model independent. Often, the algorithms may be designed with certain assumptions of the shape. Some of the commonly assumed shape distributions including normal, lognormal or the Rosin–Rammler distribution. This is particularly true of earlier instruments which had limited computational power and memory. Assumptions of certain shapes for the distribution reduced the time and resources required

for deconvolution of the intensity patterns and calculating the size distribution. With decreasing costs of computer memory and increasing computational power, more systems are being designed to be model independent.

Boxman[18] *et al.* describe various inversion procedures. In a model-independent, direct inversion technique, the recorded scattering pattern can be expressed as a set of linear equations of the form:

$$\begin{pmatrix} L_1 \\ L_2 \\ \dots \\ \dots \\ L_n \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1m} \\ a_{21} & a_{22} & \dots & a_{2m} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & \dots & a_{nm} \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \\ \dots \\ \dots \\ q_m \end{pmatrix} + \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \dots \\ \dots \\ \varepsilon_n \end{pmatrix} \tag{22}$$

The above equation can be vectorially represented as:

$$\mathbf{L} = \mathbf{A}\,\mathbf{q} + \boldsymbol{\varepsilon} \tag{23}$$

where, **L** represents the integrated light intensity measured as a function of the scattering angle,

A is the scattering matrix comprised of the calculated scattering coefficients a_{ij} ,

q is the solution vector that contains fraction of particles in each size class,

ε is the associated random measurement error.

n is the number of detector elements, and

m is the number of particle size classes.

The solution for the vector q, calculated by the least squares methods is:

$$\mathbf{q} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \mathbf{L} \tag{24}$$

Boxman *et al.* claim that the above process may not be the most efficient, as there maybe a significant error arising from the measurement errors contained in **L** and the systematic errors contained in **A**. A suggested method to overcome these drawbacks is to add an additional matrix that would suppress the oscillatory behavior of the solution vector and lead to early convergence. The use of such an additional matrix follows the Phillips–Twomey Inversion, and in such a case, equation 24 can be represented as:

$$\mathbf{q} = (\mathbf{A}^T \mathbf{A} + \gamma \mathbf{H})^{-1} \mathbf{A}^T \mathbf{L} \tag{25}$$

In equation 25, **H** represents the smoothing matrix, and, γ a smoothing scalar that represents the amount of smoothing included in the final solution. This

procedure gives the user greater control on deciding the amount of smoothing to be included in the algorithm for deconvolution. The use of non-negativity constraints and incorporation of intensity fluctuation information have been shown to increase the stability of the linear equations and thus arrive at a more reliable solution. Other techniques to improve sensitivity of instruments to particles with particular characteristics have been presented[19]. These techniques use a combination of statistical means and deconvolution procedures.

Detailed reviews about various aspects of light diffraction including the general theory, applications and related studies are available in the works of Krathovil[20] and Kerker[21].

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7. REPORTING SIZE DATA

1. Introduction
2. Standards for the Reporting of Particle Size Data
   2.1 ASTM E1617-97
   2.2 ISO 9276-1:1998
3. Particle Diameter
4. Representation of Size Data
5. Summary

1. Introduction

Reporting particle size and particle size distribution information is as critical a component as designing and conducting the experiments that generate this information. The main consideration while reporting size and size distribution data is to ensure that all pertinent information is presented, such that the experiments conducted to generate this information can be reproduced when necessary. This feature is of particular interest for comparing and communicating the particle size and size distribution data between different laboratories or between suppliers and customers. Thus, effective communication of size and size distribution data requires that pertinent information be provided in the most efficient manner.

At present, there are over 400 commercially available particle size analysis instruments. These instruments are based on a wide range of physical principles, and thus the information generated from these instruments tends to be of varied nature. Some instruments report size results as diameters, while some as surface area or projected area. The nature of the physical principle used may bias the results depending on the technique and parameters (mass, number, surface area, etc.) used for data representation. For example, results from instruments based on the principle of gravitational sedimentation tend to be more accurate when reporting particle size distribution on a mass basis than surface area. Similarly, results from instruments using the electrozone sensing principle tend to be more representative when represented on a number basis than mass basis. Particle size and size distribution data can be presented in varied forms (i.e., by a single number representing a particular feature of the distribution, in a tabular manner and/or graphically). Each representation has its own distinct advantages and shortcomings, and the choice of the representation to be used should be made judiciously. Various texts[1,2] discuss these strengths and shortcomings, and also, the means to convert from one method of representation to another. Some of the more commonly used representations will be discussed briefly in this text.

2. Standards for the Reporting of Particle Size Data

As of November 1999, there are two implemented standards that are pertinent to reporting particle size data. The ASTM E1617-97[3], Standard Practice for Reporting Particle Size Characterization Data, was originally published as E1617-94 and refers to means for reporting particle size measurement data. The ISO standard, ISO 9276-1:1998, on Representation of Results of Particle Size Analysis – Part 1: Graphical Representation[4] is the second standard that is recommended for the reporting of particle size data. Other pertinent ISO draft standards in various stages of implementation are:

- ISO/DIS 9276-2 Representation of Results of Particle Size Analysis – Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions;
- ISO/CD 9276-3 Representation of Results of Particle Size Analysis – Part 3: Calculation of means and moments of particle size distributions;
- ISO/DIS 9276-4 Representation of Results of Particle Size Analysis – Part 4: Characterization of a classification process;
- ISO/WD 9276-5 Representation of Results of Particle Size Analysis – Part 5: Validation of calculations relating to particle size analyses using the logarithmic normal probability distribution.

2.1 ASTM E1617-97

The ASTM E1617-97 standard is designed to promote the use of a standard reporting technique to help reduce inconsistencies that arise when attempting to compare particle size measurement data obtained from different measurement techniques and instruments. This standard requires that all pertinent information relating to the material being analyzed, the instrument being used for analysis, the methodology used for generating data, and the statistical approaches for evaluating the data be categorized into three levels. The nature of the report then dictates what levels need to be reported. The exchanging of analysis results between two laboratories for the purpose of comparison may thus require reporting all pertinent details, while the reporting of size data from a raw materials supplier to a customer might not require the same level of detail, depending upon the application.

Level I reporting gives fundamental information about the material being analyzed. This is of a general nature and includes details such as the material type, sample source and sample lot number pertaining to material identification. With respect to size analysis, this level of reporting requires information about the basic measurement principle of the instrument used for analysis (physical principle such as sedimentation, laser light scattering or optical analysis).

Information about size data needs to be defined by a "minimum reporting of size parameters," where the parameters being reported are a set of mutually agreed upon parameters between the supplier of the information and the party receiving the information. This level of information also requires that any bias in data arising due to the sensing technique used by the instrument be indicated by a suitable choice of diameter (see Section 3). By requiring the reporting of the physical bases for the reported parameters (e.g., number, volume or surface area distribution) this standard can help minimize errors that may arise during data interpretation. A final requirement at this level of reporting is the range of size measurement.

Level II reporting conveys in greater detail the information presented in Level I reporting. In addition to the information required for Level I, Level II requires that the instrument used for particle size analysis be explicitly identified, together with the appropriate software version, where applicable. In terms of instrumentation, this level of reporting needs a description of the experimental parameters under which the instrument was used. The basis by which calculations are performed by the instrument (where available from the manufacturer) needs to be reported together with any additional calculations conducted on the particle size data. The report also requires quantification of some basic sample statistics, including the standard deviation, number of degrees of freedom and confidence interval, and the calculations by which this statistical information is generated. The technique used for sample preparation also needs to be described in detail for this level of size reporting.

Level III reporting requires the greatest detail about both instrument parameters and sample parameters. Level III encompasses all of the information required in Level I and Level II reports together with information and description of calibration and operations conducted on the instrument, where these operations are either non-standard operations or are not specifically asked for. The operating procedures followed while conducting the size analysis need to be mentioned; if any of these procedures are designated standardized techniques, then appropriate standard designations need to be mentioned. This level of reporting also requires, if available, a statement of precision and bias of the particle size measurement data.

Thus, this standard method of size data reporting requires the users to spell out all pertinent information that may be required for comparison of particle size data from one instrument with that from another. This technique of data reporting also has significant advantages in record-keeping and tracking, when size and distribution data need to be referred to at a later date. Depending upon the application of the powder size and distribution data, the level of detail at which these data are represented can be defined by the user.

An important procedure not spelled out in this standard is the mention of the sampling technique used to create the sample for analysis. As sampling procedures vary depending upon the size of the initial batch, the nature of the material, the mode by which the batch is transported, and the nature of the technique and instrument being used for analysis, it is imperative that the technique and any instruments used for sampling be defined.

2.2. ISO 9276-1: 1998

This standard concentrates on issues pertaining to the graphical representation of particle size analysis data, particularly as represented in the form of histograms, density distributions and cumulative distributions. The distributions in questions apply not only to powders, but also to droplets and/or gas bubbles, over any size range. The standard further recommends a standard nomenclature to be followed to generate density and cumulative distributions from the measured raw data. The reference to density in this case is not to the physical property of a material, but to the fractional distribution.

An important issue highlighted in this standard is the common use of the symbols "x" and "d" to represent the particle size. While using the term "x," the standard also states that the term "d" can be used for the same purpose. The standard defines a nomenclature to distinguish between density distributions and cumulative distributions on different bases, by the use of the term $q_{(bases)}(x)$ to define the density distribution and the term $Q_{(bases)}(x)$ to define the cumulative distribution. The various bases used in this standard are number, length, surface or projected area and volume/mass. Recognizing that there is no single definition of particle size, this standard defines particle size as "the diameter of a sphere having the same physical properties; this is known as equivalent spherical diameter." The standard also defines the measures as either cumulative measures or density measures, either of which can be derived from the other by suitable integration of differentiation operations over the appropriate size range. As size distributions are often spread out over a very wide size range, the use of linear abscissa for representing the size range may not be practical. This standard defines equations to be used for representing cumulative and density distributions on a logarithmic abscissa.

3. Particle Diameter

The term "particle diameter" as a quantitative measure of the particle size should be used with caution. As is obvious, the term "diameter" would be well representative of the size of spherical particles, but "real" powders tend to be more irregular in shape with a distribution of sizes and thus "diameter" may be interpreted differently by numerous operators. Allen[2], Svarovsky[5], and other

authors have termed the various expressions for diameter as equivalent sphere diameters, equivalent circle diameters and statistical diameters depending upon the technique by which this number is calculated. Just as important is the notation for diameter, where traditional notation followed in the United States of America has used the character "d" followed by a subscript to define the manner in which the diameter has been computed. ISO standards are now referring to diameter using the character "x" with the use of the subscript still intact.

Equivalent sphere diameters refer to the diameters of regular, homogeneous spheres that would have the same property as the particle being measured. Thus, the use of the term d_v (or x_v) would refer to volume diameter and can be defined as the diameter of a regular, homogeneous sphere that has the same volume as the particle being measured. An important issue put forth by Allen is that determination of a particle size should be conducted by a technique such that the obtained results represents a property of the powder that is critical for the powder application, e.g., powders used in chemical reactions should be characterized by their surface area. Equivalent spherical diameters represent three-dimensional properties of the real particle, and thus are most reliable when used for practical applications that are influenced by volume-based properties (density, surface area, etc.) (see Table 7.1).

Table 7.1.

Definitions of Volume-Based Diameters[2,5]

Drag diameter (d_d): Diameter of a sphere that has the same resistance to motion in the same fluid (having same viscosity), moving at the same velocity as the particle

Free-falling diameter (d_f): Diameter of a sphere having the same density and the same free-falling speed as the particle in the same fluid

Surface diameter (d_s): Diameter of a sphere having the same surface area as the particle

Surface volume diameter (d_{sv}): Diameter of a sphere having the same surface to volume ratio as the particle

Stokes' diameter (d_{St}): Diameter of a free falling sphere (i.e., particle having attained the Stokes velocity) in the laminar flow region

Sieve diameter (d_A): Diameter of a sphere equivalent to the size of the minimum square aperture through which the particle will pass

Volume diameter (d_v): Diameter of a sphere having the same volume as the particle.

Equivalent circle diameters are used (see Table 7.2) when size determination is conducted by evaluating the projected profile of a particle. Thus, these diameters are used mostly for optical or electron microscopy-based techniques, where the profile of a three-dimensional particle is observed on a two-dimensional plane. While these expressions are very useful for observing and reporting the sizes of spherical particles, the results of irregular particles can be erroneous if adequate precautions are not taken. The more irregular a particle, the greater the possibility of surface details being obscured. Also, the orientation of the irregular particle at rest and the resultant projected image can significantly influence the calculated diameter. A relatively easy solution is to sample a large number of random particles in order to minimize variations. The number of particles that need to be sampled, however, needs to be evaluated on a case-by-case basis, and can vary over a wide range (from as few as a few hundred particles to many thousands of particles). Increasing availability of commercial software for image analysis, to some extent, can significantly ease and automate the process of size analysis. However, a thorough evaluation of the strengths and limitations of any software for image analysis must be conducted preferably using certified size standards. Other limitations of this group of definitions include the inability of the definition to describe the shape of the particle, especially when particles have a significant aspect ratio, and the inability to often discern two distinct particles as such due to the nature of the projected image.

Table 7.2.

Size Definitions Based on Equivalent Circle Diameter[2,5]

Projected area diameter (d_a): Diameter of a circle having the same area as the projected area of the particle at rest in a stable position
Projected area diameter (d_p): Diameter of a circle having the same area as the projected area of the particle at rest in a random orientation
Perimeter diameter (d_c): Diameter of a circle having the same perimeter as the projected area of the particle, irrespective of the particle orientation.

The definitions in the third group, the statistical diameters, are probably the most useful to define the shape of a particle (and thus, the most useful for particles with a marked aspect ratio), as these involve the calculation of a linear dimension measured with respect to a defined direction. The use of these expressions is common while using microscopy-based techniques of analysis, but also tend to be tedious (see Table 7.3). Automating the analysis tasks, using commercial software and algorithms, can help reduce the time and effort involved in conducting these analyses.

Table 7.3.

Size Definitions Based on Statistical Diameters[2,5]

Feret's diameter (d_F): Mean value of the distance between pairs of parallel tangents to the projected outline of the particle
Martin's diameter (d_M): The mean chord length of the projected outline of the particle
Unrolled diameter (d_R): The mean chord length through the center of gravity of the particle
Maximum chord diameter (d_{CH}): The maximum length of a line limited by the particle contour
Shear diameter (d_{SH}): Particle width obtained with an image shearing device.

Particle sizes are often expressed using terms such as mean diameter, median diameter and modal diameter. Though these expressions are determined from the distribution size range of the particle diameters, it is appropriate to define these terms in this section.

***Mean Diameter*:** Mean diameter of a particle system can be defined for different particle characteristics of the system under study. The arithmetic mean is calculated by dividing the sum of the diameters of all the individual particles in the distribution, by the total number of particles in the distribution. The geometric mean is calculated by calculating the nth root of the products of the diameters of the n particles constituting the system under study.

Thus, the mean diameter of a powder can be its length mean diameter, surface mean diameter, volume mean diameter or moment mean diameter. Heywood[6] has defined mathematical expression for various mean diameters, expressed according to the measured characteristics, namely, number, length, surface volume and weight.

***Median Diameter*:** The median diameter is the size at which half of all the particles in the distribution are coarser than the expressed diameter, and the remaining are finer. Thus, the median diameter is the 50 % size of a cumulative distribution curve of the particle sizes.

***Modal Diameter*:** The most frequently occurring size value of the particles under study represents the modal diameter, and thus, in a graphical representation, is the size that is represented by the peak of the differential size distribution curve.

The definition used to express the particle size should be chosen with care as often different powder distributions can give the same mean value (arithmetic average), but have significantly different shapes of distribution and size range over which the distribution is spread. Often, the use of more than one definition (e.g., stating both the mean and modal diameters) may help alleviate that confusion and may also give some information about the skewness of the distribution.

Figure 7.1 represents the particle size distribution of a powder obtained by laser light scattering. The plot shows the differential volume as a function of the particle size and indicates the occurrence of the different size measures (mode, mean and median diameters) for the same distribution.

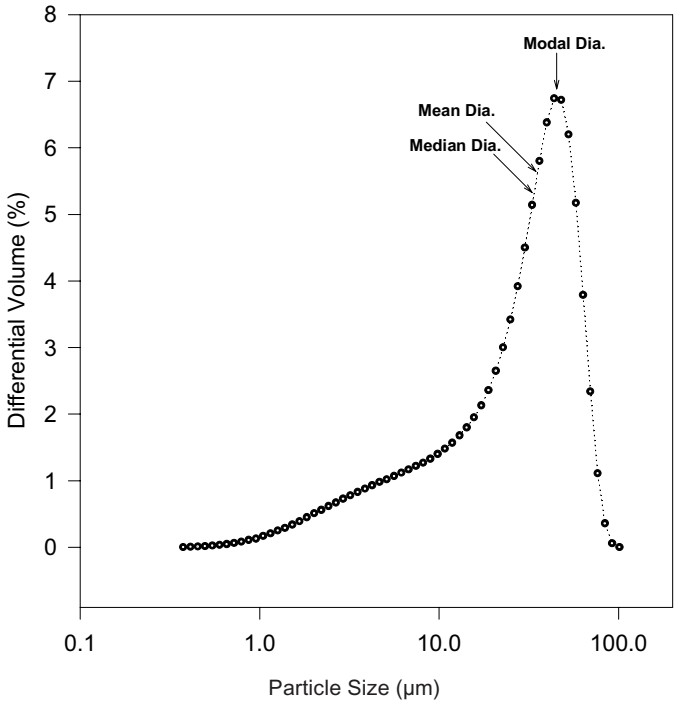

Figure 7.1.

Occurrence of Different Particle Size Measures of a Powder System

4. Representation of Size Data

Particle size and size distribution data can be represented in either a tabular or graphical form. The choice of representation used can be dependent on what information is being expressed and the applications to which this information will be used. Very often, both tabular and graphical representations are used to

convey this information, allowing the end-user to transform the data to enable conversions or comparisons with data from other sources. However, care should be taken when attempting transformation from one form of distribution to another form, due to errors associated with the assumption of a constant shape factor throughout the distribution, which is not often the case with real materials. Both forms of representation are closely related as information displayed in one form is derived from the other.

At a very basic level, tabular representations typically convey a series of size ranges and the corresponding quantity of powder observed in that size range. Thus, the size range can be the size difference between two adjacent sieves, and the corresponding quantity would be the mass of powder on each of the sieve. In case of analysis by laser light scattering, the size range may be the differences in sizes corresponding to the positions of consecutive detector elements, and the associated sample quantity would be the volume of sample giving rise to the signal incident on that element. Allen[2] and Reed[7] give suitable examples of the organization of data in typical tabular representations.

Table 7.4.

Size Data Obtained by Sieve Analysis of Glass Beads During Development of a NIST Size Standard (total mass sampled = 85.70 g)

US Sieve No.	Nominal Size Opening (μm)	Mass on Sieve (g)	Mass Fraction on Sieve (%)	Cumulative Mass Fraction Coarser (%)	Cumulative Mass Fraction Finer (%)
25	710	5.28	6.16	6.16	93.84
30	600	11.29	13.17	19.33	80.67
35	500	14.23	16.60	35.93	64.07
40	425	10.7	12.49	48.42	51.58
45	355	8.97	10.47	58.89	41.11
50	300	10.20	11.9	70.79	29.21
60	250	20.11	23.47	94.26	5.74
PAN		4.92	5.74	100	

Table 7.4 shows a typical representation of size and size distribution data that would be obtained from sieve analysis. This information provides enough raw data to conduct some basic statistical analysis and obtain information about the size distribution, such as mean, median and standard deviation. This information however, reveals very little about the shape of the distribution which can be obtained from plotting these results.

Graphical representation of size and size distribution results can be obtained either as differential distribution or cumulative distribution of the size parameter, as a function of the size. When plotting distribution data, the plots are often drawn as histograms, with the frequency of occurrence as the ordinate and the size or size range over which this frequency is observed as the abscissa. The greatest drawback of this representation arises from the finite width of the

abscissa. If the size range chosen is too wide, then slight variations in the size distribution will not be observed and the histogram will not have adequate resolution. More common representations involve plotting the size distribution data as differential distribution curves and cumulative distribution curves.

Table 7.5.

Size Distribution Data from Coulter LS 230™ Particle Size Analyzer

Eq. Spherical Dia.(µm)	Diff. Volume (%)	Cum. fraction finer (%)
0.375	0	0
0.412	0	0
0.452	0	0
0.496	0	0
0.545	0	0
0.598	0	0
0.656	0	0
0.721	1.05	1.05
0.791	11.6	12.65
0.868	24.9	37.55
0.953	24.8	62.35
1.047	12.1	74.45
1.149	1.87	76.32
1.261	2.75	79.07
1.384	11.7	90.77
1.52	8.45	99.22
1.668	0.78	100
1.832	0	100
2.011	0	100
2.207	0	100
2.423	0	100
2.66	0	100
2.92	0	100

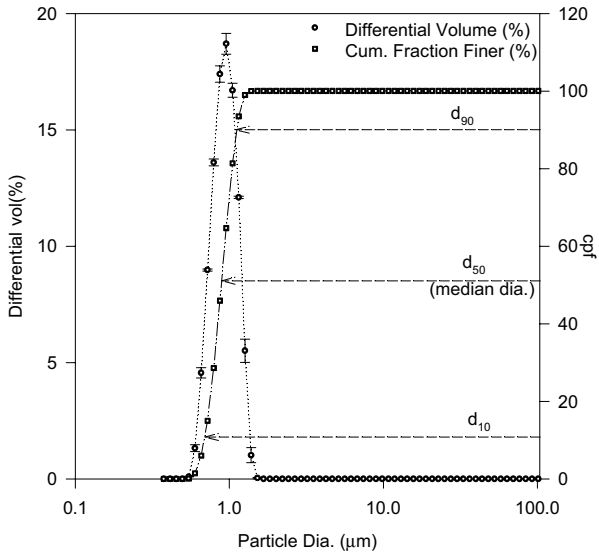

Figure 7.2.

Cumulative and Differential Distribution Plots of Nominal 1.0 µm SiO_2 Spheres

Table 7.5 shows the size distribution data obtained from a Coulter LS230™ laser light scattering particle size analyzer. The data in the left column correspond to the calculated equivalent spherical diameters. The data in the center column are the differential volumes corresponding to each of the size diameter and the data in the right column are calculated as the cumulative volume obtained from sequential summation of the differential volume. These data are plotted as differential and cumulative volume distribution curves in Figure 7.2. As is observed, the differential distribution plot gives a very good representation of the relative percentage frequency distribution (by volume) and thus can be used to estimate what are the relative amounts of particles of

different size ranges. The cumulative distribution, on the other hand, makes it easy to determine the median size (d_{50}) and the percentage distribution contained between any two sizes[2]. It also enables the determination of sizes corresponding to the d_{10} and d_{90} values with relative ease.

The d_{10}, d_{50} and d_{90} values are size values corresponding to the cumulative distribution at 10 %, 50 % and 90 %. Thus, the d_{10} value represents a size value below which 10 % of the cumulative distribution is present, and similarly d_{90} represents a size below which 90 % of the cumulative distribution occurs. Thus, from these definitions, the d_{50} value corresponds to the median diameter. Often, d_{10}, d_{50} and d_{90} values are quoted as a measure of the size distribution of the powder. However, this does not reflect the true shape of the distribution curve and can be misleading. In an attempt to overcome this drawback some have included the d_{25} and d_{75} values.

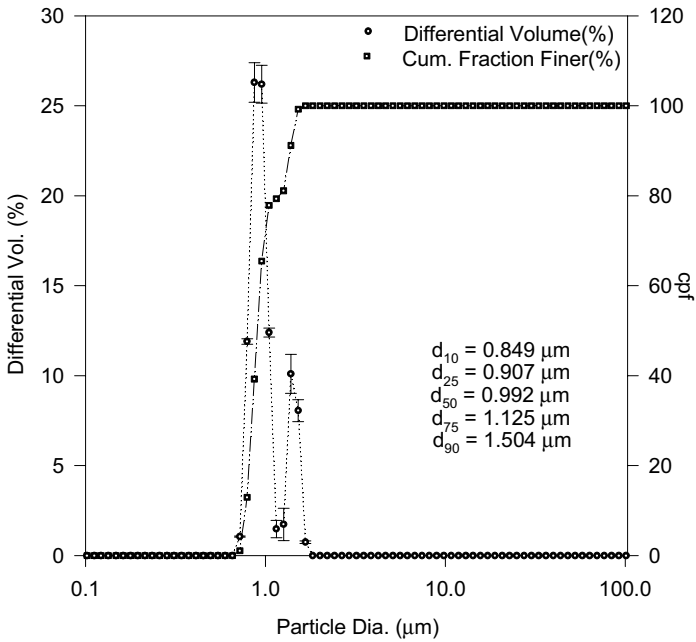

Figure 7.3.

Differential and Cumulative Distribution Plots of Powder of Bimodal Size Distribution

A cumulative distribution plot is of limited value when the powder under study may have variations in the relative distributions at different sizes, giving rise to a multi-modal fractional distribution curve, rather than a uni-modal as shown in Figure 7.2. In such an instance, the cumulative distribution curve would show an inflection, but the relative amounts cannot be easily determined. Similarly,

the use of d_{10}, d_{25}, d_{50}, d_{75} or d_{90} values would indicate very little, other than some idea of the range of powder sizes. In such instances the use of differential distribution curves would be ideal to estimate the relative amounts of powder of varying sizes. An example of this occurrence is shown in Figure 7.3, which shows cumulative and differential distributions for a SiO_2 powder system comprising of spherical particles. The d_{10}, d_{25}, d_{50}, d_{70} and d_{90} values are also listed for reference. The differential distribution shows two distinct size distributions giving rise to a bimodal distribution. The ability to obtain such information can have critical consequences in various manufacturing and quality control processes.

The choice of the technique used to represent size data is also determined by how that data will be used. A fitting example would be representation of size data of clay powders for certain whitewares manufacturing applications. In such instances, discrete numbers such as the d_{10}, d_{50} and d_{90} values would not convey much more than the size distribution of the powders. However, the slope of the cumulative distribution graph would enable determination of the packing of the powders and also some idea about the viscosity and flow behavior of the powders, all of which would directly impact the forming process and the properties of the final product.

5. Summary

The reporting of particle size and particle size distribution data can be done in various forms and techniques. The first factor to be considered is the property that is being used to characterize the particle size and size distribution. One should be aware of the errors and bias associated with measurement instruments and techniques when attempting to characterize a particular property. Similarly, conversion from distributions representing a particular property to that representing another property should be conducted with extreme care and, if possible, avoided all together. In attempting such transformations, the aspect ratio of the particles should be considered and their influence on the transformation factored in. The technique used for reporting size data should preferably address the shape and extent of distribution and some representative characteristic such as median size or moment of distribution.

While reporting of the measured data satisfies one aspect of size reporting, a comprehensive report would necessarily require reporting of various aspects of sampling, sample preparation, instrumental parameters used and any additional statistical analysis. While often cumbersome and superfluous, this additional information would enable testing for reproducibility by other testing facilities or personnel and would also provide a basis for the development of good laboratory practices for an organization.

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GLOSSARY
TERMS RELATED TO PARTICLE SIZE ANALYSIS AND CHARACTERIZATION*

ASTM: American Society for Testing and Materials

aberration[10]: any error that results in image degradation. such errors may be chromatic, spherical, astigmatic, comatic, distortion, or curvature of field; and can result from design or execution, or both

absolute powder density[6]: the mass of powder per unit of absolute powder volume

absolute powder volume[6]: the volume occupied by a powder excluding all pores and voids

absolute volume[6]: the volume of the solid matter after exclusion of all the spaces (pores and voids)

acceptable quality level[2] **(AQL or p_1)**: *in acceptance sampling*, the maximum fraction of nonconforming items at which the process average can be considered satisfactory; the process average at which the risk of rejection is called the producer's risk

acceptance number[2]: *in acceptance sampling*, the maximum number of nonconforming items in a sample that allows the conclusion that the lot conforms to the specification

acceptance sampling[2]: sampling done to provide specimens for acceptance testing; testing performed to decide if a material meets acceptance criteria

accepted reference value[4]: a value that serves as an agreed-upon reference for comparison, and which is derived as: (1) a theoretical or established value, based on scientific principles, (2) an assigned or certified value, based on experimental work of some national or international organization, or (3) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group

accuracy[2]: *of a test method,* the degree of agreement between the true value of the property being tested (or an accepted standard value) and the average of many observations made according to the test method, preferably by many observers

accuracy of measurement[7]: closeness of the agreement between the result of a measurement and the value of the measurand

aerated bulk density[6]: the minimum bulk density of a motionless powder

agglomerate[1]: several particles held together by weak cohesive forces

agglomeration: formation of aggregates *via* physical (van der Waals, hydrophobic) or electrostatic forces; the resulting structure is called an agglomerate

aggregate[1]: a cohesive mass consisting of particulate subunits

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* ***EDITORIAL COMMENTS***

1. The definition of terms in this glossary does not reflect in any way the National Institute of Standards and Technology's (NIST) preference or endorsement of these expressions.
2. Most of the definitions expressed here have been adapted as recommendations from various national and international standards agencies.
3. The use of multiple definitions for the same term reflects the varied usage of these terms for different applications and contexts.

aggregation[1]: a general term defined as any process by which particles collect to form a cohesive mass or cluster; the resulting structure is called an aggregate

air jet sieving[6]: a device in which a portion of powder in a sieve is fluidized by air passing upwards through it from a rotating slit. At the same time a negative pressure is applied to the bottom of the sieve which removes the fine particles to a collecting device

Analysis of Variance (ANOVA) [2]: a procedure for dividing the total variation of a set of data into two or more parts, one of which estimates the error due to selecting and testing specimens and the other part(s) possible sources of additional variation

angle of repose[6]: the angle to the horizontal assumed by the surface of a poured heap of powder at rest

angular aperture[10]: the angle between the most divergent rays that can pass through a lens to form the image of an object

aperture size[16]: the dimension defining an opening in a sieving medium

apparent density[17]: the mass of a unit volume of powder, usually expressed as grams per cubic centimeter, determined by a specified method

apparent particle density[6]: the mass of a particle divided by its apparent volume

apparent particle volume[6]: the total volume of the particle excluding open pores, but including closed pores

apparent powder density[6]: the mass of a powder divided by its apparent volume

apparent powder volume[6]: the total volume of solid matter, open pores and closed pores and interstices

assignable cause[2]: a factor which contributes to variation and is feasible to detect and identify

attribute data[2]: observed values or determinations which indicate the presence or absence of specific characteristics

auto-delineation[8]: the process which attempts to predict the true edge of unsharp images of particles by reference to the local gray level values; this is used to improve the accuracy of measurements and to make them less sensitive to incorrect gray level thresholding

average[2]: *for a series of observations*, the total divided by the number of observations

BSI: British Standards Institute

balanced incomplete block design (BIB) [4]: an incomplete block design in which each block contains the same number *k* of different versions from the *t* versions of a single principal factor arranged so that every pair of versions occurs together in the same number, λ, of blocks from the *b* blocks

batch[4]: a definite quantity of some product or material produced under conditions that are considered uniform

bias[2]: *in statistics,* a constant or systematic error in test results

From **ASTM E 131-98**[3]: Bias is determined by the equation:

Bias = ‘ = $(1/n)\ \Sigma_{i=1}^{n} e_i$

where, n = number of observations for which the accuracy is determined,

e_i= the difference between a measured value of a property and its accepted reference value, and

‘ = the mean value of the e_i

binary image[8]: a digitized image consisting of an array of pixels, each of which has a value of either 0 or 1; these values are normally represented by dark and bright regions on the display screen or by the use of two distinct colors

binomial distribution[2]: the frequency distribution which has the probability function:

$$P(r) = n!/ [r!(n-r)!] p^r q^{n-r}$$

where: P(r) = probability of obtaining exactly r "successes" in n independent trials,

p = probability, constant from trial to trial, of obtaining a "success" in a single trial, and,

$$q = 1 - p$$

blending[17]: the thorough intermingling of powders of the same nominal composition (not to be confused with mixing)

blinding[6]: the building up of small particles on a screening surface reducing the aperture size or closing them completely

block[2]: *in experimenting,* a group of units that is relatively homogeneous within itself, but may differ from other similar groups

Boolean operation[6]: a logical procedure where two binary images are compared pixel by pixel to produce a third binary image

bridge width[6]: the distance between the nearest edges of two adjacent holes in a perforated plate

bridging[6]: the formation of arches of particles keyed or jammed across the direction of flow

Brownian motion[6]: the random movement of small particles in a disperse phase caused by the bombardment by molecules of the surrounding medium *(thermally induced motion* – **ed. note)**

bulk density[17]: the mass per unit volume of a powder under nonstandard conditions, for example, in a shipping container (not to be confused with apparent density)

bulk sample[2]: one or more portions which (1) are taken from material that does not consist of separately identifiable units and (2) can be identified after sampling as separate or composed units

calibrant[19]: a reference material used for a calibration

calibrate[2]: to determine and record the relationship between a set of standard units of measure and the output of an instrument or test procedure

calibration : (1) the act or process of calibrating; the recorded relationship resulting from calibrating[2]; (2) the determination of a bias conversion factor of an analytical process, under specified conditions, in order to obtain meaningful results[6]; (3)*(in context of microscopy)*: the set of operations which establish, under specified conditions, the relationship between magnification values indicated by the SEM and the corresponding magnification values determined by examination of a reference material[11]

centrifugal sedimentation[6]: (1) the classification of particles by their rate of fall in a fluid accelerated by centrifugal force; (2) the grading by mass of suspended particles accelerated by centrifugal force

certification scheme[5]: certification system as related to specified products, processes or services to which the same particular standards and rules, and the same procedure apply (ISO Guide 2)

certified reference material[11]: reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainity as a stated level of confidence (ISO Guide 30:1992)

characteristic[4]: a property of items in a sample or population which, when measured, counted or otherwise observed, helps to distinguish between the items

chromatic aberration[10]: a defect in a lens or lens system as a result of which the lens possesses different focal lengths for radiation of different wavelengths

classification[17]: separation of a powder into fractions according to particle size

cluster sampling[4]: when the primary sampling unit comprises of a bundle of elementary units or a group of subunits, the term cluster sampling may be applied

coagulation[1]: formation of aggregates induced by the addition of electrolyte to a suspension; the resulting structure is termed the coagulum or coagulate, while the electrolyte additive is termed the coagulant

coagulum, coagulate[1]: in a suspension, aggregates formed by addition of eletrolyte

coarse particle[1]: state of subdivision implying that the particles have average dimensions greater than roughly 100 µm

Coefficient of Variation, CV: (1) a measure of the dispersion of observed values equal to the standard deviation for the values divided by the average of the values; may be expressed as a percentage of the average[2]; (2) *(relative measure [%] for precision)* standard deviation divided by mean value of population and multiplied by 100 (for normal distributions of data the median is equal to the mean)[14]

coincidence[6]: detection of two or more particles as a single particle

colloidal (colloid) [1]: state of subdivision implying that the particles have at least in one direction a dimension roughly between 1 nm and 1 µm. Colloids are significantly affected by Brownian (thermal) motion when suspended in a liquid

coma[10]: a lens aberration occurring in that part of the image field that is some distance from the principal axis of the system; it results from different magnification in the various lens zones. Extra-axial object points appear as short comet-like images with the brighter small head toward the center of the field (positive coma) or away from the center (negative coma)

comminution[18]: the act or process of reduction in particle size, usually but not necessarily by grinding or milling

completely randomized design: a design in which the treatments are assigned at random to the full set of experimental units

completely randomized factorial design[4]: a factorial experiment (including all replications) run in a completely randomized design

complex refractive index[14] **(N_p)**: refractive index of a particle, consisting of a real and an imaginary (absorption) part, $N_p = n_p - ik_p$

Component of Variance[2]: a part of a total variance identified with a specified source of variability

composite design[4]: a design developed specifically for fitting second order response surfaces to study curvature, constructed by adding further selected treatments to those obtained from a 2^n factorial (or its fraction)

cone and quartering[6]: a method of subdividing a dry powder sample *(see chapter on Sampling for description)*

confidence interval[2]: an interval estimate of a population parameter computed so that the statement "the population parameter lies in this interval" will be true, on average, in a stated proportion of the times such statements are made

confidence level[19]: the probability that the true value lies within a stated range (the confidence interval)

confidence limits[2]: the two statistics that define the ends of a confidence interval

confounded factorial design[4]: a factorial experiment in which only a fraction of the treatment combinations are run in each block and where the selection of the treatment combinations assigned to each block is arranged so that one or more prescribed effects is (are) confounded with the block effect(s), while the other effects remain free from confounding

confounding[4]: combining indistinguishably the main effect of a factor or a differential effect between factors (interactions) with the effect of other factor(s), block factor(s) or interaction(s)

consensus[5]: general agreement, characterized by the absence of substantial issues by any important part of the concerned interests and by a process that involves seeking to take into account the views of all parties concerned and to reconcile any conflicting arguments, (ISO Guide 2)

control chart factor[4] : a factor, usually varying with sample size, to convert specified statistics or parameters into a central line value or control limit appropriate to the control chart

control limits[2]: predetermined ranges based on the variability of past observations between which the instrument data for a test must fall to be considered valid

control[4] **(evaluation)**: an evaluation to check, test, or verify; **(authority)**: the act of guiding, directing, or managing; **(stability)**: a state of process in which the variability is attributable to a constant system of chance causes

correction[7]: value added algebraically to the uncorrected result of a measurement to compensate for systematic error

correction factor[7]: numerical factor by which the uncorrected result of a measurement is multiplied to compensate for systematic error

critical difference[2]: the observed difference between two test results, which should be considered significant at the specified probability level

cumulative oversize distribution plot[6]: a plot obtained by recording the amount of the oversize particles (y axis) against the particle size (x axis) for several different size levels

cumulative undersize distribution plot[6]: a plot obtained by recording the amount of the undersize particles (y axis) against the particle size (x axis) for several different size levels

deconvolution[14]: mathematical procedure whereby the size distribution of a particle ensemble is inferred from measurements of their scattering pattern

depletion stabilization[1]: mechanism in which particle aggregation is inhibited by the presence of free (non-adsorbed) polymer due to the creation of high-energy depletion zones (depleted of polymer compared to the bulk solution) between closely interacting particle surfaces

depth of field[10]: the depth or thickness of the *object* space that is simultaneously in acceptable focus

depth of focus[10]: the depth or thickness of the *image* space that is simultaneously in acceptable focus

design of experiments[4]: the arrangement in which an experimental program is to be conducted, and the selection of the levels (versions) of one or more factors or factor combinations to be included in the experiment; synonyms include experiment design and experimental design

detection[8]: the process by which the digitized gray level image is converted into a binary image representing the particles to be measured

determination value[2]: the numerical quantity calculated by means of the test method equation from the measurement values obtained as directed in a test method

deviation[4]: the difference between a measurement or quasi-measurement and its stated value or intended level

diffraction[14]: spreading of light around the contour of particle beyond the limits of its geometrical shadow with a small deviation from rectilinear propagation

diffusion diameter[6]: the diameter of a particle calculated from photon correlation spectroscopy, using the Stokes-Einstein equation

digitization[8]: the process of converting the continuously varying voltage output of a video signal into a discrete array of pixels whose values correspond to the intensities of the parts of the original image that they represent

discrete sample[2]: one or more units taken from a material that consists of separately identifiable units

discrete variate[2]: a variate that is a measurement based on a scale that has a limited or finite number of steps; such as a count, a rating scale, or a ratio of successes to total observations.

dispersing agent[1]: a substance which when present in small amounts facilitates the dispersion of aggregates to form a stable suspension; for example, polyelectrolytes are often used as dispersing agents in ceramic processing.

dispersion[1]: in general, a two-phase system in which particles of any kind (solid, liquid, gas) are dispersed in a continuous phase of a different composition or state; more specifically in the field of ceramics, dispersion is used to describe a suspension of solid particles in a liquid medium

drift[19]: *in instrumental methods of quantitative analysis,* a gradual change in instrument response from start to completion of a set of determinations

dry milling[18]: the process of reducing the particle size of a substance by milling without the use of a liquid medium

dry screening[18]: the process of separating small sizes of granular or powdered solids from coarser particles by passing them through a screen of desired mesh size while in the dry state

dry sieving[6]: the sieving of powders without the aid of a liquid

duplicate[2]: *in experimenting or testing,* one of two or more runs with the same specified experimental or test conditions but with each experimental or test conditions not being established independently of all previous runs

edge[6]: the boundary between regions of interest and background

edge finding[9]: one of the many edge detection methods used to detect transition between objects and background

effective aperture[10]: the diameter of the entrance pupil; it is the apparent diameter of the limiting aperture measured from the front

effective particle density[6]: the mass of a particle divided by its volume including open pores and closed pores

effective solid density[6]: the density of powder particles as determined by a given fluid displacement method

effective solid volume[6]: the mass of the particles divided by the effective solid density

electrostatic stabilization[1]: mechanism in which particle aggregation is inhibited by the presence of a mutually repulsive electrostatic potential that surrounds each particle

electrosteric stabilization[1]: mechanism in which particle aggregation is inhibited by the combined effects of electrostatic and steric interactions; usually associated with the adsorption of polyeletrolytes onto the particle surface

elongation shape factor[6]: the ratio of the length of a rectangle with two sides parallel to the longest dimension of a particle to its width

envelope volume[6]: the external volume of a particle, powder or monolith such as would be obtained by tightly shrinking a film to contain it

equivalent circular diameter[9]: the diameter of a circle having the same area as the projected image of the particle (also known as Haywood Diameter)

equivalent diameter[6]: the diameter of a sphere which behaves like the observed particle relative to or deduced from a chosen property

error (of measurement) [7]: result of a measurement minus the values of the measurand

error of the first kind[2], α: *in a statistical test,* the rejection of a statistical hypothesis when it is true

error of the second kind[2], β: *in a statistical test,* the rejection of a statistical hypothesis when it is false

evolutionary operation (EVOP) [4]: a sequential form of experimentation conducted in production facilities during regular production

experimental error[2]: variability attributable only to a test method itself

extinction[14]: attenuation of a light beam traversing a medium through absorption and scattering

factor[2]: *in experimenting,* a condition or circumstance that is being investigated to determine if it has an effect upon the result of testing the property of interest

factorial experiment (general) [4]: in general, an experiment in which all possible treatments formed from two or more factors, each being studied at two or more levels (versions) are examined so that interactions (differential effects) as well as main effects can be estimated

fine particle[1]: state of subdivision implying that the particles have average dimensions lying roughly between 1 µm and 100 µm

fineness[18]: a measurement number designation of the particle size of a material, usually reported as passing a screen of a particular standard size

fines[18]: the portions of a powder composed of particles smaller than a specified size

floc[22]: loose assembly of particles in a liquid

flocculation[1]: formation of aggregates in a suspension mediated by polymeric species, either attached to the particles or free in the suspending medium; the resulting structure is called a floc, while the polymer additive is termed a flocculant; polymer bridging is a flocculation process

flowability[6]: the ease with which a powder flows; usually expressed as an index

focal plane[10]: a plane through the focal point perpendicular to the principal axis of a lens or mirror

fouling[6]: the building up of particles onto surfaces because of the particles' stronger attraction to the surfaces than to the fluid in which they are suspended

Fourier transform (FT)[3]: the mathematical process used to convert an amplitude-time spectrum to an amplitude-frequency spectrum, or *vice versa*

fraction[17]: the portion of a powder sample which lies between two stated particle sizes; synonymous with cut

fraction factorial design[4]: a factorial experiment in which only an adequately chosen fraction of the treatments required for the complete factorial experiment is selected to be run

Fraunhofer diffraction[15]: the optical theory that describes low-angle scattering of light by particles that are large compared to the wavelength of the incident light

free falling velocity[22]: velocity of a particle through a still liquid at which the effective accelerating force of the particle is balanced by the drag exerted by the liquid on the particle

frequency distribution; differential distribution; density distribution[6]: a plot exhibiting a series of observations of values as a function of the frequency of occurrence

frequency distribution[2]: *of a population*, a function that, for a specific type of distribution, gives for each value of a random discrete variate, or each group of values of a random continuous variate, the corresponding probability of occurrence

frequency distribution[2]: *of a sample*, a table giving for each value of a discrete variate, or for each group of values of a continuous variate, the corresponding number of observations

F-test[2]: a test of statistical significance based on the use of George W. Snedecor's F-distribution and used to compare two sample variances or a sample variance and a hypothetical value

grading[6]: separation of a powder into particle size fractions

granule[1]: state of subdivision generally referring to dry particulates with dimensions lying in the 50 µm to 200 µm range; typically granules are aggregates of finer particulates, produced, for instance, by spray-drying for ease of handling during subsequent consolidation processes

gravitational sedimentation[6]: the grading of mass of suspended particles by mass accelerated by gravity

gravity feed[18]: the movement of materials from one container to another container or location by force of gravity

green density[6]: the apparent density of a green compact

gray image[9]: an image in which multiple values, not just the "black" and the "white" of a binary image, are permitted for each pixel

halo error[6]: of light microscopy and image analysis; the oversizing of objects due to halo

halo[6]: of light microscopy and image analysis; a dark or light false perimeter of a particle image

hard-aggregate[1]: an aggregate which cannot be easily redispersed by the application of moderate mechanical agitation (shaking, stirring or ultrasonication) and/or chemical treatment; typically, hard-aggregates consist of particulate subunits which have been chemically bonded or fused

heterogeneous material[20]: material in which a spot sample will have significantly different value of the characteristics under consideration from the mean value of the characteristic for the whole material

heterodisperse[1]: describes a dispersed system in which multiple size distribution modes occur; e.g., bimodal, trimodal, etc.

homogeneous material[20]: material in which a spot sample will not have a significantly different value of the characteristic under consideration from the mean value of the characteristics for the whole material

ISO: International Organization for Standardization

image analysis[9]: a processing and data reduction operation which will yield a numerical or logical result from an image

image processing/image enhancement[6]: operations on an image which produces a modified image

immersed density[12]: the mass of the powder per unit volume of suspension medium that it displaces

immersed particle density[6]: the mass of a particle per unit volume of suspension medium displaced

impaction sampling[6]: the process of selectively removing particles from a gas-borne stream by obstructing the flow of gas so that particles of higher momentum collect on a solid surface

impactor[6]: a device to remove particles selectively from a gas-borne stream by impaction onto a solid collection surface

impinger[6]: a device to remove particles selectively from a gas-borne stream into a liquid medium

incomplete block design[4]: a design in which the experiment space is subdivided into blocks in which there are insufficient experimental units available to run a complete set of treatments or replicate of the experiment

increment[19]: *in sampling,* a portion of material removed from a lot by a single operation

inspection[5]: process of measuring, examining, testing, gaging, or using other procedures to ascertain the quality or state, detect errors or defects, or otherwise appraise materials, products, services, systems or environments to a pre-established standard

instrument line shape (ILS) function[3]: the Fourier transform of the function by which an interferogram is weighted

interaction[2]: the condition that exists among factors when a test result obtained at one level of a factor is dependent on the level of one or more additional factors

intercorrelation coefficient, (r_{XX}) [3] : a measure of the linear association between the values of the same type of variable expressed as a correlation coefficient (r)

interference[2]: *in testing,* an effect due to the presence of a constituent or characteristic that influences the measurement of another constituent or characteristic

interlaboratory test comparison[5]: organization, performance and evaluation of tests on the same or similar items or materials by two or more laboratories in accordance with predetermined conditions (ISO Guide 2)

interlaboratory testing[2]: the evaluating of a test method in more than one laboratory by analyzing data obtained from one or more materials that are as homogeneous as practical

intermediate precisions[4]: the closeness of agreement between test results obtained under specified intermediate precision conditions

intermediate precision conditions[4]: conditions under which test results are obtained with the same test method using test units or test specimens taken at random from a single quantity of material that is as nearly homogeneous as possible, and with changing conditions such as operator, measuring equipment, location within the laboratory, and time

inversion[6]: the reversal of a binary image by the conversion of all the 1's to 0's and 0's to 1's

inversion procedure[6]: a back calculation method used to obtain a result (e.g., of particle size distribution from a light scattering energy pattern)

isokinetic sample[6]: sample taken at the same velocity as that in the process under test

konisampler[6]: a thermal precipitator fitted to a microscope for observing particle while being sampled

laboratory sample[2]: a portion of material taken to represent the lot sample, or the original material, and used in the laboratory as a source of test specimens

laboratory sampling unit[2]: a portion of material taken to represent one of the lot sampling units or the original material and used in the laboratory as a source of test specimens

least difference of practical importance, δ[2]: the smallest difference based on engineering judgement deemed to be of practical importance when considering whether a significant difference exists between two statistics or between a statistic and a hypothetical value

levigation[6]: the classification of particles according to their movement through a separating fluid

line start technique[12]: a technique in which a thin layer of homogeneous suspension is floated on the surface of the sedimentation liquid

lot[2]: *in acceptance sampling*, that part of a consignment shipping consisting of materials from one production lot

lot sample[2]: one or more shipping units taken at random to represent a lot and used as a source of laboratory sampling units or test specimens, or both

lower control limit[4] **(LCL)**: control limit for points below the central line

lower critical Stokes diameter[22]: Stokes diameter at which the root mean square displacement due to thermal diffusion (Brownian Motion) equals 5 % of the sedimentation distance

lower tolerance limit[4] **(LTL)**: tolerance limit that defines the lower conformance boundary for an individual unit of a manufacturing service operation

margin[6]: the region between the outside edges of the outside rows of holes and the edges of a perforated plate

mass distribution[6]: the distribution of mass of particles as a function of their size

matched test sieve[16]: a test sieve that reproduces the results of a master test sieve within defined limits for a designated material

mean square[2]: *in analysis of variance,* a contraction of the expression "mean of the squared deviation from the appropriate average(s)" where the divisor of each sum of squares is the appropriate degrees of freedom

measurement value[2]: the numerical result of quantifying a particular property or dimension

median[2]: *for a series of observations,* after arranging them in order of magnitude, the value that falls in the middle when the number of observations is odd or the arithmetic mean of the two middle observations when the number of observations is even

mesh[16]: *in a piece of woven wire cloth,* the nominal number of apertures or fraction thereof, per inch

method of attributes[4]: measurement of quality by the method of attributes consists of noting the presence (or absence) of some characteristic or attribute in each of the units in the group under consideration, and counting how many units do (or do not) possess the quality attribute, or how many such events occur in the unit, group, or area

method of least squares[4]: a technique of estimation of parameter which minimizes Σe^2, where, e is the difference between the observed values and the predicted value derived from the assumed model

method of variables[4]: measurement of quality by the method of variables consists of measuring and recording the numerical magnitude of a quality characteristic for each of the units in the group under consideration

Mie scattering[15] : the complex electromagnetic theory that describes the scattering of light by spherical 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

minimum particle size[1]: operationally defined as the smallest achievable average particle size (mean or median) measured in a well-dispersed suspension

minus sieve[17]: the portion of a powder sample which passes through a standard sieve of specified number

mixing[17]: the thorough intermingling of powders of two or more materials

mode[2]: the value of the variate for which the relative frequency in a series of observations reaches a local maximum

model matrix[14]: matrix containing light scattering vectors from unit volumes of different size classes, scaled to the detector's geometry, as derived from model computation

monodisperse[1]: describes a dispersed system in which all the particles are of the same or nearly the same size, forming a narrow (unimodal) distribution about a median value; a particle distribution may be considered monodisperse if at least 90 % of the distribution lies within 5 % of the median size

moving range[2]: the difference without regard to the sign between two successive observations

nest of sieves[6]: a set of test sieves assembled together

nominal mesh size[16]: the designated dimension of the opening of a sieve

nonconformity[2]: an occurrence of failing to satisfy the requirements of the applicable specification; a condition that results in a nonconforming item

nonparametric[2]: a term referring to a statistical technique that does not assume the nature of the underlying frequency distribution is known

normal distribution[2]: the distribution that has the probability function:

$$f(x)dx = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx$$

where, x = random variate

μ = mean of the distribution, and

σ = standard deviation of the distribution

number distribution[6]: the distribution by number of particles as a function of their size

numerical aperture[8]: product of the refractive index of the object space and the sine of the semi-aperture of the cone of rays entering the entrance pupil of the objective lens from the object point

obscuration (optical concentration) [14]: percentage or fraction of light that is attenuated due to extinction (scattering and/or absorption) by the particles

observation[2]: the process of determining the presence or absence of attributes or making measurements of a variable; a result of the process of determining the presence or absence of an attribute or making a measurement of a variable

open area[16]: the ratio of the total area of the apertures to the total functional area of the screening media, expressed as a percentage

optical axis[10]: the line formed by the coinciding principal axes of a series of optical elements comprising an optical system; it is the line passing through the centers of curvature of the optical surfaces

optical model[14]: theoretical model used for computing the model matrix for optically homogeneous spheres, with, if necessary, a specified complex refractive index, e.g. Fraunhofer diffraction, anomalous diffraction, Mie scattering

oversize[13]: portion of material composed of particles that are larger than some specific size

oversize powder[17]: particles coarser than the maximum permitted by a given particle size specification

parameter[2]: *in statistics,* a variable that describes a characteristic of a population or mathematical model

partially balanced incomplete block design[4] **(PBIB)**: an incomplete block design in which each block contains the same number *k*, of different versions from the *t* versions of the principal factor

particle[22]: a discrete element of material regardless of its size

particle size[17]: the controlling lineal dimension of an individual particle as determined by analysis with sieves or other suitable means

particle size distribution[6]: a description of the size and frequency of particles in a population

particulate[1]: of or composed of distinct particles

perforated plate[6]: a sieving medium consisting of a plate with uniformly sized holes in symmetrical arrangement

phase modulation[3]: modulation produced by rapid oscillation of one mirror of a scanning interferometer through an amplitude which is smaller than the shortest wavelength in the spectrum to produce an interferogram which is, to a good approximation, the first derivative of the conventional interferogram

pitch[11]: the separation of two similar structures, measured as the center to center or edge to edge distance

pixel[9]: a "pixel," or "picture element," corresponds to an individual sample in a digital image which has been formed by uniform sampling in both the horizontal and vertical directions

plain weave[6]: the weave in which every warp wire crosses alternately above and below every weft wire and *vice versa*

plate thickness[6]: the thickness of the plate sieving medium after perforation

Poisson distribution[2]: the distribution which has as its probability function:

$$P(r) = e^{-\mu} m^r / r!$$

where, P(r) = probability of obtaining exactly r occurrences of an event in one unit, such as a unit of time or area,

μ = both mean and variance of the distribution, and

e = base of natural logarithms

polydisperse[1]: describes a dispersed system in which many particle sizes occur; more specifically, a system in which less than 90 % of the size distribution lies within 5 % of the median size

population[4]: the totality of items or units of material under consideration

powder[1]: dry collection of particulates with a macroscopic consistency

powder volume[6]: the apparent volume of a powder as measured under specific conditions

practice[2]: a definitive procedure for performing one or more specific operations or functions that does not produce a test result

precision[2]: the degree of agreement within a set of observations or test results obtained as directed in a test method

precision[2]: *under conditions of between laboratory precision,* the multi-laboratory, single-sample, single-operator-apparatus-day (within-laboratory) precision of a method; the precision of a set of statistically independent test results all of which are obtained by testing the same sample of material and each of which is obtained in a different laboratory by one operator using one apparatus to obtain the same number of observations by testing randomly drawn specimens over the shortest practical time interval

precision[2]: *under conditions of single-operator precision,* the single-operator-laboratory-sample-apparatus-day precision of a method; the precision of a set of statistically independent observations all obtained as directed in the method and obtained over the shortest practical time interval in one laboratory by a single operator using one apparatus and randomly draw specimens from one sample of the material being tested

precision[2]: *under conditions of within-laboratory precision with multiple operators,* the multi-laboratory, single-laboratory-sample, single-apparatus-day (within-laboratory) precision of a method; the precision of a set of statistically independent test results all obtained in one laboratory using a single sample of material and with each test result obtained by a different operator, with each operator using one apparatus to obtain the same number of observations by testing randomly drawn specimens over the shortest practical time interval

pressed density[6]: the apparent density of a compact

primary particles[1]: smallest identifiable subdivision in a particulate system; primary particles may also be subunits of aggregates

principal component analysis[3]: a mathematical procedure for resolving sets of data into orthogonal components whose linear combinations approximate the original data to any desired degree of accuracy

probability function[2]: *of a continuous variate,* the mathematical expression whose definite integral gives the probability that a variate will take value within the two limits of integration

probability function[2]: *of a discrete variate,* the mathematical expression which gives the probability that a variate will take a particular value

probability level[2]: a general term that reflects the stated proportion of times an event is likely to occur

probability sample[4]: a sample of which the sampling units have been selected by a chance such that, at each step of selection, a specified probability of selection can be attached to each sampling unit available for selection

process average[2]: for the items produced, the true and unknown level of (1) the fraction of nonconforming items, or (2) a characteristic of the items as determined by a specific test method

production lot[2]: that part of one manufacturer's production made from the same nominal raw material under essentially the same conditions and designed to meet the same specifications

proficiency testing[5]: determination of laboratory testing performance by means of interlaboratory test comparisons (ISO Guide 2)

quality[5]: totality of characteristics of an entity that bear on its ability to satisfy stated or implied needs

random cause[2]: one of the many factors which contribute to variation, but which are not feasible to detect and identify since they are random in origin and usually small in effect

random error[7]: result of a measurement minus the mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions

random error of result[4]: a component of the error which, in the course of a number of test results for the same characteristic, varies in an unpredictable way

random sampling[2]: the process of selecting units for a sample of size n in such a manner that all combinations of n units under consideration have an equal or ascertainable chance of being selected as the sample

randomization[4]: the procedure used to allot treatments at random to the experimental units so as to provide a high degree of independence in the contributions of experimental error to estimates of treatment effects

randomized block experiment[2]: a kind of experiment which compares the average of k different treatments that appear in random order in each of b blocks

randomized block factorial design[4]: a factorial experiment run in a randomized block design in which each block includes a complete set of factorial combinations

receiver pan[6]: a pan which fits snugly under a sieve to collect fine particles

reference material[11]: a material or substance one or more of whose property values are sufficiently homogeneous, stable, and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials (see ISO Guide 30:1992)

reference standard[11]: a reference material, generally of the highest metrological quality available, from which measurements are derived

refractive index[3]: the phase velocity of radiant powder in a vacuum divided by the phase velocity of the same radiant power in a specified medium. When one medium is a vacuum, n is the ratio of the sine of the angle of incidence to the sine of the angle of refraction

rejection number: *in acceptance sampling,* the minimum number of nonconforming items in a sample that requires the conclusion that the lot does not conform to the specification

relative refractive index (m) [14]: complex refractive index of a particle, relative to that of the medium, $m = N_p/n_m$

repeatability[6]: a measure of precision and expressed as a standard deviation; the precision of successive measurements of the same sample carried out subject to all of the following conditions:

(a) the same measuring instrument;

(b) the same method of measurement;

(c) the same conditions of use;

(d) the same observer;

(e) the same location;

(f) repetition over a short period of time

repeatability (of results of measurements)[7]: closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

NOTES

1. These conditions are called **repeatability conditions**.
2. Repeatability conditions include:
   - the same measurement procedure;
   - the same observer;
   - the same measuring instrument, used under the same conditions
   - the same location;
   - repetition over a short period of time.
3. Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

replicate[2]: *in experimenting or testing,* one of two or more runs with the same specified experimental or test conditions and with each experimental or test conditions being established independently or all previous runs; to repeat a run so as to produce a replicate

reproducibility[6]: a measure of precision and expressed as a standard deviation; the precision of measurements of the same sample where individual measurements are carried out under changing conditions, such as the following:

(a) the measuring instrument;

(b) the method of measurement;

(c) time;

(d) the conditions of use;

(e) the observer;

(f) the location

reproducibility (of results of measurements) [7]: closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement.

NOTES

1. A valid statement of reproducibility requires specification of the conditions changed.
2. The changed conditions may include:
   - principle of measurement;
   - method of measurement;
   - observer;
   - measuring instrument;
   - reference standard;
   - location;
   - conditions of use;
   - time.

3. Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

4. Results are here usually understood to be corrected results.

residual error[4]: the difference between the observed result and the predicted value (estimated treatment response); observed result minus predicted value

resolution[6]: a quantitative expression of the ability of a measuring device to distinguish meaningfully between closely adjacent values of the quantity indicated

response variable[4]: the variable that shows the observed results of an experimental treatment

Reynolds number[6]: the dimensionless number which defines the flow pattern of a fluid surrounding a particle

riffler[6]: a device for dividing a stream of particles into representative samples

robustness[4]: insensitivity of a statistical test to departures from underlying assumptions

ruggedness[4]: insensitivity of a test method to departures from specified test or environmental conditions

run[2]: *in experimenting or testing,* a single performance or determination using one of a combination of experimental or test conditions

sample[19]: a portion of a material intended to be representative of the whole

sample[2]: (1) a portion of a lot of materials which is taken for testing or for record purposes; (2) a group of specimens used, or observations made, which provide information that can be used for making statistical inferences about the population(s) from which the specimens were drawn

sample, final[21]: sample obtained or prepared under the sampling plan for possible subdivison into identical portions for testing, reference or storage

sample, gross[19]: a single large sample obtained by placing in a single container two or more increments taken from a lot

sample, laboratory[19]: a subsample selected from the properly prepared gross sample of a lot for submission to one or more laboratories for chemical analysis

sample, prepared[19]: a sample on which comminution, division, blending or other procedures have been performed to make the sample ready for analysis

sample, spot[20]: a sample of specified quantity taken from a specified place in the bulk material, gross sample or laboratory sample, or at a specified place and time in a stream and representative of its own local environment

sample, test[19]: a subsample selected from the properly prepared laboratory sample which has a suitable sample weight or volume for one or more determinations by chemical analysis

sample, umpire[19]: a laboratory sample submitted to a laboratory of recognized capability chosen to resolve a difference

sample division[21]: the process in sample preparation where the mass of the sample is decreased by partition or extraction without change in particle size

sampling dimension[21]: a dimensionless number characterizing the distribution of sampling increments in space relative to the powder; the volume of each sampling increment is not taken into consideration

sampling fraction[4]**, f**: the ratio f of the number of sampling units selected for the sample to the number of sampling units available

sampling increment[21]: a quantity of material taken as sample from a larger quantity

sampling plan[2]: a procedure for obtaining a sample

sampling plan result[2]: the number obtained for use in judging the acceptability of a lot when applying a sampling plan

sampling sequence[21]: the sequence of sampling partitions and extractions and necessary sample preparation steps that result in the reduction of the primary sample to representative test portion

sampling unit[2]: an identifiable, discrete unit or subunit of material that could be taken as part of a sample

sampling with replacement[4]: a procedure used with some probability sampling plans in which a selected unit is replaced after any step in selection so that this sampling unit is available for selection again at the next step of selection, or at any other succeeding step of the sample selection procedure

scattering[14]: general term describing the change in propagation of light at the interface of two media

scattering pattern[14]: angular or spatial pattern of light intensities originating from scattering, or the related energy values taking into account the sensitivity and the geometry of the detector elements

screen[6]: a sieve or sieving medium used for separating particles in a manufacturing process

screen mesh[18]: the average number of openings per linear inch of material

screening design[4]: a balanced design, requiring relatively minimal amounts of experimentation, to evaluate the lower order effects of a relatively large number of factors in terms of contributions to variability or in terms of estimates of parameters for a model

sensitivity criterion[2]: a quantitative measure of the relative merit of two test methods, that combines the estimated variance of each method with the ability of the method to measure differences in the property of interest

sensitivity ratio[2]**, SR**: *in comparing two test methods,* the ratio of the sensitivities of the test methods with the large sensitivity in the numerator

shading[6]: the combined effect of uneven illumination, optical path and camera characteristics, which causes a variation in the image background light intensity distribution of an image

sieve[16]: a plate, sheet, or woven wire cloth, or other device, with regularly spaced apertures of uniform size, mounted in a suitable frame or holder, for use in separating material according to size. The terms sieve and screen can be used interchangeably

sieve analysis: (1) the act of obtaining a particle size distribution using sieves[16]; (2) the particle size distribution of a particulate or granular solid or sample thereof, when determined by passage through and retention on a graded set of sieves[18]

sieve classification[17]: the separation of powder into particle size ranges by the use of a series of graded sieves

sieve fraction[17]: the portion of a powder sample which passes through a standard sieve of specified number and is retained by some finer sieve of specified number

sieve mesh number[6]: the number of apertures occurring in the surface of a sieve per linear inch

sieve size of a particle[6]: the smallest sieve aperture through which a particle will pass if presented in the most favorable attitude

sieving[6]: the operation of determining the size distribution of particles in a powder by using a series of sieves

sieving diameter[6]: the diameter of the aperture of the mesh of the sieve which just allows the passage of the particle

sieving medium[6]: a network of perforated sheets used for separating particles according to their size

sifter[6]: a type of screening machine having a rotary motion substantially in the plane of the screening surface, used for the screening of powders

significance level[2]**, α**: the stated upper limit for the probability of a decision being made that a hypothesis about the value of a parameter is false when in fact it is true

single sampling[2]: *in acceptance sampling,* a sampling plan for which the decision to accept or reject a lot is based on a single sample

size fraction[6]: the portion composed of particles between two given size limits, expressed in terms of mass, volume surface area or numerical frequency

smoothing, relaxation[6]: the processing of a digitized image whereby each pixel is considered in turn and its value modified by reference to its neighbors

specification[2]: a precise statement of a set of requirements to be satisfied by a material, product, system, or service that indicates the procedures for determining whether each of the requirements is satisfied

specimen[18]: a specific portion of a material or laboratory sample upon which a test is performed or which is selected for that purpose

spherical aberration[10]: a lens defect in which the image forming rays passing through the outer zones of the lens focus at a distance from the principal plane, different from that of the rays passing through the center of the lens

sphericity shape factor[6]: the ratio of the surface area of the particle to that of a sphere of the same volume

spinning riffler[6]: a rotary sample divider *(description in Chapter 2 on Powder Sampling)*

stable suspension[1]: a suspension that has sufficient kinetic stability to prevent the occurrence of significant aggregation as measured over a relevant time frame; stability may be ascertained by suitable experimental means, such as particle size, turbidity, or sedimentation measurements

stage graticule; reticle[6]: a reference scale used to calibrate an eyepiece graticule

standard deviation[2]**, s**: *of a sample,* a measure of the dispersion of variates observed in a sample expressed as the positive square root of the sample variance

standard error of calibration[3] **(SEC)**: a measure of the calibration accuracy determined by the following equation:

$$SEC = \left(\frac{1}{n-p-1} \sum_{i=1}^{n} e_i^2 \right)^{1/2}$$

where:

n = the number of observations in the calibration data set,

p = the number of independent variables in the calibration, and

e_i = the difference between a measured value of a property and its accepted value

standard error of performance[3] **(SEP)**: a measure of accuracy determined by the following equation:

$$SEP = \left(\frac{1}{n-1} \sum_{i=1}^{n} (e_i - \bar{e})^2 \right)^{1/2}$$

where:

n = the number of observations for which the accuracy is determined,

e_i = the difference between a measured value of a property and its accepted value, and

‘ = is the mean of all e_i

Standard Reference Material® (SRM®): Certified reference material (CRM) issued by NIST. A SRM is a well-characterized material produced in quantity to improve measurement science. It is certified for specific chemical or physical properties, and is issued by NIST with a certificate that reports the results of the characterization and indicates the intended use of the material.

standardization[5]: correlation of an instrument response to a standard of known accuracy

state of statistical control[2]: a condition in which a process, including a measurement process, is subject only to random variation

statistic[2]: a quantity that is calculated from observation on a sample and that estimates a parameter of a population

steric stabilization[1]: mechanism in which particle aggregation is inhibited by the presence of an adsorbed polymer layer that is firmly anchored to the particle surface so as not to desorb during particle collisions in general, a steric stabilizer has one portion of its structure that exhibits low solubility in the dispersion medium and/or high affinity for the particle surface, and the other portion is soluble in the medium

stereology[6]: the quantitative study of three dimensional structures from two dimensional sections or projections of them

Stokes diameter[13]: equivalent diameter of the spherical particle that has the same density and terminal settling velocity as the real particle in the same liquid under creeping (laminar) flow conditions

Stokes' law[6]: the equation which determines the free-falling velocity attained by a particle under viscous flow conditions and allows calculation of particle size

Stokes-Einstein equation[6]: the equation which relates the pace of Brownian motion to the diameter of the particle in motion

subsieve fraction[17]: particle all of which will pass through a 44 μm (no. 325) standard sieve

sum of squares[2]: *in analysis of variance,* a contraction of the expression "sum of the squared deviations from the appropriate average(s)" where the average(s) of interest may be the average(s) of a specific subset(s) of data or of the entire set of data

surfactant[6]: a substance which reduces surface tension

suspension[1]: a liquid in which solid particles are dispersed

systematic error[7]: mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions minus the value of the measurand

systematic error of result[4]: a component of the error, which in the course of a number of test results for the same characteristic, remains constant or varies in a predictable way

systematic sampling[2]: the process of selecting units in a sample in accordance with a specific order or location in time or space, or both

tap density[17]: the mass per unit volume of a powder that has been placed in a specified container and has been settled under specified conditions by mechanical action

terminal settling velocity[13]: velocity of a particle through a still liquid at which the force due to gravity on the particle is balanced by the drag exerted by the liquid on the particle

test determination[4]: (1) the process of deriving from one or more test observations (observed values) the presence or absence of an attribute or the value of a characteristic or dimension of a single test specimen, or (2) the attribute (presence or absence) or value derived from the process

test method[2]: a definitive procedure for the identification, measurement, and evaluation of one or more qualities, characteristics, or properties of a material, product, system, or service that produces a test result

test portion[20]: the portion withdrawn from the test sample and entirely used in the test or observation

test result[2]: a value obtained by applying a given test method, expressed as a single determination or a specified combination of a number of determinations

test sample[20]: the sample prepared from the laboratory sample from which the test portions are withdrawn

test sieve: (1) a sieve that meets all of the minimum requirements of ASTM Committee E-11[16]; (2) a frame supporting a sieving medium intended for particle size analysis, and conforming to a standard specification[6]

test sieving[6]: the use of test sieves in a prescribed manner to perform separation of particles into size classes

threshold[6]: a gray level value which separates regions of interest from background in a gray level image

throughput[3]: the vector product of the area and solid angle of a beam at its focus and the square of the refractive index of the medium in which the beam is focussed

tolerance limits (specification limits)[4]: limits that define the conformance boundaries for an individual unit of manufacturing or service operation

tolerance specification[4]: the total allowable variation around a level or state (upper limit minus lower limit), or the maximum acceptable excursion of a characteristic

tolerances[2]: *in mathematics,* prescribed limits of variation for specified properties of a particular material based on observed values obtained by specified test methods and on samples that are representative of the material

traceability[5]: the property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons (ISO Guide 2); the ability to trace the history, application or location of an item or activity and like items or activities by means of recorded identification. (ANSI/ASQC A3-1987, A)

treatment[4]: a combination of the levels (versions) of each of the factors assigned to an experimental unit, synonym treatment combination

treatment combination[2]: *in experimenting,* one set of experimental conditions

true density; true particle density[6]: the mass of particle divided by its volume, excluding open pores and closed pores

trueness[4]: the closeness of agreement between the population mean of the measurements or test results and the accepted reference value

t-test[2]: a test of statistical significance based on the use of Student's *t*-distribution and used to compare two sample averages or a sample average and a hypothetical value

Type A operating characteristic curve[2]: an operating characteristic curve which describes the operation of a sampling plan, where the size of the lot being sampled is taken into consideration

Type B operating characteristic curve[2]: an operating characteristic curve which describes the operation of a sampling plan, where items are drawn at random from a theoretically infinite process

ultrasonic probe[6]: a point source of ultrasonic vibration

ultrasonication[1]: application of high-energy, high-frequency sonic energy to a suspension in order to disperse aggregates

uncertainity[4]: an indication of the variability associated with a measured value that takes into account two major components of error: (1) bias, and (2) the random error attributed to the imprecision of the measurement process

underflow[6]: that portion of the feed material which has passed through a screening surface

undersize[13]: portion of material composed of particles that are smaller than some specific size

undersize control screen[6]: a screen used for the removal of undesirable fines from a material

universe (population)[4]: the totality of the set of items, units, or measurements, etc., real or conceptual, that is under consideration

unstable suspension[1]: a suspension that lacks kinetic stability as measured over a relevant time frame; a highly unstable suspension is one that is subject to rapid aggregation

upper control limit[4] **(UCL)**: control limit for points above the central line

upper tolerance limit[4] **(UTL) (upper specification limit)**: a tolerance limit applicable to the upper conformance boundary of an individual unit of a manufacturing or service operation

validation[19]: proof, with reference materials or materials traceable to them, that a method is acceptable for all elements in its scope

variable[2]: a quantity to which any of the values in a given set may be assigned

variables data[2]: measurements which vary and may take any of a specified set of numerical values

variance[2] **(s^2)** : *of a sample,* a measure of the dispersion of variates observed in a sample expressed as a function of the squared deviations from the sample average

variance[2] **(σ^2)**: *of a population,* a measure of the dispersion of members of the population expressed as a function of the sum of the squared deviations from the population mean

variate[2]: a measured value that includes a random error of measurement; a variable with which a probability distribution is associated

verification[5]: checking or testing to assure conformance with the specification

vibrating screen[6]: a screen oscillated by mechanical, electrical or ultrasonic means

volume distribution[6]: the distribution by

volume of particles as a function of their size

warp[6]: all wires running lengthwise of the cloth as woven

weave[6]: the pattern formed when warp and weft wires cross each other

wedge wire screen[6] **(profile wire deck)**: a screening surface comprising wires of wedge shaped cross-section spaced from each other at a fixed dimension. The underflow thus passes through an aperture of increasing cross-section

weft; shoot[6]: all wires running crosswise of the cloth as woven

well-dispersed[1]: a state that describes a stable suspension in which the minimum particle size has been achieved; operationally defined by the observance of a constant (minimum) particle size distribution during the dispersion process

wet milling[18]: the grinding of materials with sufficient liquid to form a slurry

wet sieving[6]: the sieving of particles with the aid of a liquid

wire diameter[6]: *sieving*, the diameter of the wire in the woven cloth

wire screen[6]: a screen produced by a wire weaving process (or by pressure welding) of two layers of parallel wires set at right angles to form apertures of nominally uniform size

woven wire cloth[6]: a sieving medium of wires which cross each other to form the apertures

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ANNEX 1
SOME FORMULAE PERTAINING TO PARTICLE SIZE REPRESENTATION

1. Mean Particle Size

For a powder system comprising of spherical particles, with a fractional distribution function $f_N(a)$, the total number of particles in the system (N) are thus defined by[1]:

$$N = \int_{x_{\min}}^{x_{\max}} f_N(x)dx$$

The length of all the particles in the system can be summed and represented as:

$$L = \int_{x_{\min}}^{x_{\max}} x f_N(x)dx$$

where, x is the length of each particle.

Thus, the mean length, $\bar{x}_L = L/N$

$$\bar{x}_L = \frac{\int_{x\min}^{x\max} x f_N(x)dx}{N}$$

Similarly, a mean size can be defined in terms of the surface area and volume, and so mean surface area, $\bar{x}_A$ can be calculated as:

$$\bar{x}_A = \sqrt{\frac{\int_{x\min}^{x\max} x^2 f_N(x)dx}{N}}$$

and the mean volume, $\bar{x}_V$ as:

$$\bar{x}_V = \sqrt[3]{\frac{\int_{x\min}^{x\max} x^3 f_N(x)dx}{N}}$$

2. Size Distribution Functions

Size distributions of powders can be represented by various mathematical functions, including[1]:

(i) Log-Normal Distribution: Typically observed for granulated powders produced by spray-drying, milling of fine grained minerals and calcined aggregates:

$$f(\ln x) = \frac{1}{\sqrt{2\pi}\,\ln\sigma_g}\exp-\frac{\left(\ln x_i - \ln x_g\right)^2}{2\left(\ln\sigma_g\right)^2}$$

where, $f(\ln x)$ is the frequency function in a number, volume or mass basis,

x_g is the geometric mean size, and,

σ_g is the geometric standard deviation indicating the range of sizes.

(ii) Rosin-Rammler Distribution: Typically observed for some milled, coarse-grained materials:

$$F_M(x) = 1 - \exp-\left(\frac{x}{x_{RR}}\right)^n$$

where, $F_M(x)$ is the cumulative mass fraction finer than size x,

x_{RR} is the size parameter for which $F_M(x)$ =0.37, and,

n^{-1} is an index of the dispersion of size.

(iii) Gaudin-Schuhmann (GS) Distribution: Typically observed for coarse industrial minerals produced by processes of industrial crushing and grinding:

$$F_M(x) = \left(\frac{x}{x_{\max}}\right)^n$$

where, x_{max} is the apparent maximum particle size obtained by extrapolation, and n is the constant indicating the range of sizes present in the powder.

3. Relationship between Fractional and Cumulative Distributions

Fractional distributions can be calculated from the obtained cumulative

$$f(x) = \frac{dF(x)}{dx}$$

distribution, or *vice versa*, from the relationship:

where, $f(x)$ is the function describing the fractional distribution, and $F(x)$ is the cumulative fraction finer than x.

In this case, the distributions can be on a number or mass basis.

Conversion between Different Basis of Representation

For a powder system following a log-normal distribution of particle size, the following equations can be used for conversion from one distribution to another[2]:

$$\ln x_{NL} = \ln x_{gN} + 0.5 \ln^2 \sigma_g$$

$$\ln x_{NS} = \ln x_{gN} + 1.0 \ln^2 \sigma_g$$

$$\ln x_{NV} = \ln x_{gN} + 1.5 \ln^2 \sigma_g$$

$$\ln x_{NM} = \ln x_{gN} + 2.0 \ln^2 \sigma_g$$

where,

x_{gN} is the geometric mean (median) of the number distribution,

σ_g is the geometric standard deviation,

x_{NL} is the length mean diameter of the number distribution of the particles,

x_{NS} is the surface area mean diameter of the number distribution of the particles,

x_{NV} is the volume mean diameter of the number distribution of the particles, and

x_{NM} is the moment mean diameter of the number distribution of the particles.

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ANNEX 2
NIST RM/SRMs RELATED TO PARTICLE SIZE CHARACTERIZATION

Standard	SRM No.	Certified Value	Attribute
Silicon Nitride Powder	659	0.3 µm to 3.0 µm	Particle Size Distribution
Silicon Nitride Powder	1899 1900	10.67 m^2/g 2.79 m^2/g	Surface Area
Zirconia Powder	1978	0.3 µm to 2.2 µm	Particle Size Distribution
Zirconia Thermal Spray Powder	1982	20 µm to 90 µm	Particle Size Distribution
Alumina and Silica-alumina Powder	8571* 8572* to be replaced	158 m^2/g 291 m^2/g	Surface Area
Tungsten Carbide Cobalt Powder	1984/1985#	10 µm to 60 µm	Particle Size Distribution
Zeolite Powder	2850#, 2851#, 2853#	0.3 µm to 3.0 µm	Particle Size Distribution
Silica Sand	8010*	40 µm to 400 µm	Particle Size Distribution
Glass Beads	1021#, 1003, 1004#, 1017, 1018, 1019	1 µm to 2450 µm	Particle Size Distribution
Etched Si chip	2090	0.2 µm to 3000 µm	SEM Magnification
Graphitized Rayon Fibers	2069 b	2 mm to 4mm	SEM Performance

* Reference Material (RM) # RM/SRM under development

Sales and information about SRMs can be obtained from:

Standard Reference Materials Program
National Institute of Standards and Technology
100 Bureau Drive
Room 204, Building 202
Gaithersburg, MD 20899-2322
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