With the likely release of engineered nanoparticles into the aquatic environment, developing appropriate analytical methods for occurrence surveys has become a priority. To this end, the stepwise method development towards the quantification of silver nanoparticles (AgNP) in surface water using asymmetric flow field flow fractionation (AF4) and inductively coupled plasma mass spectrometry (ICP-MS) is reported. The analysis of natural and otherwise complex samples is challenging and yields uncertainty about the accuracy and precision of measurements. Therefore, a practical tool to assess relative accuracy among separation protocols using light scattering (LS) detection was developed. This assessment metric was applied to optimization of cross flow ($V_x$) protocols in AF4 separation interfaced with LS detection using mixtures of polystyrene beads. AF4 has several instrumental parameters that may have a direct effect on separation performance. A sensitivity analysis utilizing orthogonal fractional factorial design and graphical analysis was applied to ascertain the relative importance of five AF4 primary/instrumental factor settings when analyzing synthetic freshwaters containing AgNPs. The most important and significant AF4 primary/instrumental factors were buffer concentration and $V_x$ velocity, while the least impacting was $V_x$ ramp time. Optimal settings were also generated for each of the factors within the range of settings explored. A parallel orthogonal fractional factorial design was employed to evaluate the effects of 5 environmental factors including natural organic matter (NOM) content on the separation. None of these water quality characteristic effects or interactions were found to be significant although investigations with fluorescence spectroscopy into potential Ag$^+$-NOM and AgNP-NOM interactions suggested that these interactions affect the molar mass and physical conformation of the NOM particles in the sample. Finally, the developed methodology was evaluated for accuracy in a natural water sample. Isotope enriched silver ions were used to characterize and quantify silver speciation following AF4 separation. Silver quantitation was reproducibly achieved within 10% of a spiked “challenge” concentration of AgNPs in lake water using the method of standard addition to compensate for natural matrix and system complexity, demonstrating the applicability of the developed method for the accurate measurement and speciation of AgNPs in the aquatic environment.

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