Issues in Particle Size Analysis

R. Hogg
Department of Energy and Mineral Engineering,
The Pennsylvania State University

Abstract

Important issues that arise in the acquisition, presentation and interpretation of particle size data are discussed. Presentation of size distributions as relative quantity versus size, representation of quantity by number, mass, etc., and procedures for inter-conversion of the different forms are described. Definitions of various kinds of average sizes are presented. Limitations on their use and the importance of precise definition are emphasized. Definitions of size for irregular particles, the role of particle shape and implications with regard to comparability of analytical results based on different principles and procedures are evaluated. Different types of measurement procedures are classified according to whether they involve measurements on individual particles, on separated classes of particles or on complete assemblages. The restrictions and constraints, such as size limitations and resolution which apply to these types, are discussed.

Keywords: particle size distribution, average size, surface area, size definition, size measurement, limitations and constraints on sizing procedures

Introduction

The size distribution in particulate materials is of major importance in determining system behavior and is a primary focus of most characterization efforts. Various procedures can be applied for size analysis and instruments are available based on a range of different principles. The choice of a suitable analytical method for a specific application depends on the nature of the material and the reason(s) for performing the analysis.

This paper is not intended to be a comprehensive review of procedures for particle size analysis. Details of specific procedures and their relative strengths and weaknesses have been given by Allen [1]. The primary objective here is to highlight some important issues related to the acquisition, presentation and interpretation of particle size data. Emphasis is on powders and liquid suspensions, but some reference to aerosol measurements is included for completeness.

Size Distribution

Particle systems normally involve a collection of sizes – complete uniformity is extremely rare. Consequently, it is generally necessary to express the results of an analysis in the form of a distribution: relative quantity versus particle size. The latter is usually represented by a characteristic linear dimension. Quantity is most commonly given as the fraction of the total number, mass or volume of particles that fall into some size range. Alternatively, but less frequently used, quantity can also be represented by fractional area or length. A useful generalization [2,3] is to present the distribution by a particle size density function \( q_r(x) \) defined such that:

\[
q_r(x) = \text{fractional quantity that has size between } x \\
\text{and } x + dx
\]  

(1)

where \( x \) is size and \( r = 0, 1, 2, \) or 3 corresponding to number, length, area or volume respectively. The different forms are the same only for sets of identical particles; the differences between forms increases with distribution width. The mass and volume distributions are identical unless density varies systematically with size.

Distributions can also be expressed in cumulative form by the particle size distribution function \( Q_r(x) \) where

\[
Q_r(x) = \text{fractional quantity finer than size } x
\]  

(2)

and
The above represent the distribution in continuous form, which is appropriate since size is generally a continuous variable. However, size data often appear in discrete form as the relative quantity in finite size intervals, such that

\[ q_i = \text{fractional quantity in size interval } i \]  \hfill (4)

and

\[ Q_r(x_i) = \sum_{j=1}^{i-1} (q_r)_j \]  \hfill (5)

where size 1 represents the smallest size present. Alternatively, the cumulative form may be defined as

\[ Q_r(x_i) = \sum_{j=i+1}^{m} (q_r)_j \]  \hfill (6)

where size m is the minimum size and size 1 corresponds to the maximum. In both cases, \( Q_r(x) \) represents the fraction finer than the lower limit of interval i. The choice of whether size 1 should represent the smallest or largest may depend on the application. In applications to size reduction processes size 1 is usually designated as the largest and m as an arbitrary minimum, while the reverse is more convenient for crystallization or agglomeration.

In practice, distributions are normally presented in either the discrete, incremental form (\( q_i \)), or the cumulative \( Q_r(x) \). The cumulative form offers some advantage in that size x is uniquely defined whereas the incremental form refers to a finite range. Furthermore, because \( Q_r(x) \) is by definition a monotonic function, it is typically easier to fit to an algebraic form than the more complex \( q_i \). On the other hand, the cumulative form tends to obscure fine detail in the distribution, while graphical presentation of the incremental form offers a clearer picture of the distribution of sizes. It should be noted that the incremental distribution \( q_i \) is not a direct estimate of the density function \( q_r(x) \), which can be approximated by

\[ q_r(x_i) \approx \frac{(q_i)_{i}}{\Delta x_i} \]  \hfill (7)

in which \( \Delta x \) is the size interval width, which typically is arranged to vary with size. Direct experimental determination of the density function is rarely practical.

Quantity representation by number, mass/volume etc. is usually dictated by the procedure used to acquire the data. Transformation from one representation to another, e.g. \( Q_r(x) \) to \( Q_r(x) \) can be accomplished using [2,3]:

\[ q_r(x) = \frac{x^{r-1} q_r(x)}{\int_0^x x^{r-1} q_r(x) dx} \]  \hfill (8)

with

\[ q_r(x) = \frac{d Q_r(x)}{dx} \]  \hfill (9)

Alternatively

\[ (q_i)_{i} = \frac{Q_r(x)_{i}}{m \sum_{i=1}^{m} (q_i)_{i}} \]  \hfill (10)

where \( \bar{x} \) is the average size in interval i. While such transformations are mathematically straightforward, their application requires accurate knowledge of the complete distribution, especially the “tails”. For example, in transforming from the volume \( r = 3 \) to the number \( r = 0 \) distribution, the integral in Equation 8 includes the term \( 1/x^3 \) and is therefore dominated by the finest sizes for which information on the quantity present is typically subject to the largest errors. Conversely, the reverse transformation, number to volume, is dominated by the largest sizes, for which serious statistical errors in particle counting are common. Examples of such transformations are given in the appendix.

Average sizes

If average sizes are to be used, it is critical that they be clearly defined because of the essentially infinite number of possibilities that exist for any distribution. Median sizes are defined such that

\[ Q_r(x_{m, r}) = 1/2 \]  \hfill (11)

Typically, median sizes are estimated directly from plots of the cumulative distribution \( Q_r(x) \) or by numerical interpolation of the data. Modes are given by maxima in the size density function. Mean sizes can be defined by the moments of the distribution:

\[ M_{s,r} = \int_0^\infty x^s q_r(x) dx \]  \hfill (12)

where \( M_{s,r} \) is the mean moment of the distribution \( q_r(x) \) and s can take on any value. Each moment defines a mean size:

\[ \bar{x}_{s,r} = M_{s,r}^{1/s} \]  \hfill (13)

The value of the median, mode or any particular mean increases as \( r \) increases.

Surface Area

The surface area of a collection of particles is an important characteristic in its own right and can
also be used as a measure of average size. Different measures of the surface area of a particle can result in quite different values. The geometric area is defined on the basis of an assumed macroscopic shape (sphere, cube, etc.), neglecting small-scale surface irregularities and roughness, and is directly related to size. The external area includes any such microscopic features. Cracks and pores within particles provide additional internal area, which may be independent of particle size. The total area is the sum of the external and internal contributions; its relation to size will generally depend on the relative magnitude of the two contributions.

The geometric surface area, commonly expressed as the volume or mass specific surface, \( S_v \) or \( S_m \) (surface area per unit volume or mass) can be estimated from the particle size distribution. For a sphere of diameter \( x \), \( S_v = 6/x \) which, for a collection of particles, can be used to define a specific surface mean diameter, \( \bar{x}_{sv} \) such that

\[
\bar{x}_{sv} = \frac{6}{S_v}
\]

(14)

The specific surface area can be estimated from moments of either the number or volume distribution using \([2, 3]\)

\[
S_v = k_{2,3} \frac{M_{2,0}}{M_{3,0}} = k_{2,3}M_{-1,3}
\]

(15)

where \( k_{2,3} \) is the area to volume shape factor (\( = 6 \) for spheres). Because of the inverse relationship to size, accurate estimates require precise knowledge of the fine “tail” of the size distribution.

Some examples of the estimation of surface area and various average sizes are given in the appendix.

Surface area can be determined directly by adsorption measurements (usually gas) which normally yield the total area. The permeability of a bed of particles to fluid flow can be used to estimate the external area. Comparisons of the different measurements can provide information on shape factors, surface roughness and internal porosity.

**Definition of Size**

In order to express the size of a particle as a single, linear dimension, it is strictly necessary to define its shape and to indicate which characteristic dimension is being used, e.g. diameter of a sphere, side of a cube etc. In practice, most particles are irregular in shape and simple definitions are not available. Probably the nearest thing to a unique size definition would be particle volume. Unfortunately, procedures for measuring particle volume are quite limited, especially for very small particles. The usual approach is to define size as an equivalent sphere diameter i.e. the diameter of a sphere that would be the same in some respect as the particle. Definitions and applications of some commonly used equivalent-sphere diameters are presented in Table 1.

In the case of isometric particles, for which three mutually perpendicular dimensions have the same magnitude, variations among equivalent-sphere diameters determined by different procedures can be expected to be small. However, for elongated or flattened particles variations may be quite large. Furthermore, there may appear to be variations within a set of identical particles due to orientation effects. For sizing procedures that involve gravity or inertial forces, differences in density will also lead to variations in equivalent-sphere diameter.

**Particle Size Determination**

**Sampling**

As in any characterization procedure, sampling is a critical step in the determination of particle size distributions. Procedures for avoiding physical bias in sampling particulate materials have been discussed at length by Gy \([4,5]\) and, with particular reference to size analysis, by Allen \([1]\). Statistical errors can be minimized through the use of a sufficiently large sample. A formula for estimating the required sample size can be obtained by consideration of the statistics of random mixtures \([6]\). A simplified version is given by:

\[
M \approx \frac{2\rho x_m^3}{\varepsilon^2 q_m} \text{ (grams)}
\]

(16)

where \( M \) is the required sample weight, \( \rho \) is the solid density \((g/cm^3)\), \( x_m \) is the maximum size present (cm), \( q_m \) is the smallest relative amount of that size that would be considered significant and \( \varepsilon \) is the acceptable relative error. Examples of required sample sizes are shown in Table 2.

It is clear from the table that sample size can be critical in analyses of materials containing particles larger than 1mm, but is typically satisfied automatically (by instrument requirements) in sub-sieve analyses.

**Types of Measurement Procedures**

While it is common to speak of particle size measurement, it should be recognized that procedures for determining size distribution involve measurement of both size and relative quantity. For many procedures, the actual measurement is of quantity while size is inferred from the response to external forces.
Experimental procedures generally fall into one of three groups depending on whether measurements are made on:

1. individual particles
2. classes of particles separated according to size
3. all sizes simultaneously

In the first type, individual particles are examined one at a time and their size is determined either by direct measurement as in microscopy/image analysis or through their response to some kind of sensing system as in automatic particle counters. Quantity is typically determined by simple counting, leading to a direct measure of the number size distribution. In the case of electrical sensing methods, which estimate particle volume through the reduction of electrical conductivity by electrolyte displacement, an alternative to counting is to determine the volume distribu-
tion directly by accumulating individual particle volumes.

The second group includes sieving, sedimentation and cascade impactors and involves size classification based on ability to pass through an aperture, differential settling in a fluid or particle inertia in a flow stream. Size is not measured directly but is assigned on the basis of aperture size, settling time or flow velocity (by calibration). Relative quantity is commonly determined by direct weighing of the classified material. Concentration measurement by attenuation of radiation is often used for quantity determination in sedimentation systems. Sieving and impaction give a direct measure of the incremental mass distribution; sedimentation normally yields the cumulative form.

Methods based on radiation scattering (light or sound) generally fall into the third group. The complete distribution is estimated by comparing scattering intensities for a range of angles, frequencies etc., with predictions from scattering theory. In effect, iterative procedures are used to find the distribution that gives the closest fit to the scattering data. Results are generally reported as a volume distribution. Dynamic light scattering, sometimes referred to as quasi-elastic light scattering (QELS) or photon correlation spectroscopy (PCS), uses autocorrelation procedures to evaluate fluctuations in scattering intensity at a fixed angle, typically 90°. Characteristic time-scales for the fluctuations are used to estimate diffusion coefficients due to Brownian motion which are related to size through the Stokes-Einstein relationship. Estimates of the size distribution are obtained by curve-fitting to standard forms.

Restrictions and Constraints

All experimental test procedures have relative advantages and disadvantages. Besides differences between systems operating on the same basic principle, there are inherent problems associated with each of the general approaches.

**Size Limitations:** Most of the available techniques have an optimum range of applicability. While this range can be quite broad – imaging techniques such as microscopy, for example, can cover the entire range from molecular to astronomic – the practical limits for any specific application are usually much narrower. At any particular scale, image analysis is generally limited to a size range of not much more than 10:1. The lower end is limited by resolution and the upper by counting statistics. Similar constraints apply to other analytical procedures.

An important distinction can be made between two basic types of size limits:
- **Measurement limits**
- **Detection limits**

Measurement limits arise when a procedure recognizes the existence of particles outside of the range of applicability and provides a measure of their quantity. Sieving procedures provide a good example of measurement limits. Size information is provided only over the range of sieve sizes used but the quantities coarser than the coarsest sieve and finer than the finest are readily determined. Detection limits occur when particles outside of the range are invisible to the system and are assumed to be absent. This type is normally associated with the lower end of the range. Apparent size distributions obtaining using systems subject to measurement and detection limits are compared in Fig. 1.

Procedures based on individual particle counting are especially prone to detection limits. For imaging methods, the problem can be addressed by the use of progressively higher magnification. However, since observations at a particular magnification are essentially subject to detection limits, construction of the overall size distribution requires matching of the separate data sets obtained at the different magnifications. Problems associated with the matching procedures can be a major source of errors in the application of image analysis to systems with broad size distributions.

Automatic counters based on light scattering or electrical sensing are usually subject to an absolute limit. Such instruments are inappropriate for use with materials containing undersize particles. The results of measurements for which substantial quantities are reported at sizes adjacent to the lower limit should be regarded as questionable.

Methods that involve size separation are generally

![Fig. 1](image-url) **Fig. 1** The effect of lower size limits on size distribution measurements.
subject only to measurement limits. Grossly oversize particles can present problems in sedimentation because of their very high settling rate which leads to difficulty in preparing uniform initial dispersions. Oversize particles can lead to blockage of orifices in cascade impactors applied to airborne particles. However, high settling velocities tend to eliminate such particles prior to entering the device.

Lower detection limits are typical also for radiation scattering systems. Scattering by particles smaller than the wavelength of the incident beam is relatively weak and insensitive to scattering angle. Since information on how scattering from such particles is handled in the algorithms used to estimate size distribution is not generally available to the user, the exact nature of these limits is unclear. Again, reported distributions showing large quantities close to the lower limit should be treated with caution. Modern, commercial scattering systems often claim “full-range” capability, from < 1µm to about 1 mm. This is certainly advantageous for samples whose size range is not known a priori. However, its value is limited by the need to minimize settling of coarse particles so as to maintain a homogeneous suspension in the field of view. For low-density materials, this can be achieved by dispersion in liquids of similar density but this is impractical for higher density solids such as most minerals.

The existence of a finite range of applicability for most sizing procedures can present problems in the analysis of materials containing a broad range of sizes – soil samples, for example, may include particles ranging from pebbles 1 cm or larger down to submicron clay particles. Particle modification processes such as comminution often involve progressive reduction in size from as large as tens of centimeters to micron and sub-micron sizes. In such cases, it is usually necessary to employ more than one procedure for complete characterization of the material or evaluation of the process.

The first step in implementation of a two-stage size analysis is to separate the material into a coarse and a fine fraction at some intermediate size. Since sieving generally provides the sharpest separation, this is usually the preferred method for making the separation and, by extension, for analysis of the coarse fraction. The fine fraction can be analyzed by an appropriate method such as light scattering or sedimentation. Because the two measurement procedures involve different definitions of size, there remains the question of matching the two parts of the complete distribution. A simple, and usually effective, solution is to provide significant overlap between the two sets of measurements, for example by sieving down to 400 US mesh (37 µm) and performing the sub-sieve analysis on a -200 mesh (74 µm) fraction. The complete distribution is obtained by adjusting one of the sets of sizes so as to produce a smooth, continuous cumulative curve. An example of the evaluation of the complete distribution from a two-stage analysis is given in Fig. 2.

Applications to processes such as comminution are also sensitive to detection limits at the finest sizes. Evaluation of ultrafine grinding processes often requires analysis of sets of size distributions starting from a relatively coarse feed to final products that may extend well into the submicron range, thus necessitating the two-stage approach. The use of sedimentation methods for the sub-sieve stage, while tedious, generally provides the greatest accuracy. Because of their operational simplicity, light scattering procedures present an attractive alternative. However, uncertainty with regard to their lower size limit means that these methods should be used with caution. Standard light scattering systems can be extended into the submicron range but claims of further extension to still finer sizes are of dubious valid-

![Figure 2: Example of the combination of sieve and subsieve data to obtain an overall size distribution. Procedure:](image)
Angular scattering patterns for such particles are relatively insensitive to size, while scattered intensity at any angle decreases so drastically with size that contributions from fine particles are overwhelmed by those from coarser material.

The validity of light scattering data for ultrafine material can be assessed using supplementary measurements of surface area by gas adsorption whose accuracy actually increases with decreasing size. An example of this approach is shown in Fig. 3 based on data for the grinding of quartz from a feed size of about 50µm to a final product with a maximum size of about 0.3µm. It can be seen from the figure that the measured areas are in direct proportion for the coarser products with an approximately 4:1 ratio of the gas adsorption area to that from light scattering, reflecting the role of irregular shape and surface roughness. For the finer products, obtained after grinding for more than 8 hours, the BET area shows a steady increase relative to that derived from light scattering. This deviation is attributed to the failure of the light scattering system to account fully for particles smaller than about 0.2µm.

Resolution: Different procedures for size analysis vary in their ability to discriminate between sizes. Methods such as microscopy and automatic particle counters that involve measurements on individual particles generally provide the highest resolution. Those such as light scattering that estimate the size distribution from the collective response of the whole system are typically less able to discriminate and tend to smooth over fine detail in the distribution. Dynamic light scattering, for which the distribution is typically estimated by fitting to a standard form, tends to have quite low resolution. Procedures such as sieving, impaction and sedimentation, which include separation by size, fall somewhere between the other two groups. Sieving provides excellent discrimination at the actual aperture sizes but gives no information on intermediate sizes. The situation is similar for cascade impactors, although the sharpness of separation is lower. Sedimentation methods can give information at any size but resolution is also limited by low separation sharpness.

Resolution is particularly important in the analysis of narrow size distributions, low resolution invariably leading to an apparent broadening of the distribution [7]. Precise description of the “tails” of the distribution is critical to some applications. For example, a single oversize particle in an abrasive powder used for surface polishing can lead to catastrophic results [8]. High resolution is a necessity for the analysis of such materials.

Operational Constraints: In addition to factors such as precision, resolution, reproducibility, etc., there are other requirements that influence the appropriateness of the different procedures for specific applications. These include response time, versatility, requirements for operator skill and experience, equipment cost and availability and on-line capability. Response time is critically important in quality control and, especially, direct process control applications. Laser scattering/diffraction systems are particularly attractive for such applications. Instrument response times are typically a few minutes so that dispersion stability is not critical. As a consequence, sample preparation is usually fairly straightforward. Automatic particle counters also offer very rapid instrument response. However, problems with aperture blockage and/or sensing zone contamination tend to reduce reliability and render sample preparation more critical. Microscopy and the separation-type procedures such as sieving, sedimentation and impaction for which response times can be several hours are obviously unsuitable for such applications.

Versatility in terms of applicability to a variety of materials and physical conditions can be important where access to a broad range of equipment may be limited. Light scattering systems can be applied to most materials, cover a broad range of sizes and can be applied to particles suspended in liquid or gas, but require relatively expensive, dedicated equipment. Sieving requires fairly low-cost equipment but is generally limited to particles coarser than about 20 µm. Sedimentation methods are mostly restricted to particles in liquid suspension while impactors are only applicable to aerosols.

Some procedures require considerable skill and
experience on the part of the operator in order to ensure reliable, accurate results, while others need only a basic knowledge of the operating procedure. Modern light scattering systems and, to some extent, automatic counters generally fall into the latter category while sieving, sedimentation and especially microscopy/image analysis and cascade impactors are more demanding. In all cases, however, sufficient experience and understanding of the process, to identify suspect results etc., is desirable.

Of the standard, laboratory procedures, light scattering offers the greatest potential for on-line applications. Problems include the substantial dilution often needed for slurry systems and deposition on cell windows in aerosol measurements. Acoustic measurements on slurries can be made at high concentrations, but resolution is generally low for these methods and the presence of air bubbles can lead to serious errors.

Errors occur in all measurements. In size analysis, errors can be associated with size and/or quantity. As noted previously, with the exception of imaging methods, size is generally assigned, by theory or calibration, rather than by actual measurement. Consequently, most of the error typically occurs in the quantity measurement. Even with image analysis, size estimation can be made reasonably accurate and errors usually arise from counting statistics, especially in determination of the volume distribution - a single particle of size 10 units is equivalent to 1000 of size one unit. At the same time, while the image size may be accurately determined, the actual particle size is typically overestimated due to preferred orientation.

Errors in analysis by sieving can generally be attributed to failure to ensure that all particles small enough to pass through each opening actually do so. Blinding of fine sieves by adhesion and/or bridging over openings can seriously exacerbate this problem. The result is that sieving tends to overestimate size and, if blinding occurs, to narrow the apparent distribution.

Errors in analysis by automatic counters commonly result from failure to recognize the detection limit and from the problem of coincidence - simultaneous passage of more than one particle through the sensing zone. The latter can be minimized by choosing a sufficiently low concentration. However, if the concentration is too low, background noise can become significant, leading to false counts. Complete dispersion of the particles is obviously a requirement but, because of the low concentrations used and the rapid response time, reagglomeration is not usually a problem. Bias in sampling can also lead to errors, particularly in the use of electrical sensing methods. Typical procedures involve pre-dispersion of the particles in an appropriate (usually aqueous) solution followed by addition to the electrolyte used in the measurement. A common approach is to add the dispersion drop-wise from a pipette or eyedropper until the desired concentration is reached. Preferential settling of the larger particles in the pipette can produce significant bias. The recommended procedure is to transfer and rinse out the entire amount of a small quantity in the pipette and repeat as needed.

Most sedimentation systems for particle size analysis involve measurement of the relative concentration of particles remaining in suspension at some depth after some time of settling. The depth and time define the settling velocity and, through the use of Stokes law, the size of the largest particles remaining, while the relative concentration is equal to the fraction finer than that size. Stokes law is strictly valid only for small particles, typically finer than about 50µm for gravity settling of minerals in water. This is often considered to establish an upper size limit to the procedure. However, this problem is easily surmounted through the use of Haywood correlations [9] or the expressions presented by Concha and Almendra [10]. In practice, the upper limit is dictated by problems in making measurements at very short times. Similarly, the lower size limit is often ascribed to the effects of Brownian motion. It seems more likely, however, that this limitation is due primarily to other factors such as sampling errors and thermal gradients, etc. [1,11]. The lower size limit can be reduced through the use of centrifuges, at the cost of increased complexity of the experimental procedure and data analysis [1]. It should be noted that reduction of the lower size limit is accompanied by an equivalent reduction in the upper limit.

Errors in sedimentation size analysis are normally associated with the concentration measurement. In the case of sampling types such as the classical Andreasen pipette, errors can occur due to disturbance during sampling, cross-contamination between samples and inaccurate concentration measurement. X-ray attenuation is often used for in situ concentration measurement thus avoiding problems associated with sample extraction. Absorption of X-rays by suspended solids depends on the atomic weight of the elements involved. When only light elements are included, as in silicate minerals and especially organics, relatively high solids concentrations are required
to ensure reliable concentration estimates. This can lead to hindered settling effects that slow down the overall settling process leading to apparently finer distributions. Particle interactions can also affect the relative settling rates among different sizes thus invalidating the size-separation basis of the technique and can cause an apparent narrowing of the distribution. Stabilization of the suspension to eliminate reagglomeration of the particles during the rather long settling times normally required is critically important. Unexpectedly narrow apparent distributions, especially those showing a sharp cut-off in the fine sizes, are often an indication of inadequate stabilization of the suspension.

Errors in size analysis by light scattering can be attributed to the resolution problems noted previously and to orientation effects for non-spherical particles. Such particles are assigned a size based on the cross-sectional area presented to the incident light. The size assigned is interpreted as a volume diameter and is usually larger than the true value, especially for flattened particles. The result is that light scattering systems typically report size distributions that are coarser than those obtained by other methods [7].

The restrictions and constraints associated with widely-used analytical procedures are summarized in Table 3.

### Nanoparticles

Since most of the analytical procedures described above have lower size limits close to one micrometer, determination of nanoparticle size distributions presents particular problems. Imaging methods, by electron microscopy for example, can give quite accurate measures of individual particle sizes and reasonable descriptions of narrow size distributions. However, for relatively broad distributions these methods are subject to serious problems associated with the need to use several magnifications to ensure adequate coverage of the size range and the subsequent uncertainties in matching the different sets of data. Production of suitable, well-dispersed images may also be difficult.

Dynamic light scattering is specifically applicable to particles in the nano-size range. However, procedures for the direct determination of the distribution of sizes remain to be developed. Generally, distributions are estimated by curve-fitting to standard forms. Problems associated with the extension of standard light scattering procedures into the nano-size range were discussed in a previous section of this article.

Centrifugal sedimentation is probably the most appropriate method for determining nanoparticle size distributions. However, procedures generally involve a high degree of operator skill and equipment availability is rather limited.

### Conclusions

The distribution of sizes present is a principal characteristic of any particulate system. Presentation of size analyses should always include specification of the basis of the distribution (number, volume etc.) and some indication of the definition of size used. Average sizes can be useful characteristic parameters if clearly defined. Analytical procedures generally express size as an equivalent sphere diameter defined as the diameter of a sphere that would give the same response as the particle. It follows that different methods often give different results. Procedures based on different principles are all subject to inherent restrictions and constraints; further restrictions, applicable to commercial equipment, are generally

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**Table 3 Performance characteristics of experimental procedures for particle size analysis**

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<th>Method</th>
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<th>Operational Constraints</th>
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* At any given magnification
beyond the scope of this paper.

It is recommended that the following be kept in mind in selecting the appropriate analytical procedure for a specific application:

- The definition of size used – e.g. “sieve diameter”, “area diameter”, “Stokes diameter”, etc.
- The basis for representing quantity in size ranges – number, volume, mass
- The range of applicability – since most methods can only be used over a limited range of sizes it may be necessary to use more than one method to cover a broad range of sizes and combine the data to obtain the complete distribution
- The nature of the size limits:
  - Measurement limits: information is obtained only in the range of applicability of the method but the relative amounts falling outside of the range are measured
  - Detection limits: particles outside of the range are not detected and assumed to be absent

Measurement limits are preferred; lower detection limits are especially troublesome. Upper limits can usually be avoided by pre-classification of the particles – commonly by sieving. This approach is generally impractical for lower limits due to the difficulty of precise classification at very fine sizes
- Resolution – the ability to discriminate among the sizes present and to indicate fine detail in the size distribution
- Reproducibility/repeatability – replicate analyses should agree closely
- Ease of use – the need for special operator skills
- Response time – applicability for on-stream analysis or quality control
- Special considerations – reaction with suspending liquids (e.g. water); dispersion/deaggregation problems etc.
- Sample size constraints – some procedures require relatively large samples
- Appropriateness to the particular application – e.g. the use of aerodynamic methods for airborne particulates.

Nomenclature

\[ \begin{align*}
A_s & : \text{ particle projected area (random orientation)} & [L^2] \\
A_{sr} & : \text{ particle projected area (stable rest plane)} & [L^2] \\
d_a & : \text{ projected area diameter (random orientation)} & [L] \\
d_{as} & : \text{ projected area diameter (stable rest plane)} & [L] \\
d_v & : \text{ surface diameter} & [L] \\
d_s & : \text{ Stokes diameter} & [L] \\
d_{sv} & : \text{ Specific surface mean diameter} & [L] \\
d_v & : \text{ volume diameter} & [L] \\
g & : \text{ acceleration due to gravity} & [L/T^2] \\
k_{x_2} & : \text{ surface/volume shape factor} & [-] \\
M & : \text{ sample weight} & [M] \\
M_s & : s^b \text{ moment of size distribution } q_i(x) & [L^b] \\
q_m & : \text{ specified minimum detection level} & [-] \\
q_r(x) & : \text{ particle size density function} & [L^{-1}] \\
(q_r)_i & : \text{ incremental size distribution} & [-] \\
Q_r(x) & : \text{ cumulative size distribution} & [-] \\
S & : \text{ particle surface area} & [L^2] \\
S_B & : \text{ BET (gas adsorption) surface area} & [L^2] \\
S_{LS} & : \text{ surface area by light scattering} & [L^2] \\
S_m & : \text{ mass specific surface area} & [L^2/M] \\
S_v & : \text{ volume specific surface area} & [L^2] \\
v & : \text{ settling velocity} & [L/T] \\
V & : \text{ particle volume} & [L^3] \\
x & : \text{ particle size} & [L] \\
x_i & : \text{ lower limit of size interval } i & [L] \\
x_i & : \text{ mean size in interval } i & [L] \\
x_{m} & : \text{ maximum size} & [L] \\
x_{50}(x) & : \text{ median size of distribution } q_r(x) & [L] \\
x_r(x) & : x^b-based mean size of distribution } q_r(x) & [L] \\
x_s & : \text{ specific surface mean diameter} & [L] \\
\varepsilon & : \text{ specified sampling error} & [-] \\
\mu & : \text{ fluid viscosity} & [M/LT] \\
\rho & : \text{ solid density} & [M/L^3] \\
\Delta \rho & : \text{ density difference} & [M/L^3]
\end{align*} \]

References

Appendix: Manipulation of Particle Size Data

Examples of size distribution transformations are given in Table A1 and Fig. A1. The procedure for transforming a measured number distribution to the corresponding volume distribution is shown in Table A1. The results of transformations from number to volume and vice versa, based on reasonable estimates from the same actual distribution, are illustrated in Fig. A1. Specifically, the “measured” distributions are simulated assuming a 100g sample for the volume distribution and a count of 1000 particles for the number distribution. The figure clearly demonstrates the pitfalls typically encountered in making such estimates. In each case the “calculated” distribution differs substantially from its “measured” equivalent with the major discrepancies in the tails. In principle, the estimates can be improved by increasing the amount of sample used in the analysis. However, the required increase may be very large indeed as illustrated in Fig. A2 in which it can be seen that increasing the total number of particles counted from 1,000 to as much as 100,000 still leaves considerable error in the estimated volume distribution.

Illustration of graphical estimation of median sizes is included in Fig. A1. Examples of the calculation of specific surface area and some average sizes are given in Table A2. The dominant contribution of the fine sizes in the estimation of quantities such as surface area that are inversely related to size is readily apparent from the third column of the table.

Fig. A1 Examples of size distribution transformations: number to volume and volume to number.

Fig. A2 Effect of total number of particles counted N on transformation of number to volume distribution.
Table A1: Estimation of volume distribution by transformation from measured number distribution

<table>
<thead>
<tr>
<th>Interval Boundary, µm</th>
<th>Interval Mean size, x, µm</th>
<th>Measured Number Distribution, ((r = 0))</th>
<th>Calculated Volume Distribution, ((r = 3))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cum. (Q_o)</td>
<td>Incr. (q_o)</td>
</tr>
<tr>
<td>125.0</td>
<td>105.1</td>
<td>1.00</td>
<td>0.000</td>
</tr>
<tr>
<td>88.4</td>
<td>74.3</td>
<td>1.00</td>
<td>0.001</td>
</tr>
<tr>
<td>62.5</td>
<td>52.6</td>
<td>1.00</td>
<td>0.002</td>
</tr>
<tr>
<td>44.2</td>
<td>37.2</td>
<td>0.99</td>
<td>0.004</td>
</tr>
<tr>
<td>31.3</td>
<td>26.3</td>
<td>0.99</td>
<td>0.007</td>
</tr>
<tr>
<td>22.1</td>
<td>18.6</td>
<td>0.99</td>
<td>0.011</td>
</tr>
<tr>
<td>15.6</td>
<td>13.1</td>
<td>0.98</td>
<td>0.02</td>
</tr>
<tr>
<td>11.0</td>
<td>9.29</td>
<td>0.96</td>
<td>0.033</td>
</tr>
<tr>
<td>7.81</td>
<td>6.57</td>
<td>0.92</td>
<td>0.057</td>
</tr>
<tr>
<td>5.52</td>
<td>4.65</td>
<td>0.87</td>
<td>0.095</td>
</tr>
<tr>
<td>3.91</td>
<td>3.28</td>
<td>0.77</td>
<td>0.259</td>
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<tr>
<td>2.76</td>
<td>2.32</td>
<td>0.51</td>
<td>0.291</td>
</tr>
<tr>
<td>1.95</td>
<td>1.64</td>
<td>0.22</td>
<td>0.120</td>
</tr>
<tr>
<td>1.38</td>
<td>1.16</td>
<td>0.10</td>
<td>0.050</td>
</tr>
<tr>
<td>0.98</td>
<td>0.82</td>
<td>0.05</td>
<td>0.030</td>
</tr>
<tr>
<td>0.69</td>
<td>0.02</td>
<td>0.020</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Sum: 1214.78 1
### Table A2 Estimation of average sizes from volume distribution

<table>
<thead>
<tr>
<th>Interval mean Size, ( x ) (( \mu m ))</th>
<th>Incremental Volume Distribution, ( q_3(x) ) (mm(^3))</th>
<th>( q_3(x)/x )</th>
<th>( xq_3(x) ) (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>840.90</td>
<td>0.001</td>
<td>0.00</td>
<td>0.457</td>
</tr>
<tr>
<td>594.60</td>
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<td>0.00</td>
<td>0.867</td>
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<td>420.45</td>
<td>0.004</td>
<td>0.01</td>
<td>1.490</td>
</tr>
<tr>
<td>297.30</td>
<td>0.008</td>
<td>0.03</td>
<td>2.321</td>
</tr>
<tr>
<td>210.22</td>
<td>0.016</td>
<td>0.07</td>
<td>3.275</td>
</tr>
<tr>
<td>148.65</td>
<td>0.028</td>
<td>0.19</td>
<td>4.187</td>
</tr>
<tr>
<td>105.11</td>
<td>0.046</td>
<td>0.44</td>
<td>4.850</td>
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<td>74.33</td>
<td>0.068</td>
<td>0.92</td>
<td>5.089</td>
</tr>
<tr>
<td>52.56</td>
<td>0.092</td>
<td>1.75</td>
<td>4.839</td>
</tr>
<tr>
<td>37.16</td>
<td>0.112</td>
<td>3.02</td>
<td>4.168</td>
</tr>
<tr>
<td>26.28</td>
<td>0.124</td>
<td>4.71</td>
<td>3.253</td>
</tr>
<tr>
<td>18.58</td>
<td>0.124</td>
<td>6.66</td>
<td>2.300</td>
</tr>
<tr>
<td>13.14</td>
<td>0.112</td>
<td>8.54</td>
<td>1.474</td>
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<tr>
<td>9.29</td>
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<td>9.91</td>
<td>0.855</td>
</tr>
<tr>
<td>6.57</td>
<td>0.068</td>
<td>10.42</td>
<td>0.450</td>
</tr>
<tr>
<td>4.65</td>
<td>0.046</td>
<td>9.93</td>
<td>0.214</td>
</tr>
<tr>
<td>3.28</td>
<td>0.028</td>
<td>8.58</td>
<td>0.093</td>
</tr>
<tr>
<td>2.32</td>
<td>0.016</td>
<td>6.71</td>
<td>0.036</td>
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<tr>
<td>1.64</td>
<td>0.008</td>
<td>4.75</td>
<td>0.013</td>
</tr>
<tr>
<td>1.16</td>
<td>0.004</td>
<td>3.05</td>
<td>0.004</td>
</tr>
<tr>
<td>0.82</td>
<td>0.002</td>
<td>2.75</td>
<td>0.002</td>
</tr>
<tr>
<td>0.58</td>
<td>0.001</td>
<td>1.38</td>
<td>0.000</td>
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<tr>
<td>0.41</td>
<td>0.000</td>
<td>0.63</td>
<td>0.000</td>
</tr>
<tr>
<td><strong>Sum:</strong></td>
<td><strong>1.000</strong></td>
<td><strong>82.45</strong></td>
<td><strong>40.238</strong></td>
</tr>
</tbody>
</table>

**Estimates:**

**Specific Surface Area:**

\[ S_v = 6 \sum q_3(x)/x = 0.495 \, \mu m^2/m^3 \]

**Specific Surface Mean Diameter:**

\[ \bar{x}_{sv} = 6/S_v = 1/ \sum q_3(x)/x = 12.13 \, \mu m \]

**Volume Mean Diameter:**

\[ \bar{x}_{13} = \sum xq_3(x) = 40.24 \, \mu m \]

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### Author’s short biography

**Richard Hogg**

Richard Hogg is Professor Emeritus of Mineral Processing and GeoEnvironmental Engineering at the Pennsylvania State University. He received a B.Sc. from the University of Leeds and the M.S. and PhD degrees from the University of California at Berkeley. Dr. Hogg’s research interests include fine particle processing, particle characterization, and colloid and surface chemistry.