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Electronic Supplementary Information 2

An approach to estimating the contribution of signal noise to the diameter uncertainty of individual silver nanoparticles and resolution of spICP-MS analysis

Lidia Ivanova Kaynarova, Deyana Liubomirova Georgieva * and Violeta Milenkova Stefanova

Department of Analytical Chemistry and Computer Chemistry, University of Plovdiv "Paisii Hilendarski"; 24 Tzar Assen Str., 4000 Plovdiv, Bulgaria
*E-mail: georgieva@uni-plovdiv.bg.

S2.1. Instrumental parameters optimization

For best ICP-MS performance a targeted optimization of instrument parameters was carried out with respect of better signal to noise ratio on ^{107}Ag. For this purpose, a signal of silver ionic standard (1 µg L^{-1}) was monitored at 10 ms dwell time during variation of two set of parameters, related to: i) ionization conditions in plasma (sampling depth and nebulizer flow rate) and ii) ions focusing (extraction lenses voltages). To ensure a maximum ionization efficiency the RF power of the plasma was maintained at 1.55 kW. The sample flow rate also was kept constant at 0.342 mL min^{-1}. The results from target optimization are presented on Figure S1 (A-D) as normalized signals of Ag versus the particular instrumental parameter. On the second axis of the graphs the variation of signal RSD % is given to represent the stability of measurements. Normalized signals (in %) are calculated with respect to the corresponding maximum signal measured when varying the influencing parameter in the specified range.

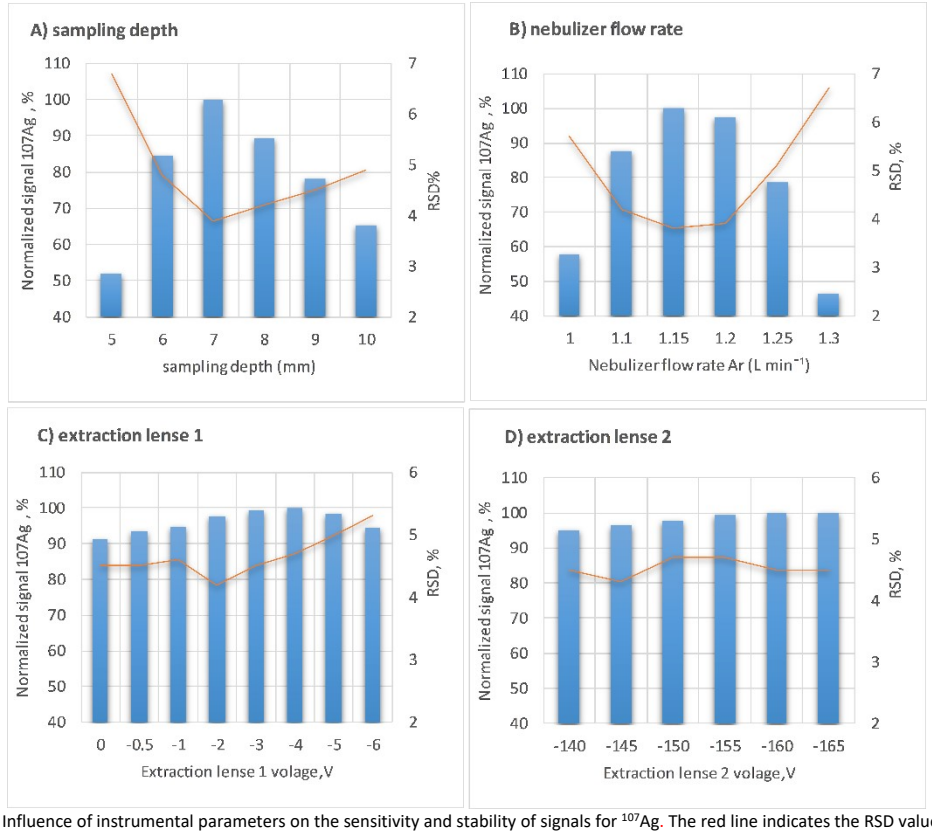

Figure S2.1 Influence of instrumental parameters on the sensitivity and stability of signals for ^{107}Ag. The red line indicates the RSD value in % on second axis. Constant values during optimization are: A) nebulizer gas flow rate – 1.2 L min^{-1}. B), sampling depth - 7 mm, C) and D) sampling depth 7, nebulizer flow rate 1.15

Most pronounced effect on signal sensitivity have a nebulizer flow rate and sampling depth position, which are fundamentally related to the ionization efficiency of analyte and the extraction of ions from the plasma zone of their maximum population.

The sampling depth is very sensitive parameter (Fig. S2.1A). The marked decrease in sensitivity, accompanied by noise deterioration at lower sampling depths, is probably due to inefficient ionization of Ag, while at high sampler depths, it is rather due to a combination of ion beam lateral diffusion and recombination processes, with a decrease in temperature along the central plasma channel. The optimum sampling depth also depends on the properties of the specific nanoparticle's material as well as the design of the ICP-MS instrument used, but it is a critical factor that significantly affects the analytical performance of the single particle applications therefore it should be optimized in each particular case. The results obtained in our study are in accordance with the previously published work (1). The authors reported the similar significant influence of the sampling depth on both Ag NPs and ion signals, that show the ionization maximum at the same sampling zone. The maximal ionization, reported by authors in (2) is around 4-5 mm sampling depth, which differs from the results in our study. Perhaps the reason is that in the cited article, the High matrix interface (HMI) with an additional dilution gas was used.

The nebulizer flow rate, on the one hand, affects the formation of fine aerosol droplets, thus being directly related to the transport efficiency of the analyte to the plasma. On the other hand, the rate of this gas flow is critical with respect to the residence time in the hot zone of the discharge, and is therefore directly related to the ionization efficiency and also would affect undesired ion cloud expansion. The expected strong influence of this parameter (Figure S2.1B) shows that a good signal-to-noise ratio for Ag^+ is achieved in a very narrow range of flow variation (i.e. between 1.1 - 1.2 L min^{-1}).

The voltage of both extraction lenses (Figs. S2.1, C and D) has a considerably lower effect on the level and stability of the silver signal. In the studied ranges, the variation of the potential of extraction lens 1 reflects in no more than 9% loss of sensitivity, and for extraction lens 2, respectively, less than 5%. Whereas, with extraction lens 1, a slight effect of degradation of reproducibility may be observed at potentials lower than – 3V, the second extraction lens has no effect on noise.

1. Lee W-W, Chan W-T. Calibration of single-particle inductively coupled plasma-mass spectrometry (SP-ICP-MS). J Anal At Spectrom. 2015;30(6):1245–54.
2. Kálomista I, Kéri A, Galbács G. Optimization of plasma sampling depth and aerosol gas flow rates for single particle inductively coupled plasma mass spectrometry analysis. Talanta. 2017;172:147–54.

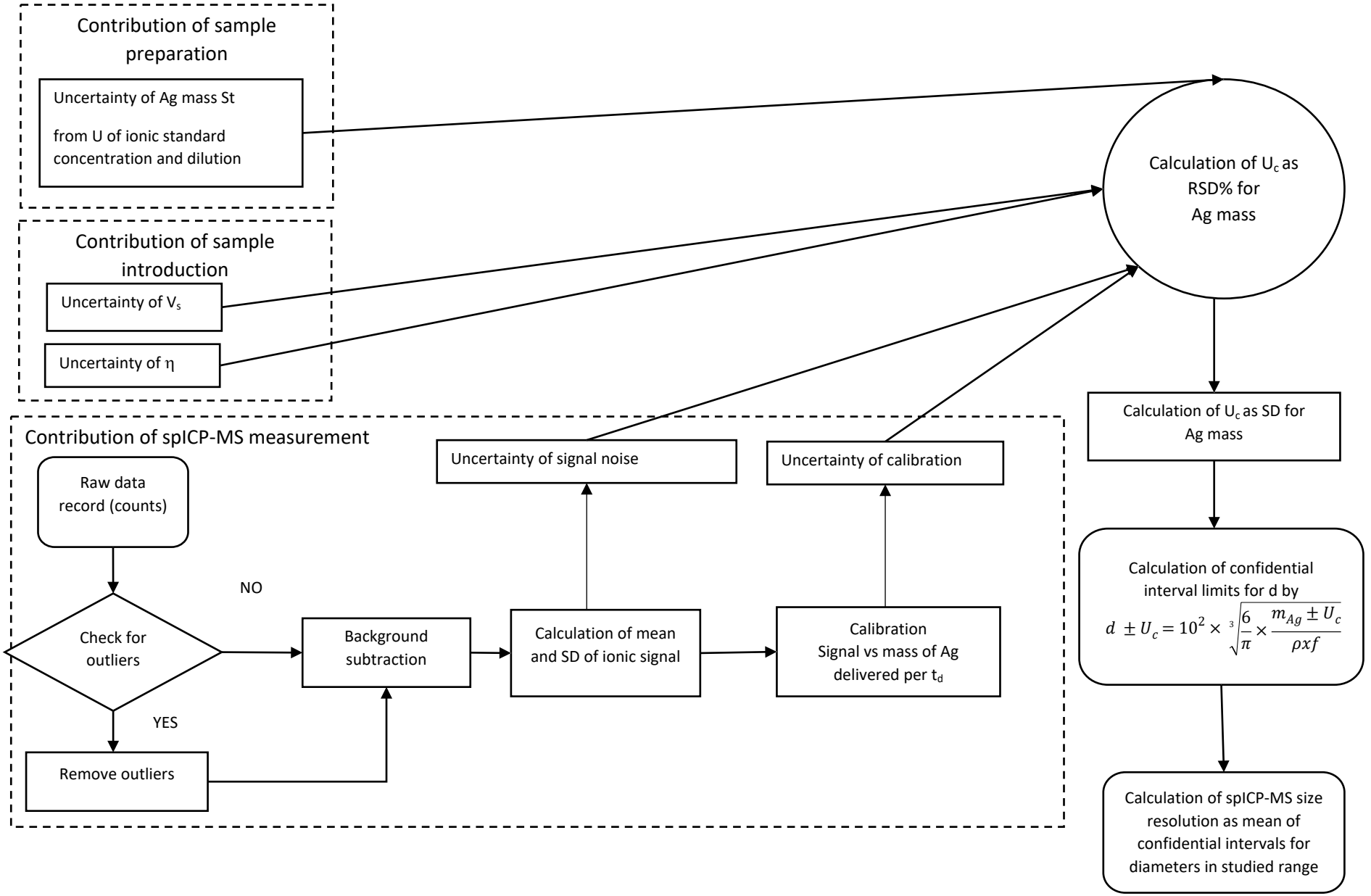

Figure S2.2 A flow-chart diagram for NPs size uncertainty estimation and spICP-MS size resolution determination using ionic standard calibration approach.