Supplementary information

Injector choice

Torches with injectors of 1 and 2.5 mm internal diameter have been tested. For SP ICP-MS analysis, torch with an injector of minimal internal diameter of 1 mm is usually recommended to limit the quantity of analyte entering the plasma and promote the passage of one NP per dwell time. However, it is obvious that, considering the same gas and sample flow, 2.5 mm internal diameter allows a higher analyte quantity to pass to the plasma, and so leads to a better sensitivity. Indeed, a signal to background ratio for ^{56}Fe (S/B) of 67 was obtained with 1 mm injector diameter compared to 305 with 2.5 mm one. Note that the main risk of using 2.5 mm diameter injector is to detect several nanoparticles per spike. SP ICP-MS analysis of 30 nm IONP suspensions gave a median size of around 30 nm with 1 and 2.5 mm injector diameter proving that only one NP was detected in a dwell time. Thus, for this work a 2.5 mm injector diameter was chosen.

Mathematical treatment

Figure $1_{SI,}$ obtained for a silver NP suspension, illustrates well the principle of SP ICP-MS with a signal distributed between two groups: a first one representing the background, and a more intense one representing the NPs. Threshold position, that is to say the intensity of the signal that separates background from NPs, is generally determined by the iterative method well described in the work of Pace et al. [1]. Signal data are averaged and a standard deviation (σ) is calculated. All data above the mean plus 3σ are removed, and the same treatment is done on remaining data until the mean still unchanged. The obtained mean is considered as the threshold. With the aim of validating the methodology developed by these authors, the same methodology has been applied to a standard of 60 nm silver NP suspension (Figure 1_{SI}). Figure 1_{SI} shows that the sample background signal is well separated from the NP one. Threshold

position should be between these two types of signals.

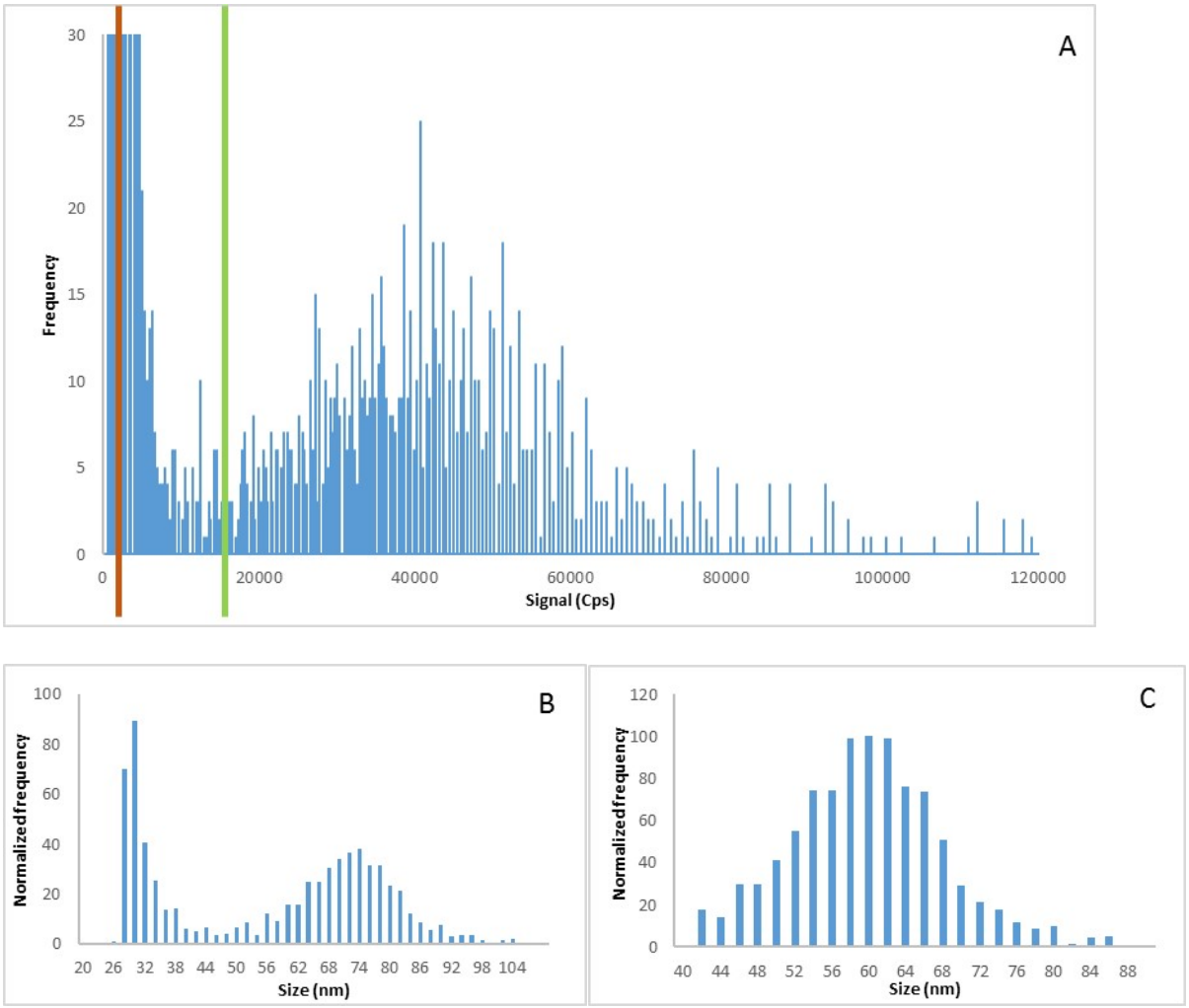

Figure 1_{SI}. Signal distribution of a silver 60 nm NP suspension measured in single particle ICP-MS mode (A). In red, the threshold position determined by iterative method. In green, threshold visually determined. Particle size distribution obtained after threshold determination with iterative method (B) and with visual determination (C).

However, when applying iterative method, the threshold position has been found to be very low in the background signals (in red, Figure 1_{SI} A). Therefore, we modified the iterative method in order to have a well-determined threshold position with a standard silver NP suspension showing a well-distinguished distribution NP signal towards the background one. It seems to be evident that a too strong contribution of background is responsible for an under-evaluated

threshold. Accordingly, we have added supplementary steps to the iterative method. Blank values are statistically analysed and values that are present at a frequency of more than 10% are suppressed from sample data. By this way, the most frequent values of blank are not taken into account in the calculation of threshold by iterative method. This modification leads to a well determined threshold position of the 60 nm silver NP suspension (Figure 2_{SI}).

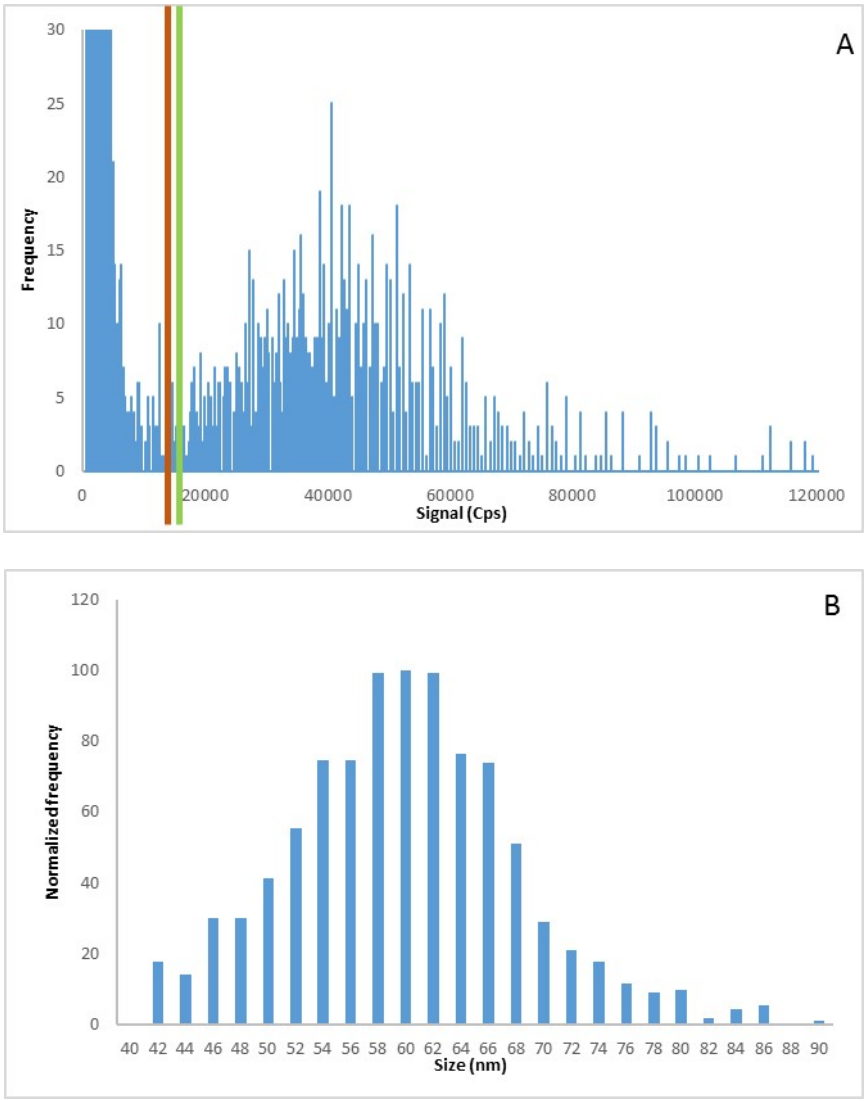

Figure 2_{SI}. Threshold determination of a 60 nm silver NP suspension, in green by a visual determination, and in red by the method developed in this study (A). Particle size distribution obtained after threshold determination with the method developed in this study (B).

1 H. E. Pace, N. J. Rogers, C. Jarolimek, V. A. Coleman, C. P. Higgins and J. F. Ranville, *Anal. Chem.*, 2011, **83**, 9361–9369.