ABSTRACT

Accurate particle size distribution information is a prerequisite for understanding mechanical, electrical, and chemical properties of refractories. While a number of techniques are now available for measuring the particle size distribution above a few microns, few are capable of high resolution, accurate results below a few microns.

Sedimentation techniques, in general, allow high resolution particle size measurements compared to various light scattering and diffraction techniques. Coupled with a disc centrifuge, measurements into the deep submicron are possible. By mechanically scanning the source/detector, measurement time is reduced significantly. Unlike light scattering and diffraction techniques, the mass distribution is obtained directly, without the need to correct for the sample's optical properties.

An X-ray disc centrifuge with a mechanically scanned source/detector is discussed that yields high resolution, accurate size results down to 10 nm. After a brief review of the principles, examples are given with special emphasis on the accuracy compared to light scattering techniques.

Introduction

In the beginning of particle size measurements there were sieves, then microscopes, followed by electrozone counters and sedimentation devices. Recently, various forms of light scattering, principally, laser light scattering and diffraction have been used.

Is it necessary to use laser scattering to measure particle size distributions? There are two answers to this question: yes, if you believe that only recently developed methods are valuable; no, if you believe that the principles of physics have not changed much during the past 10 or 20 years.

Perhaps a more interesting question is this: What characteristics of the measured distribution matter most — accuracy, precision, resolution, reproducibility? Or, do speed and simplicity outweigh every other
consideration? Accuracy is defined as the difference between the true and measured values. It is a measure of the systematic errors. Precision is defined as the ability to repeat a measurement under the same conditions. It is a measure of the random errors. Resolution is defined as the ability to distinguish between different sizes in the same sample. It is the ability to distinguish a real multimodal or a real shoulder or a real tail. Reproducibility is defined as the ability to repeat measurements from instrument-to-instrument or operator-to-operator or sample-to-sample. It is closely related to precision but with one variable allowed to change from measurement-to-measurement.

The measurement time for modern laser diffraction instruments is undoubtedly shorter than for sedimentation techniques. Though, the measurement times for sedimentation have been reduced to just a few minutes for not too broad distributions using a scanning head source/detector. In addition, sample preparation, instrument cleanup, and data analysis and printout times combined are now comparable to measurement time. Thus, measurement time is often not the limiting factor in throughput.

The precision is around 1% to 2% for sedimentation, closer to 1% with experience. This precision applies to the median or mean diameters; whereas, the precision for the 10th and 90th percentile diameters is slightly worse. Machine-to-machine reproducibility is similar. The precision for laser diffraction instruments is better than 1%, this being its main advantage. Machine-to-machine reproducibility is a major problem because of design changes and software variations. Given the proprietary nature of the algorithm for solving what is essentially an ill-conditioned problem, a change in the algorithm often leads to very different results, especially below a few microns. Since the various manufacturers use different algorithms for the portion of the distribution below a few microns, this is yet another reason why results do not agree well among laser diffraction instruments.

Theory

Particle Size

The particle size in a sedimentation device is calculated using Stokes’s Law. Excellent reviews exist in the literature. In brief, the equation of motion for a particle of mass $m_p$ and diameter $D$ with density $\rho_p$ falling in a gravitational field, through a liquid of density $\rho_f$ with viscosity $\mu_f$ is:

$$m_p \cdot \frac{d^2 x}{dt^2} = m_p \cdot g - m_f \cdot g - F \cdot \frac{dx}{dt}$$

The right side of this equation is a balance between the force of gravity, buoyancy, and the frictional force. This second order, homogeneous, differential equation with constant coefficients can be solved exactly. The transient part of the solution decays within milliseconds. The remaining part can most easily be obtained by setting $d^2x/dt^2$ to zero, and solving for the constant, terminal velocity, $dx/dt$. Integrating from $t = 0$ to time $t$ yields:

$$t = \frac{(18 \cdot \eta_f \cdot x)(g \cdot \Delta\rho \cdot D^2)}{m_p \cdot \frac{d^2 x}{dt^2}}$$

where $\Delta\rho = \rho_p - \rho_f$ and, for a sphere, the frictional coefficient $F$ is given by:

$$F = 3 \cdot \pi \cdot \eta_f \cdot D$$

A similar equation of motion is obtained for a particle in a centrifuge with rotational speed $\omega$:

$$m_p \cdot \frac{d^2 r}{dt^2} = m_p \cdot \omega^2 \cdot r - m_f \cdot \omega^2 \cdot r - F \cdot \frac{dr}{dt}$$

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The solution for the time \( t \) it takes particles to travel from a radial distance \( S \) to the position of the detector \( r \) is given by:

\[
t = \left[ 18 \cdot \eta_f \cdot \ln(r/S) \right] \left[ \omega^2 \cdot \Delta \rho \cdot D^2 \right]
\]

These equations are for the line start technique, where the particles are layered onto the surface of the liquid. All the particles start at the same position. In the homogeneous start technique, where the particles are uniformly distributed throughout the liquid, the raw signal, using X-rays, is proportional to the cumulative mass distribution \( F(D) \), if and only if the particles fall in straight lines. In the case of the centrifuge, corrections for radial dilution are necessary. Here \( F(D) \) is given by an integral equation, called the Karnack equation.

**Limits to Particle Size**
The largest size that can be measured with accuracy is limited by an assumption in deriving Stokes's Law. It is assumed that the flow is not turbulent. This is ensured when the Reynold's number is less than, roughly, 0.2. The Reynolds number, \( Re \), is defined by:

\[
Re = (\rho_f \cdot dv/dt \cdot D/\rho_f)
\]

This condition puts an upper limit on particle size given by:

\[
D_{\text{max}} \leq \left[ (18 \cdot \eta_f^2 \cdot 0.2) / (\rho_f \cdot \Delta \rho \cdot g) \right]^{1/3}
\]

For high density, pure refractory metals with a density around 20 g/cm\(^3\), in liquids with a viscosity of 5 cP, the maximum particle size is around 75 micron. For the WO\(_4^{2-}\) compounds, with densities around 8 g/cm\(^3\), in liquids with a viscosity of 1.2 cP, the maximum particle size is around 40 micron. In principle, it is possible to measure larger sizes using much more viscous liquids. In practice, such liquids are difficult to use: pumping is hard, cleanup time increases, and ensuring a homogeneous dispersion is not easy.

At the low end the competition between sedimentation and diffusion limit the smallest size that can be measured in gravity. Below a micron or so, depending on particle density, motion due to diffusion becomes more important than motion due to gravitational settling. If not taken into account, the application of Stokes's Law to calculate size is wrong. By applying a centrifugal force, the particle size can be extended down to approximately 10 nm for materials like tungsten.

**Detection**
In modern instruments, the appearance time of a particle is detected using either X-rays or light. X-rays are absorbed in proportion to mass. So a direct mass detector obtains. No corrections are necessary. The only limit is one of sensitivity. For particles comprised of atoms of low atomic numbers, the signal is weak. Typically, for atomic numbers below 13 (aluminum), the signal is weak. For refractory materials the signal is very strong.

All materials either absorb or scatter light. Therefore, detection based on light is quite sensitive. Unfortunately, nontrivial light scattering corrections must be applied to the measured signals before a mass-weighted distribution is obtained. These corrections are based on Mie scattering theory, and they require the refractive index of the particle at the wavelength of the light source. Refractory materials may scatter and absorb light, and this manifests itself in the real and imaginary parts of the refractive index (RI). Literature values of the real and imaginary parts of the RI for such materials are not readily available. Nor are inexpensive, routine instruments for measuring these values.
To illustrate the problems, see Figure 1. Here the extinction efficiency, $Q_{\text{ext}}$, is calculated as a function of particle size from 0 to 10 microns for TiO$_2$. The turbidity must be divided by $Q_{\text{ext}}$ to obtain the differential mass distribution. Errors in the final size distribution may arise if $Q_{\text{ext}}$ is not well known. Notice that $Q_{\text{ext}}$ is not a simple function, especially below a few microns. This is the problem. Accuracy suffers when $Q_{\text{ext}}$ is not known. X-ray detection does not suffer from this problem.

**Experimental Setup**

Measurements shown in the results section were obtained with a Brookhaven BI-XDC, a size distribution analyzer that combines gravitational and centrifugal sedimentation for particle sizing using an X-ray source and photomultiplier detection. The source/detector are mounted on a digital stage that can be scanned across the liquid in which the particles sediment in order to speed up the measurement. Total measurement time depends on the breadth of the distribution. Times from 5 minutes to 20 minutes are common.

Typical liquid volumes vary from 10 to 25 mL, with a nominal concentration of 0.1% by volume for strong X-ray absorbers such as the refractory metals. Multiplying by the particle density yields a reasonable estimate of the mass concentration. For example, with a particle density of 10 g/cm$^3$, the mass concentration is 1 gm per 100 mL of liquid. The typical concentrations in the BI-XDC are 3 times smaller than those in a Micromeritics's Sedigraph, because the path length through which the X-rays pass is 3 times longer. This allows measurements in a concentration range where hindered settling, and the inaccuracies that arise from it, are less.

Particle size distribution results are only as good as the sample preparation techniques allow. In principle, as many as three separate steps are required for creating a stable dispersion starting with a dry powder: wetting, dispersing, stabilizing. Each step may require a separate chemical additive, although any two steps can usually be achieved with a single agent. For oxides and other hydrophilic surfaces, a wetting agent is not always required. For pure metals, a good wetting agent is pure methanol. This lowers the contact angle, allowing liquid to spread over the surface. Once wetted, a dispersing agent may be required to keep the particles apart. Such agents attach themselves to the particle surface, displacing the wetting agent. Dispersing agents provide a repulsion between particles. Mechanical energy may be required to break apart loosely aggregated particles, allowing the dispersing agent to do its job. We have found that ammonium citrate works well as a dispersing agent for many metal powders. Finally, a long-term stabilizing agent may be required if the integrity of the final dispersion is required for long periods. Stabilizing agents either displace dispersing agents or adsorb onto parts of the particle surface not occupied by the dispersing agent. Surfactants and polymers that incorporate imidazole compounds are useful for stabilizing pure metals. Proper choice of wetting, dispersing, and stabilizing agents ensures the least amount of mechanical energy will be required for breaking apart aggregates, and such agents will also ensure the reproducibility of stable dispersions. Too often a dispersion is created by subjecting the particle/liquid system to high amounts of mechanical energy, which, in the long term, does not create a reproducible, well-dispersed system.

Samples are introduced into the disc through an injection port using a syringe. The highest signal (minimum X-ray absorption) corresponds to the liquid without particles, including any wetting or dispersing agents; the lowest signal (maximum X-ray absorption) corresponds to the liquid with particles homogeneously dispersed. To achieve this condition, the disc is rocked back-and-forth, causing the suspension to thoroughly mix. [In a Sedigraph, which does not include a centrifuge, nonhomogeneities may occur when vortices, created by the inlet/outlet ports, inadvertently act as mini-centrifuges. Under these circumstances the initial conditions are not homogeneous. This may explain the occasional appearance of pseudo aggregate peaks.] When the start button is pushed on the BI-XDC, the disc achieves a constant speed in just under 1 second. Disc speeds from 500 to 6,000 RPM are possible with stability of ± 0.01%.
Results

Since the sedimentation technique using X-rays has been used for more than 25 years, the results presented emphasize what can be done with a centrifuge as well as the theoretical limits discussed above.

Repeatability of better than 1% in the mass median diameter is shown by the 5 TiO$_2$ results that nearly perfectly overlay in Figure 2. Measurement time was 5 minutes per run. The centrifuge was run at 1,500 RPM.

According to theory, the largest size of SiO$_2$ particles in water that can be measured accurately is on the order of 80 µ, and this limit is reached in Figure 3. In this case the measurement was done with gravity only.

Lead zirconate titanate, PZT, is a ceramic material used in electrical insulators. Figure 4 shows the cumulative and differential mass distribution. The differential distribution is a smooth, unimodal, lognormal-like distribution with particles as small as 30 nm. Notice too the excellent repeatability of the results. These runs were made in under 10 minutes using 4,500 RPM. Measurements have been made down 10 nm using carbon black and a disc centrifuge photosedimentometer. Given the much higher density of refractory materials, this same lower limit should easily be obtainable with the BI-XDC.

Two samples of Kromasil, a glass bead materials, were mixed: one with a mass median diameter of 5 µ and one with 13 µ. Figure 5 shows the individual cumulative distributions, and the curve obtained upon mixing. Figure 6 shows the differential distribution that obtains. The two modes are approximately 3:1 apart. It is possible with narrow peaks to distinguish sizes only 1.3:1 apart. In comparison, instruments based on diffraction require much greater differences to distinguish individual peaks. The resolution of sedimentation techniques is inherently much higher.

Figure 7 shows the cumulative mass distribution results on three tungsten samples obtained from the Teledyne Wah Chang company in Albany, Oregon. Dry powders were wetted with a few drops of methanol to form a paste. The sample labeled W-10 Fe was dispersed in an aqueous solution of 0.1 % by weight tetra-sodium pyrophosphate; whereas, the samples labeled WA55 773C and WA30 757C, were dispersed in a 20% by weight ethylene glycol and water solution. Fifty watts of ultrasonic energy was applied for approximately five minutes to all three samples prior to running. Notice that all three samples have significant fractions of particles in the size range where light scattering corrections must be applied to get accurate results.

Summary

Sedimentation devices, especially ones with X-ray detection, have a significant edge in accuracy and resolution, especially for particle sizes where the extinction efficiency is not constant, usually below a few microns. Unfortunately, from the standpoint of quality control, a wrong answer, one that is very repeatable, but still wrong, is often preferred by novices. Laser diffraction instruments do not fractionate the distribution prior to detection. Sedimentation devices do. Therefore, the diffraction instrument must mathematically deconvolute the sum of all the light scattering patterns from all the particles registered during the entire measurement. On paper this is easy; in practice it leads to artifacts, often concealed by smoothing the result assuming some shape to the distribution function such as a lognormal. It seems that smooth, lognormal differential distributions, force-fit to the real results are preferred. Yet, for those who want accurate, well-resolved results, a sedimentation device, with X-ray detection, has much to offer. For particle sizing below a few microns, the addition of a centrifuge allows fast, accurate results even well below the size where diffusion competes with sedimentation.
References


**Figure 1.** Light extinction efficiency, $Q_{\text{ext}}$, versus particle size for TiO$_2$. The efficiency is a nontrivial correction that must be used to correct data obtained with turbidity, light scattering or diffraction detectors.
Figure 2. Overlay of five different runs of the cumulative undersize distribution by mass for TiO₂ using the centrifuge mode on the BI-XDC x-ray disc centrifuge. The repeatability is excellent.

Figure 3. Cumulative undersize distribution by mass for SiO₂ up to 80 microns using the gravitational mode on the BI-XDC. The upper limit is set by a maximum Reynolds number of 0.2.
Figure 4. Cumulative undersize and differential size distribution by mass of lead zirconate titanate down to 30 nm using the centrifuge mode of the BI-XDC.

Figure 5. Cumulative undersize distribution by mass for two separate and one mixed sample of Kromasil, a glass bead. The gravitational mode of the BI-XDC was used.
Figure 6. Differential size distribution by mass of the mixed Kromasil sample showing complete resolution of the two peaks.

Figure 7. Cumulative undersize distribution by mass for three tungsten samples. The very high density of these materials must be considered in all phases of sampling and sample preparation as well as measurement. These results from the BI-XDC show that all three have sizes where light scattering corrections become important.