A Novel Ultrasonic Method for Characterizing Suspensions of Nanoparticles

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ABSTRACT

The Ultrasonic Pulsed Doppler (USPD) method is a novel, inexpensive and rapid means to characterize nanoparticle suspensions. Using only a single transducer, and applicable with almost arbitrary sample volumes, USPD measures the ultrasonic backscatter in the 15 Mhz range from moving particles as small as sub-ten nanometers. Particle motion spreads the backscatter over a range of frequencies and the shape of a high resolution power spectrum (bin widths of several Hz) is analyzed to determine the backscattered power that is the measure of the suspension concentration. A typical measurement can be made in about 30 minutes. USPD may also be able to characterize the size and mechanical properties of nanoparticles. Measurements can be made on batch samples and for particle streams, which can support quality assurance applications. To date, backscatter measurements have been made for islets of Langerhans, particle beads (40 nm – 150 μm), dendrimers and titanium dioxide colloids.

Keywords: nanoparticles, ultrasonics, concentration measurement, particle size distribution, quality assurance

1 INTRODUCTION

The Ultrasonic Pulsed Doppler Methodology was originally developed as a simple, inexpensive and rapid means to measure the concentration of Islets of Langerhans in preparations for transplantation for treatment of Type I diabetes. Subsequently, we have endeavored to extend its capabilities downward in particle size and have found that it can measure concentration for single-digit nanometer-sized particles.

The technique is a based on the measurement of ultrasonic backscatter from moving particles. In the 15 Mhz frequency range, the wavelength of the interrogating signal is much larger than the diameter of the particles and Rayleigh scattering occurs. The outgoing scattered wave $p_s(r)$ at a distance r from a particle modeled as a fluid sphere of radius a in response to an incident plane wave $p_i(r)$ can be expressed in terms of an angular distribution factor Φ:

$$\Phi = \frac{r p_s(r)}{p_i(r)} = \frac{1}{3} k_0^2 a^3 \left[\frac{\kappa_1 - \kappa_0}{\kappa_0} - \frac{3(\rho_1 - \rho_0)}{2\rho_1 + \rho_0} \right] \qquad (1)$$

where k_0 is the acoustic wavenumber ω/c. The two terms in brackets represent the contrast between the particles' mechanical properties and those of the suspending medium. The first represents the compressibility contrast, where κ_0 is the compressibility of the medium and κ_1 is that of the particle. The second is the density contrast, where ρ_0 is that of the medium and ρ_1 is that of the particle. The former term represents monopole reradiation uniform in all directions while the latter represents dipole radiation. This has a cosine directivity which for backscatter yields the minus sign ahead of the density term. Typically the compressibility contrast dominates the backscatter.

The second important feature of USPD is the measurement of Doppler shifted backscatter due to motion of the particles. By measuring backscatter at frequencies differing from that of the interrogating signal, clutter due to reflections of the interrogating signal is eliminated. Consequently, the noise floor of the USPD measurements is set by the electronics and not the acoustical conditions in the measurement volumes. Doppler shifts can be generated by three sources of particle motion. First, the fluid can be stirred, leading to motions both toward and away from the transducer. Second, if the fluid is flowing through a conduit (e.g. exiting a manufacturing or other processing step) this motion can supply the needed Doppler shift. Finally, if it is of sufficient power, the interrogating signal itself can give rise to acoustical streaming, whereby a velocity away from the transducer is generated by the nonlinear deposition of momentum into the fluid.

2 SYSTEM ARCHITECTURE

A sketch of the USPD system in Figure 1 shows a batch processing chamber as it is presently configured.

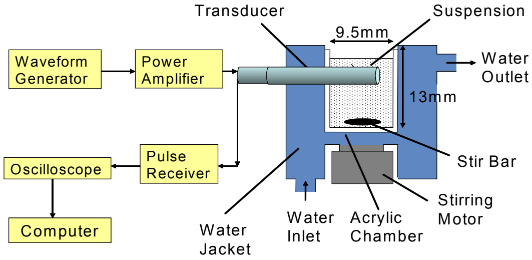

Fig. 1: Schematic of USPD Batch System

In this system the sample suspension is confined in a thermally-jacketed vessel containing a stirrer bar. A single transducer extends into the chamber horizontally. In the figure it is shown extended into the fluid. In this position, the system can be self calibrated by measuring the reflectivity of the back wall of the chamber. For backscatter measurements the transducer face is flush with the inside wall of the chamber.

The transducer is focused, so that there is a volume about 1.7 mm from the transducer face in which the ultrasonic fields are concentrated and strongest. It is in this volume that most of the backscatter is generated. Consequently, the size and shape of the container is not a critical element and as long as a uniform flow through the focal volume is maintained the measurement can be made. This suggests that USPD can be used in almost arbitrary fluid volumes.

A conceptual configuration that can support real-time monitoring of a particle manufacturing process is shown in Figure 2 below. Here the flow of the particles gives rise to the requisite Doppler shifts. The transducer is shown outside the flow region, connected acoustically to it by a window.

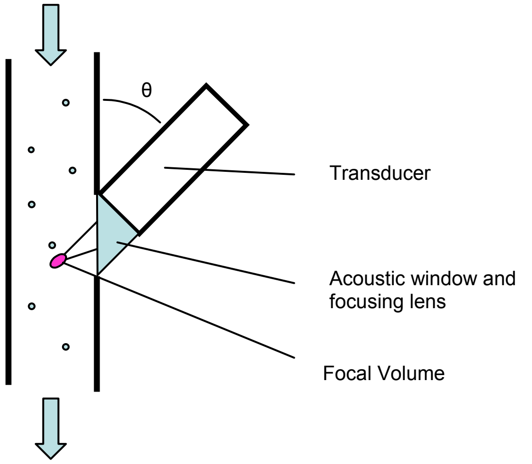

Fig. 2: In-Line Monitoring of Particle Streams

The electronics suite includes a signal generator that generates the interrogation signal, a series of tone bursts separated by quiet periods during which the backscattered signal is detected. The signal from the signal generator is then, if necessary, amplified and sent to the transducer. The backscattered signal is detected by the same transducer and the total electronic signal containing both interrogating and backscattered signals is sent to a pulse receiver for additional amplification and signal conditioning.

The deep-memory oscilloscope (presently a LeCroy 6030 series) is the heart of the system. It performs the A/D function and then an FFT of the entire signal to produce a very high resolution power spectrum with a several-Hz bin width. The shape of these high resolution power spectra contains the information required to compute the concentration and other properties of the suspensions. Individual power spectra are then averaged to make a single concentration measurement. At present, 250 power spectra can be analyzed in approximately 8 minutes to form a useful average power spectrum. Typically three such averaged spectra are sufficient for a high precision measurement. With increasing processing speed the time required may be reduced.

3 SIGNAL PROCESSING

As indicated above, the key signal characteristic is the power spectrum of the backscattered signal generated by the digital oscilloscope. Figure 3 illustrates the power spectra for water (no particles) and a 10% wt/wt solution of 40 nm carboxylated polystyrene beads.

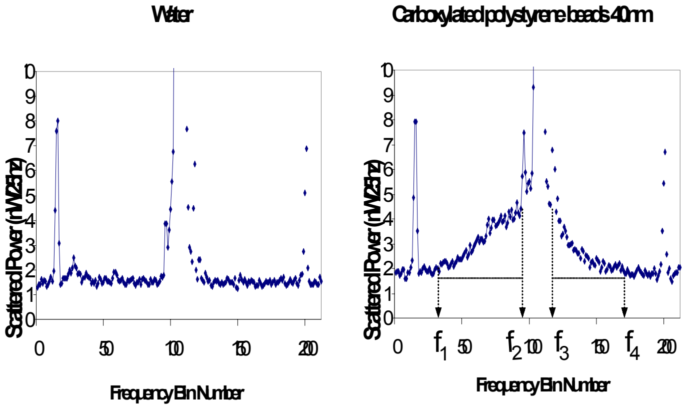

Fig. 3: Examples of Power Spectra with and without particles

On the left side of Figure 3, the power spectrum for plain water shows a main peak associated with the interrogating signal centered at frequency bin 106. On either side of this peak are flat regions representing the noise floor of the measurement and containing two spurious peaks around bins 10 and 200 associated with the electronics. The right side of Figure 3 shows a spectrum in the presence of the particles. Here, there is significant power in triangular regions of the spectrum below and above the main peak, with the limits of this power denoted by frequencies f_1 and f_2 below the peak and f_3 and f_4 above it. The total backscattered power is proportional to the area of the two triangles adjacent to the main peak. The concentration measured is proportional to this backscattered power and to the square of the angular distribution function in Eq. (1).

4 APPLICATIONS

Ultrasonic backscatter by the USPD system has been demonstrated over a broad range of particle systems, including:

Islets of Langerhans (~ 150 µm)
Stem Cell Spheroids (~ 150 µm)
Cells (~ 20 µm)
Polymer Beads (40 nm - 150 µm)
Perfluorocarbon Emulsions (~ 100 nm)
Carbon Nanotubes (10 nm diameter)
Dendrimers (4 nm)
Titanium Dioxide Colloids (4 nm)

An example of a high-precision concentration calibration curve, that for human islets, is shown below in Figure 4. Currently, work is progressing on development of concentration curves for particles at 50 nm and smaller.

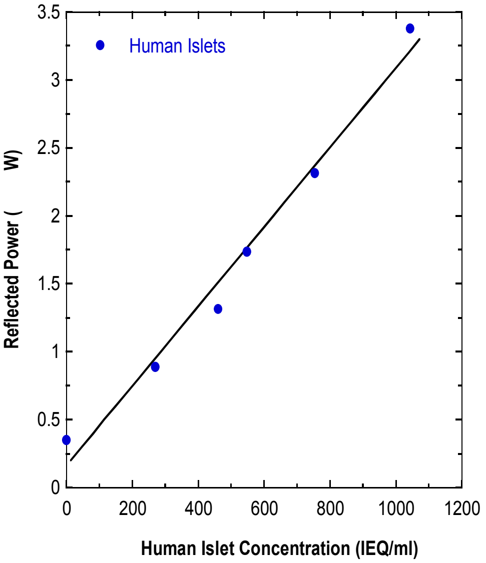

Fig. 4: Concentration Calibration Curve for Human Islets

Other potential applications of USPD include monitoring of physical properties of particles by making use of the dependence of their backscatter on particle size, compressibility and density. Measurements of these properties may allow real-time tracking of modifications to particles as they are functionalized for specific applications.

5 CONCLUSIONS

The USPD system has shown promise as a tool for rapid measurements of concentration and possibly particle size and compressibility for submicron particles using batches of materials or with streams of particles for manufacturing process control. This system promises to be simpler and less expensive than competing methods, and it may provide information related to the mechanical properties of the particles that cannot be easily obtained in any other way.

USPD technology is protected by pending U. S. patents.