Particle Characterization

Flow Pressurization Eliminates Bubbles for More Accuracy.

Bubbles create major issues when characterizing nanoparticles in solution because the characterization techniques typically utilize light scattering, specifically when determining size distribution and stability. Bubbles are much larger than nanoparticles and will scatter exponentially more light while interfering with particle movement, giving inaccurate results. Bubbles are often introduced when samples are pipetted into small cuvettes that are commonly used for dynamic light scattering (the prevailing method for calculating the size distribution of nanoparticles in solution). A larger issue is that bubbles are spontaneously formed during zeta potential measurements. Zeta (ζ) potential is a physical parameter which is representative of a particle's surface charge and can be directly related to the particle's stability in solution. To quantify zeta potential, a voltage is applied to the solution; the electrically directed speed of the particles is determined through a light scattering technique, known commonly as Phase-Analysis Light Scattering (PALS). Electrolysis, an insidious reaction that occurs in all zeta potential measurements, leads to bubble generation.[1-4] With typical zeta potential measurements, great care and laborious workarounds are needed to avoid or eliminate bubbles.[3]

Electrolysis is a phenomenon based on fundamental principles; when a direct electric field is applied to a conducting solution, an otherwise non-spontaneous decomposition reaction occurs. Due to its high degree of electrical conductivity, low voltages can be applied to a saline solution and electrolysis will occur. The end result is water splitting into its constituent elements, hydrogen and oxygen. At room temperature and pressure, this inevitably leads to gas formation at the site of the reaction. Visually, this can be seen by bubbles forming at each electrode; the cathodic electrode reaction will result in hydrogen gas evolution (Reaction 1)[1] while the anodic electrode reaction will result in oxygen gas evolution (Reaction 2)[1] at applied voltages above 1.7 V.[2]

Reaction (1) $2\ H^+ (aq) + 2\ e^- \rightarrow H_2 (g)$

Reaction (2) $H_2O (l) \rightarrow O_2 (g) + 4\ H^+ (aq) + 4\ e^-$

The DelsaMax PRO offers simultaneous dynamic light scattering (DLS) and zeta potential measurements with rapid speed, with 32 independent detectors working in conjunction. With a particle diameter sizing range of 0.4 nm to 10,000 nm for DLS and a particle radius sizing range of 1 nm to 7,500 nm for zeta potential, the DelsaMax PRO represents the latest generation of light scattering technology for measurements in the submicron range. However, even with rapid speed, a small inner-electrode spacing of 1.6 mm and platinum electrodes—which minimize gas

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evolution[4]—the DelsaMax PRO still may generate bubbles during zeta potential measurements in highly conducting aqueous solutions. To minimize erroneous measurements due to bubble formation, the DelsaMax PRO can be connected to the DelsaMax ASSIST. The DelsaMax ASSIST pressurizes the flow cell of the DelsaMax PRO by first closing the inlet and outlet valve for sample flow; then a separate gas source pressurizes the closed system up to 500 psi (~34 bar).

Intuitively, the overall effect of the DelsaMax ASSIST can be thought of as the reverse of opening a pressurized soda bottle. When depressurized, the gas solubility in the soda drops and bubbling starts. The DelsaMax ASSIST reverses this natural phenomenon by re-pressurizing the flow cell. The pressurization system eliminates bubbles from the flow cell in three highly effective ways. The effects are governed by the following equations. Note in Equation 1, c represents the saturated gas concentration in solution while k_H is Henry's law constant. In Equation 3, γ is surface tension and R is the radius of the bubble.

Equation (1) $$\rho = k_H \cdot c$$

Equation (2) $$PV = nRT$$

Equation (3) $$\Delta P = \frac{2\gamma}{R}$$

First and most important, the solubility of gas in solution increases with increasing partial pressure (ρ), commonly known as Henry's law (Equation 1). Thus, evolved gas bubbles will dissipate into solution, eliminating bubbles and the spurious results caused by the light that bubbles scatter. Secondly, as dictated by the ideal gas law (Equation 2), gas at the same temperature and higher pressure will occupy a lower volume; an order of magnitude increase in pressure leads to a corresponding order of magnitude decrease in bubble volume, resulting in a 100-fold decrease in light scatter intensity due to bubbles. Finally, the decreased bubble volume leads to increased radius of curvature of the bubbles and higher surface tension. The higher surface tensions leads to increased Laplace pressure (the difference in pressure between the gaseous inside of a bubble and the aqueous outside, ΔP, Equation 3), leading to bubble collapse.

The utility of the DelsaMax ASSIST with the DelsaMax PRO is demonstrated in Figure 1. 100 nm latex control beads (Control Particles, L100, PCS Latex) were diluted by adding three drops of beads in 10 ml of carbonated water (generic seltzer water purchased from a local grocery store). The solution was immediately injected into the DelsaMax ASSIST which was connected to the DelsaMax PRO. The system was then pressurized with a nitrogen gas source (Event Schedule SOP can be found on the DelsaMax website). Trials were run at 25° C, four acquisitions/run, and five seconds/acquisition. The six trials ran in an unpressurized state (4.9 psi) had an average diameter of 4,306 ± 1,680 nm. The light scattered by CO_2 bubbles led to highly skewed diameters. The six trials ran in a pressurized state (29.9 psi) had an average diameter of 104.4 ± 7.0 nm. The result agrees well with the latex bead assay sheet value of 100.32 ± 12.313 nm. Figure 2 is a plot of the Phase-Analysis Light Scattering (PALS) forward monitor amplitude during each trial run. The forward monitor amplitude is the measure of the unscattered and unabsorbed light transmission through the flow cell. A high value of PALS forward monitor amplitude indicates minimum obscuration, which is to be expected from the optically clear solution; a low value near 0 indicates nearly complete obscuration. For this particular experiment, a near-zero PALS forward monitor amplitude could only be caused by bubble formation throughout the entire flow cell volume.

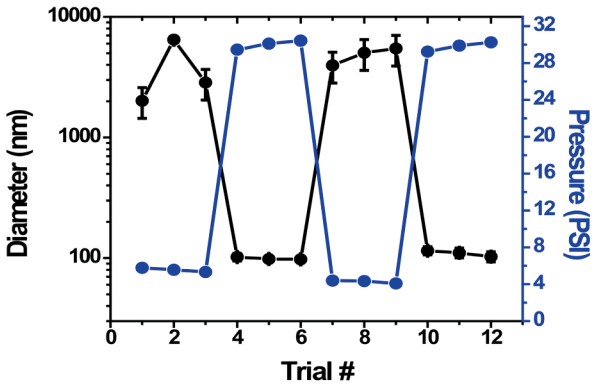

Figure 1. Plot of reported 100 nm bead diameter vs. flow cell pressure. At ambient pressure, bubble formation of evolving CO_2 gas from the seltzer water dominates the light scattering signal, giving spurious results. In a pressurized state above 2 bar, the gas bubbles either collapse or dissolve into solution, allowing the true size distribution of the 100 nm standard latex beads to be measured. Error bars in the graph are the trial polydispersity.

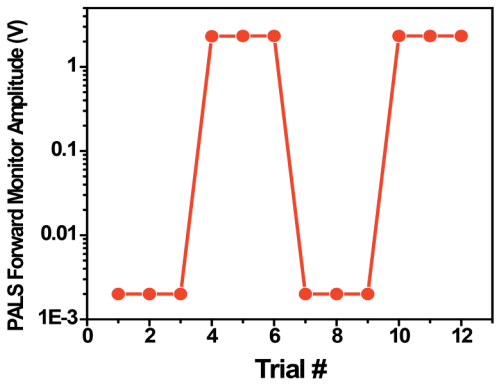

Figure 2. Plot of Phase-Analysis Light Scattering (PALS) forward monitor amplitude over the course of each trial. During trials 1 through 3 and 7 through 9, when the flow cell is in an unpressurized state, bubbles scatter and obscure the light, leading to a forward monitor amplitude of 0.002 V. In a pressurized state, the flow cell is nearly optically clear, with only minimal light scattering from the dilute 100 nm latex beads, leading to a high PALS forward monitor amplitude above 2 for all pressurized trials.

1. Pauling, Linus. *General chemistry* (Courier Dover Publications, 1988).

2. Chang, Moon-Hwan; Dosev, Dosi; and Kennedy, I; ζ-Potential analyses using micro-electrical field flow fractionation with fluorescent nanoparticles—*Sensors and Actuators B: Chemical.* 124.1; 172-178: (2007).

3. Kumar, Pradip and Bohidar, H B; Interaction of soot derived multi-carbon nanoparticles with lung surfactants and their possible internalization inside alveolar cavity—*Radian Journal of Experimental Biology;* 48.10; 1037-1042: (2010).

4. Wu, Chien-Hsien; Chen, Jia-Kun; and Yang, Ruey-Jen; Electrokinetically driven flow control using bare electrodes—*Microfluidics and Nanofluidics;* 3.4; 485-494: (2007).