Comparison of Particle Sizing Methods

This document is a slightly irreverent, but honest, comparison of several different particle sizing methods. It is by no means an attempt at an exhaustive survey of the particle sizing field, since such a survey would require a good size text book or two. My primary objectives are

1) to help potential buyers of particle sizing instruments (especially those without a lot of particle sizing experience) sort through the often exaggerated claims of instrument performance, and

2) to help them appreciate that all particle sizing methods have both advantages and limitations. These advantages and limitations should be understood and weighted before choosing a particle sizing instrument.

I urge potential customers to be very cautious about accepting the performance claims of any instrument manufacturer, and to be cautious about accepting at face value the results of any particle sizing instrument. The truth is that while a certain particle sizing application may be dominated by one sizing method, other applications are dominated by other methods.

The most sophisticated particle sizing customers often use completely different sizing methods for different applications, and even use two different methods for the same application; these customers understand that the best choice of sizing method depends upon both the nature of the sample and what characteristics of the size distribution are most important.

One method can never suit all samples. There is no instrument from Zero to Infinity!

If you read this document and find what you believe to be a substantial error of fact, please contact via email and tell us what you think is wrong.

Particle sizing methods can be separated into three basic classes: ensemble methods, counting methods, and separation methods. Each of these classes is covered in a separate section below.

I. Ensemble Methods
The ensemble methods collect mixed data from all of the different size particles in a sample at the same time, and then digest the data to extract a distribution of particle sizes for the entire population.

Common ensemble techniques are
Low Angle Laser Light Scattering,
Photon Correlation Spectroscopy,
Back-scattering Spectroscopy, and others.

Low Angle Laser Light Scattering (LALLS)

How it Works
This method passes a laser beam through a sample of particles, and collects light intensity data at different (low) scattering angles away from the axis of the laser beam. Intensity data is collected at many different angles (up to 64 in most instruments).
Mie theory light scattering calculations are applied to the intensity data to generate a distribution of particle sizes that is consistent with the observed light intensities at the observed angles.

LALLS is applied to relatively low concentration samples, so that there is a minimum of multiple scattering (where light scattered from one particle is scattered by a second particle before reaching the detectors), since multiple scattering makes it difficult to generate an accurate size distribution based on scattering angles. To learn more about light scattering see the excellent book: _Absorption and Scattering of Light by Small Particles,_ by Craig F. Bohren and Donald R. Huffman; Wiley Interscience, 1983.

Advantages

. Very fast data collection; in most cases no more than a minute or two. . Very broad dynamic range (commonly claimed from <0.1 micron up to millimeter sizes).
. Relatively simple to use.
. Can measure both powders (with suitable powder sampling equipment) and fluid suspensions.
. Testing is non-destructive, so samples can be recovered if necessary.
. The method is widely used (perhaps too widely used!), so many people are familiar with the method and have confidence in the results.

Disadvantages

. Relatively low resolving power. Narrow, side-by-side peaks must be at least 15% - 20% different in size to be resolved. A perfectly narrow peak is reported with a peak width of -15% to 20% of the mode diameter. The entire distribution is represented by a set of 128 to 256 data points over the entire size range, so truly high resolution measurement is not possible.
. Accuracy depends on the accuracy of the optical parameters (refractive index, light absorption) available for the particles, as well as the accuracy of information about particle shape, since these are all used to calculate the scattering properties of the particles. Light absorption characteristics are often unknown and must be "estimated".
. Mixtures of particles with different optical properties can't normally be measured.
. Unusual particles give can give erroneous results. Big particles with fine internal structure or porosity, or long thin fibers, can yield results that are very far from correct.
. Strongly absorbing particles can present problems because they may not produce a usable scattering signal.
. There is a great leap of faith required. The calculations used to generate the distribution are complex and often proprietary, so it is very difficult to verify instrument performance except in the simplest of cases.

One well known manufacturer says in their literature: "The method is an absolute one set in fundamental scientific principles. Hence there is no need to calibrate an instrument against a standard - in fact there is no real way to calibrate a laser diffraction instrument."
Perhaps this manufacturer has not spoken to the many customers who have purchased a LALLS instrument and concluded that it produces absolutely wrong results in their application. Is this why calibration is not needed?

Anecdote on LALLS
Some years ago, this author attended a customer's evaluation of a LALLS instrument that was produced by a very well known instrument manufacturer.

The customer prepared three unidentified polymer latex samples: a narrow -0.28 micron mean, a narrow -0.39 micron mean, and an equal mixture of both. The LALLS instrument accurately reported the mean sizes of the two individuals, but reported only a single, relatively broad peak for the mixture. When the identities of the samples were revealed, the instrument representative said "You should have told me that there were multiple peaks. ", then adjusted some software parameters, and finally generated a curve with two partially resolved peaks.
Said the customer: "What if I didn't know there were two peaks?"

Photon Correlation Spectroscopy (PCS)

How it Works
Light scattered from small particles «-3 microns) varies rapidly in intensity due to Brownian motion of the particles. The variation in intensity over very short times can be "auto correlated" to extract information about the velocity distribution of the particles that scattered the light. The average size of the particles (quite accurate) and some information about the size distribution is calculated.

Advantages
. A minimum amount of information about the sample is needed to run an analysis. Even mixtures of different materials can be accurately measured; only the viscosity of the medium must be known accurately.
. Very small minimum measurable particle size. . Only a tiny sample is needed.
. The analysis is fast and simple.
. Testing is non-destructive, so samples can be recovered if needed.

Disadvantages
. Extremely low resolution; particles must differ in size by 50% or more for PCS to reliably detect two peaks.
The method does not really provide much "size distribution" data, only a mean size and estimate of standard deviation.
. A small quantity of a small size particle can easily be "lost" in a much larger quantity of a large size particle.
. Only small particles <-3 microns (with significant Brownian motion) can be measured, all larger particles are beyond the instrument's range.

Back-scattering Spectroscopy

How it Works
An intense light beam, usually a laser, is directed into a suspension of particles, and the angular intensity distribution of light scattered backward, at high angles, is measured. (As opposed to LALLS where the scattered light is at "low angles", close to the original beam direction.) Light scattering calculations are applied to the scattering data to generate a particle size distribution. Back scattering is often applied to high concentration samples that are either "in process" or that can't be diluted without changing the size distribution.

Advantages
. Can measure samples that are too concentrated for most other sizing methods, including on-line measurements of particles (if there is an optical window available).
. Relatively simple operation... No sample preparation needed. . Non-invasive/non-destructive test method

Disadvantages

. The particle size distributions are low resolution, even compared to LALLS. Multiple scattering from high concentration samples hurts potential resolution.

. The optical properties (refractive index/absorption) and shape of the particles must be known to generate accurate results.

. Materials that absorb light strongly can present problems, because the back-scattering signal is very weak.

II. Counting Methods

The counting methods all characterize the sample distribution one particle at a time, basically by accumulating counts of particles with similar sizes. Some common counting methods are:

the electrozone counter,

the light counter,

the time of *flight counter,*

and the microscope (optical or electron).

In each of these methods, particles are classified and placed in "size bins", one particle at a time. These methods all must insure that multiple particles are not counted together and cause errors in the reported size distribution ("co-incident counting").

The accuracy and resolution of these methods depend on how accurately the size of each particle can be characterized during the (usually) very brief time that it is counted.

Electrozone Counter

How it Works

The electrozone counter was pioneered by the Coulter Company many years ago for blood cell counts in hospitals, where it is still widely used.

Particles are suspended in an electrically conductive fluid (usually saline water with emulsifier) and forced to flow through a small orifice. Conductors are placed in the fluid on either side of the orifice, and the electrical resistivity of the orifice is monitored as particles pass.

Each particle produces a sharp "spike" in electrical resistivity as it passes the orifice, and the total area (time x height) under the spike is approximately proportional to the volume of the particle. Each of the spikes is classified according to total area, and a particle count is placed in a bin that corresponds to the appropriate particle size. After many thousands of particles have passed the orifice, the bin counts are converted to a particle size distribution, and the distribution is finally adjusted to account for the statistically finite probability of "co-incident" counts.

Advantages

. Suitable for a relatively broad range of sizes (0.5 micron to >300 microns, using different orifice sizes).

. Simple in concept, and easy to calibrate with known size standards. . Quick analysis time

. Gives repeatable results with many kinds of samples, including many non- spherical particles.

. Resolution comparable to LALLS; adjacent narrow peaks that differ by about 15%-20% can be resolved.

Disadvantages

. Dynamic size range is limited to about 30 in a single run (from about 2% of the orifice size to about 60% of the orifice size).

Analysis of broader distributions requires pre-separation of samples according to size (for example, via sieves), so that the individual fractions can be run using different orifices. This makes analysis of broad distributions more difficult and the results more doubtful.

. Samples must be suspended in a conductive fluid; saline water may not be convenient for many kinds of samples.

. The particles must normally be electrical insulators.

. While the minimum size for the method is about 0.5 micron, experience has shown that measurements below 2 - 3 microns are often very difficult due to stray oversize particles that get trapped in the orifice and cause plugging. Particles below 0.5 micron can't be measured by this technique under any circumstances.

. Resolution near the lower limit of the instrument is often not as good as in the middle of the measurable range.

The Light Counter

How it Works

The light counter is very much the optical equivalent of the electro zone counter. Particles are forced through a counting chamber, where a focused laser beam is partially blocked as the particle passes. The reduction in light intensity reaching a detector is related to the optical cross section of the particle, and this is converted to a size distribution.

Advantages

. Suitable for a relatively broad range of sizes (-0.5 micron to >2,000 microns, using different size sensors).

. Simple in concept, and easy to calibrate with known size standards. . Quick analysis time - normally less than 3 minutes

. Gives repeatable results with many kinds of samples.

. Resolution comparable to LALLS (at least for larger spherical particles); adjacent narrow peaks that differ by about 15%-20% can be resolved.

Disadvantages

. Dynamic size range is limited to about 100-200 for a single run. Analysis of broader distributions requires measurement using two different size sensors.

. Resolution appears to suffer with smaller particles.

. Non-spherical particles reduce resolution, because the cross section of the particle is evaluated rather than it's volume. The cross section for a given particle weight will depend on both particle shape and orientation as it passes through the detector.

A second detector beam perpendicular to the first would allow a better measurement of volume, but to this author's knowledge, only single beam instruments are produced.

. It is impossible to measure particles below 0.5 micron, and measurements below 1 - 2 microns may be of lower accuracy than over the rest of the measurement range.

The Time of Flight Counter

How it Works

This technique is targeted for dry powders, although very dilute particulate suspensions in water can be "nebulized" and the particles measured after the water has evaporated.

Sizes are measured as follows: an air stream containing particles is drawn through a fine nozzle into a partial vacuum, producing a supersonic "barrel shock envelope" of air. Particles accelerate in the air flow according to size, with smaller particles accelerating more rapidly than larger particles. The particles then pass two focused laser beams. The first laser beam detects each particle and starts a time-of-flight clock, while arrival at the second laser beam stops the clock.

The time of flight is recorded, and the individual times of flight are converted into a size distribution by classifying into bins that are a little over 1.5% apart. Coincident counts are discarded by computer software.

Advantages
. Works with dry powders.
. Can be easily calibrated with known size standards.
. Broad total measurement range, -0.2 to 700 microns. . Fast analysis time, normally about 1 minute.
. Fair resolution, at least for particles above 0.5 micron, where narrow adjacent peaks that differ by -20% can be resolved.

Disadvantages
. Liquid suspensions of particles may be difficult or impossible to measure.
. Particles <0.2 micron can't be measured; measurements below 0.5 micron will likely be low resolution.
. Non-spherical particles will be reported as smaller than correct, but the magnitude of the error is not known.
. High resolution analysis is not possible due to physical limitations of the method.

Microscope Counting

How it Works
Most everyone is familiar with how to use an optical microscope. With an appropriate calibration scale, an operator can characterize a distribution of particles by visually classifying and manually accumulating counts of particles in different size ranges.
Automated optical counting systems (with video camera and computer) eliminate most of the drudgery of this type of analysis. Similar counting techniques can be applied to the images produced by electron microscopes. Optical microscope counting is also used in some "on-line" analysis systems, where in-process particles are viewed with a microscope through a suitable optical window.

Advantages
. Microscopic evaluation allows you to "really" see the particles and evaluate their range of shapes and sizes. The method inspires great confidence in the results.
. A quick look with a microscope often gives a great deal of information that other methods are unable to give.
. The microscope can be "calibrated" by looking at known size standards.

Disadvantages
. The method inspires too much confidence in some cases. It may be difficult to collect enough data to give a reliable result. A single 30 micron particle that is not counted represents the same weight of material as 27,000 particles of 1 micron that are counted.
. Analysis time can be very long, especially for electron microscope analysis.
. The number of particles measured is usually small compared to other particle sizing methods, so representative sampling becomes critical.
. It is normally not possible to determine if two or more particles are just "touching" or if they are permanently stuck together; in other words, really just one bigger particle. This can lead to significant errors in reported size distribution.
. Sample preparation for electron microscopes is slow, expensive, and requires considerable technical expertise.
. Anything more that a quick look with an optical microscope soon becomes very tedious.

Anecdote on Electron Microscope Counting
In 1995 *the first overseas distributor for the Disc Centrifuge was contracted. Under the terms of the contract, the distributor agreed to purchase* a *Disc Centrifuge for demonstrations and sample evaluations. This distributor had sold other particle sizing instruments, and* so *had on hand several polystyrene calibration standards. These standards were immediately evaluated with the new Disc Centrifuge.* A *panicked FAX soon arrived in the USA: "Why* is *this instrument producing FALSE peaks in calibration standards?!!!". As* it *turned out, there were no false peaks, only real ones. The manufacturer of the calibration standards used an electron microscope to characterize polystyrene latexes, and so permanent clusters of* 2, 3, *and* 4 *primary particles were reported in the microscope evaluation as* single particles that were only "touching" each other. These clusters showed up on the disc centrifuge as *narrow bands of larger particles, each representing half* a *percent or less of the sample weight. Sonication with emulsifier did not break down the clusters, but when* a *standard was allowed to settle for* a *day, and* a *sample then withdraw from near the top of the settling particles, the "false"peaks completely disappeared.*

III. Separation Methods

Separation methods all apply an outside separation force to the particles in a distribution to physically separate the particles according to size. Since particles of different sizes are physically separated, the burdens of accurate characterization of individual particles (counting methods) and of calculating a distribution from mixed data (ensemble techniques) are reduced or eliminated. The accuracy of these methods depends upon whether the particles react to the separation force as expected. The resolution of these methods depends on how completely the particles are separated according to size. Common separation techniques include

> *sieves,*
> *gravitational sedimentation,*
> *the disc centrifuge,*
> *capillary hydrodynamic fractionation,*
> *sedimentation field flow fractionation,*
> and others.

Sieves

How they Work
Sieves (or "screens") are one of the oldest particle sizing methods, and are used in both the laboratory and in very large (tons per hour) production equipment to separate one size particle from another.
The most common type of sieve is a woven cloth of stainless steel or other metal, with wire diameter and tightness of weave controlled to produce roughly rectangular openings of known, uniform size. The sizes of sieve openings have been standardized, so that there is reasonably good consistency between sieves from the same manufacturer and sieves from different manufacturers, at least in terms of their specifications.

A series of sieves can be stacked on top of each other, with the coarsest sieve on top and the finest on the bottom, thus forming a sieve "column".

A sample is introduced on top of the coarsest sieve, and progresses down through the column due to vibration, shaking, fluid flow, or some combination of these. Particles progress until they reach a sieve where the openings are too small for them to pass, whereupon they are "retained". The weight of sample retained on each sieve produces a crude distribution of sizes. Conventional woven sieves are limited to a minimum size opening of -20 microns, but reach maximum sizes of several centimeters.

Some smaller non-woven sieves are also available (chemically or electrically etched metal films); these generally have round openings.

Advantages
. Simple and inexpensive.
. Inspires great confidence in the results.

Disadvantages
. Limited to relatively coarse particles. . Usually labor intensive
. The reported distribution depends very much on the shape of the particles and the duration of the test, since the sieve will (in theory) pass any particle with a smallest cross-section smaller than the nominal opening. Long thin particles will give very different results when compared to spherical particles of the same weight. A short duration test will give different results than a long duration test
. Difficult to calibrate, except in a very crude fashion.
. The reported distribution is low resolution; narrow particle families must be -35-40% different in size to be resolved.
. The sieve openings tend to plug with particles that are close to, but very slightly larger than, the opening size. This leads to blocked sieves and incorrect results.
. The uniformity of sieve opening size is normally far from perfect, so the reported results can vary significantly from one sieve "column" to the next.
. The finer sieves are fragile and prone to damage. Sieves require routine inspection for damage, and should be tested on a regular basis using a well characterized "standard" sample.

Gravitational Sedimentation

How it Works
A sample of particles is uniformly suspended in a fluid of known density and viscosity, and allowed to settle due to gravity. Larger particles in the distribution settle faster than smaller particles, approximately according to Stokes' Law. Usually the particles sediment to the bottom of the container, but if they are lower in density than the fluid, they float toward the top of the container.
The concentration of particles remaining in the fluid is continuously monitored via x- rays or a light beam at a known distance from the top (or bottom) of the container. As particles settle out of the suspension, the concentration of particles remaining in the detector beam falls with time; this data is converted to an "integral" or "cumulative" type distribution of particle size by applying Stokes' Law to the concentration versus time data. Alternatively, the height of the sediment layer that accumulates with time can be recorded and used to calculate a weight distribution. The method allows a very simple apparatus (even a graduated cylinder) to generate a particle size distribution.

Advantages
. Simple in concept, inspires confidence in the results. . Instrument can be relatively inexpensive.
. Absolute accuracy is excellent with spherical particles that do not settle too fast or too slow.
. Easy to confirm performance with particle size standards.

. Good resolution; uniform families of particles <10% different in size can be completely resolved.
. Overall range is quite broad, from -1 micron to >500 microns

Disadvantages

. Limited in size to relatively large (>0.5 - 1 micron) particles except when the particles are extremely dense. Brownian motion of very small particles combined with long sedimentation times can lead to substantial errors in the reported size distribution.
. Analysis time is very slow for small particles - up to 12 hours or more.
Very small particles «-0.2 - 0.5 micron) are often not measurable.
. Large particles (>25 microns) do not follow Stokes' Law if their rate of sedimentation produces turbulent flow of fluid around the particles. This can lead to errors if not accounted for by the instrument software.
. Non-spherical particles, such as long thin fibers are reported as smaller than correct unless correction factors for particle shape are applied. The light scattering properties of non-spherical particles can also present problems when a light beam is used to measure the concentration of particles.
. Practical dynamic range is limited to about 25, unless there are multiple detector beams or the detector beam is moved during the analysis in the direction opposite the particles' movement (Scanning Detector).

The Disc Centrifuge (DC)

How it Works
The disc centrifuge is a hollow, optically clear disc with a central opening on one side. The opposite side of the disc is centrally mounted on a drive shaft that rotates at a known speed, from -600 - 900 RPM up to -24,000 RPM. The empty spinning disc chamber is partly filled with liquid that is held against the outside edge of the chamber by centrifugal force, forming a ring inside the chamber.

The liquid ring has a slight density gradient: the liquid at the outside edge of the ring is slightly more dense than that near the inside edge. A small volume of a dilute suspension of particles is injected into the center of the spinning disc, and quickly reaches the liquid surface. Particles sediment from the surface toward the outside edge of the chamber at rates that depend on particle size, with large particles moving much faster than small. A detector beam (usually a light beam) passes through the liquid near the outside edge of the disc, and particles passing the beam reduce the intensity in proportion to their concentration.
Since all of the particles in the sample start sedimentation at the same place and at the same time, particles of the same size all reach the detector beam at the same time. The time to reach the detector beam versus beam intensity is converted to a size distribution using both Stokes' Law (modified slightly for use in a centrifuge) and Mie theory light scattering calculations.

Advantages

. Extremely high resolution; narrow particle families <5% different in diameter can be completely resolved, 2% different partly resolved.
. Relatively broad overall size range, from <0.01 micron to >40 microns. . Dynamic range up to 1000 or more with disc speed ramping during analysis.
. Very accurate results with spherical particles. . Easy to calibrate using size standards.
. Most measurements require only 3 - 15 minutes.
. Recently extended to allow measurement of low density particles.

Disadvantages

. Not suitable for particles >-50 microns

. Maximum dynamic range of -75 when disc speed is fixed (not ramped during the analysis).

. Non-spherical particles are reported as smaller than correct unless the operating software accounts for particle shape; for example, rods three times as long as wide are reported -8% smaller than correct.

. Analysis times are long for very small particles «0.05 micron) with density close to the liquid density.

. Absolute accuracy of the distribution depends on knowing both optical properties and particle shape.

Capillary Hydrodynamic Fractionation (CHDF)

How it Works

A very fine capillary tube (a few microns inside diameter) carries a flow of emulsifier in water. At the start of an analysis, a very dilute suspension of particles is added to the flow just upstream of the capillary. As the particles move down the capillary they diffuse across the capillary bore, due to Brownian motion. Over time, each of the particles resides at all possible distances from the center of the capillary, thus experiencing all possible velocities. The flow velocity profile within the capillary tube is approximately parabolic, with the highest velocity at the center. At any instant, a particle moves at a speed close to the speed of the fluid at that particle's center.

The center of a particle of diameter D can only approach the capillary wall to distance of D/2; each particle is excluded from residing closer to the wall than half it's diameter. On average, large particles have a higher velocity down the capillary than small particles, because large particles never experience the lowest flow velocities that are near the capillary wall. Large particles reach the end of the capillary first, very small particles reach the end last. A detector (optical, ultra-violet, or other) following the capillary measures the concentration of particles as they exit the capillary.

Advantages

. Fast analysis time; - 7 to 10 minutes in all cases. . Small minimum particle size, -0.01 micron.

. Minimum of information needed about optical characteristics. . Performance can be verified with calibration standards.

Disadvantages

. Limited to particles below -1-2 microns; larger particles have too little Brownian motion.

. Aqueous emulsifier medium only.

. Very poor resolution; narrow families must differ in diameter by 35% to be physically separated in the capillary (mathematical enhancement of the original distribution improves resolution to -10%-15%, but adds uncertainty to the results - artifact peaks generated by the enhancement process are sometimes a problem).

. Capillary plugging is a common problem.

. Non-spherical particles may not be correctly measured

Sedimentation Field Flow Fractionation (SF3)

How it Works (Condensed version)

An SF3 instrument consists of a rotating disc that has a closed flow chamber located near the outside edge of the disc. This flow chamber has a cross section of -1 - 3 mm X several mm, resembling a hollow belt strapped around the rotating disc.

Fluid is continuously pumped through the flow chamber while the disc is spinning at up to several thousand RPM. A sample run begins with the disc spinning at the highest speed. The rotational rate is gradually reduced during the run. At the start of a run, a suspension of particles is added to the fluid stream. The particles are driven by g-force toward the outside edge of the flow chamber (if higher in density than the fluid), or toward the inside edge of the chamber (if lower in density than the fluid). Large particles are effectively "pinned" against the chamber wall by g-force, and initially make little or no progress along the length of the chamber. Small particles (with greater Brownian motion) form a "cloud" of particles that hover above the chamber wall.

The smaller the particles, the higher the Brownian cloud. The liquid velocity profile inside the chamber is parabolic (just as in CHDF), so smaller particles spend more time in the higher velocity portions of the flow, and make faster progress (on average) along the length of chamber, exiting the chamber first (just the opposite of CHDF). As the speed of rotation falls, the g-forces fall as well, allowing larger and larger particles to spend time away from the chamber wall, and thus moving along the length of the chamber.

There is a "transition" point where the g-forces become low enough that large particles (those too big to have significant Brownian motion) essentially "roll" or "slide" down the length of the chamber due to the lateral hydraulic force applied by the fluid flow. After this transition point is passed, larger particles move faster than smaller particles, because their centers are located at higher flow velocity than smaller particles (the same as CHDF). Particles are detected in the liquid flow leaving the chamber with a light, ultraviolet, or other detector. (Is that all clear?)

Advantages

. Broad dynamic range (especially if both "Brownian" and "rolling" modes are included).
. Very good resolution with small «3-5 micron) particles; narrow peaks as little as 5% different in size can be resolved.
. Performance easily verified with calibration standards
. Not dependent on particle geometry in "Brownian" mode

Disadvantages

. Extremely complicated algorithm for size separation, very difficult for many people to understand clearly - reduces confidence in the results.
. Complicated mechanical construction with critical high speed rotating seals; has a history of mechanical/maintenance problems. Many very expensive SF3 instruments collect dust in the corners of laboratories around the world.
. Relatively long run times, can be up to 1 hour or more.
. Separation in the "rolling/sliding" mode would appear to be a very complicated function of both size and shape.