# Extension of the linear dynamic range for nanoparticle sizing using single-particle ICPMS by matrix addition

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Single-particle inductively coupled plasma mass spectrometry (spICPMS) is currently the method of choice for analyzing metal nanoparticles by ICPMS, as it allows for particle sizing and determination of the particle number concentration. In spICPMS, ICPMS signals are recorded at high time resolution, such that individual particles ionized in the plasma produce a detectable burst of ICPMS signal; the frequency and intensities of single-particle signals are proportional to, respectively, the number and mass (i.e. size) of nanoparticles in a sample. Even though 6 to 12 orders of magnitude linear dynamic range are routinely achieved for ICPMS analysis of dissolved metals using conventional continuous liquid introduction, this linear calibration range is not currently accessible for the analysis of particulate samples directly introduced into the plasma. Efficient vaporization, ionization and atomization are key for a wide linear calibration range. However, because discrete particles vaporize at different positions along the plasma depending on their size, both the ionization efficiency of particles and the ion-collection efficiency of the mass analyzer are affected by particle size, which limits the linear calibration range. Large particles require long residence time in the ICP for complete vaporization and ionization; however, long residence time increases the diffusional losses of ions generated early in the plasma. For the analysis of small nanoparticles (< 20nm), highest sensitivity is obtained with the ICP pushed closed to the mass analyzer sampling orifice to avoid diffusional losses. However, when the system is optimized for analysis of small particles, larger particles may not spend enough time in the plasma to get efficiently ionized. For such an optimization, the calibration curve is non-linear, and potentially even double-valued, for high-mass particles due to incomplete vaporization and only possesses one order of magnitude linear dynamic range. Ideally, one would wish to achieve efficient ionization for all particles at one common sampling position along the ICP (i.e. one residence time in the ICP) while minimizing non-linear calibration of low-mass particles caused by diffusional losses. Here, we explore extending the dynamic range of NP calibration by adding excess matrix to all solutions: excess matrix salt engulfs each particle introduced into the ICP so that the mass of individual analyte particles —regardless of nanoparticle size— is insignificant compared to the total mass of the composite particulates. The addition of the matrix salt shifts the size-dependent optimal sampling position for analyte nanoparticles to a common position and extends the linearity of the single-particle calibration. A proof-of-principle study was conducted using microdroplets, which were used as proxy for other mass-limited discrete samples, in combination with an ICP-Time-of-Flight Mass Spectrometer. In this study, different gold concentrations in microdroplets represent variably sized nanoparticles and, without matrix addition, produce gold-concentration dependent optimum ICP sampling positions. When a matrix of highly concentrated lithium solution (500 mg/g) was added to the gold solutions, a shift in optimal ICP sampling position was observed and conserved for all gold concentrations. Thereby one single sampling position allowed for an increase of the linear calibration of the mass of Au in microdroplets from one to three orders of magnitude. The end goal is to extend the linear calibration range for discrete samples over 4 orders of magnitude to enable the measurement of different sizes of nanoparticles ranging from 20 nm up to 250 nm at one single sampling position.