Ultra-high resolution particle size analysis with the CPS disc centrifuge

Introduction

All methods of particle size analysis can be characterized by three parameters: the accuracy of the reported size distribution, the repeatability of the reported size distribution, and the resolution of the distribution. This document discusses the excellent resolution that can be achieved using the CPS Disc Centrifuge.

What is resolution?

Resolution of a size measurement method is the ability of the method to see a size distribution clearly. All size measurement methods report a distribution that is more or less "fuzzy" compared to the true distribution, much as an out of focus lens produces a fuzzy image. A lens can be very slightly out of focus (higher resolution) or far out of focus (lower resolution). Different particle sizing methods and different instruments have vastly different resolutions, even though nearly all particle sizing instrument manufacturers claim that their instruments have "high resolution". In order to rationally evaluate instrument resolution, we must first have a clear definition of resolution.

For this document, resolution of a size measurement method is defined in two ways, which give the same result. First, resolution is the minimum fractional size difference between two perfectly narrow families of particles which allows the two reported peaks to overlap by less than 5% of their total area. Resolution is stated as a percentage:

$$\text{Resolution} = 200 \times (D_1 - D_2)/(D_1 + D_2)$$

Where D_1 is the diameter of the larger family, and D_2 is the diameter of the smaller family. For example, if we find that two families can be resolved with D_1 of 1.05 micron 1 and D of 0.95 micron, then the instrument resolution is 10%. Second, we can express the same resolution value in terms of the reported peak width for a single family of particles that are perfectly uniform in size, compared to their reported median diameter:

$$\text{Resolution} = 100 \times (D_{95} - D_5)/D_{50}$$

Where D_{95} is the diameter larger than 95% of the entire reported distribution, and D_5 is the diameter larger than 5% of the entire reported distribution. These two resolution calculations give the same value for resolution.

Theoretical resolution of the CPS disc centrifuge

Particles sediment in the CPS Disc Centrifuge according to Stokes' Law. Particles sediment at rates that are proportional to the square of the particle diameter; 1 micron particles sediment 4 times faster than 0.5 micron particles. At the start of a typical analysis, all particles are located in a thin band at the fluid surface. When particles arrive at the instrument's detector beam, they have separated from particles of different size, so the detector beam measures only a small slice (a "differential") of the whole size distribution. This is why we call the disc centrifuge method "differential sedimentation". Figure 1 shows a close-up of the sedimentation process.

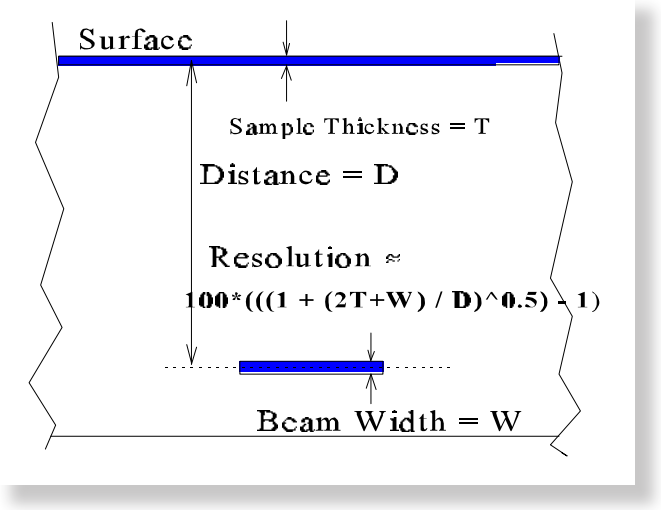


Figure 1 - Resolution of the CPS Disc Centrifuge

The theoretical resolution depends on three factors:

- the width of the detector beam,
- the thickness of the initial sample band, and
- the sedimentation depth.

As the sedimentation depth increases, the theoretical resolution increases as well, because the physical separation of particles of different size becomes larger. The equation in Figure 1 calculates the resolution as a function of the three variables. The detector beam width is approximately 0.5 mm. The sedimentation depth depends on how much fluid is added to the centrifuge, but with a typical set-up of the instrument, the depth is in the range of 10 mm. The initial sample band width depends on the volume of sample that is injected into the disc. With a sample volume of 0.1 ml, the initial sample ring has a thickness of approximately 0.066 mm. Using these typical values, we can calculate the theoretical resolution: ~ 3.11%.

Quantum Design EUROPE
Quantum Design GmbH
Breitwieserweg 9
D-64319 Pfungstadt
Please contact: Stefan Wittmer
✆ +49 6157 80710-63, wittmer@qd-europe.com
Find your local contact at www.qd-europe.com
CPS Instruments Europe

Ultra-high resolution particle size analysis with the CPS disc centrifuge

The theoretical resolution can be improved by reducing the detector beam width, increasing the sedimentation depth, and reducing the thickness of the initial sample Figure 2 band. For example, if the sedimentation depth is increased to 20 mm (about the maximum practical depth in the CPS Disc Centrifuge) and the sample volume is reduced to 0.05 ml, then the theoretical resolution improves to ~1.4%. This means that two perfectly narrow peaks only 1.4% different in diameter could be completely resolved.

Factors that reduce resolution of the CPS disc centrifuge

Actual instrument resolution is always slightly worse than the theoretical resolution described above. There are three factors that all can reduce resolution. Theses factors are: Brownian motion of the particles during sedimentation, sedimentation instability (streaming), and a broader than expected initial sample band that comes from the injection process. Each of these potential broadening factors is discussed below.

Brownian motion

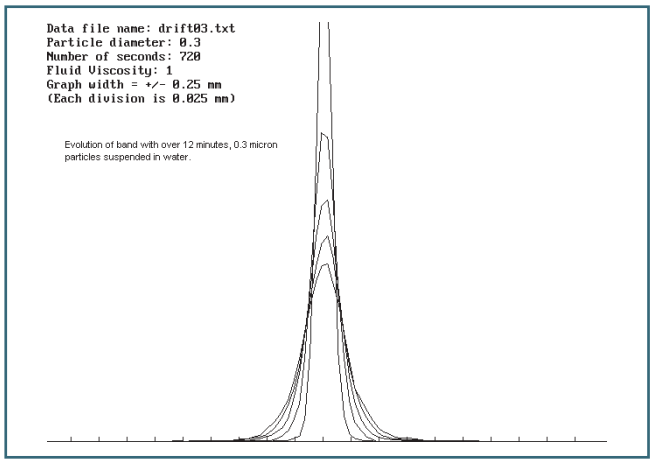


Figure 2

Random diffusion of particles during the sedimentation will cause some particles to arrive at the detector beam earlier than expected (larger apparent diameter), and some particles to arrive later than expected (smaller apparent diameter). Brownian motion is a true diffusion process, with a calculable diffusion constant that depends on both particle size and fluid viscosity. In general, the mean absolute diffusion distance during a brief time (say 1 second) is proportional to the inverse square root of the particle diameter. A "random-walk" simulation of Brownian motion shows how the diffusion progresses. Figure 2 shows how an initially thin band of 0.3 micron diameter particles (0.02 mm initial band thickness) broadens over 12 minutes in a fluid with viscosity of 1 centipoise.

After 12 minutes, 95% of the particles are found in a Gaussian shaped band ~0.125 mm wide around the original position. If we were to measure a perfectly narrow family of 0.3 micron particles that required 12 minutes to reach the detector beam, then the band would reach the detector with an increase in band width equal to ~0.125 mm. In order to estimate the effect of Brownian motion on resolution, we can add the Brownian diffusion to the initial sample thickness. This yields an estimated resolution of:

$$100x(((1+(2T+W)/D)^{0.5})-1)=$$
$$100x(((1+(2x(0.033+0.125)+0.5)/20)^{0.5})-1)=2.02\%$$

After accounting for the effects of Brownian motion over 12 minutes, the CPS Disc Centrifuge should still resolve peaks near 0.3 micron diameter that differ by as little as 2%, compared to 1.4% in the absence of Brownian motion.

For particles larger than 0.3 micron, or particles with sedimentation times less than 12 minutes, the effect of Brownian motion on resolution will be considerably less. For example, 0.5 micron particles arriving at the detector after 4 minutes form a band less than 0.02 mm wider than the initial sample thickness, so the resolution in this case would be ~1.5%, only very slightly different that the resolution would be without Brownian motion.

For particles that are significantly smaller than 0.3 micron, or that reach the detector more slowly, the effect of Brownian motion will be considerably more. For example, 0.05 micron particles that require 45 minutes to reach the detector will arrive as a band ~ 0.4 mm wide; with a total sedimentation depth of 20 mm, resolution in this case would be ~3.8%. Particles of 0.05 micron diameter that reach the detector after 90 minutes form a band that is about 0.75 mm wide; with a total sedimentation depth of 20 mm, the resolution in this case would be ~7.9%.

Initial sedimentation instability

All analyses in the CPS Disc Centrifuge must be conducted in the presence of a density gradient, where the fluid at the outside edge of the disc chamber is of slightly higher density than the fluid near the surface. In the absence of a density gradient, differential sedimentation is unstable: an injected sample sediments "en-masse" rather than as individual particles. This instability is sometimes called "streaming". The instability is caused by the effect of the (more dense) suspended particles on the net density of the fluid in which they are suspended. If the net density of the sample suspension is higher than the fluid inside the rotating disc,

Ultra-high resolution particle size analysis with the CPS disc centrifuge

then the sedimentation will become unstable. During the entire analysis, the fluid that is just "below" a band of particles (that is, fluid slightly further from the center of rotation) must be equal to or higher in density than the net density of the fluid that hold the band of particles. This requirement for stability can be expressed mathematically as the following differential:

$$\partial\tilde{n}/\partial R \geq 0$$

Where ñ is the net fluid density, and R is the distance from the center of rotation. This requirement means that it is impossible to have an instantaneous, "step-like" increase in suspended particle concentration without inducing instability. In fact, there will always be some (very brief) instability immediately following sample injection until the above equation is satisfied. The effect of instability is a broader than expected initial sample band, and so lower than expected resolution.

We can estimate the effect of instability by comparing the net sample density with the steepness of the density gradient inside the disc centrifuge. For example, suppose we inject a sample of polystyrene particles with a concentration of 0.05% by weight (typical for a polystyrene sample), and that the fluid in the centrifuge ranges from 1.0178 g/ml (5% sucrose solution) to 0.9981 g/ml (water) over a sedimentation distance of 20 mm. The steepness of the gradient is:

$$(1.0178 - 0.9981) / 20 = 0.000985 \text{ (g/ml)/mm}$$

The density of polystyrene is 1.050 g/ml, so a 0.05% dispersion in water at 20o C has a density of 0.998126 g/ml, or 0.000026 g/ml higher than pure water. The distance over which this increase in density can be supported by the density gradient is:

$$0.000026 / 0.000985 = 0.0264 \text{ mm}$$

In other words, the leading edge of the sample band can not be less than 0.0264 mm wide in order to maintain stable sedimentation if the polystyrene concentration in the sample is 0.05%. The initial sample thickness (based on injected sample volume of 0.05 ml) is ~0.033 mm. Initial instability will add about 0.0264 to the initial band thickness. Higher or lower sample concentrations will lead to a proportionally larger or smaller contribution from initial instability.

Materials with higher density (for example polyvinyl chloride, density 1.385 g/ml) provoke additional instability unless a proportionally steeper density gradient is used. In nearly all cases, the effects of instability can be kept quite small by using relatively low sample concentration and an appropriate density gradient.

With 0.05% of 0.3 micron polystyrene particles, 0.1 ml sample volume, a 20 mm sedimentation distance, and the above described density gradient, the expected resolution of the instrument (including the effect of Brownian motion over 10 minutes of sedimentation) is ~ 1.8 - 1.9%.

Injection effects

The injection process can impact resolution in two ways. First, the injection is not instantaneous, but actually takes place over a period of about 0.1 second. This means that all particles do not start the sedimentation process at exactly the same time. Second, the physical impact of the sample striking the fluid surface inside the disc can cause some initial mixing of the sample into the gradient fluid, so that the initial sample band is not as narrow as the volume of the injected sample would suggest.

Injection timing

The effect of injection timing on the reported width of a perfectly narrow family of particles depends on the total sedimentation time. The % increase in reported peak width is given by:

$$100 \times ((1 + (T_i / T_s))^{0.5}) - 1)$$

Where T_i is the time required for injection, and T_s is the time required for the particles to reach the detector beam. At a sedimentation time of 60 seconds and with an injection time of 0.1 second, the increase in width is ~0.083%. This contribution is very small compared to the other factors that impact resolution. At sedimentation times longer than about 1 minute, injection timing will always have negligible impact on resolution. With much shorted sedimentation times, the effect can be significant. For example, if a peak reaches the detector in 10 seconds, the increase in reported width from injection timing will be ~ 0.5% of the peak diameter; or about 25% of the total reported width. The overall impact of injection timing is actually a little less than indicated by the above equation, because if particles begin sedimentation at slightly different times, the effect of initial instability (as described in the above section) will be reduced. Reduced initial instability partially offsets the effect of injection timing.

Quantum Design EUROPE
Quantum Design GmbH
Breitwieserweg 9
D-64319 Pfungstadt
Please contact: Stefan Wittmer
✆ +49 6157 80710-63, wittmer@qd-europe.com
Find your local contact at www.qd-europe.com
CPS Instruments Europe

Ultra-high resolution particle size analysis with the CPS disc centrifuge

Physical impact

It is difficult to predict the effect of physical impact of the sample on the fluid surface. However, experience has shown that the initial mixing (band broadening) is relatively small in nearly all cases, especially when the total sedimentation distance is ~20 mm. The rotating disc can be viewed using a synchronized strobe light, and the mixing from physical impact of the injection can be seen; it is clearly <1 mm, although an exact value is difficult to measure. When the sample is prepared using a fluid that is significantly lower in density than the fluid at the top of the density gradient, the mixing is drastically reduced (<<1 mm). For example, if the gradient consists of sucrose in water, the sample can be prepared in a mixture of 8% ethanol in water, with a density of ~0.985 g/ml. With this type of sample preparation fluid, the sample does not penetrate the density gradient surface very far; the sample fluid tends to quickly "float" and spread across the fluid surface. While it is not possible to exactly predict the effect of physical impact, the contribution to reported width of a perfectly narrow beam should be <1% in all cases, and likely will be well under 0.5% if the sample is prepared in a lower density fluid.

Actual resolution of the CPS disc centrifuge

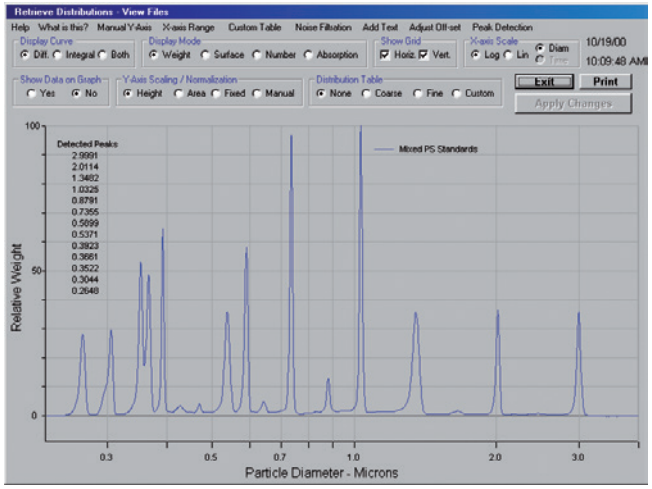


Figure 3

When all of the factors that impact resolution are taken into account (Brownian motion, initial instability, inject effects), the expected resolution at a particle diameter of 0.3 micron is in the range of 1.9% to 2.5% when the instrument is set up with a sedimentation depth of 20 mm. This means that two perfectly narrow families that differ in diameter by 1.9% to 2.5% should overlap by not more than 5% of their peak area.
Figure 3 is an image from the CPS Disc Centrifuge operating software, showing the particle size distribution for a mixture of several "U.S. NIST traceable" polystyrene calibration standards.

Data was collected from 4 microns to 0.2 micron. This analysis was run at 20,000 RPM, with a fluid depth of ~20 mm. Total analysis time to reach 0.2 micron was 11.7 minutes. You can see in the distribution that the different standards vary considerably in width. For example, compare the width of the peak at 1.348 microns with the peak at 1.032 microns; the 1.032 micron peak is clearly more narrow.

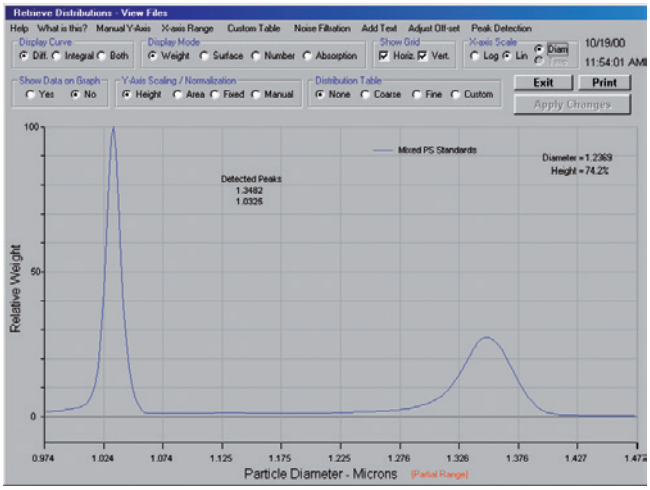


Figure 4

The difference in width between these two peaks is shown more clearly in Figure 4, where only a portion of the distribution is displayed. The peak at 1.0325 micron has a 95% width of only 3% of its mean diameter. This means that the resolution of the instrument must be better than 3%, since the measured width includes both the real width (which can never be zero!), plus the contribution of the instrument.

Figure 5 shows the portion of the distribution between 0.223 micron and 0.413 micron, including several different peaks. There are several interesting features in this part of the distribution. The narrowest of the peaks, at 0.392 micron, has a 95% peak width of only ~2.6% of it's mean diameter, which proves that under these conditions the instrument has resolution better than 2.6%, since the measured width includes both true width (which can't be zero) plus the contribution of the instrument. The peak at 0.3044 micron has shoulder on its trailing edge, which suggests something went wrong during the emulsion polymerization of this standard, or that the standard is actually a mixture of two emulsion polymerization batches with very slightly different peak sizes.

Quantum Design EUROPE
Quantum Design GmbH
Breitwieserweg 9
D-64319 Pfungstadt
Please contact: Stefan Wittmer
✆ +49 6157 80710-63, wittmer@qd-europe.com
Find your local contact at www.qd-europe.com
CPS Instruments Europe

Ultra-high resolution particle size analysis with the CPS disc centrifuge

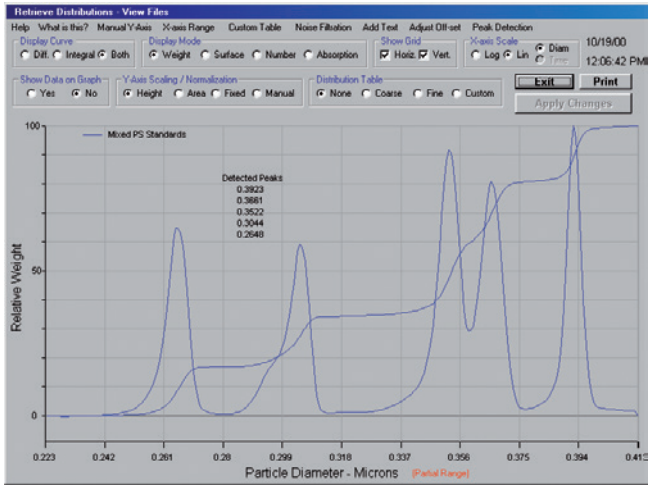


Figure 5

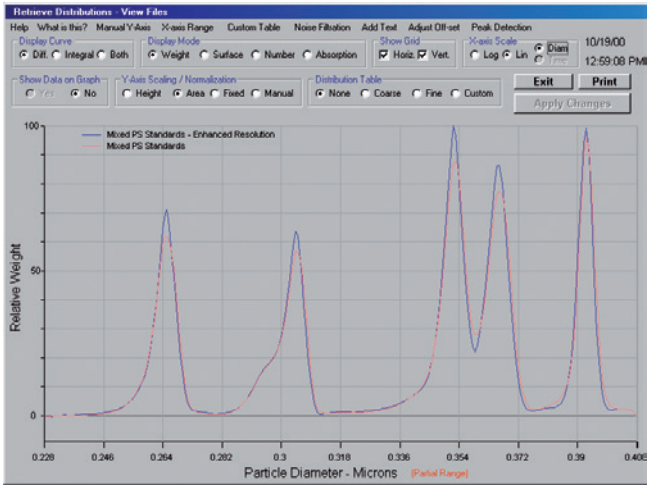


Figure 6

The most interesting feature in Figure 5 is the pair of peaks at 0.3522 micron and 0.3661 micron. These two peaks differ in size by 3.9%, and they are almost completely resolved, but what makes this pair interesting is that they were sold as a single calibration standard of 0.36 micron mean size! Whatever particle sizing method was used to characterize this calibration standard, it was not capable of seeing that this latex is actually a ~50:50 mix of two different size emulsion polymerization batches.

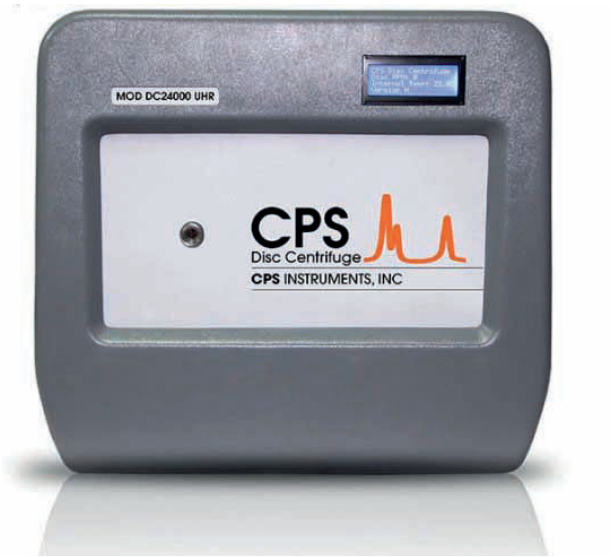
Enhancing resolution in the CPS disc centrifuge

The most important factors that impact instrument resolution are known (detector beam width, sample thickness, Brownian motion) and can be mathematically modeled. It is possible to enhance the instrument's resolution by mathematically treating the distribution data that comes from the instrument to remove the effects of these factors. The process of removing a known effect from an unknown distribution is sometimes called "deconvolution". CPS has included in the operating software an optional deconvolution method to reduce the effect of the detector beam width. Methods to remove the effects of other factors have been identified but not yet coded into the software.

Figure 6 shows a comparison of two separate runs of the same sample as in Figures 3, 4, and 5, but with ~50% of the effect of the detector beam width removed from one of the distributions by deconvolution. The two distributions in Figure 6 are plotted with equal total area under the curves. The resolution of the enhanced curve is clearly better than the normal curve. The 95% peak width for the 0.3923 micron peak is only ~2.27% of its mean size (compared to ~2.6% without enhancement).

What are your resolution needs?

If you have a sizing application that requires the highest possible resolution, then CPS can add deconvolution functions for Brownian motion and initial sample thickness to the operating software. These additions should yield resolution of better than 1%. Let us know what your resolution needs are.



Quantum Design EUROPE
Quantum Design GmbH
Breitwieserweg 9
D-64319 Pfungstadt
Please contact: Stefan Wittmer
+49 6157 80710-63, wittmer@qd-europe.com
Find your local contact at www.qd-europe.com
CPS Instruments Europe