

**THE REQUIRED AMOUNT OF DATA FOR THE ANALYSIS OF
THE SILVER NANOPARTICLE SIZES BY SP-ICP-MS**

Silver nanoparticles (Ag NPs) are known for their antiseptic properties. Ag NPs have a wide range of applications, for example, in medicines, cosmetics and consumer products. Regular contact of silver nanoparticles with humans determines the relevance of monitoring the characteristics of nanomaterials, including the nanoparticle size. Methods of electron microscopy, X-ray diffraction, light scattering and others have proven themselves well in the analysis of NPs, however, the requirements for a high concentration of NPs in the sample and the composition of the matrix are known. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a promising method for analyzing the NP sizes, which allows working with extremely low NP concentrations with satisfactory reproducibility and productivity [1, 2].

It is known that SP-ICP-MS is able to register a statistically significant number of NPs in a short measurement time [1, 2]. However, with variable concentrations, the total possible number of registered NPs for a given fixed measurement time is limited by the choice of the dwell time (which determines the total number of dwell time windows, and, in turn, depends on the size of the analyzed NPs) and the estimated calculated resolution between the signals of single NPs (necessary to comply with the requirement to register the signal from each single NP in a single dwell time window) [3]. Thus, if the dilution of the sample is correctly selected for these analysis conditions, the measured number of NPs may not be sufficient to construct a reliable particle size distribution.

The purpose of this study is to demonstrate the change in the image of the signal distribution of single NPs with increasing measurement time in the SP-ICP-MS-analysis of NP sizes.

MATERIALS AND METHODS

Monodisperse 100 nm Ag NPs (Sigma-Aldrich, USA) were used as a model object. The reference dispersion of Ag NPs was diluted with deionized water to an Ag NPs content of approximately 1500 particles/ml and sonicated.

Measurements were carried out on an inductively coupled plasma mass spectrometer iCAP RQ (Thermo Fisher Scientific, USA) in a time resolved analysis mode. The signal was monitored at m/z 107 at 15 ms dwell time, the parameters of the mass spectrometer were similar to those

described in [4]. The calculated resolution between the signals of single 100 nm Ag NPs in this work was 50 dwell time windows.

RESULTS AND DISCUSSION

The array of signal intensities obtained in 30 minutes of data registration was divided into fragments corresponding to signal registration during 1, 2, 3, 4, 5, 10, 15, 20, 30 minutes with the corresponding number of single dwell time windows.

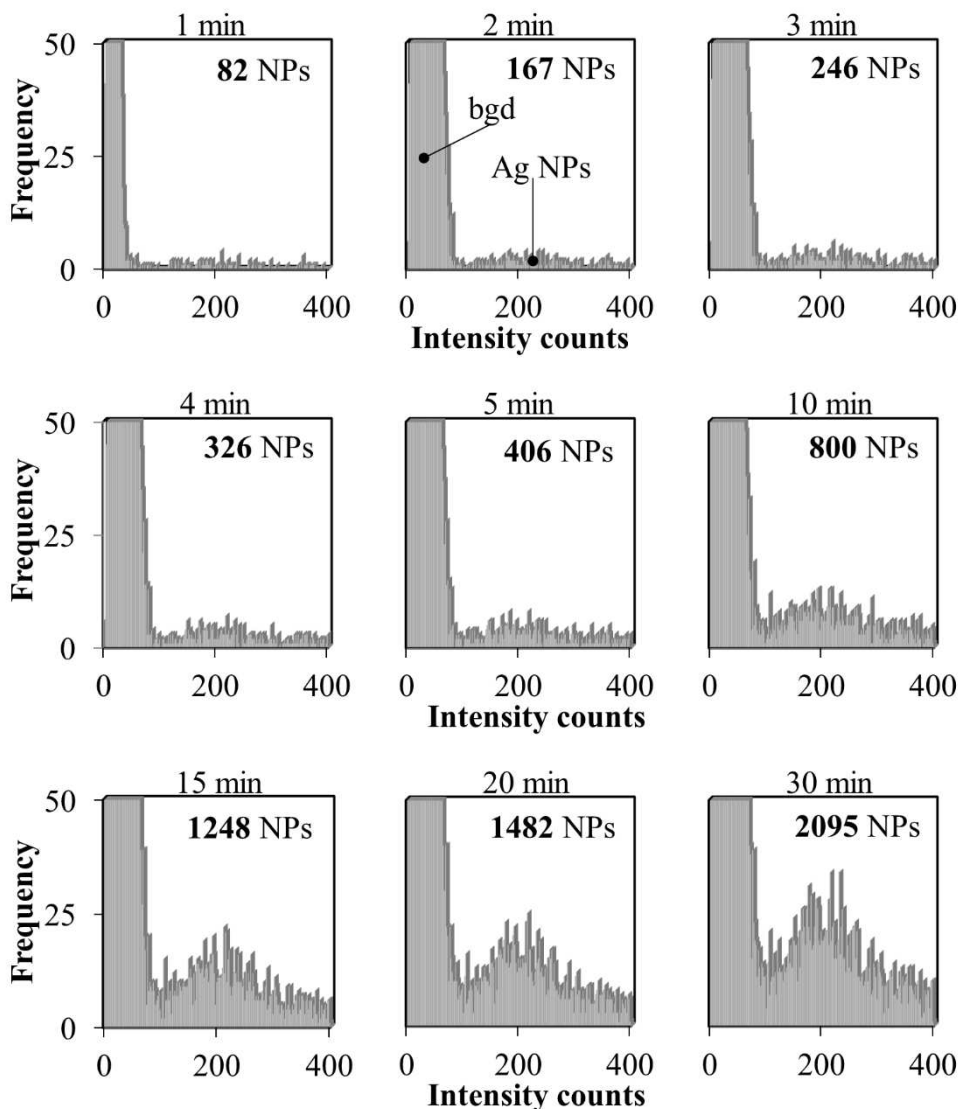


Fig. 1. Signal distributions and the number of registered 100 nm Ag NPs with a total measurement time from 1 to 30 minutes.

Fig. 1 shows the signal distributions of the 100 nm Ag NPs standard dispersion, where the left part of the distribution in each case is represented by the background signal distribution with an intensity of up to 110 counts;

then - the Ag NP signal distribution with an intensity of more than 110 counts. It should be noted that even in the case of a monodisperse standard sample, the NP signal distribution is represented by a wide range of intensities due to the peculiarities of signal registration in SP-ICP-MS, when the NP signal can be registered fragmentally (giving increased or reduced intensity).

As the measurement time increases, the change in the number of registered Ag NPs is quite proportional. The greatest change in signal frequency was observed in the range of intensities 210-220 counts, representing the most common averaged intensity of a single 100 nm Ag NPs. A noticeable maximum of the 100 nm Ag NP signal distribution was revealed when registering signals of approximately 400-500 single NPs with a total measurement time of 5 minutes or more. Up to this point, the Ag NP signal distribution was not sufficiently reliable, since the number of registered NPs was too small to obtain a real NP signal distribution.

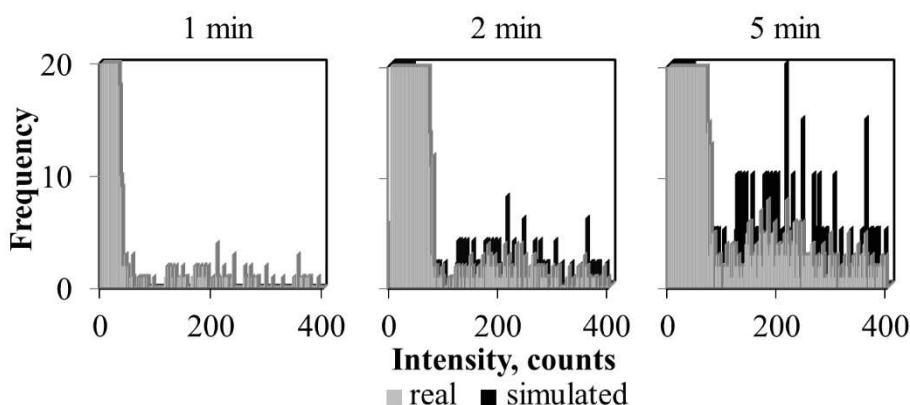


Fig. 2. Real and simulated distributions of 100 nm Ag NP signals with a total measurement time of 1, 2 and 5 minutes.

Simulation of the distribution of NP signals from a smaller data array confirmed the assumption that the distribution of 100 nm Ag NP signals with a small number of registered NPs (up to approximately 350 particles, which corresponds to 4 min of measurement in this experiment) does not objectively reflect the average signal intensity of a single 100 nm Ag NP and gives relatively overestimated frequencies in the area of nearby intensities. Fig. 2 shows a comparison of the 100 nm Ag NP signal distributions recorded during 2 and 5 minutes with the signal distributions obtained by a multiple increase in the frequencies of the signals recorded during 1 min. It is noticeable that with an increase in the measurement time, the greatest increase in frequency actually occurs in the area of the average intensity of a single 100 nm Ag NPs (210-220 counts), whereas a

multiple increase in the number of NPs for a data array that does not reflect this average intensity leads to an overestimation of the frequencies of nearby intensities.

Thus, for 100 nm Ag NPs under given conditions, the 5 minutes total measurement time allowed registering a sufficient number of NPs to determine the maximum of the signal intensity distribution corresponding to the average intensity of a single 100 nm Ag NPs.

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