

# Acoustic Attenuation Spectroscopy for Process Control of Dispersed Systems

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## Abstract

Acoustic Attenuation Spectroscopy (AAS) is a powerful technique for the measurement of Particle Size Distribution (PSD) of concentrated colloids – in most cases without the need for sample dilution, i.e. at process conditions. While AAS has been used successfully in the laboratory, it has not been widely employed for Process Control purposes. This paper describes a new flow-through (Process Online) measurement approach that can make AAS into a suitable Process Control tool for widespread use in most industrial production settings, in particular for PSD measurement and control. This approach basically consists of splitting ultrasonic sound waves by using stepped reflectors and/or transducer delay rods which provide multiple measurement gaps without the use of moving parts.

## Introduction

Acoustic Attenuation Spectroscopy (AAS) is commonly used to measure particle size distributions (PSD) in the range 5 nm to 100 microns of aqueous, as well as, non-aqueous colloidal samples such as Chemical Mechanical Polishing (CMP) slurries, Ceramic Slips, Printing Inks, Minerals, Catalysts, Metal Oxides, Pigments, Cosmetics, O/W and W/O emulsions, and others<sup>1-5</sup>.

AAS consists of measuring the attenuation (dB/cm or dB/cm/MHz) of sound waves traveling through the colloid as a function of the Frequency of the sound waves (MHz). These colloids may be flowing and/or being stirred while the measurement takes place (thus, particle settling is prevented).

Commonly measured attenuation levels are in the range of near zero to over 100 dB/cm in the frequency range 1-100 MHz. The percent solids level (discrete-phase concentration) of measured samples is typically in the range 0.1 to 60% volume although Greenwood et. al. have used long-path measurements on lower-concentration samples<sup>6</sup>. Sound speed spectra can be readily measured in addition to attenuation. Sound speed data is useful in verifying the quality of the attenuation data. It can also be employed to infer molecular-level phenomena in colloidal samples<sup>7</sup>.

## Current AAS Laboratory Systems

Figures 1 and 2 below show schematic representations of tone burst Through-Transmission and Echo-based attenuation measurements. In either case, measurements are made at several accurate gaps in order to maximize the frequency range of the attenuation spectra. Thus, these measurements require the use of expensive High-Resolution/Accuracy translation stages or stepper motors (within micron-level positioning resolution/accuracy) that also offer minimal pitch and yaw specifications<sup>5</sup> (for optimal

transducer alignment). The measured acoustic attenuation spectra are used to calculate PSD data whose accuracy and resolution are enhanced by broad frequency-range (1-100 MHz) measurements<sup>4, 8-13</sup>.

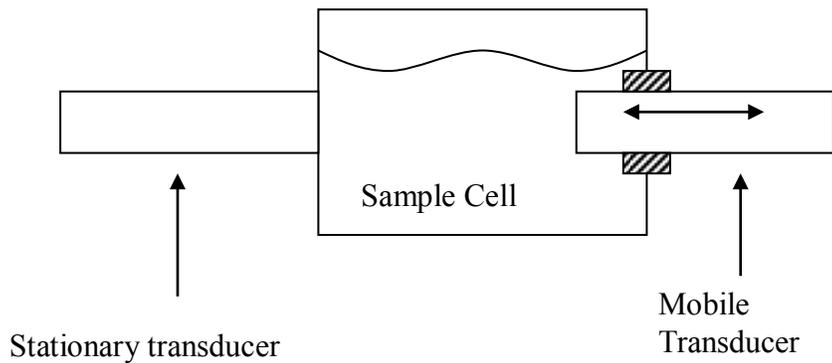


Fig. 1. Sample Cell for Through-Transmission Attenuation Measurements.

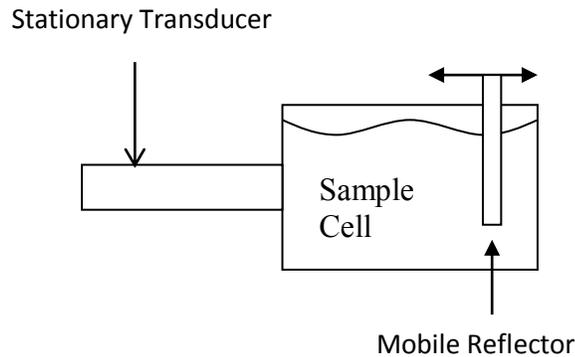


Fig. 2. Sample Cell for Echo-Based measurements using a Mobile Reflector introduced through the top of the liquid sample. A stationary transmitter/receiver transducer is used.

Fig. 3 presents measured attenuation data by a tone-burst echo based APS-100 Acoustic Particle Sizer instrument (Matec Applied Sciences, Northborough, MA USA) of a 4% wt silica sample (MP1040 from Nissan Chemical, mean nominal particle size of 110-120 nm). The bottom curve is for pure water. The two closely overlaid spectra are measured plus a third-order polynomial fit that exhibit close agreement.

Fig. 4 shows the corresponding PSD data for this MP1040 sample. This data –calculated using Carasso et. al.'s model<sup>13</sup>- shows a fairly narrow PSD with a mean volume-average particle size of 115 nm, and 114 nm Area-Average, which are in good agreement with its manufacturer's nominal value.

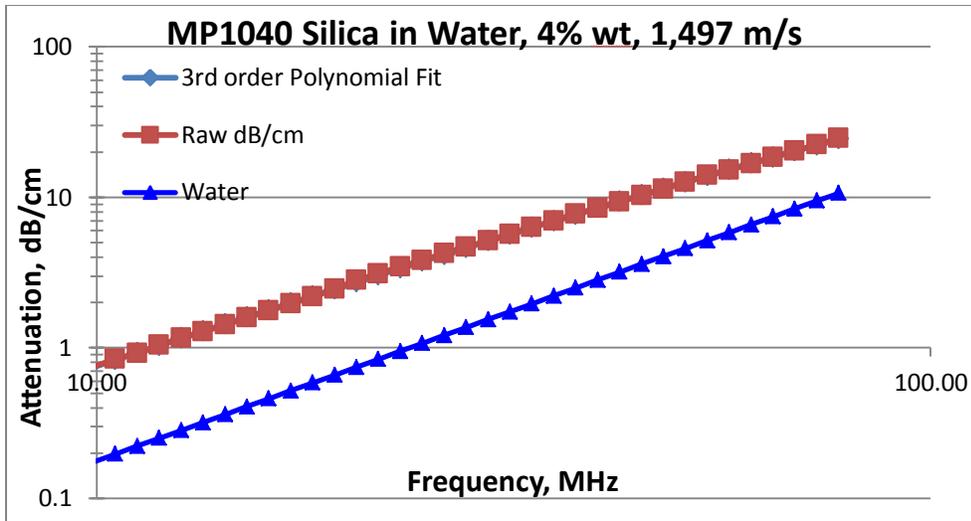


Fig. 3. Measured attenuation spectra for a MP1040 silica sample.

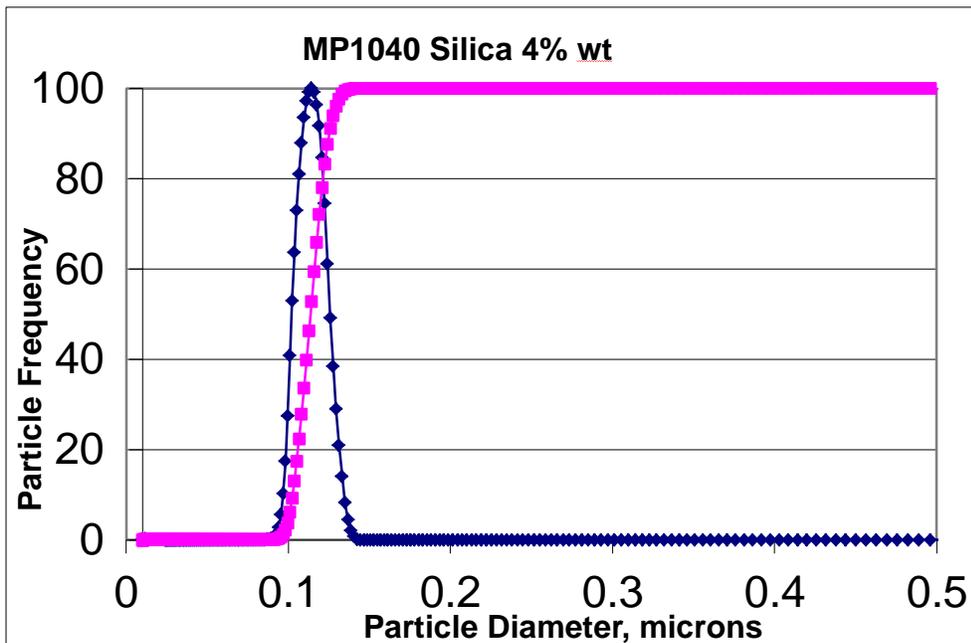


Fig. 4. Particle Size Distribution from AAS measurement of MP1040 silica sample.

Despite the advantages AAS offers for PSD analysis in laboratory applications, it suffers from the following drawbacks for Process/Online applications:

- A. High-Resolution Motion Stage/Stepper motor required in order to perform measurements at multiple gaps:
  - Higher initial cost.
  - Maintenance requirements which reduce uptime cycles.

- B. Abrasion issues (Transducers/Reflectors, Seals) from flowing slurries. This factor is compounded by the fact that many slurries are designed to be highly abrasive, e.g. CMP Semiconductor slurries.
- C. Relatively Long Data Spectrum Acquisition (~couple of minutes) which prevents real-time spectrum acquisition. One difficult scenario occurs when the flowing colloid's percent solids fluctuates frequently. These colloid-concentration fluctuations can make the acquired attenuation spectrum inaccurate as attenuation levels increase with volume fraction of the colloid's discrete phase.

### Proposed Process Online System

Desirable features of an AAS Process Online System are as follows:

- A. No Moving Parts
- B. Minimized Abrasion
- C. Attenuation measurements at multiple gaps
- D. Fast Spectrum Acquisition (< 30 seconds)

These provide the following benefits:

- Reduced initial and maintenance costs
- Increased reliability
- Maximum uptime
- Near Real-Time data spectrum acquisition.

Figures 5 and 6 show representations of proposed online sample cells for acoustic attenuation and sound speed spectrum measurements that meet the above requirements. These show a transmitter/receiver transducer plus a stepped reflector. This reflector arrangement provides 3 stationary mirror surfaces that provide three different ultrasonic measurement gaps. More than one transducer element can be placed on the delay rod in order to widen the frequency range of the measurement. For brevity, this type of arrangement will be referred to as AREPA (Acoustic REflection Particle Analysis). This arrangement provides multiple acoustic paths without the need for a motion stage while minimizing abrasion effects. Thus, this measurement approach provides reduced initial and operational costs, increased reliability, and maximum uptime. Measurements are relatively fast (near real time) since there is no need to reposition reflectors or transducers. A delay rod –usually Quartz of 2.5 to 5 cm diameter- and a transducer element are pictured.

As described by Reed et. al.<sup>3</sup>, these reflector-based measurements use the delay rod's internal echo waveform as a reference to calculate attenuation data. This approach enjoys increased accuracy through

the use of cross correlation of the reference and liquid echo waveforms. AREPA measurements are more suitable for less concentrated colloid measurements as the sound travels twice in the gap thereby resulting in higher attenuation levels.

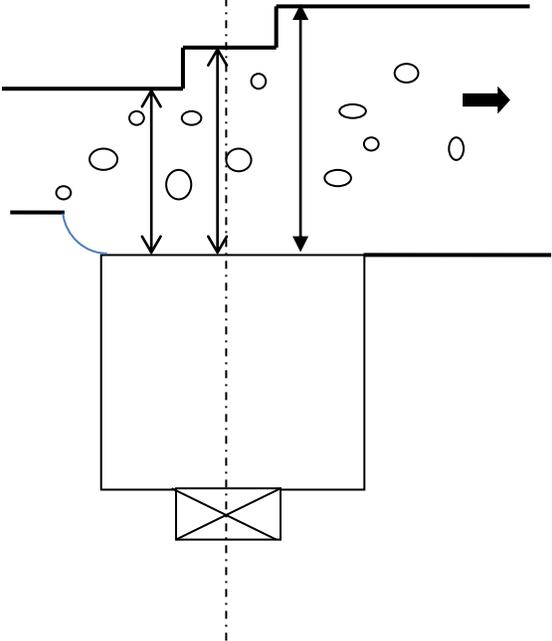


Fig. 5. Acoustic Reflection Particle Analysis (AREPA) on line sample cell showing three reflector surfaces on a single stepped reflector component. A transducer delay rod and transducer element are shown.

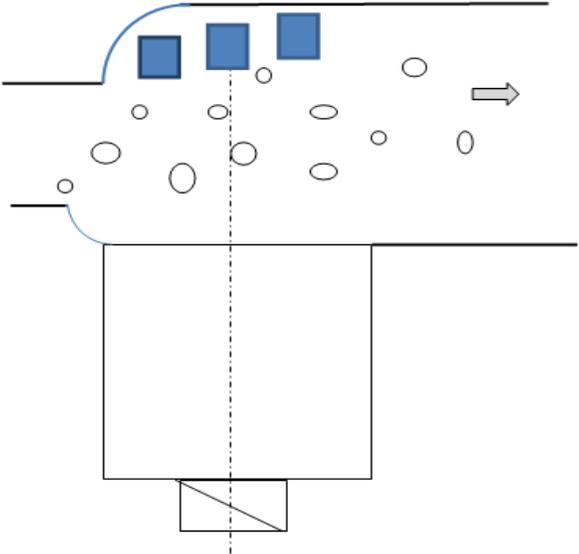


Fig 6. AREPA sensor incorporating three separate reflectors for multi-path ultrasonic measurements.

Alternatively, a through-transmission based sample cell would allow characterization of higher percent solids level samples because the sound waves travel only once in the gap (for attenuation measurement

purposes). For brevity, this measurement will be referred to here as TTAPAS (Through-Transmission Acoustic Particle Analysis System).

Figure 7 describes a TTAPAS flow-through cell for use in online/process-control applications. Multiple measurement paths (gaps) can be achieved by precision machining steps on the wet end of one of the delay rods. As mentioned above, multiple transducer elements could be placed on the delay rods in order to widen the frequency range while using a single delay rod. Two or more steps would be required for these measurements.

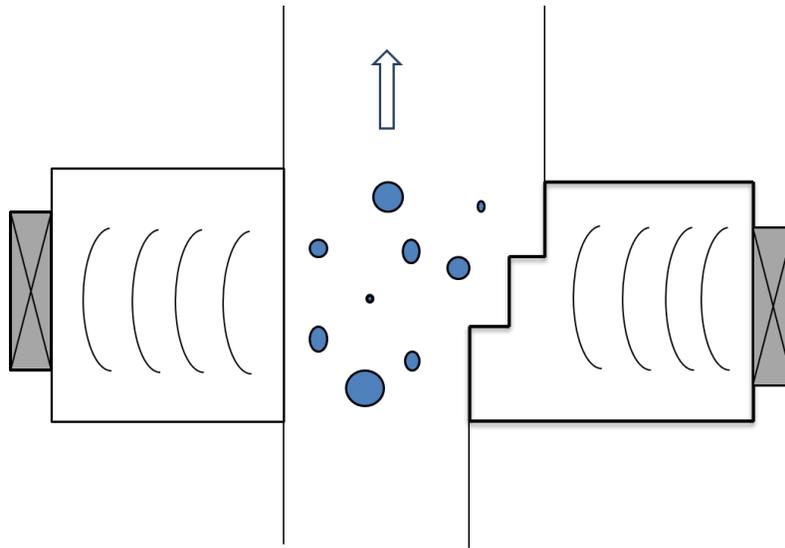


Fig. 7. TTAPAS through-transmission cell arrangement for attenuation and sound speed measurements.

The steps on the reflector and transducer configurations described above can have various shapes such as rectangular, circular etc. Some of these alternative arrangements would include stacked disc-like surfaces; however, these would likely be more prone to abrasion issues.

These online systems could be placed either in process pipes (inline) or on a bypass pipe as shown in Fig. 8. Valves (CVV) are pictured at either side of the flow-through AREPA/TTAPAS cell. These valves can be used for periodic sensor calibration and/or cleaning by stopping colloid flow while allowing calibration solvent (without particles) to flow through the sensor. Calibration consists of comparing the measured solvent spectrum (aqueous or non-aqueous) to a “golden” (calibrated) one and calculating corresponding calibration factors for each measurement frequency. This approach is similar to Reed et. al.’s calibration<sup>3</sup> except that it can be extended to the use of non-aqueous solvent spectra as calibration fluids in order to avoid using water in non-aqueous applications. These “golden” non-aqueous solvent spectra are actual physical properties that can be produced (once) on off-line (lab) acoustic instruments that have been water calibrated as typically done.

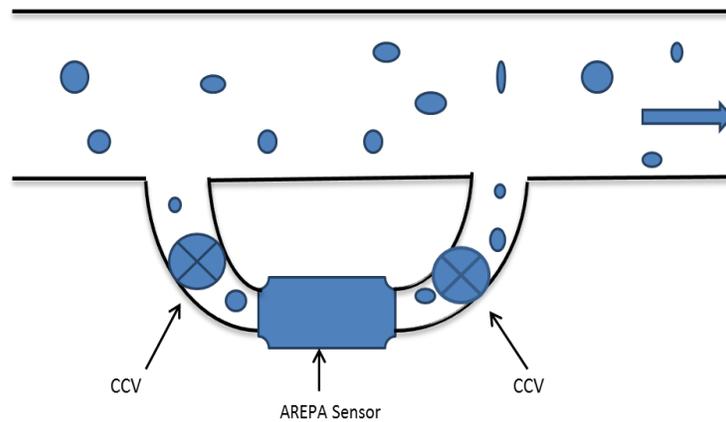


Fig. 8. AREPA (or TTAPAS) online sensor installed on a process bypass line. The two CCV's (Calibration/Cleaning Valves) can be manipulated to temporarily stop sample flow in order to allow cleaning and/or calibration fluid to flow through the sensor (cleaning/calibration fluid pipes not shown).

#### Attenuation and Sound Speed Data

Figure 9 presents echo waveforms from a 3-step reflector on a DI water sample. The two steps on the reflector unit are each 0.4 cm deep. The middle reflector is nearly rectangular and 0.64 cm wide. This reflector unit was precision machined so that each reflector has the same surface area facing the transducer. Not shown is the reference echo traveling back and forth within the 2.5cm diameter quartz delay rod.

Four echoes are observed originating from the reflector surface closest to the transducer. From left to right, these are echoes 1, 2, 4, and 5. These decay in amplitude as expected. Echo number 3 is the first echo from the middle reflector surface while the last echo emanates from the farthest reflector from the transducer.

These sound wave amplitudes/characteristics need to be incorporated into the sensor calibration for accurate acoustic attenuation spectrum data. These spectra will then be used in the particle size distribution computations.

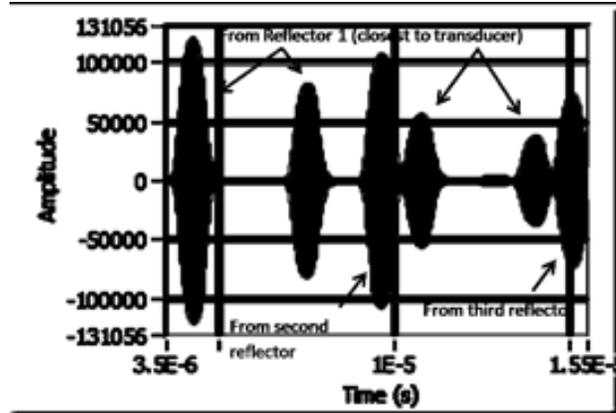


Fig. 9. Waveforms (18 MHz) from a two-step (three equal-area reflector surfaces) AREPA cell on a DI-Water sample; step depths= 2 x 0.4 cm, total reflector diameter= 2.54 cm, center reflector width= 0.64 cm, transducer-element diameter= 1.9 cm, 21.1 °C.

#### Transducer Element Diameter Effect

Because this arrangement in essence divides the sound wave, i.e. its energy, into as many reflector surfaces, it is possible to adjust the amplitude of each reflected (or transmitted in the TTAPAS case) sound wave by manipulating each step's surface area. For example, the farthest step (gap) can be manufactured to have a larger area –and thus increased echo amplitudes- than the closer ones in order to make better measurements at longer paths.

Radial location of each step is also important. The center step in a three-step reflector (or delay rod in TTAPAS) reflects more energy than the edge surfaces. Thus, the center reflector can be constructed with a smaller surface area than the others.

Figure 10 below presents waveforms on a system identical to Fig. 9 except that the transducer element is 0.64 cm. The center reflector is also 0.64 cm wide. As can be observed, the echoes from the two edge surfaces are minimal compared to the center one.

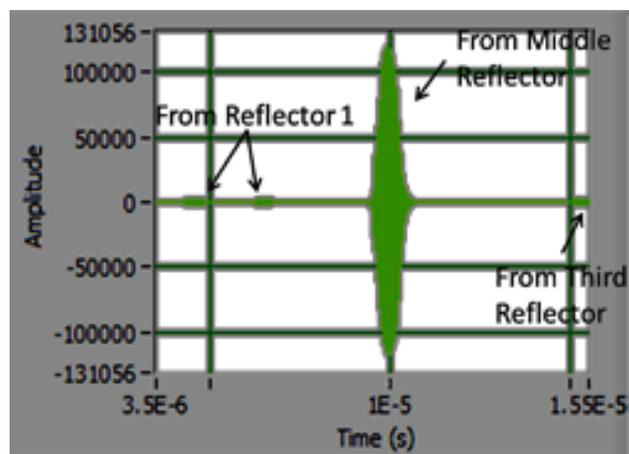


Fig. 10. Waveforms (18 MHz) from a two-step (three equal-area reflector surfaces) AREPA cell on a DI-Water sample; step depths= 2 x 0.4 cm, total reflector diameter= 2.54 cm, center reflector width= 0.64 cm, transducer-element diameter= 0.64 cm, 21.1 °C.

#### Particle Size Distribution (PSD) Data

Fig. 11 presents particle size distribution (PSD) data for a 4% wt MP1040 silica sample (Nissan Chemical) measured using a three-reflector (2 x 0.4cm steps) AREPA sample cell. The three reflectors were precision machined to be flat and parallel to each other. The transmitter/receiver transducer was finely aligned to the reflectors.

The sample cell was calibrated using DI Water prior to these measurements. The corresponding PSD computations were performed using the Carrasso et. al.<sup>13</sup> computational model.

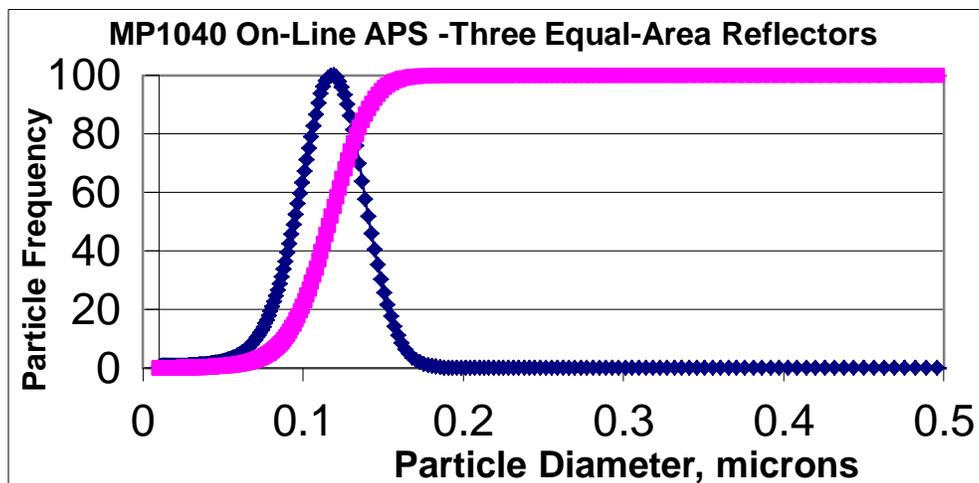


Fig. 11. PSD data for a 4% wt silica sample using a three-reflector AREPA sample cell.

#### Particle Size Distribution for Process Control

PSD curves are not practical as set points. Instead, numerical set points are preferable. Mean particle size data can be readily available for such purposes. However, mean particle size values can be misleading as any single mean particle size can be produced by an infinite number of PSD curves<sup>14</sup>. Moreover, as shown in the hypothetical example in figure 12, it is possible for a sample with a mean particle size of 150 nm not to contain a single 150 nm particle.

Figure 12 shows two distributions that could be obtained from a Low-Resolution (ensemble) technique along with a (bimodal) high-resolution one such as by a fractionation or TEM technique. Light-scattering based devices may actually tend to report only the larger particle size population because the larger particles tend to mask the smaller ones due to the larger particles' higher light-scattering efficiency.

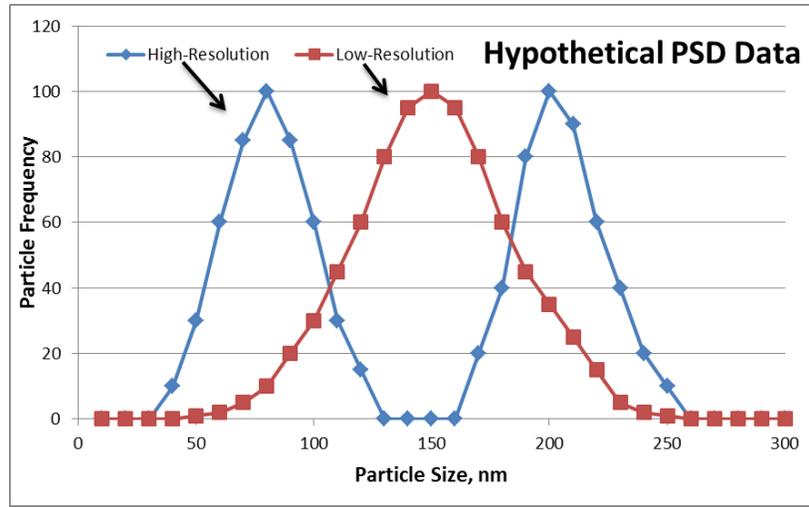


Fig. 12. Two hypothetical PSD curves generated by low (unimodal)- and high-resolution (bimodal) sizing techniques.

Figure 13 presents three particle size distributions measured from three different samples by a CHDF3000 instrument (Capillary Hydrodynamic Fractionation, Matec Applied Sciences, Northborough, MA USA). These three PSD's are noticeably different, yet produce the same mean particle size of 180 nm. Various properties of these samples such as rheology, film gloss, percent solids loading, etc. would be very different even though they are reported to have the same mean particle size.

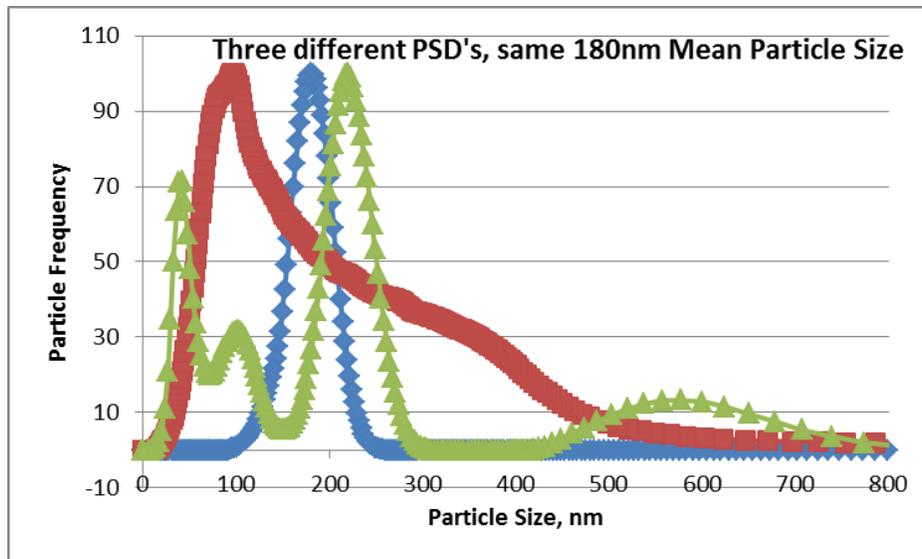


Fig. 13. Three samples measured by a CHDF3000 instrument produce the same 180nm mean particle size value despite their different PSD curves.

CONCLUSIONS

Acoustic Reflection Particle Analysis (AREPA), and Through-Transmission Acoustic Particle Analysis System (TTAPAS) show strong promise for particle size distribution measurement in process control/Online scenarios. Both approaches eliminate the use of moving parts while minimizing abrasion issues. Thus, costs are reduced and uptime is maximized.

Regarding process control set points, Volume-, Area, and Number-average particle size data could be used. Volume-average (fourth power dependence on particle diameter) is highly sensitive to larger particles, i.e. it can shift sharply if small numbers of large particles are detected; Number-average data (first power dependence on particle diameter) are strongly affected by small particles, especially those below 100 nm. Area-average data are less prone to sharp fluctuations due to detected minor populations and thus would appear more suitable to be used as a set point for process control.

Another approach would be to use ratios of mean particle size data. Based on the discussion above, the ratio of Volume/Area averages would provide a more stable control figure than the polydispersity index (PDI, which is equal to the ratio of volume to number average values). PSD Percentile figures, e.g. 90%, are also useful in maintaining suitable process control goals.

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