A Guide to Choosing a Particle Sizer©

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Introduction

The choice of a particle size analyzer has never been more difficult. There are several techniques from which to choose and variations within each technique. Sales literature claims of specification and performance have become highly inflated, confusing the first-time buyer; the result has been to hinder and not help the decision making process. Many particle sizing instruments were originally designed to address specific problems. Although some have found additional uses, there is still some truth to the notion that certain techniques are best suited for particular tasks. The idea that one instrument will suit every particle sizing need, and hence solve all problems, is not supported in practice.

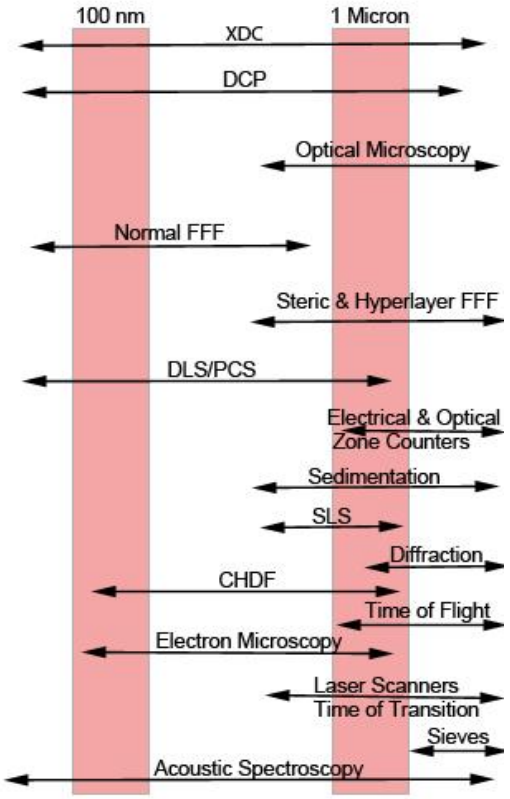
Limited in scope

This guide does not specifically address imaging problems, shape analysis, single particle counting, nor sizing of airborne particles. Examples are drawn from particle sizing in liquids where the amount of material is not of primary concern; the "dirty water" or microcontamination problem is excluded.

This document is a brief summary based on many years of experience with the modern methods of particle size analysis; it is not definitive. New techniques and new applications of old techniques appear at an ever increasing rate. Yet, the concepts presented here are general enough to be of value for several years to come. The author would welcome any comments you may have and is always available to answer any specific questions.

Figure 1

Commercially Available Particle Sizing Techniques
(Mostly Liquid Suspensions).



Legend:
XDC: Scanning X-ray Disc Centrifuge
DCP: Disc Centrifuge Photosedimentometer
FFF: Field Flow Fractionation DLS: Dynamic Light Scattering
PCS: Photon Correlation Spectroscopy
SLS: Static Light Scattering
CHDF: Capillary Hydrodynamic Fractionation

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Classifications

Particle sizing techniques can be classified in several ways.

Size Range: Many interesting applications in particle size analysis center around 1 micron. Figure 1 shows several commercially available techniques for particle sizing with a purposefully "fuzzy" demarcation around 1 micron.

Why is the region around 1 micron so important? There are several reasons.

First, this region is roughly the dividing line between sedimentation and centrifugation. For particles that are dense and/or larger, sedimentation works well. For particles that are not dense and/or smaller, centrifugation works well. Since both density and size play a role, the choice of technique depends on both of these properties.

Second, this region is roughly the dividing line between Fraunhoffer Diffraction (FD) and light scattering. For particles that are larger, the classical FD technique is independent of the refractive index of the particle. For particles that are smaller, the scattering pattern depends significantly on the refractive index of the particle.

Third, measurements become increasingly difficult with zone counting (ZC: electro- and photozone) techniques below this region. Electrozone techniques suffer from signal-to-noise problems, and photozone techniques suffer from diffraction effects as do optical scanners. In addition ZC techniques suffer from increasing coincidence errors at these smaller sizes. Fourth, the ability to resolve images with an optical microscope becomes increasingly difficult below about a micron.

All of the statements above are generalizations. Yet they provide good, first-order, estimates of the practical working limits of any one technique. In special cases these limits may be exceeded. But be wary of size range claims without qualification.

Imaging vs. Nonimaging: Instruments based on imaging are, potentially, capable of measuring shape, structure, and texture in addition to concentration and size. They can, ideally, distinguish between different compositions. Imaging techniques include optical and electron microscopy, video, holography, and photography. Image analyzers are often, but mistakenly, thought of as the primary method of particle size analysis.

Yet image analysis has many disadvantages and difficulties. Typically, too few particles are measured to give reliable statistical results. Manual image analysis is subjective, slow, and labor intensive. Like other single particle counters, image analyzers may suffer from coincidence effects. When automated and computerized, the cost mounts, and coincidence effects may be more difficult to recognize.

Non-imaging techniques yield equivalent spherical diameters (ESD). This is the diameter of a sphere that would give the same result as the actual particle. Thus, different techniques may yield different equivalent spherical diameters for the same particle. These differences are valuable: They reveal information on the shape, structure, or texture of the particle. Nevertheless, if definitive information of this type is required, then an image analyzer is necessary.

Degree of Separation: Another major classification is the degree to which particles are separated prior to measurement. There are three categories here: single particle counting; fractionation, both partial and high resolution; and ensemble averaging.

Single particle counters (SPCs) include image analyzers, electro- and photozone counters, and particle scanners. Like image analyzers, SPCs suffer from coincidence counting effects. The zone counters are also subject to clogging of the zone. Additionally, electrozone counters normally require high salt concentrations to work properly, and this may cause aggregation. Yet SPCs are the preferred choice when particles must be counted as well as sized.

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Fractionation techniques include sieving, sedimentation, centrifugation, and various forms of particle chromatography. Depending on how the measurement is carried out, the particles may be partially separated or more of less completely separated. The difference is crucial when high resolution results are required. As a class, the fractionation techniques are relatively slow.

Ensemble averagers include Fraunhofer Diffraction (FD) and all forms of light scattering. The signal, from which the size distribution information is calculated, is a sum over all the signals from all the particles during the entire measurement. Thus, the results are an average over an ensemble of particles. As a class, ensemble averagers are fast, easily automated, and can be, at least in principle, put on-line. In general the resolution is, however, poor.

Weighting: A size distribution has two coordinates. The size, which is, most often, an equivalent spherical diameter, is plotted on the x-axis; and the amount in each size class, which is plotted on the y-axis. The amount is usually given as either the number or volume or mass of particles. If the particle density is the same for all sizes, then the volume and mass descriptions are equivalent.

Each particle sizing technique weights the amount observed differently. For example, light scattering on really small particles is weighted by the intensity of scattered light which varies as the 6th power of the diameter. A few large particles can dominate the scattered light signal obscuring the presence of small particles. Electrozone techniques weight by the volume of the particle which varies as the cube of the diameter.

Although it is a simple matter to write the equations for converting from one type of weighting to another, the results calculated this way are often in error. Perhaps some particles were not measured at all. Perhaps the measured distribution is significantly broader than the true distribution. Or, in the hybrid techniques, different ranges are weighted differently. In all these cases the errors in the transformed data are much exaggerated due to weighting.

Whenever possible use a particle sizing technique that gives the desired weighting without transformation. If absolute counts are needed, then get a single particle counter. If mass is important, then get an instrument that responds to mass. If a few particles in the tail of the distribution are important, then get an instrument that is capable of identifying these.

Information Content: The last major classification includes the amount of information required to solve a particular problem in particle sizing.

Frequently only a single number is required to answer a question in particle sizing. That number might be the average size or it might be a cumulative specification such as 90% of the particles are less than a stated size. For quality assurance or process control, this single number may be sufficient. Techniques that give only a single number include the following: a turbidity measurement at one wavelength; end-point titration of the surface groups; and the Blaine test for large particles in a powder sample.

Sometimes a second number is required. Perhaps it is the width of the distribution (testing for monodispersity) or two cumulative sizes, for example the 90th and 10th percentile values (characterizing the usefulness of rutile as a pigmenting agent). In the submicron range, DLS is a technique which reliably yields a measure of the width as well as an average of the size distribution.

Additional size distribution information, often hard to come by reliably, might be the skewness of a single, broad distribution; the size and relative amounts of several peaks in a multi-peaked distribution; or the existence of a few particles at one extreme of the distribution. Where the distribution has several, closely spaced features, a high resolution technique is necessary. More complete size distribution information is often required in the pigment and coatings industry.

Finally, a word of caution: Many of the modern methods of particle size analysis purport to give complete size distribution information. Often they don't. Computers are marvelous devices for storing, retrieving, and massaging data. With the exception of, perhaps, image enhancement, rarely can a computer improve resolution in par-

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ticle sizing applications. That is the job of the basic technique.

Specifying a Particle Sizer

Specifications are of two types: quantitative and qualitative. If you need to run 30 samples each day, then you have quantified a throughput specification. One example of a qualitative specification is ease-of-use.
Short lists of both types of specifications follow. The lists are by no mean definitive. They do, however, provide a good starting point for focusing on questions you will need to answer before an informed choice can be made.

Quantitative Specifications
- Size Range
- Throughput
- Accuracy
- Precision
- Reproducibility
- Resolution

Qualitative Specifications
- Support
- Ease-of-Use
- Versatility
- Life Cycle Cost

Size Range: Everyone wants the zero-to-infinity machine. It appears to solve lots of problems: only one instrument is required, now and for the future; less bench space is required; operator learning curves are reduced to one. Its universality is so appealing that zero-to-infinity machines are currently the rage. Witness the birth of the hybrid instruments. They combine more than one technique. But there are several limitations with the zero-to-infinity machines, not the least of which is: they do not exist.

First, there are theoretical limitations with any single technique. Diffraction is normally limited to sizes much larger than the wavelength of the light source. Sedimentation is limited at the high end by turbulence (large Reynolds numbers) and at the low end by diffusion. In fact, it is not hard to find the theoretical limitations in any technique. They lie either in the basic assumptions or in the resulting equations used to calculate the results.

Second, there are limitations associated with the implementation of the technique in practical instruments. To ensure a good dynamic signal response, the detectors in diffraction devices are located in such a way that the raw size classes are, typically, logarithmically spaced. This may mean that the last size class covers fully half the total size range. Accelerating a centrifuge is useful for speeding up the measurement, but it often broadens the real size distribution.

Third, there are limiting cases which become, incorrectly, generalized to cover all types of samples. DLS is a useful technique for particles which remain suspended. Low density materials stay suspended long enough to make useful measurements, but high density materials may not. Colloidal gold can be measured with a centrifuge down to about 0.01 micron because of its high density. Colloidal polystyrene, whose density is very low, cannot be measured much below 0.05 micron using the same centrifuge. Diffusion makes the results suspect, and the measurement is painfully slow.

Table I
Categorizing Particle Size Specifications

Quantitative Specification	Qualitative Specifications
Category I: Academic Use	
1. Accuracy	1. Life Cycle Cost
2. Resolution	2. Versatility
Category II: Research & Development	
1. Precision	1. Versatility
2. Resolution	2. Support
	3. Cost
Category III: Quality Assurance	
1. Throughput	1. Ease of Use
2. Reproducibility	2. Support
	3. Repair/Maintenance

Fourth, there are limitations when subranges, or different techniques, are spliced together. Usually each subrange requires a change in something: a lens, an aperture, a speed of rotation, etc. In principle this is possible. In practice it is difficult to splice distributions together without

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producing artifacts. These are often taken to be real by novices. Some manufactures use smoothing to hide these artifacts, yet this may then result in a significant loss of resolution. Different techniques use different weightings and are subject to different theoretical limitations, especially at their extremes. Yet it is at the extremes where they are spliced together.

Although instrument makers often claim they have the perfect, universally applicable instrument, the "zero to infinity" machine, the vast majority are limited, in particular at the extremes of the size range.

Recommendation:
Estimate an average and a range for your particular problems. Have a few test measurements made to support your estimates. Look for an instrument that can cover the range without using the extremes claimed in the specifications. Choose an instrument that is suited to the task. There are no free lunches, and there are no zero-to-infinity particle sizers.

Throughput: The concept of throughput is most important to a quality control laboratory where a large number of samples must be run in one day. Speed of analysis is sometimes a consideration even for one measurement. Process control applications are an example.

Some techniques are relatively slow: Image analysis and sedimentation on small, low density particles, are but two examples. Some techniques are relatively fast: most forms of light scattering. In some particle sizing applications, throughput is not even a consideration. In others, it is a dominant consideration. The novice often assumes that the measurement duration is sufficient to characterize the typical time per sample. This is a mistake. The total time includes: sampling, sample preparation, measurement, calculation, formatting and printing, and clean up. In some cases warm-up or calibration or instrument adjustment may also add significantly to the overall time per experiment. Automated instruments may need time-consuming wash/rinse cycles. Sometimes the measurement duration is only a fraction of the actual time per sample.

Recommendation:
Estimate the throughput you require. Compare to vendor claims. Be sure to consider the total duration as defined above.

Accuracy: Accuracy is a measure of how close an experimental value is to the true value. Often, the true value is not known. Perhaps the particles are not spherical. Perhaps no truly accurate measurements have been made by which to compare the results. In these cases, accuracy becomes difficult to assess.

Accuracy depends on knowing the sample variables (shape, density, refractive index, etc.) and instrument variables (calibration, alignment, temperature). Good accuracy implies good sampling and sample preparation techniques have been used. Sometimes accuracy is important; sometimes it is not. Materials used in the coatings industry need to be characterized accurately. The large particles affect the film forming capability of the coating; the medium size particles affect the light scattering properties; and the small particles control the rheology. In quality and process control applications, relative changes from batch-to-batch are much more important than accuracy. In these cases, reproducibility is the main specification.

Relative numbers are acceptable unless they have to be compared with other techniques or absolute requirements. Then accuracy becomes paramount.

Accuracy has often been defined by the historical use of an instrument in a particular field. Although not really a definition, its practicality, however, cannot be ignored. New instrumentation should agree or, at least, correlate with the historical results. But if this argument is carried too far, then bad measurements are perpetuated. Most instruments claim accuracy when tested with spherical standards. There are very few reliable standards. There are, however, reference materials for checking precision, reproducibility and resolution. While useful, these are not absolute standards, and, as such, should not be confused with them.

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Recommendation:
Even if you are only interested in relative changes, test an instrument with reference materials just to verify the precision, resolution and reproducibility claims.

Precision: Instrument precision is a measure of the variance in repeated measurements on the same sample. Precision limits resolution, reproducibility and accuracy. Precision is a useful criterion by which to assess instruments even if the accuracy cannot be determined. The precision of a measurement may be +/- 1%, yet the absolute accuracy might be much worse. It is common to have good precision but poor accuracy.

Reproducibility: Reproducibility is a measure of the variance from sample-to-sample or instrument-to-instrument or operator-to-operator, etc. If you only have one instrument and one operator, then questions of reproducibility may not be of much interest. But if you have several plant operations, with several operators, all using the same manufacturer's model, then check reproducibility. If it is much worse than the basic precision of any one instrument, then look for the source of the error. Is it preparation differences, or variations from one instrument to the other?

Variations in instrument performance are much greater than most novices would guess. These can occur because of a change in production technique, detector response, software, or a combination of all three.

Recommendation:
Always perform round-robin tests using the same sample; this can reduce or eliminate sample variations. Send an exact set of common operator instructions with the sample to minimize operator variations. The results should quantify instrument-to-instrument variations.

Resolution: Resolution has two quite distinct definitions in particle sizing. The first definition concerns the minimum detectable differences between different runs. It answers the question, "Can the differences between two samples be resolved?" This definition is closely related to the precision of the measurement.

The second definition concerns the minimum detectable differences between features of the size distribution in one run. The simplest example is the ratio between two peaks in a bimodal distribution. If the minimum ratio is 2-to-1, then the resolution is rather low. If it is1.1-to-1, then it is rather high. Ensemble averaging instruments, all forms of light scattering and diffraction in particular, are medium to low resolution instruments.

Beyond a certain point resolution is not determined by the number of channels in a SPC, nor by the number of reported size classes, nor by the resolution of the output devices (CRT, printer) used to format the results. Yet, many manufacturer's specifications would have you believe that resolution is defined in one of these ways. Resolution is, fundamentally, a function of the basic signal-to-noise ratio of the instrument. Reporting more than the fundamental resolution is like magnifying the noise: more numbers are obtained, but they are meaningless.

Above one micron it is quite common for ground material to exhibit very broad distributions. In this case resolution is seemingly not very important.

Do not be fooled by this common assertion. If the fundamental resolution of an instrument is undetermined, then how does one know if the broad distribution is really hiding practical and, possibly, significant information? Are those long tails real? After all, low resolution instruments often smear out the distribution producing unrealistically long tails.

Recommendation:
Test resolution by mixing narrowly distributed and previously measured samples - - the reference standards.

Accuracy, precision, resolution, and reproducibility are functions of the size range. Errors are greatest at the extremes. If possible, do not purchase an instrument for measurements at the

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extremes. A common mistake is to check an instrument in its midrange and then proceed to use it at one or another of the extremes.

Be skeptical of claims of accuracy, precision, etc. if these really refer only to the average size. If it is not clear from the manufacturer's literature, then ask for clarification. The average of any distribution is least subject to variation. Even instruments with poor resolution and instrument-to-instrument reproducibility may yield results with 1% or 2% precision in the average for any one instrument. Higher moments, such as the measure of width or skewness and the tails of the distribution, are more sensitive to uncertainties. So pay particular attention to the variance in some of these more sensitive statistics when evaluating instrumentation.

Support: Support is defined here as good technical support. Is the manufacturer familiar with your particular problem? Can they suggest sample preparation techniques? To support you after the sale, does the manufacturer offer adequate training, good technical manuals, and experts available to help you interpret results?

The instrument manufacturer should have a laboratory with other instruments available with which to validate the usefulness of the proposed instrument. Sample preparation techniques are often the key to good measurements, and the manufacturer should guide you in this aspect of particle sizing. A continuing program of development by the manufacturer will ensure the user that the instrument will not become obsolete in the near future.

Recommendation:
Judge the level of support you will need. Question instrument manufacturers on how they will provide support. Ask for references to verify anv claims that are made.

Ease-of-Use: There is nothing more subjective than the concept of ease-of-use. In one limit it means automated sample preparation, automated instrument control, and automated data analysis and printout - - all unattended.

Some manufacturers strive for this under the banner of the "one button" instrument.

Other users think that an instrument is incomplete without a complete data archiving, retrieval, and data base management system. These objectives are hardly "one button". They require a rudimentary knowledge of desktop computer operation.

Recommendation:
If ease-of-use is important to your application then be sure to watch measurements being made before you purchase. Make sure that the entire process - - sample prep, measurement, data analysis, and cleanup -- is demonstrated.

Versatility: Versatility is here defined as the ability to measure a wide variety of samples and sizes under a variety of sample preparation conditions. For example, the electrozone technique requires a conducting liquid, which is most often water with an electrolyte (salt) added. For many applications this condition is not restrictive; for others it is. Electron microscopes cannot be used on samples that sublime under a vacuum. Some instruments work with almost any liquid; others do not. Either the technique may be limited, or its implementation by a particular manufacturer may be.

Recommendation:
Try to estimate a realistic range of samples and the corresponding size ranges that you intend to measure. Experience shows that it is usually better to choose dedicated instruments that do a good job for their intended purpose rather than going for the "zero-to-infinity" machines which do a poor job on a variety of samples.

Life Cycle Costing: Instrument cost is the least and the most significant part of purchasing an instrument. If the instrument cannot perform the appointed tasks, it is no bargain at any price. If it can do the job properly, it may be a bargain at twice the price.

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Particle sizing instruments vary in price from a few hundred dollars (pipettes, turbidimeters, simple microscopes) to a few hundred thousand dollars (electron microscopes complete with image analysis software). As of the publication of this article, most modern instruments range from $15,000 to $60,000 with the majority around $30,000. But the initial cost of an instrument is only part of its total cost.

The total price of an instrument is best judged in terms of the life cycle cost. This includes initial price, operating cost, and maintenance and repair costs. Every instrument needs some type of maintenance. It may be as simple as cleaning air filters once every 3 months. It may be as difficult as replacing mechanical parts or aligning an optical system. To some, these are not difficult tasks; to others they are. Every instrument will, sooner or later, require repairs. Any vendor who denies this is not worthy of further consideration.

Recommendations:
Ask the vendor for a list of users who have had the instrument for at least one year. Ask these users for their experience with maintenance and repairs. Ask the vendor what the typical problems have been, and what cures are necessary. Ask about maintenance. Compare the user and vendor responses.

Summary: The mix and priority of quantitative and qualitative specifications you use in making your decision will, to some extent, be determined by your intended use.

Although it may be dangerous to pigeonhole your intended use by putting it into one of the three categories shown in Table 1, it may also help you to focus on what factors are most important in solving your particle sizing problem.

Remember, many users do not fall into such neat categories. And, one person's research may be another person's quality assurance. But if you recognize a pattern in one of these categories that fits your needs, do not hesitate to use them to organize your thinking. Ultimately, you will make a better choice.

Before ending this guide it is worthwhile mentioning two aspects of particle sizing that, so for, have been ignored -- sampling and sample preparation. It is fair to say that the majority of variation in particle sizing measurements is ultimately traceable to either incorrect sampling or sample preparation. Particle size analysis results are only applicable when the samples drawn are representative and the dispersion techniques appropriate.

Sampling and sample preparation are precursors to particle sizing. As such they are often not directly addressed by manufacturers of particle sizing instrumentation. Yet they are probably the most important sources of error.

Problem areas to consider:

- Unrepresentative samples.
- Large and/or dense particles trapped, or segregated, before they reach the sensing zone.
- Inadequately dispersed samples in the submicron range.

When deciding which instrument to purchase it is common to send samples to several manufacturers. The biggest problem in comparing results obtained this way lies in the assumption that all the samples were prepared in the same manner. It is a common failing to assume the first measurement reported is correct. (This is also true when comparing any new particle size result to the historical data base.) A better approach is this: Prepare equally representative samples; determine the best method for dispersing the sample; and then advise each manufacturer to disperse the sample in the same way.

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Table 2
Common Traps and Pitfalls in Buying Particle Size Instruments

1. Ignoring correct sampling and sample preparationwhen comparing instruments and techniques.
2. Trying to satisfy several different requirements with one instrument.
3. Misunderstanding the best use for different techniques.
4. Using values that are computed rather than measured.

Table 2 lists a few of the more common traps and pitfalls that can lead to an incorrect choice of particle sizing instrument.

Recommendations:
Never purchase an instrument until you have verified, usually by altering the sampling and/or sample preparation techniques, that the results make sense. For example, make measurements using two different types or levels of dispersion energy. Or compare results using two different techniques, but the same sample preparation. Look for consistency in results. They may not agree exactly, but they should be consistent: broad distributions should remain broad, bimodals should remain bimodals.

Volumes have been written about the fundamentals of particle sizing. The bibliography contains a few references to guide the interested reader.

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