Silver nanoparticle characterization using Single Particle ICP-MS (SP-ICP-MS) and Asymmetrical Flow Field Flow Fractionation ICP-MS (AF4-ICP-MS)

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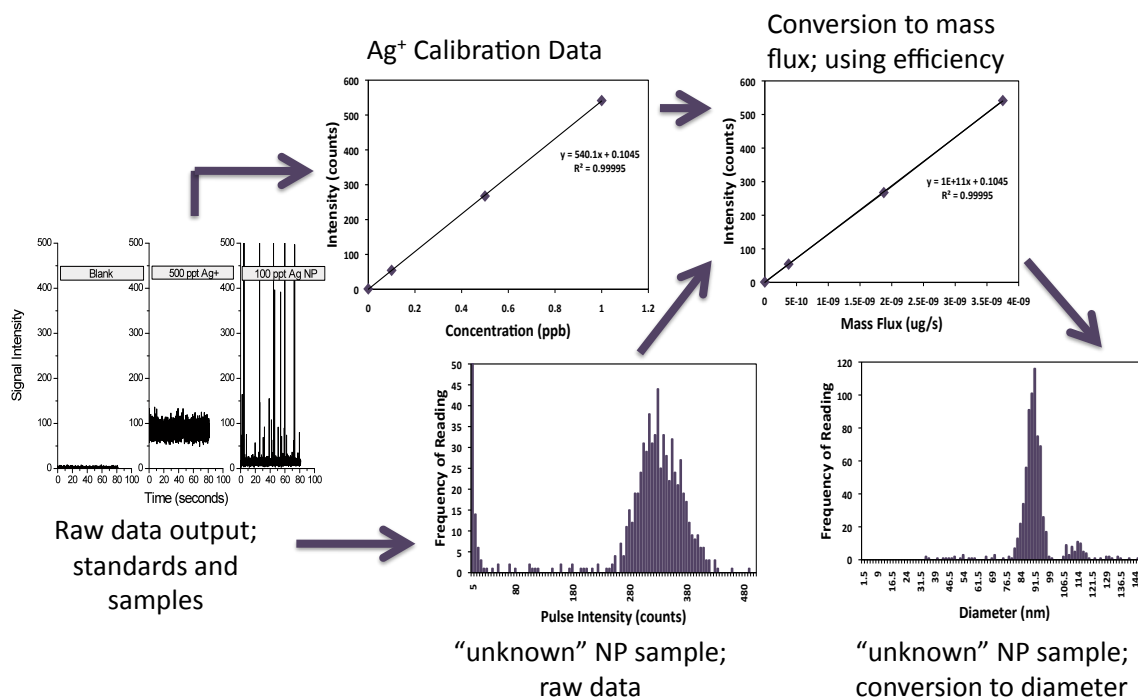
Figure S-1: Here, we relate pulse height to nanoparticle size. The ICP-MS is a mass-based technique where particle size is determined by relating the pulse intensity to an elemental mass. Following the figure above, as in traditional ICP-MS analysis, the first step in this process is to create a dissolved standard calibration curve. This relates the ICP-MS detector signal intensity to the concentration of the analyte entering the plasma. The next step is to determine the relationship between the concentration of the dissolved analyte and the total analyte mass (m_p) that enters the plasma during each dwell time. This relationship between analyte concentration and the mass observed per event is mass flux, which is highly dependent on the transport efficiency (η_n). The transport efficiency must be calculated for each instrument and under the given run conditions for the mass flux to be accurate. In this way, the mass flux calibration curve relates signal intensity (counts/event) to a total mass transported into the plasma in a given dwell time. Finally, the intensity of each individual pulse can then be transformed using the mass flux calibration curve to determine the particle mass. The ionization efficiency of the NP is presumed to be 1 (particles are 100 percent ionized) in most circumstances.

From here, one can convert the mass to particle diameter, d (nm), using the particle density ρ (g/cm^3), and assuming 1) spherical geometry of the particle, and 2) capturing the complete ion cloud from the NP in one dwell time.

$$d = \sqrt[3]{\frac{6 * m_p}{\pi * \rho}}$$

See Pace et al. (2011) for additional details.

H. E. Pace, N. J. Rogers, C. Jarolimeck, V. A. Coleman, C. P. Higgins, and J. F. Ranville, Analytical Chemistry **83**, 9361 (2011).
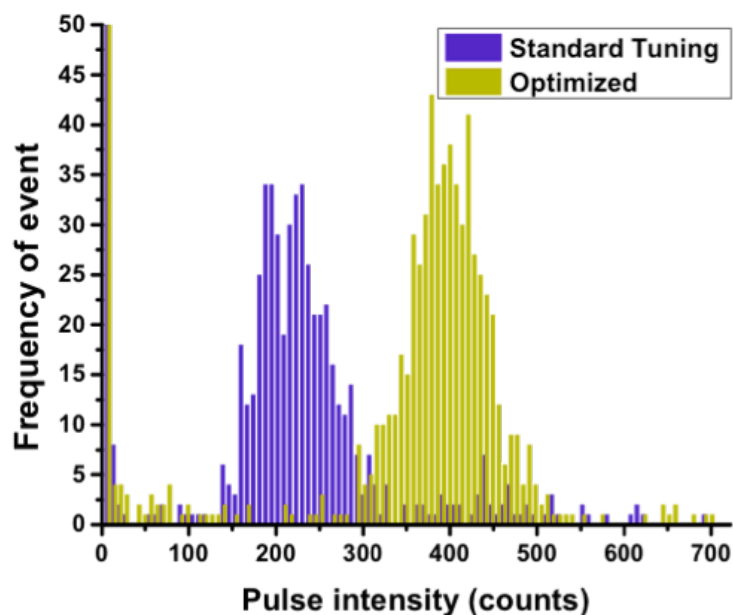
Figure S-2: It is clear that after tuning optimization, the pulse intensity is significantly higher for the same 100 nm Ag NP solution. Optimization consisted of tuning the instrument for maximum sensitivity of analyte metal by adjusting sample introduction flow rate and increasing nebulizer gas flow rate. The outcome gave parameters that were not necessarily optimal during a standard daily tune for traditional ICP-MS analysis, such as higher than normal oxide levels, but a significant increase to sensitivity during SP-ICP-MS analysis was gained, with no apparent pitfalls.
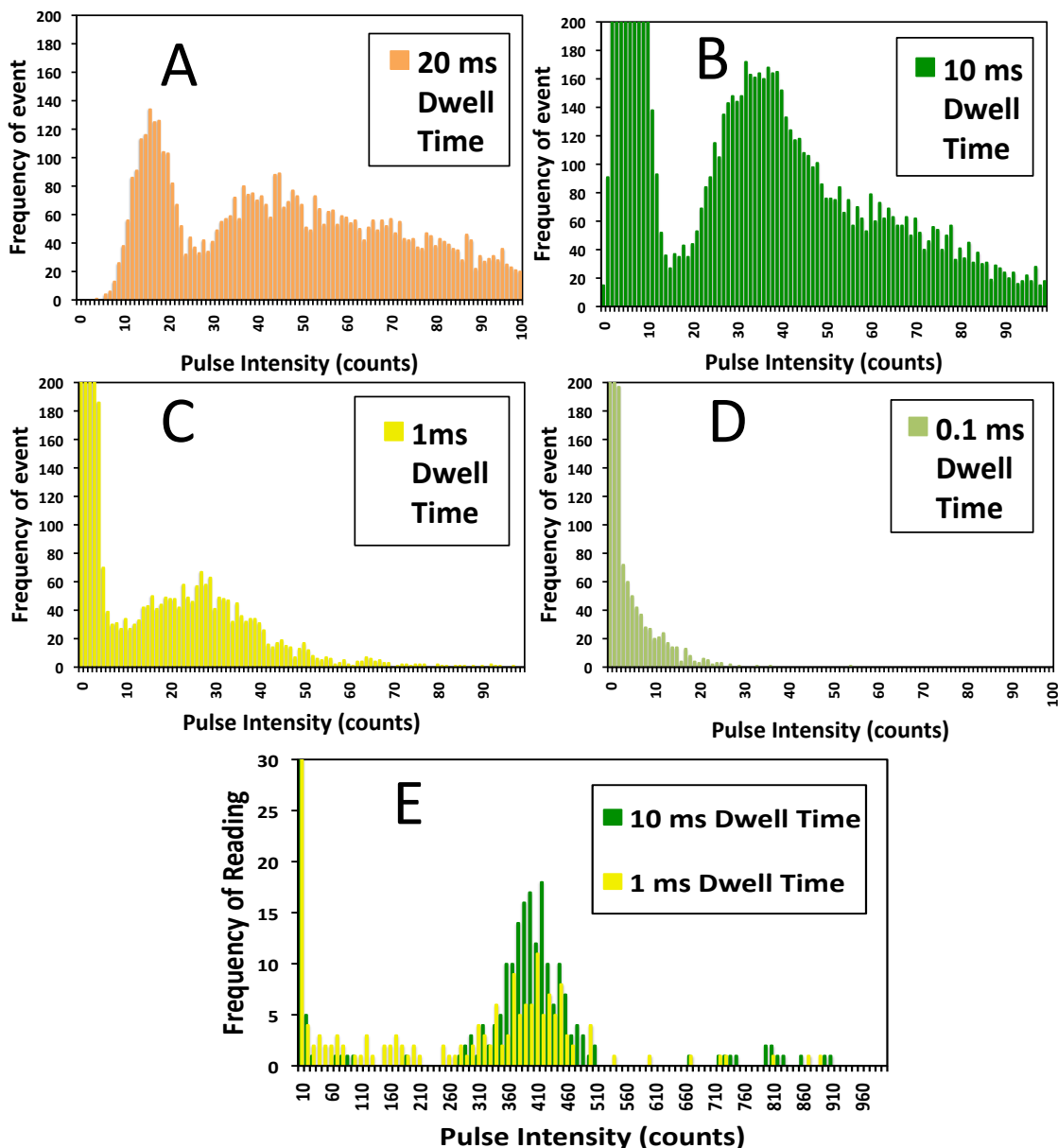
Figure S-3: Through dwell time optimization analysis, we found that 10 ms dwell times consistently provided the most accurate results for a variety of sample concentrations and NP sizes. Using 40nm Ag NPs, Figure 1 A-D show the change in histogram shape by varying the data collection parameters. For long dwell times, 20ms, (A), it is clear that coincidence of particles in a single dwell time is masking the mono-disperse nature of the sample. Conversely, a 0.1 ms dwell time that is too short (D); particles are not being completely analyzed as ions cannot be transported from the plasma to the detector in such a short time. When looking at the two moderate dwell times with the 40nm particles (B and C), it is less clear which is optimal. By using 100nm particles at the 10 and 1 ms dwell times (E) we note that the incomplete analysis of particles at 1 ms dwell times becomes more evident with the appearance (increase) of smaller, intermediate particle sizes that were not originally present.