The Effect of the Plasma Sampling Depth and the Flow Rate of the Aerosol Dilution Gas on the Performance of Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS) Measurements

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Abstract
Single Particle Inductively Coupled Plasma Mass Spectroscopy is a modern technique available for the characterization of nanoparticles. Optimization of the measurement conditions can increase the potential of the technique, especially with regards to the minimum detectable particle size (typically ca. 15 nm). To this end, in this work we explored the effects of changing the (interface) sampling depth and the on-line aerosol dilution by the High Matrix Introduction (HMI) function on an Agilent 7700X ICP-MS.

Introduction
Inductively coupled plasma-mass spectroscopy (ICP-MS) is one of the most prominent techniques of modern analytical chemistry that allows us to detect metals as well as several non-metals in ultra trace analytical concentrations. The effective and robust inductively coupled plasma ion source combined with the selective and highly-sensitive detector of mass spectrometry result in ng/L or attogram limits of detection.
A few decades ago the idea surfaced that ICP-MS may be utilized to measure (characterize) single nanoparticles [1]. As an advantage of this method, the single particle inductively coupled plasma spectroscopy (SP-ICP-MS), we can mention that the measurements can be executed in solution phase (sol form) that makes the sample preparation simpler. The traditional nanoparticle analyzing techniques, e.g. scanning electron microscopy (SEM), transmission electron microscopy (TEM), and the dynamic light scattering (DLS) are often time consuming and impractical [2]. In our experience, SP-ICP-MS can indeed detect nanoparticles at a low concentration (even 10^3-10^4/mL) that is typical for environmental samples [3] and can provide size and number concentration, as well as compositional information within a short time (5-60 minutes).
In ICP-MS spectrometry, it is practical to optimize the main experimental parameters in order to achieve the best performance. One of these settings is the interface sampling depth, that determines the depth within the central analytical channel in the plasma from where ions are extracted by the interface. According to the zone model [4], there is an optimum zone (highest concentration of ions) in the central channel where the concentration of the singly charged ions of the isotope is at maximum. This optimum sampling depth changes with the element and also with the setting of relevant other instrumental parameters (e.g. plasma RF power, carrier gas flow rate, etc.). ICP-MS manufacturer Agilent Technologies equips 7700-range instruments with a High Matrix Introduction (HMI) function. Originally, this function was developed for the handling of concentrated sample matrices (up to ca. 2.5%, as opposed to ca. 0.2% with regular ICP-MS instruments). This HMI option operates by adding an extra tangential Ar gas to the aerosol carrier flow, thereby enabling on-line aerosol dilution. This can also be helpful, when analysing nanosols.

At present, our research group actively investigates the possibilities for increasing the performance of SP-ICP-MS analyses and for eliminating spectral interferences [5]. Within these activities, the present report describes the results of our latest investigations dealing with the tuning of the interface sampling depth and the HMI gas flow rate. To our knowledge, no such previous reports have been published.

Eyperimental

The experimental instrument was an Agilent 7700X type ICP-MS with an Agilent I-AS autosampler. The sample uptake rate was 400 μL/min performed by a MicroMist nebulizer. During the SP-ICP-MS experiments, the data acquisition software was used in Time Resolved Analysis (TRA) mode with an integration time of 6 ms and measurement time of 100 seconds. All measurements were performed at ^{197}Au.

Agilent technologies Multi-Element Standard 3 was used to prepare Au solutions in different concentrations. Gold nano sols were prepared from PELCO NanoXact 40 and 60 nm Au nano sol standards (Ted Pella Inc., USA) stabilized with tannic acid. High purity deionized water (Millipore Elix Advantage 3+ Synergy, USA) was used during sol preparation. The particle concentration was $5 \cdot 10^4$/mL. To ensure the homogeneity of the sols and to avoid the aggregation of the nano particles we applied ultrasonic treatment with an Ultrasonik 300 Instrument (Ney, USA).

Results and discussion

A calibrating series was prepared from the gold stock a solution to produce solutions of 0, 1, 5 and 10 ppb concentration. We observed that for solutions, the intensity of the signals increased with the decrease of the sampling depth. The sampling depth difference of 14 mm (between 6 and 20 mm) resulted in about one full order of magnitude change. We determined the sensitivity that belongs to each sampling depth value and it was found that the highest sensitivity was featured by the lowest value of sampling depth (6 mm). As can be seen in Figure 1, with the increase of the sampling depth the sensitivity decreases.

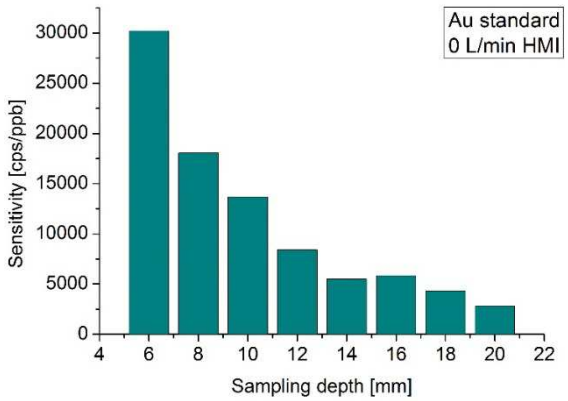

Figure 1. Sensitivity values in function of sampling depth

For nano sols (both the 40 nm and 60 nm Au particles) we observed the same tendency: with the decrease of the sampling depth the nano particle signal increased. About 6 times higher signals could be achieved by adjusting the sampling depth between 6 and 20 mm. The histograms in Figure 2. illustrate our observations (please note that the counts on the abscissa are related to the particle size and hence the signal). It can also be observed that the histogram peaks become significantly broader at lower sampling depth values, which can decrease the

dynamic size range of SP-ICP-MS measurements. On the other hand, the number of detection events is fairly constant in the range of 6 to 20 mm, which allows one to perform accurate particle number concentration measurements.

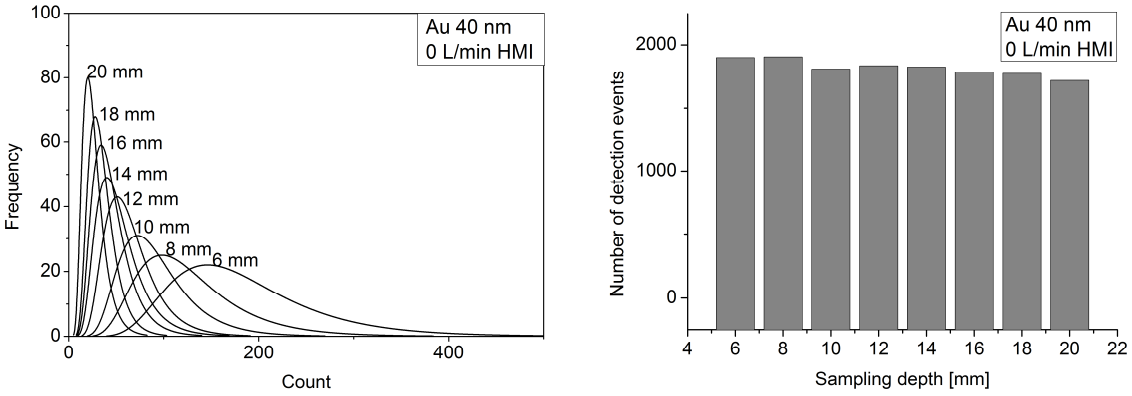

Figure 2. The signal histograms (left) and the number of detection events (right) for a 40 nm Au sol recorded with different sampling depth values

The observation of the effects of HMI was also performed by using both standard solutions and the nano sols. We also performed a cross-optimization by varying the sampling depth too. We investigated the effects of three settings of the HMI flow: 0, 0.5 L/min and 1.0 L/min. The experiments were executed first with the Au solution. Figure 3. shows the results for the example of the 10 ppb solution. The case of no HMI flow was already discussed. Setting 0.5 L/min HMI we found that the signal intensity decreased. Moreover, the intensity maximum moved to the 16 mm sampling depth value for all concentrations respectively (not shown in Figure 3). Using the aerosol dilution causes the flow rate to increase, which in turn results in a shift of the optimum sampling depth. A further increase in the HMI flow to 1.0 L/min was found to suppress the signal even more and the optimum sampling depth shifted to an even higher value (20 mm). These changes were experienced for all concentration and can be explained the same way as in the case of 0.5 L/min HMI. The overall suppression effect of HMI flow on the signal was several orders of magnitude.

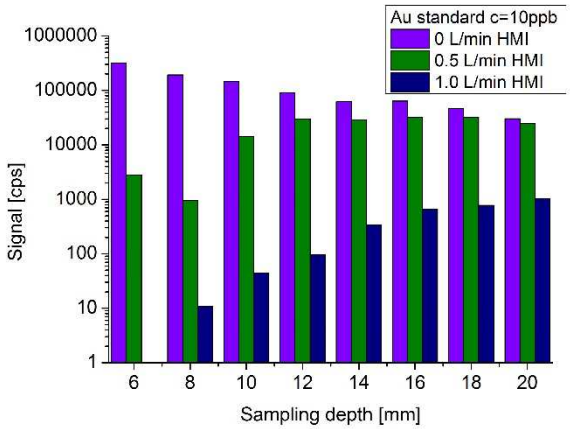

Figure 3. The variation of the signal of 10 ppb Au solution as a function of HMI flow rate and the sampling depth

The signal from nano particles were only investigated for the HMI flow equals 0.5 L/min case, as with higher HMI settings for all depth values and even for this one at lower (6-12 mm) depth values, the nanoparticle signal was so low that it could not be separated from the background signal in the histograms. The peak of the nano particles was most separable from the background at 16 mm sampling depth; at higher depths the background and particle signals started fusing together again. This is demonstrated in Figure 4.

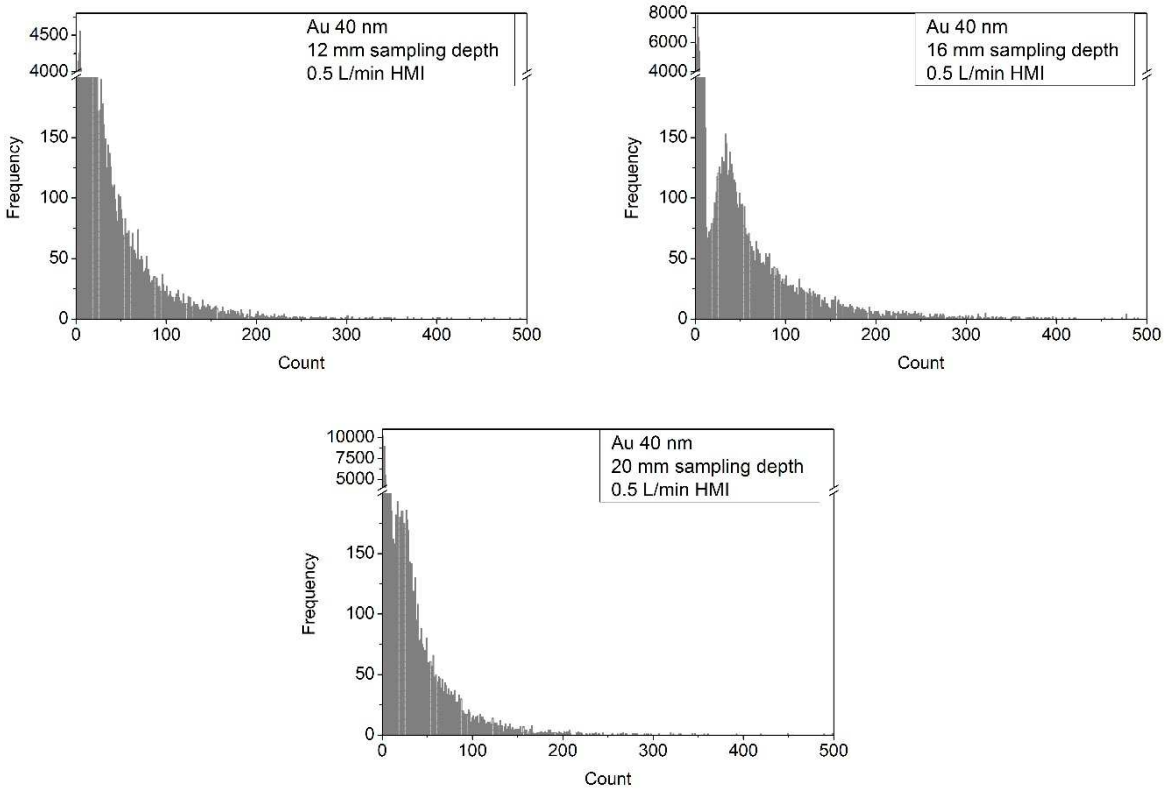

Figure 4. The effect of changing the sampling depth on signal histograms as obtained for a 40 nm gold sol with the indicated HMI and sampling depth settings

Conclusions

According to our expectations, the HMI flow and the sampling depth have a substantial influence on the performance of SP-ICP-MS measurements. It was established that by the optimization of sampling depth, a factor of 6 signal increase (or decrease) can be realized. Upwards from 6 mm sampling depth, the number of detection events were fairly constant, but the histogram peaks became narrower. Thus, this optimization can be used to find conditions under which the best size detection limits can be achieved within the lowest possible measurement time. Using the HMI flow was found to greatly reduce the signals, which may be useful for the on-line dilution of nano sol samples, but it must be accompanied by a concurrent optimization of the sampling depth, as HMI shifts the sampling depth optimum towards significantly higher values.

References

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