PARTICLE SIZE MEASUREMENT

1. Introduction

The size distribution of particles in a wide variety of particulate systems is of paramount importance in the chemical processing industries. For example, the compacting and sintering behavior of metallurgical powders, the flow characteristics of granular material, the hiding power of paint (qv) pigments (qv), and the combustion efficiency of powdered coal (qv) and sprayed fluids, are all heavily influenced by the size of the constituent particles (see FLOW MEASUREMENT; METALLURGY, SURVEY; POWDERS, HANDLING, BULK POWDERS).

A particle is a single unit of material having discrete physical boundaries that define its size, usually in micrometers, μm ($1\,\mu m = 1 \times 10^{-4}\,cm = 1 \times 10^{-6}\,m$). The size of a particle is usually expressed by the dimension of its diameter. Traditionally, particle science was limited to particulate systems within a size range from 10^4 to $10^{-2}\,\mu m$, although the recent interest in nanotechnology is pushing the lower limit of interest down by one order of magnitude.

A limitation of the linear dimensional size descriptor is that only particles having simple or defined shapes, eg, spheres or cubes, can be uniquely defined by a linear dimension. The common solution to this problem is to describe a no spherical particle to be equivalent in diameter to a sphere having the same mass, volume, surface area, settling speed (uniquely defined parameters), or other defined parameters as the particle in question (Fig. 1). Therefore, a particle can be described as behaving as a sphere of diameter d.

Although this approach makes unique spherical particle size characterization possible, it does not come without important adverse consequences; the main one being that the reported size of a particle becomes dependent on the physical parameter used in the measurement. A flaky particle falling through a liquid under the influence of gravity is expected to behave as a sphere having a somewhat smaller diameter than that of the same particle measured on the basis of volume equivalence. In reporting particle size data, it is therefore necessary to specify the method by which the data were generated. Shape is a parameter that usually influences equivalent sizes, but is not taken into account in most measurement techniques. The variations in diameter equivalence for any specific nonspherical particle can generally be attributed to the shape of the particle. Furthermore, it is reasonable to expect variations in particle shape to cause apparent size variations within a particle population, thereby causing artifacts, eg, widening of the measured size distribution of the population. Because of this shape dependence, a limited amount of shape information can be inferred from ratios of spherical equivalence, referred to as shape factors, as obtained by different methods.

The choice of parameter used in the determination of size distribution should include consideration of the information needed in the interpretation of the data. For example, in the case of a manufacturer of paint pigment, the size parameter that best describes the hiding power (performance of the pigment) is the projected area of particles. A powdered catalyst manufacturer is primarily concerned with surface-area equivalence.

2. Data Representation

Particulate systems composed of identical particles are extremely rare. It is therefore useful to represent a polydispersion of particles as sets of successive size intervals, containing information on the number of particle, length, surface area, or mass. The entire size range, which can span up to several orders of magnitude, can be covered with a relatively small number of intervals. This data set is usually tabulated and transformed into a graphical representation. Size distributions can also be reduced to a single average diameter, eg, the mean, median, or mode.

2.1. Distribution Averages. The most commonly used quantities for describing the average diameter of a particle population are the mean, mode, median, and geometric mean. The mean diameter, $\bar{d}$, is statistically calculated and in one form or another represents the size of the entire particle population. It is useful for comparing various populations of particles.

The simplest calculation of the mean, referred to as arithmetic mean (count mean diameter) for data grouped in intervals, consists of the summation of all diameters forming a population, divided by the total number of particles. It can be expressed mathematically by equation 1:

$$\bar{d} = \frac{\sum n_i d_i}{\sum n_i} \tag{1}$$

where n_i is the number of particles in group i having midpoint diameter d_i. This diameter is commonly referred to as D[1,0] because the diameter terms in the numerator of the equation are of the power (d^1), and there are no diameter terms(d^0) in the denominator of the equation. There are several additional definitions of the mean that are commonly used for various types of comparisons. The most appropriate definition of the mean diameter to be used in any specific application should be the one corresponding most closely to the relevant property of the particle system under study.

The mean volume diameter (mass diameter) is the arithmetic mean diameter of all the particle volumes or masses forming the entire population and, for spherical particles, can be expressed as in equation 2:

$$\bar{d}_m = \bar{d}_v = \left(\frac{\sum n_i d_i^3}{\sum n_i}\right)^{1/3} \tag{2}$$

and used when the contribution of particles of various sizes to the total mass of the particles is of importance. This diameter is commonly referred to as D[3,0].

Similarly, the diameter of average surface area (mean surface area diameter), can be expressed as in equation 3:

$$\bar{d}_s = \left(\frac{\sum n_i d_i^2}{\sum n_i}\right)^{1/2} \tag{3}$$

and is used when the surface behavior of the particle system is of importance. This diameter is commonly referred to as D[2,0].

The diameter of average mass and surface area are quantities that involve the size raised to a power, sometimes referred to as the moment, which is descriptive of the fact that the surface area is proportional to the square of the diameter, and the mass or volume of a particle is proportional to the cube of its diameter. These averages represent means as calculated from the different powers of the diameter and mathematically converted back to units of diameter by taking the root of the moment. It is not unusual for a polydispersed particle population to exhibit a diameter of average mass as being one or two orders of magnitude larger than the arithmetic mean of the diameters. In any size distribution, the relation in equation 4 always holds.

$$\bar{d} < \bar{d}_s < \bar{d}_v \tag{4}$$

All definitions of the mean given (eqs. 1–3) are based on the number of particles being measured, and therefore are limited to techniques that give information on individual particles. Since several particle sizing techniques measure particle parameters that are related to bulk quantities, eg, surface area, volume, mass, or other quantities that do not include number of particles, different averages need to be used. The two most important means aside from the ones defined in equations 1–3 are the surface area mean, or Sauter mean diameter referred to as D[3,2], and the volume mean diameter, or the De Broukere mean diameter, referred to as D[4,3]. The Sauter mean diameter is expressed mathematically in equations 5.

$$\mathrm{D}[3,2] = \bar{d}_{sm} = \frac{\sum s_i d_i}{S} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{5}$$

where s_i is the total surface area, $n_i \pi d_i^2$, of the particles within group i and S is the total surface area for the entire population being measured. This diameter is related to the efficiency of liquid atomization (1). For a powder sample consisting of smooth spheres, which may be a reasonable assumption for a wide variety of particle systems, the surface area (measured by gas adsorption techniques), the mass, and the density of a sample are sufficient to calculate the Sauter diameter using the following relation, ρ_p is the density of the particles and M is total mass.

$$\mathrm{D}[3,2] = \bar{d}_{sm} = \left(\frac{6}{\rho_p}\right)\frac{M}{S} \tag{6}$$

The De Brouckere diameter, for spherical particles of uniform density, can be written as in equation 7, where m_i is the total mass of the particles in group i and M is the total mass for all groups.

$$\mathrm{D}[4,3] = \bar{d}_{mm} = \frac{\sum m_i d_i}{M} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \tag{7}$$

The difference between the calculations of the various types of means is probably the most confusing aspect in averaging distributions, and is a common source of confusion when attempting to compare data from different instruments.

The mode of a distribution is simply the value of the most frequent size present. A distribution exhibiting a single maximum is referred to as a unimodal distribution. When two or more maxima are present, the distribution is called bimodal, trimodal, etc. The mode representing a particle population may have different values depending on whether the measurement is carried out on the basis of particle number, surface area, mass, or volume.

The median particle diameter is the diameter that divides half of the measured quantity (mass, surface area, number), or in other words divides the area under a frequency curve in half. It is important to note that the median for any distribution takes a different value depending on the measured quantity. The median, which is a useful measure of central tendency can be easily estimated, especially when the data are presented in cumulative form. The median is the diameter corresponding to the fiftieth percentile of the distribution, and is commonly referred to as D50, or D0.5

Another frequently used average is the geometric mean, which is particularly useful for log-normal or wider (spanning over a decade) distributions. The geometric mean diameter, d_g, is calculated using the logarithm values of the measured diameters. For example, the geometric count mean diameter is given in equation 8. Similar equations can be written for the geometric surface and volume mean diameter.

$$\ln d_g = \frac{\sum n_i \ln d_i}{N} \left(d_g = \exp\left[\frac{\sum n_i \ln d_i}{N}\right]\right) \tag{8}$$

2.2. Tabular. A typical distribution as measured by modern instrumentation can include size information on tens of thousands and even millions of individual particles. These data can be listed in a computer and then sorted into a series of successive size intervals, keeping track of the measured quantity, eg, number, surface area, or mass, within each group. For narrow size distributions it may be sufficient to group the data in linear intervals, eg, 0–1, 1–2, 2–3 μm, and then list the intervals as a percent value of the whole.

Grouping into linear intervals has the disadvantage of not maintaining the resolution of the distribution constant across its width. For example, for an experiment where particle diameters are measured and classified in linear intervals from 0 to 200 μm, each interval 2 μm in width, the resolution of an interval, which can be defined as the ratio of the width of the interval to the mean interval size, would have a value of 0.5 for the first band (0–2 μm) and a value of 0.01 for the last band (198–200 μm). Classifying data on a geometric scale, eg, 1–2, 2–4, 4–8, 8–16, has the virtue of maintaining a consistent band resolution over the entire distribution. Typical particle size data are given in Table 1, along with the percent represented by each interval. This interval can be based on the total number of particles measured, the total sample weight, total volume, or any other basis upon which data might be acquired.

Cumulative frequency data, whether on a number, surface area, or mass basis, allows for easy estimates of the total number, surface area, or mass of particles less than a given size. For the data in Table 1, 12 particles out of 1000 (1.2%) had a diameter <2 μm, 7.4% <4 μm, etc. This type of representation is particularly useful for comparing multiple distributions.

2.3. Graphical. A tabular presentation offers the ultimate in precision because all data can be listed exactly as acquired, but a graphical representation offers a much easier way to compare data than tables. The two common types of plots are the frequency histogram, sometimes referred to as differential plots, and the cumulative frequency plots. Normally, the percentage of particles in a given size interval, called the frequency, is plotted against size as shown in Fig 2. It is standard practice to plot data that have been grouped in geometric progression on a logarithmic scale (Fig. 2**b**). Information on sizes within the individual intervals is not utilized. Differential frequency plots have the advantage of providing a means of comparing data from different distributions by quickly conveying information on the relative amounts in the various group intervals, provided that intervals in each distribution are identical.

The second type of graphical representation, the cumulative frequency, shown Fig. 3 for the data in Table 1, is most useful when several distributions need to be compared, especially when the intervals of the various data sets are not identical. Cumulative distributions by number are generated by summing the contributions of all the particles less than a certain diameter range and plotting this total contribution versus the lower boundary of the diameter range. From Table 1, because the 1.2% in the 1–2 μm interval is finer than 2 μm, the amount of finer material is 1.2%, the amount finer than 4 μm is 7.4%, etc. Although not as frequently encountered as the cumulative less (finer than), the cumulative greater (coarser) than a certain size can be plotted by simply reversing the order of summation of the frequency histogram to obtain the amount greater than a given diameter. Note that cumulative plots tend to conceal detail because of smoothing effect. This effect can be minimized by employing greater numbers of smaller increments when justified by the data. A plot of the particle diameter as a function of the cumulative surface area and mass (or volume) can also be used (see Fig. 3).

3. Sampling

Sampling of powders is carried out at two different levels. First, there is the taking of a sample from a gross supply of powder, eg, a rail car or a large heap. Soot sampling is actually covered by the ASTM and British Standard Institute's protocol. Discussions of gross sampling procedures are available (2-7). Sampling from larger (ie, tons) supplies of powders can be achieved using the thief sampler (Fig. 4**a**) or alternatively a powder sample can be taken from a flow of powder using a device, eg, that shown in Fig. 4**b**. When a sample in the order of 100 g to 1 kg has been obtained, a representative sample for use in size characterization equipment must then be taken. Some of the modern methods of size characterization require as little as 1 mg of powder, thus obtaining a representative sample can be quite difficult. If the powder flows well and does not contain too many fines, a device known as the spinning riffler (Fig. 4**c**) can be used. A spinning riffler consists of a series of cups that rotate under the powder supply. The time of one rotation divided into the time of total powder flow should be as large a number as possible. Although this device has been shown to be very efficient, problems can be encountered on very small (1 mg) samples, and the powder must be processed several times. Furthermore, if the powder is cohesive and does not flow well, the equipment is not easy to use. A silica flow agent can be added to the powder to enable the powder to flow (8).

4. Measurement Methods

A wide variety of particle size measurement methods have evolved to meet the almost endless variability of industrial needs. For example, distinct technologies are required if *in situ* analysis is required, as opposed to sampling and performing the measurement at a later time and/or in a different location.

All of the modern particle sizing technologies can be classified into three broad classes: (*1*) methods that fractionate particles according to size prior to detection and measurement, (*2*) methods that rapidly count and measure particles individually (particle counters), (*3*) methods that measure numerous particles simultaneously (ensemble techniques). Depending on the type of information that needs to be extracted form the size analysis, one type of technology may be advantageous over another. For example, particle counters offer the ultimate resolution, but may suffer from poor counting statistics for wide distributions, ensemble techniques are high precision, but can suffer from lack of accuracy for bimodal, or more complex distributions, while fractionation techniques offer fairly high resolution, high accuracy, but generally lower throughput. Some of those methods have been developed or adapted to measure the size distribution of dry or airborne particles, or particles dispersed in liquids.

Every method, with the exception of imaging technologies, provides the measurement of an equivalent spherical diameter in one form or another. The spherical diameter information can be deduced indirectly from the behavior of the particles passing through restricted volumes or channels under the influence of gravity or centrifugal force fields, and from interaction with many forms of radiation, or ultrasonic waves.

5. Fractionation Methods

The fractionating techniques described here are sieving, sedimentation, hydrodynamic chromatography, and field flow fractionation. This family of methods includes several distinct technologies in which the particles are separated by size before being detected and measured. Some of the fractionation techniques operate from first principle and do not need calibration, while others need calibration. Both the dynamic range and the resolution of these techniques are governed by the efficiency of the separation process they utilize. The resolution is typically better than ensemble techniques, but below that of counting methods. The dynamic range depends on the particular technique being utilized; wet and dry sieving can be used for measuring particles in the size range from 5 to several thousand microns, centrifugal, and gravimetric sedimentation is useful for particles from ~0.1 to 100 μm, and hydrodynamic chromatography and field flow fractionation are used for the particles smaller than a few micrometers.

5.1. Sieving. This is the uncontested oldest and still one of the most widely employed sizing methods in which particles are classified according to the degree to which they are retained on a series of sieves having different opening dimensions. This technique is straightforward and requires simple equipment, but without attention to details it can lead to erroneous results (9). The sieves, particularly those of finer meshes, are often damaged by careless handling and tend to become clogged with irregularly shaped particles unless agitated, but become distorted by too much agitation (10). Furthermore, it is always a concern to determine when all the particles that might pass through the sieve have done so. Nevertheless, attempts to automate the procedure have not met with notable success (11–15).

A typical sieve is a shallow pan having a wire-mesh bottom or an electroformed grid. Opening dimensions in any mesh or grid are generally uniform within a few percent. Sieves are available having openings from 5 μm upward in several series of sizes in geometric progression. Woven wire-mesh sieves have approximately square openings; electroformed sieves have round, square, or rectangular openings. Wire sieves tend to be sturdier and less expensive, and have a greater proportion of open area. They are much more frequently employed than their electroformed counterparts except in the very fine particle range where only electroformed sieves are available (16).

Dry-sieving is typically performed using a stack of sieves having openings diminishing in size from the top downward. The lowest pan has a solid bottom to retain the final undersize. Powders are segregated according to size by placing the powder on the uppermost sieve and then shaking the stack manually, or using a mechanical vibrator (17,18), or with air pulses of sonic frequency (19,20) until all particles fall onto sieves through which they are unable to pass, or fall into the bottom pan. The unit powered by sonic energy shown in Fig. 5, when used properly can efficiently vibrate the sample using very flexible diaphragms. In another device, sieves are employed one at a time within a container from which passing particles are captured by a filter. Agitation on the sieve is provided by a rotating air jet (21). The material retained by the sieve is recorded and recycled to the next coarser sieve until all the powder is exposed to the desired series of sieves or all material passes.

Wet-sieving is performed using a stack of sieves in a similar manner except that water, or another liquid that does not dissolve the material, is continually applied to facilitate particle passage. A detergent is frequently added to promote particle dispersion. This enhanced dispersion is essential at the fine end because under dry conditions, electrostatic and surface forces greatly impede clean passage and isolation of sizes. To accelerate the screening process, a partial vacuum is sometimes applied (22,23). Ultrasonic energy dislodges irregular particles trapped in sieve opening, provided it is applied in moderate density; a maximum of 0.45 W/cm^2 at a frequency of 40 kHz has been recommended (10).

The particle mass retained by each sieve is determined by weighing after drying when necessary, and each fraction is designated by the sieve size it passed and the size on which it was retained. The sieve diameter of a particle is therefore defined as the size of the sieve aperture through which the particle in question just passes through. Mass fractions of the particles are then presented in tabular or graphical form.

Sieve analysis is the workhorse of the mineral processing industry to assess ore crushing for mineral release; in heavy construction work to evaluate soils, sand, and gravel for foundation stability, in powder metallurgical operations for porosity control, and in agriculture for grading seed quality and uniformity.

5.2. Sedimentation. Measurement of the settling rate for particles under gravitational or centrifugal acceleration in a liquid provides the basis of a variety of techniques for determining particle sizes. Gas-phase sedimentation (qv) has been investigated (24), but difficulties achieving adequate particle dispersion and the effect of electrostatic charging have restricted this application. In liquid-phase sedimentation, the particles initially may be distributed uniformly throughout a liquid (homogeneous start) or concentrated in a narrow band or layer at the liquid's surface (line start). The particle movement is monitored using light or X-ray beams.

The particle size determined by sedimentation techniques is an equivalent spherical diameter, also known as the equivalent settling diameter, defined as the diameter of a sphere of the same density as the particle that exhibits an identical free-fall velocity. Thus it is an appropriate diameter upon which to base particle behavior in other fluid-flow situations. Variations in the particle size distribution can occur for no spherical particles (25,26). The upper size limit for sedimentation methods is established by the value of the particle Reynolds number(*Re*), given by equation 9:

$$\mathrm{Re} = \frac{dv\rho_p}{\eta} \tag{9}$$

where d is the particle diameter, ρ_p is the particle density, η is the liquid viscosity, and v is the terminal velocity of the particle, which can be determined from Stokes' law, given by equation 10:

$$v = \frac{2gd^2(\rho_p - \rho)}{18\eta} \tag{10}$$

where ρ is the liquid density, and g is the gravitational constant. One of the key implications of the Stokes law is that the larger particles settle at a faster rate, which is proportional to the square of the diameter ($v \propto d^2$). Therefore, the settling rate of a 10 μm particle will be 100 times that of a 1 μm particle.

Several distinct configurations of instruments used to measure the Stokes' diameters of particles are available. These variations include gravitational versus centrifugal sedimentation (2), X-ray detection versus light detection (27), scanning versus fixed detectors (28–31), and line versus homogeneous start (2,7). All of these variations come with important consequences that are reflected in the size distribution values generated by these instruments. Therefore, close attention to the actual configuration of a system is important prior to selection to ensure optimum performance for the particular task for which the sizer is intended. Gravitational sedimentation is intended for larger and higher density particles, which exhibit a relatively high settling rate, in order to obtain a distribution in a reasonable amount of time. The use of centrifugal force to accelerate the settling rate of particles is essential to monitor the movement of smaller, lower density particles. For particles where the diameters are close in value to the wavelength of light, the light intensity scattered by the particles is a strong function of particle diameters, and therefore optical correction factors are required for accurate measurements (32–34). Instruments using X rays for the detection of particle concentration do not need optical correction. Scanning detectors speed up the analysis, but reduce the resolution of the measurement. Line starts yield a differential distribution that can be characterized by a higher resolution than homogeneous starts. The latter generates a cumulative distribution in a shorter amount of time. Therefore, if resolution is preferred to throughput, a line start system having fixed detectors might be the ideal configuration.

In X-ray sedimentation, a collimated beam of X rays permits particle concentration detection as a function of mass. The relationship between the fraction of X-rays transmitted and the mass concentration of particles of atomic weight >12 is expressed as in equation 11:

$$\ln T = -\Delta\mu L C_f \tag{11}$$

where $\ln T$ is the natural logarithm of the transmittance relative to the suspending liquid, $\Delta\mu$ is the difference in the X-ray mass-absorption coefficient of the solids and the liquid, L, is the distance through the suspension in the direction of transmission, and C_f is the particle concentration. The weight percent (P_f) of particles finer than size d_f, is given by equation 12:

$$P_f = 100\frac{\ln T_f}{\ln T} \tag{12}$$

where T_f is the transmittance after time t at the distance h and T is the transmittance at the starting time. Particles having an atomic weight <12 are not efficient X-ray absorbers, and therefore are not suited for X-ray detection, and therefore optical particle detection need to be used.

Instead of monitoring X-ray transmission, some instruments use visible light to monitor concentration (35). This optical technique is generally referred to as turbidimetry or photoextinction. Light is usually used for low particle concentrations and detection of low molecular weight particles.

Centrifugal sedimentation permits evaluation of smaller diameters, but adds mechanical complexity. Both line start and homogeneous start techniques can be used within a centrifuge tube or a disk (Fig. 6). If a centrifuge tube is used in the line start mode (36), a thin layer of suspension is established above a clear liquid filling most of the tube. The layer containing the particles must be formed of a liquid slightly less dense than the other liquid but completely miscible with it. In the homogeneous start mode, the particles are mixed with the liquid to form a homogeneous suspension. The tube is then transferred to the centrifuge and spun at a predetermined rpm, or accelerating rpm for wider size distributions. A disadvantage of using a line start procedure is the possibility of streaming, in which filaments of suspension break through the interface between the suspension and clear liquid and carry down faster than they normally would fall. This problem can usually be overcome by employing a very dilute suspension and placing a second layer of intermediate density and interfacial tension beneath the suspension layer (37).

The relatively high rotation speeds of disk centrifuges (see Fig. 6) cause any liquid within the disk cavity to arrange itself to have an essentially flat air–liquid interface. Particles within the liquid migrate radially outward. The change in concentration from a homogeneous suspension at a particular radius from the center of rotation can be measured. The same is true when a thin layer of suspension is injected onto clear liquid already established in the disk. The interfacial region is somewhat perturbed by such an injection but only a small portion of clear liquid is affected. Figure 6 shows the inclusions of a cusp in the rotor face and a method of sample injection to minimize interface disturbance in a two-layer operation. In the case of the disk cavity being filled initially with homogeneous suspension, acceleration and Coriolis forces cause undesirable disturbances. Such disturbances are minor for the very small ($<1\,\mu m$) particles, however, for which centrifuges are primarily used.

Sedimentation analysis is suitable for a wide variety of materials and is used for both quality control and research work, eg, agglomeration studies (38), and gives well-defined, relatively high resolution results. The technique has been employed in the evaluation of soils, sediments, pigments, fillers, phosphors, clays (qv), minerals, photographic halides, and organic particles (39,40).

5.3. Field-Flow Fractionation. Field-flow fractionation is a general name for a class of separation techniques that fractionate a particle population into groups according to size. The work in this area has been reviewed (41).

Particles of different size are separated by differential retention time in a stream of liquid flowing through a thin channel. The channel is subjected to a force field applied perpendicular to the flow, thereby confining the particles to be separated to specific regions of the channel. The particular region of the channel the particles will occupy is dependent on the type of field applied, and the size of the particles. As the eluent flows along the channel in a laminar parabolic flow profile, the combined effect of the field and the flow is to separate the particles according to their size. The basic principle of the technique for sedimentation FFF is illustrated in Figs. 7 and 8. In this particular type of FFF, the flow field, or the driving force perpendicular to the eluent flow is a gravitational field (Fig. 7) and a centrifugal force field (Fig. 8).

A fractogram of the separation by field-flow fractionation is shown in Fig. 7**c**. In addition to gravitational and centrifugal force fields, several other types of fields, such as Flow FFF, Electrical FFF, Steric FFF, and Lift-hyperlayer FFF have been used to confine species to specific regions within the flow channels (42).

5.4. Hydrodynamic Chromatography. Hydrodynamic chromatography (HDC) is a fractionation method where the particles carried in an elution fluid are separated in column packed with spherical material. The actual separation takes place within the interstitial void spaces within the column. The various size species eluting from the column at different time are detected by a ultraviolet (uv) detector. The larger particles tend to remain in the central regions of the eluent flow, where the velocities are higher, and the smaller particles tend to migrate closer to the walls thereby experiencing lower eluent velocities. This instrument is calibrated with a series of standards of known sizes. This technology has been used for measuring the size distribution of colloidal systems such as latex, organic pigments, carbon black, emulsions, and liposomes.

6. Particle Counting Methods

Particle counting methods, also referred as stream methods, the particles to be analyzed are moved through a sensing zone where they are detected and analyzed one at a time. The family of methods does not operate on physics first principles, and therefore need to be calibrated. They offer the ultimate in resolution, but can suffer from poor counting statistics when the data is converted from a number distribution to a mass or volume distribution where the size range is greater than one decade. Because of the inherently low dynamic range of these techniques, most of the modern instruments come equipped with multiple sensors, or magnifying optics to increase their dynamic ranges.

6.1. Computer-Automated Image Analysis. Particle characterization by image analysis consists of examining and measuring the size or shape of particles that have been magnified. The pioneering studies of particle characterization by imaging technologies were carried out in the late 1960s and early 1970s (43,44). The projected area of the profiles were estimated by direct comparison with sets of reference circles, known as a reticule, engraved on the eyepiece of the microscope. The ever-increasing power of data processing capability coupled with the high performance and falling costs of television cameras and scanners has led to the development of highly sophisticated and powerful image processing and analysis systems that took place in the 1980s, and early 1990s (7). Image analyzers can extract information from negatives, photomicrographs, or directly from microscopic (both optical and electron) images by scanning or digitization techniques. Further advances in microelectronics, eg, fast frame grabbers, have led to the transformation of the highly sophisticated image analyzer of the 1990s into a much faster particle size and shape analyzer. This new breed of instruments, as shown in Fig. 9 has gained considerable popularity within the past decade. The particles to be analyzed are dynamically presented to the instrument as dry particles carried in a gas stream, or falling from a vibration feeder, or as liquid dispersions moving through thin flow cells. This type of dynamic image analysis system is normally used for particles $>5.0\,\mu m$ in diameter. The major advantage of this type of fast imaging system is that a much larger number of particles can be analyzed than in conventional image analysis systems.

Several diameter definitions are used in particle image measurements. Some of the most common are illustrated in (Fig. 10). There are several distinct Feret's diameters: GFD (Greatest Feret's Diameter) is the greatest distance between two parallel lines that do not intersect the particle. LFD (Least Feret's

Diameter) is the smallest distance between two parallel lines that do not intersect the particle, HFD (Horizontal Feret's Diameter) is the distance between two parallel lines in the vertical direction that do not intersect the particle, and VFD (Vertical Feret's Diameter) is the distance between two parallel lines in the horizontal direction that do not intersect the particle (45). The Martin's diameter, is the chord length that divides the projected particle into two equal areas with respect to a fixed direction; VMD being the Vertical Martin's Diameter, and HMD being the Horizontal Martin's diameter (46). The Equivalent Circular Area diameter (ECAD) is the diameter of a circle having the same projected area as that of the particle. The Equivalent Circular Perimeter diameter (ECPD) is the perimeter of a circle having the same perimeter as the measured particle. The Least Bounding Rectangle (LBR) is the smallest rectangle that completely encloses the particle. The fiber length (FL) is the length of a rectangle that has the same area and perimeter as the particle, and the fiber width (FW) is the width of a rectangle that has the same area and perimeter as the particle.

Some of the basic diameters illustrated in Fig. 10 can be used to characterize particle shape (47). The two most commonly used shape factors are the aspect ration (AR), and the sphericity. The aspect ratio is a measure of the elongation, or length/width ratio of the particle. The aspect ratio can be computed in a number of ways; it can be derived form the ratio of the greatest Feret's diameter (GFD) to the least Feret's diameter (LFD), or the ratio of the length of the least bounding rectangle (LBR) to the width of the least bounding rectangle, or the ratio of the fiber length (FL) to the fiber width (FW). The reciprocal of the aspect ratio is the chunkiness. The sphericity of the projected image of a particle ($4\pi A/P^2$) is a measure of the deviation from a perfect circle. It is a number between 0 and 1, with 1 representing a perfect circle.

A decision-making process called thresholding establishes the particle boundary (48,49). This boundary is taken as the point where signal amplitude is midway between the optical density of the background and the optical density corresponding to the particles. A small error in boundary location is insignificant when relatively large particles are present, but can become critical for smaller particles. The magnitude of uncertainties stemming from the error in the boundary location can be considerably higher for a projected surface-area measurement as compared to a length measurement. The mathematical transformation from length or projected surface area to volume further magnifies the measurement uncertainties.

For accurate and repeatable particle size measurement, important sample preparation requirements, eg, representative sampling, particle concentration for minimum number of touching particles, efficient and uniform particle transport to the sensing zone for particle detection and counting must be considered carefully. In order to minimize the probability of touching particles, each image should not contain more than ~5–10 particles. Because the resolution limit of a digitized image corresponds to one pixel, the maximum resolution between two sizes is, to a large extent, governed by the magnification of the image. The precision, or repeatability of the method, is related to the total number of particles counted, the width of the distribution, and the number of pixels forming the smallest particle. The proper balance between resolution, precision, and accuracy is obtained when the amount of material dispersed in any given field of view corresponds to roughly 5–10 particles per field at the magnification where the smallest particle in the distribution covers roughly 10 pixels.

Serious biases in the measured size distribution can be caused by particles touching the edge of the field of view. Simply ignoring the portion of any particle falling outside the field of view, or even tagging and discounting any particle touching the border, erroneously generates a finer distribution because larger particles have a much greater probability of touching the border of a finite field. Therefore, in addition to ignoring any particle touching the border of the field, it is necessary to incorporate a correction factor to adjust the count in each size class. The correction factor is dependent on the actual size of the field as compared to the particle size as follows:

$$C = \frac{Z_1 Z_2}{(Z_1 - F_1)(Z_2 - F_2)} \tag{13}$$

where C is the correction factor, Z_1 and Z_2 are the horizontal and vertical dimensions of the field of view, respectively, and F_1 and F_2 are horizontal and vertical Feret diameters of a particle, respectively.

Calibration of the image analyzer to convert pixel lengths to micrometers is necessary to ensure that all measurements are traceable back to the standard meter. The calibration is performed using certified stage micrometers, as provided by such organizations as the National Institute for Testing Technologies (NIST).

Microscopy (qv) is the preferred technique when particle identification or, shape evaluation is important in addition to size. Shape characterization is used in the abrasives (qv) industries, pollution or contamination assessment, and forensic studies (see FORENSIC CHEMISTRY).

6.2. Resistazone Counters. The basic principles used in a resistazone counter are illustrated in Fig. 11. The particles to be characterized are suspended in a conducting electrolyte and drawn through an orifice situated between two electrodes as shown. The presence of a particle within the zone alters the electrical resistance of the electrolyte in the inspection zone. The change in the resistance of this electrolyte plus particle system can be used to measure the size of the particle. In such a system one must take into account the possibility of multiple occupation of the zone. Advanced versions of this instrument electronically edit the pulse caused by the presence of the particle to determine if it is moving directly down the middle of the inspection zone.

6.3. Optical Counters. Optical counters have been widely used to monitor cleanroom technology and for monitoring particulate level in oil, and other fluids. Instruments manufactured by Royco Inc. (Menlo Park, Calif.) are available for studying aerosols and particles in liquids. The HIAC counter (HIAC Instruments, Monte Claire, Calif.) is a widely used stream counter for particles in fluid. One of the more recently developed optical counters is available from Particle Sizing Systems (Santa Barbara, Calif.). The configuration of a light obscuration sensor, is shown in Fig. 12. A general review of stream optical counters is available (2).

6.4. Time-of-Flight Instrumentation. In the late 1980s and 1990s, an instrument variously known as the Galai particle size analyzer or the Brinkmann size analyzer was used to characterize the size of particles by confining the particles to be characterized in an inspection zone scanned by a laser beam. This instrument is now marketed under the name of Ankersmid. The size of a particle is deduced from the time required for the laser beam to traverse a particle in the inspection zone. The basic configuration of the instrument is shown in Fig. 13. This particular system can also be used to provide shape information because the equipment is provided with logic modules for image analysis using a video camera to inspect the measurement zone. Another time-of-flight analyzer is the Lasentec Instrument. This system is has been used for on-line monitoring of particles in a slurry or a suspension.

The AeroSizer, manufactured by TSI is equipped with a special device called the AeroDisperser for ensuring efficient dispersal of the powders to be inspected. The aerosol particles to be characterized are aspirated into the inspection zone that operates at a partial vacuum. As the air leaves the nozzle at near sonic velocities, the particles in the stream are accelerated across an inspection zone where they cross two laser beams. The time of flight between the two laser beams is used to deduce the size of the particles. The instrument is calibrated with latex particles of known size. A stream of clean air confines the aerosol stream to the measurement zone. This technique is known as hydrodynamic focusing. A computer correlation establishes which peak in the second laser inspection matches the initiation of action from the first laser beam. The equipment can measure particles at a rate of 10,000/s. The output from the AeroSizer can either be displayed as a number count or a volume percentage count.

7. Ensemble Methods

Although ensemble methods are the least accurate and suffer from the lowest resolution as compared to the other classes of techniques, they are the most widely used within virtually all industries. Despite those inherent disadvantages, ensemble measurement techniques are popular because they are typically simple to use, offer high throughput, and generate high precision data, and do not require calibration.

7.1. Photon Correlation Spectroscopy. Photon correlation spectroscopy (PCS), also commonly referred to as quasielastic light scattering (QELS) or dynamic light scattering (DLS), is a technique in which the size of submicrometer particles dispersed in a liquid medium is deduced from the random movement of the particle undergoing Brownian diffusion. This technique has been used for a wide variety of materials (50–52). The basic principle of the technique is illustrated in Fig. 14.

A laser beam is focused into the cell where the particles to be measured are dispersed. A small fraction of the incident light is scattered by the particles and collected by the photomultiplier tube (PMT). The intersection between the focused laser beam and the line of sight of the PMT defines the measuring volume of the instrument. The particles in the measuring volume scatter light, a portion of which is scattered towards the PMT. The overall intensity of light collected by the PMT is the result of the superposition of the scattered wave from all the particles in the measuring volume. A set of stationary particles would produce a uniform light intensity over time, but in reality the particles dancing under Brownian diffusion create a fluctuating intensity signal. The particle size information is extracted from the analysis of this randomly fluctuating signal. Although these fluctuations are random in nature, buildup and decay times roughly correspond to the average time required for a pair of particles to move by half a wavelength with respect to each other. The diffusion coefficient, D, of the particles under study can be obtained from the autocorrelation of the intensity fluctuations collected by the detector. The hydrodynamic radius of the particles, d_{H}, is then calculated from the diffusion coefficient using the Stokes-Einstein relation:

$$d_{\mathrm{H}} = \frac{kT}{6\pi\eta D} \tag{14}$$

where k is Boltzmann's constant, T is the absolute temperature, η is the viscosity of the liquid medium, and d_{H} is the hydrodynamic diameter. Typically, this type of instrumentation is capable of measuring particles in the size range upward from 0.005 μm, where the scattered light intensity becomes too small to be detected, to roughly 1 μm at which size the particles tend to settle. For suspensions having broad distributions, or for multimodal distributions, the extraction of the particle size distribution from the autocorrelation function becomes extremely difficult, and not totally reliable. Photon correlation spectroscopy generally works well for narrow, unimodal distributions. The technique has been used for the study of microemulsions, liposomes, and many other colloidal dispersions (see COLLOIDS).

7.2. Ultrasonic Spectroscopy. This technology basically consists of using ultrasound to probe particles that are homogeneously suspended in a liquid, thereby exploiting the inherent advantage that sound waves can propagate through opaque dispersions. The raw data collection, in which the size distribution is buried, consists of measuring the loss in energy as the sound waves interact with the particles.

Two distinct approaches are being used to extract particle size data from the attenuation spectrum: an empirical approach based on the Bouguer-Lambert-Beer law (53) and a more fundamental or first-principle approach (54-56). The first-principle approach implies that no calibration is required, but certain physical constants of both phases, ie, speed of sound, density, thermal coefficient of expansion, heat capacity, thermal conductivity, attenuation of sound, viscosity for fluid phase, and shear rigidity for solid phase, are required for accurate measurements. The measuring principle is illustrated in Fig. 15. A sonic wave is sent through the dispersion, which is mechanically agitated to maintain a homogeneous suspension, and its attenuation measured by the receiver transducer. The distance traveled by the sonic wave is accurately known. The attenuation measurement is repeated for a series of frequencies ranging from 1 to 150 MHz. The attenuation of the signal results from the various extinction mechanisms: viscous, thermal, scattering, and diffraction. An iterative algorithm is used in which the theoretical attenuation spectra associated with a particular size distribution closely matches the measured spectra.

Ultrasonic spectroscopy technology, developed in the early 1990s, is proving useful in the lubricant and food industries for measurement of oil-in-water emulsions at process concentrations. As this technology further develops and matures, it is anticipated to find a wider range of industrial applications.

7.3. Laser Diffraction Equipment. Laser diffraction instruments are by far the most common types of instrumentation used for particle size characterization in the chemical industry. Although these instruments inherently have poor resolution, and often suffer from poor accuracy, they owe their popularity to ease of use, high throughput, wide dynamic range, and low maintenance requirements. They are generally good quality control instruments when used properly.

The size distribution of a population of particles in suspension is measured from the angular variation in the intensity of light scattered by the particles. Modern instruments are equipped with modules for liquid dispersion as well as aerosol dispersion for wet or dry analysis. The particles whose diameters are much larger than the wavelength of light scatter predominantly in the forward direction and the particles with a diameter that is of the same order as the wavelength will scatter more efficiently at wider angles. Therefore, the angular scattering pattern of a population of particles is the signature of the size distribution function of the particle population. Figure 16 illustrates the basic principle behind laser diffraction instruments for the determination of particle size distribution.

As an electromagnetic wave encounters a particle, a number of processes can occur, depending on the size and optical properties of the particle. Light–particle interaction can take place through external reflection, internal reflection, absorption, and diffraction. If the particle diameter is large compared to the wavelength, (particles $>10\,\mu\text{m}$ in diameter) diffraction is the only significant phenomenon that needs to be considered. If the particle diameter is of the same order as the wavelength, a more complex scattering theory is applied where all light–particle interactions need to be considered. As a result, the reliability of laser diffraction instruments is greatly diminished in the size range below a few microns in diameter. Comparison of particle data from a diffractometer with that from an image analyzer (Fig. 17) indicates that there is some difference between size distributions as determined by the two methods.

8. Selection of Equipment

Because of the diversity of technologies for particle sizing applications, each of which explores the size distribution from a different perspective, the size distribution as generated by different methods generally do not agree. A careful evaluation of the particulate system to be evaluated must be carried out before attempting to select a particular family of technology, and corresponding instrument. Items that will affect the quality of the data, which need to be considered are the size range, accuracy, detection limits, and resolution of any particular technology. Other important items are initial instrument cost, operational cost, throughput, reliability, and quality of maintenance program from the manufacturer. Instrument validation is a must prior to committing to any particular technology.

BIBLIOGRAPHY

"Size Measurement of Particles" in *ECT* 1st ed., Vol. 12, pp. 472–497, by K. T. Whitby, University of Minnesota; in *ECT* 2nd ed., Vol. 18, pp. 310–324; in *ECT* 3rd ed., Vol. 21, pp. 106–131, by C. Orr, Micrometrics Instrument Corp.; in *ECT* 4th ed., Vol. 22, pp. 256–278, by R. Trottier, Aluminum Co. of America, and B. Kaye, Laurentian University; "Size Measurement of Particles" in *ECT* (online), posting date: December 4, 2000, by R. Trottier, Aluminum Co. of America, and B. Kaye, Laurentian University.

CITED PUBLICATIONS

1. R. A. Mugele and H. D. Evans, *Ind. Eng. Chem.* **43**, 1317 (1951).
2. B. H. Kaye, *Direct Characterization of Fineparticles*, John Wiley & Sons, Inc., New York, 1981.
3. Technical data, Spinning Riffler, The Gilson Co. Inc., Worthington, Ohio, and Quantachrome Corp., Boynton Beach, Fla.
4. C. H. Murphy, *Handbook of Particle Sampling and Analysis Methods*, VCH Publishers, Weinheim, Germany, 1984.
5. K. Sommer, *Sampling of Powders and Bulk Materials*, Springer-Verlag, New York, 1986, p. 291.
6. *British Standard Methods for the Determination of Particle Size Powders*, Part I, *Subdivision of Gross Sample Down to 0.2 Milliliters*, BS3406 Part I, British Standards, London, 1961.
7. T. Allen, *Particle Size Analysis*, 4th ed. Chapman and Hall, London, 1992.
8. B. H. Kaye, J. Gratton-Liimatainen, and John Lloyd, *Part. Part. Syst. Charact.* **12**(4), 194 (Aug. 1995).
9. K. Leschonski, *Powder Technol.* **24**, 115 (1979).
10. J. Hidaka and S. Miwa, *Powder Technol.* **24**, 159 (1979).
11. K. Schonert, W. Schwenk, and K. Steier, *Aufbereit. Tech.* **15**, 368 (1979).
12. B. H. Kaye and N. Robb, *Powder Technol.* **24**, 125 (1979).
13. B. H. Kaye and M. R. Jackson, *Powder Technol.* **1**, 43 (1967).
14. R. W. Bartlet and T. H. Chin, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **256**, 323 (1974).
15. C. Orr, D. K. Davis, and R. W. Camp, *Powder Technol.* **24**, 143 (1979).
16. A. Rudolph, C. Peters, and M. Schuster, *Aufbereit. Tech.* **33**, 384 (1992).
17. K. T. Whitby, *Symposium on Particle Size Measurement*, ASTM Special Technical Publication No. 234, ASTM, Philadelphia, Pa., 1959, p. 3.
18. J. E. English, *Filtr. Sep.* **11**, 195 (1974).
19. H. O. Suhm, *Powder Technol.* **2**, 356 (1968–1969).
20. C. W. Ward, *Powder Technol.* **24**, 151 (1979).
21. B. J. Wahl and P. Larouche, *Am. Ceram. Soc. Bull.* **43**, 377 (1964).
22. J. D. Zwicker, *Am. Ceram. Soc. Bull.* **45**, 716 (1966).
23. H. B. Carroll and B. Akst, *Rev. Sci. Instrum.* **37**, 620 (1966).
24. F. S. Eadie and R. E. Payne, *Iron Age* **174**, 99 (1954).
25. D. W. Moore and C. Orr, Jr., *Powder Technol.* **8**, 13 (1973).
26. C. Bernhardt, *Part. Part. Syst. Charac.* **8**, 209 (1991).

27. B. B. Weiner, D. Fairhurst, and W. W. Tscharnuter, *ACS Symp. Ser.* **472**(2), 184 (1991).
28. M. Weber, B. Cai, and L. Kunath, *Aufbereit. Tech.* **31**, 351 (1990).
29. J. P. Olivier, G. K. Hickin, and C. Orr, Jr., *Powder Technol.* **4**, 257 (1970–1971).
30. P. Sennett, J. P. Olivier, and G. K. Hickin, *Tappi* **57**, 92 (1974).
31. P. K. Herrmann, *Keram. Z.* **31**, 275 (1979).
32. M. J. Devon, T. Provder, and A. Rudin, in Ref. 45, p. 134.
33. M. J. Devon and co-workers, in Ref. 45, p. 154.
34. K. F. Hansen, *ACS Symp. Ser.* **472** (2), 169 (1991).
35. C. C. McMahon, *Cer. Bull.* **49**, 794 (1970).
36. R. L. Hoffman, *J. Colloid Interface Sci.* **143**, 232 (1991).
37. B. Scarlet, M. Rippon, and P. J. Lloyd, *Proceedings of the Conference on Particle Size Analysis*, The Society for Analytical Chemistry, London, 1967, p. 242.
38. G. Staudinger and M. Hangl, *Part. Part. Syst. Charac.* **7**, 144 (1990).
39. C. J. Thomas and D. Fairhurst, in K. Sharma and F. J. Micale, eds., *Proceedings of the Fine Particle Society Symposium*, Plenum Press, New York, 1989, p. 213.
40. J. C. Thomas, A. P. J. Middelberg, J. F. Hamel, and M. A. Snoswell, *Biotechnol. Prog.* **7**, 377 (1991).
41. K. D. Caldwell, in H. G. Bart, ed., *Modern Methods of Particle Size Analysis*, Vol. 73, Monographs on Analytical Chemistry and its Applications, John Wiley & Sons, Inc., New York, 1984.
42. C. J. Giddings, *Field-Flow Fractionation: Analysis Macromol., Colloidal, Particulate Mate.*, **260**, 1456 (1993).
43. H. H. Heywood, *Proc. Second Lunar Sci. Conf.* **13**, 1989 (1971).
44. H. H. Hausner, *Symposium on Particle Size Analysis*, Loughborough, U.K., 1967.
45. L. R. Feret, *Assoc. Int. l'Essai Mater. Group D* (Zurich) **2** (1931).
46. G. Martin, C. E. Blythe, and H. Tongue, *Trans. Ceram. Soc.* **23**, 61 (1924).
47. R. XU, O. Andreina Di Guida, *Powder Technol.* **132**, 145 (2003).
48. J. S. Glass, *Chem. Eng. Prog.* **68**, 58 (1972).
49. J. C. Russ, *Computer Assisted Microscopy—The Measurement and Analysis of Images*, North Carolina State University, Raleigh, 1990.
50. R. Pecora, ed., *Dynamic Light Scattering, Applications of Photon Correlation Spectroscopy*, Plenum Press, New York, 1985.
51. D. S. Horne, *Proc. SPIE-Int. Soc. Opt. Eng.* **1430**, 166 (1991).
52. N. Ostrosky, D. Sornette, P. Parker, and E. R. Pike, *Opt. Acta*, **28**, 1059 (1981).
53. U. Krauter and U. Riebel, *Proceedings of the First International Particle Technology Forum*, Part 1, *Particle Characterization*, American Institute of Chemical Engineers, New York, 1994, p. 30.
54. F. Alba, C. L. Dobbs, and R. Sparks, *Proc. SPIE-Int. Soc. Opt. Eng.* **1430**, 36 (1991).
55. P. S. Epstein and R. R. Carhart, *J. Acoust. Soc. Am.* **25**, 533 (1953).
56. J. R. Allegra and S. A. Hawley, *J. Acoust. Soc. Am.* **S1**, 1545 (1972).

REMI TROTTIER
STEWART WOOD
The Dow Chemical Company

Table 1. **Particle Size Distribution**

Diameter range, μm	Number	Percent, %	Cumulative finer % (high size)
1–2	12	1.2	1.2
2–4	62	6.2	7.4
4–8	185	18.5	25.9
8–16	250	25.0	50.9
16–32	295	29.5	80.4
32–64	172	17.2	97.6
64–128	22	2.2	99.8
128–256	2	0.2	100.0

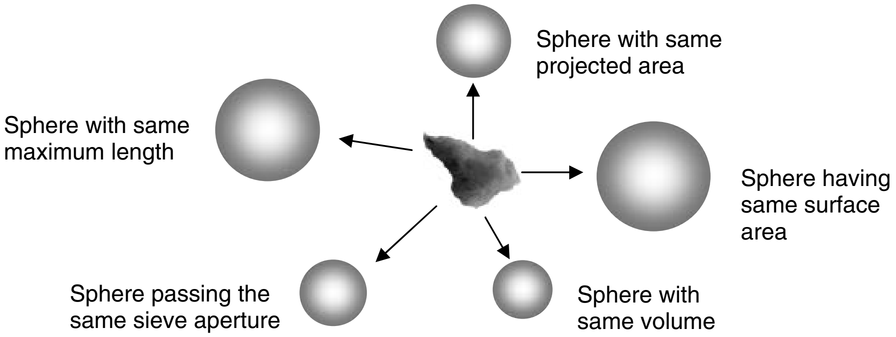

Fig. 1. Nonspherical particles can have a number of different diameters depending on which parameter of the particle happens to be measured.

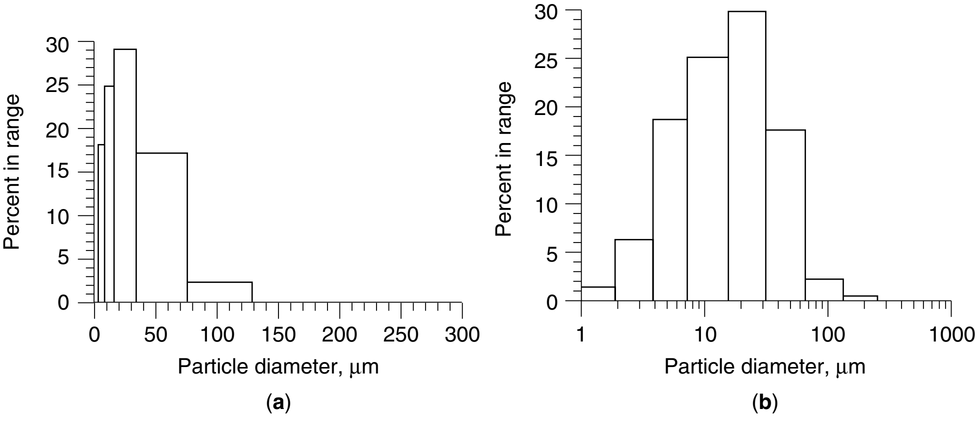

Fig. 2. Histograms of the data from Table 1, plotted on (**a**) a linear and (**b**) a logarithmic scale.

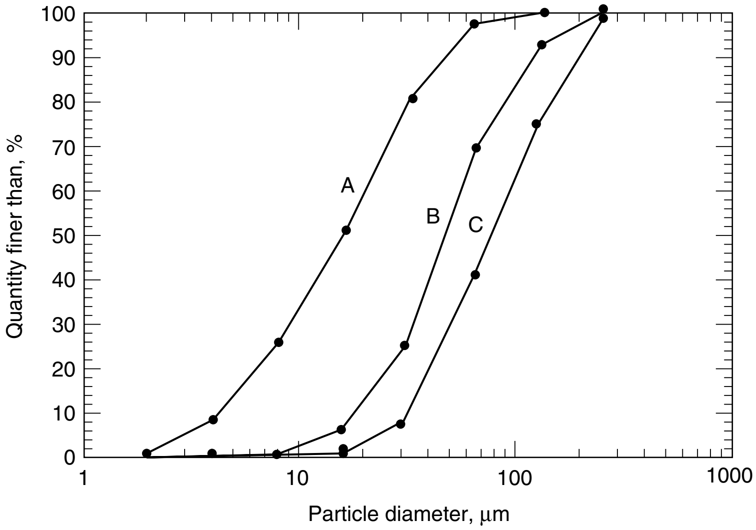

Fig. 3. Cumulative frequency distribution plotted by A, number; B, surface area; and C, volume, for the data in Table 1.

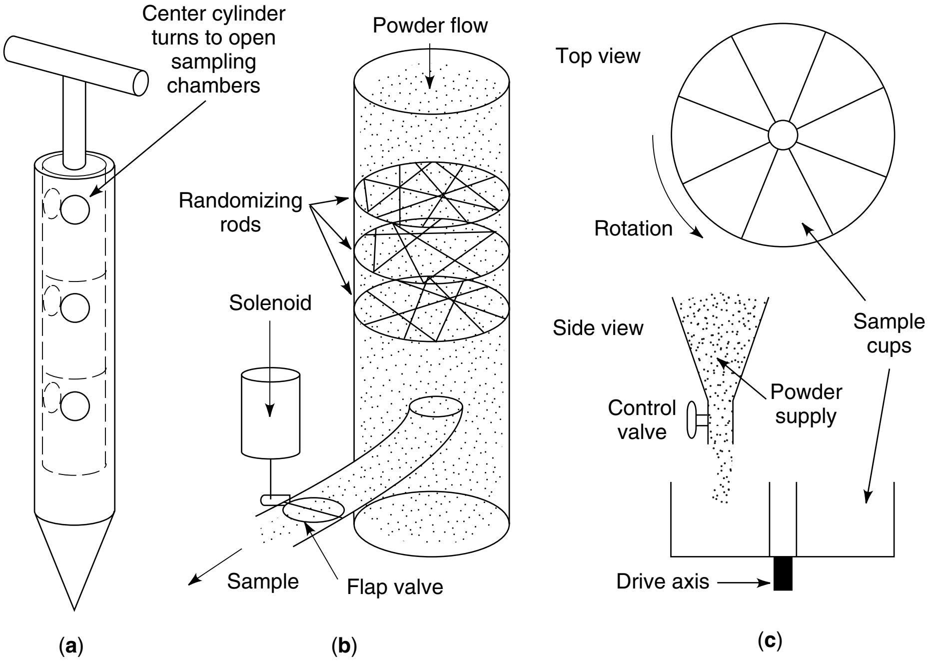

Fig. 4. Types of samplers for obtaining small (1 mg to several g) representative samples from a bulk supply of powder: (**a**) thief sampler; (**b**) passive sampler; (**c**) spinning riffler.

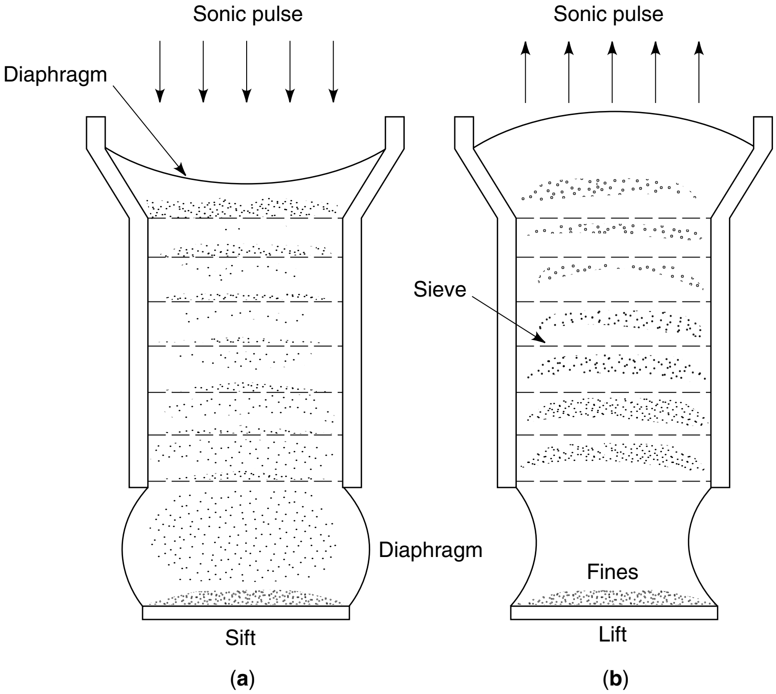

Fig. 5. Dry-siever employing sonic frequency: (**a**) particles falling through sieves on downward sonic pulse; and (**b**) particles lifted by upward sonic pulse.

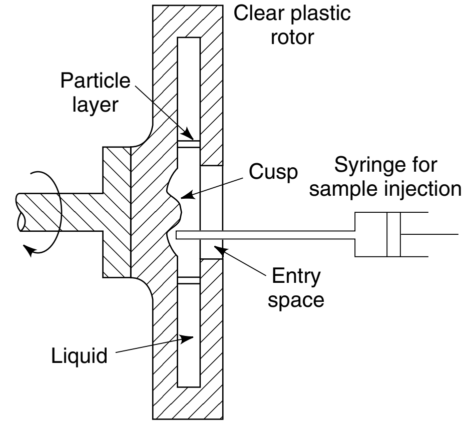

Fig. 6. Disk profile showing injection method.

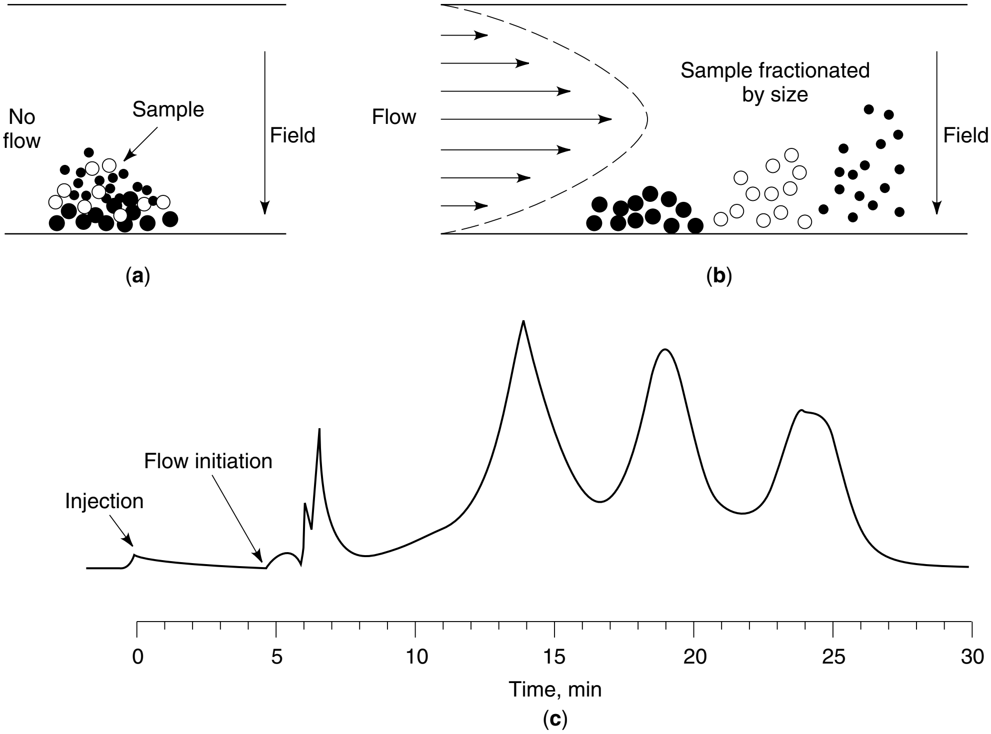

Fig. 7. Principles of field-flow fractionation: (**a**) sample equilibrium position before flow is initiated, (**b**) fractionated sample after flow initiation, and (**c**) a fractogram for silica particles subjected to a flow rate of 39.1 mL/h.

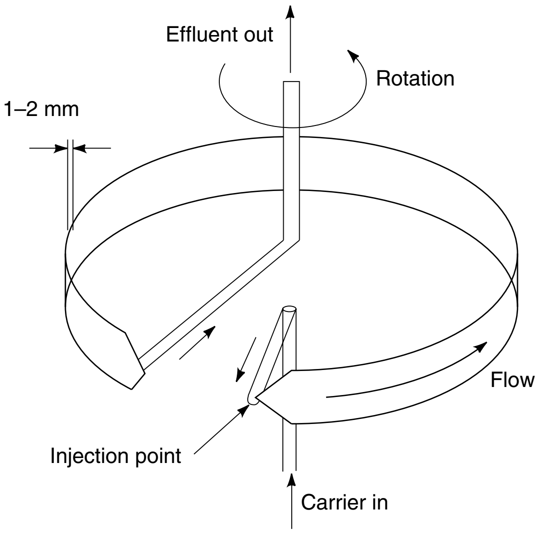

Fig. 8. Centrifugal sedimentation field-flow fractionation equipment deposits particles along the circumference of the disk by size. The fluid enters and leaves the disk axially.

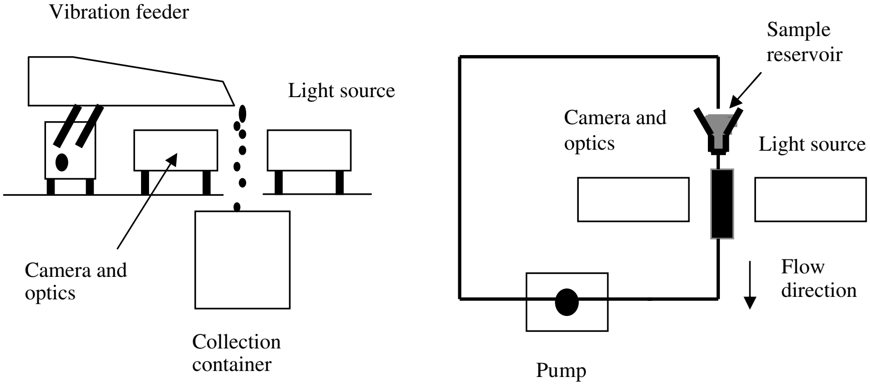

Fig. 9. Dynamic image analysis systems: (**a**) dry dispersion system, and (**b**) wet dispersion system.

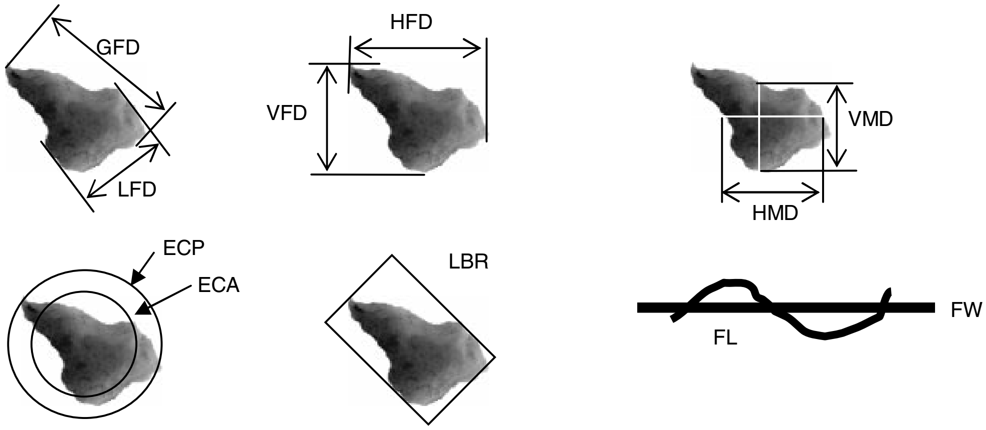

Fig. 10. Visual representation of diameters frequently used in image analysis.

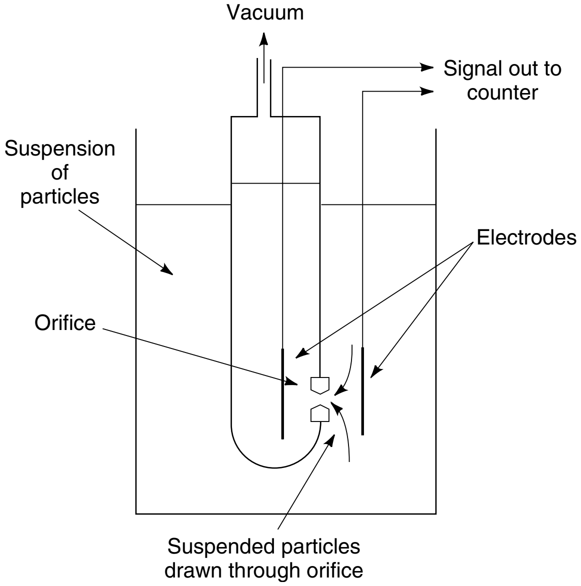

Fig. 11. Simplified schematic of an electrozone stream counter.

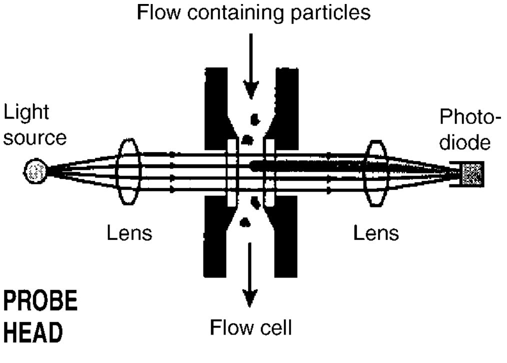

Fig. 12. Schematic representation of the internal structure of a light obscuration sensor.

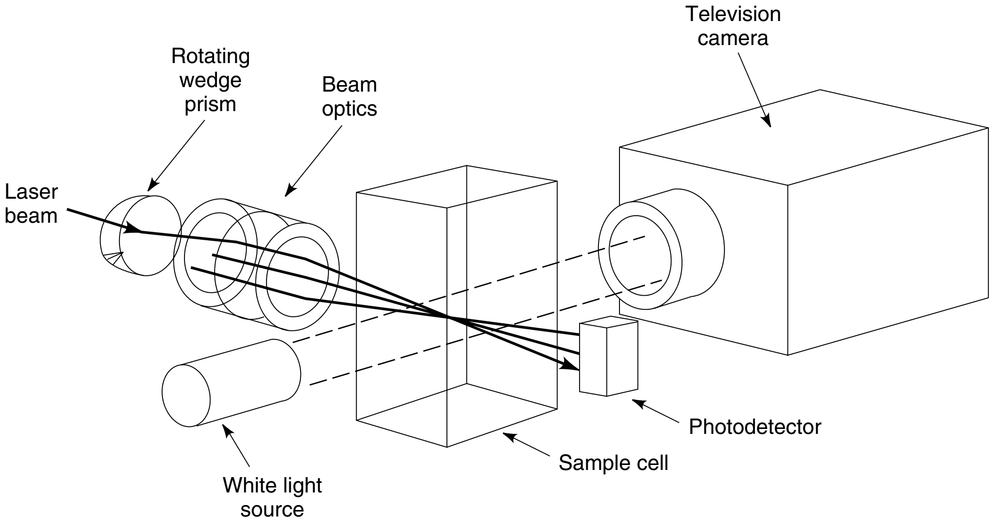

Fig. 13. Schematic representation of the Ankersmid particle size analyzer showing both the laser-based time-of-flight sizing equipment and the CCD camera for direct image analysis of the suspension in the interrogation zone.

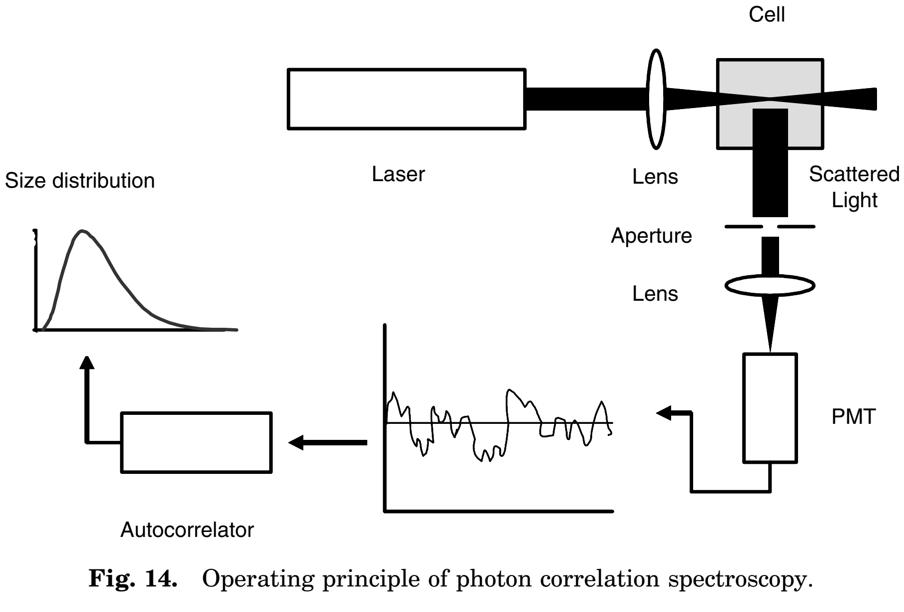

Fig. 14. Operating principle of photon correlation spectroscopy.

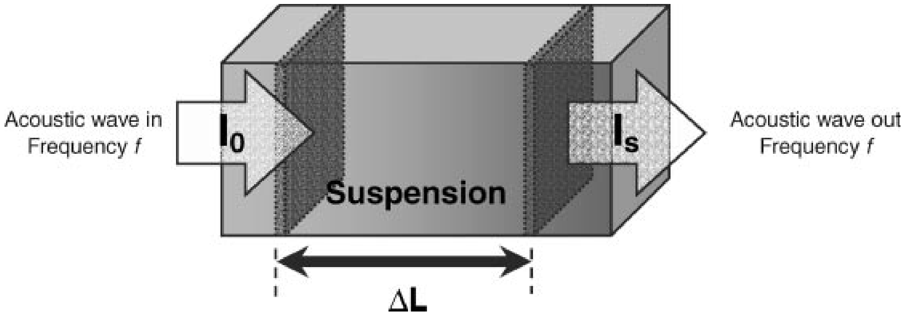

Fig. 15. Measurement of the attenuation spectrum used to calculate the size distribution of high concentration dispersion.

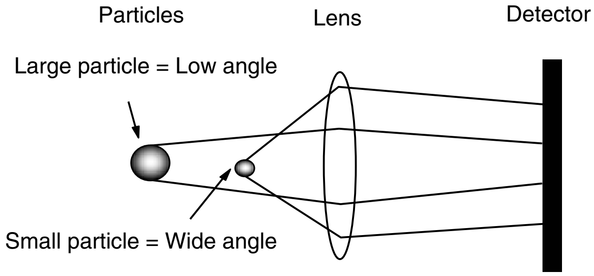

Fig. 16. Finer particles diffract light at wider angle than coarser particles.

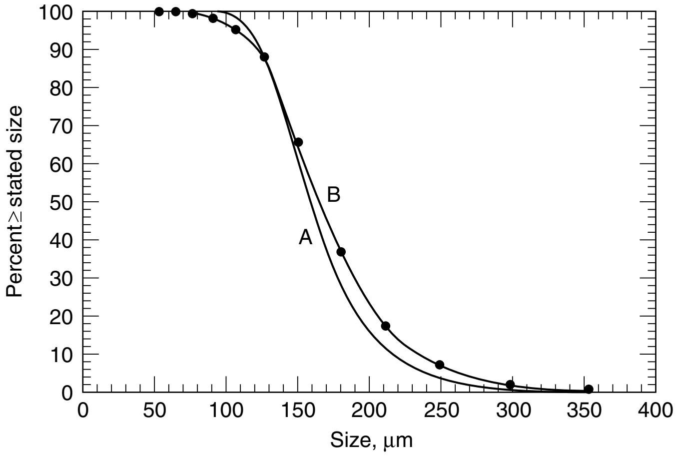

Fig. 17. Size data for a metal powder obtained by A, image analysis, and B, on a diffractometer.