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Expanding the detectable nanoparticle size range by High Resolution ICP-MS

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Overview

Purpose: To overcome the challenge of detecting smaller nanoparticle sizes with high absolute sensitivity of high resolution (HR) ICP-MS using the spICP-MS approach.

Methods: Samples containing nanoparticles were analyzed directly with a Thermo Scientific™ Element XR™ HR-ICP-MS by single particle ICP-MS (spICP-MS).

Results: The highest sensitivity of the Element XR HR-ICP-MS and the Thermo Scientific™ Element 2™ HR-ICP-MS enables detection of smallest nanoparticles.

Introduction

The small nanoparticle size and high surface to mass ratio compared to ionic species of the same analyte, has a strong influence upon the analytes' physiochemical and toxicokinetic properties. Smaller silver nanoparticles are shown to have more significant effects than larger nanoparticles or $AgNO_3$ [1]. Therefore, there is a trend for single particle ICP-MS towards reducing the smallest detectable nanoparticle size. This is however, hampered by the sensitivity and background of most instrumentation. The smaller the nanoparticles which have to be detected, the higher sensitivity of the ICP-MS required to be able to detect these small particles.

Therefore, the Element XR HR-ICP-MS instrument with its high inherent sensitivity and low dark-noise was used in this study to demonstrate its capabilities to detect small nanoparticles.

Methods

Sample preparation

After sonication, samples were diluted in 2 mM sodium citrate. The diluted samples were sonicated again before analysis.

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Sample analysis

Samples were analyzed directly by the Element XR HR-ICP-MS using the conditions shown in Table 1. The sample flow and nebulization efficiency were determined gravimetrically. The detection sensitivity was determined with an ionic silver standard.

Table 1. Element XR HR-ICP-MS parameters for Ag nanoparticle determination

Parameter	Value
RF power	1250 W
Sample gas flow	1.2 L/min
Nebulizer	Quartz, self aspirating
Spray chamber	Cyclonic
Isotope monitored	^{109}Ag
Detection mode	Triple
Dwell time	3 ms (0.001 s sample time, 4 % mass window)
Sample flow	0.14 mL/min
Nebulization efficiency	0.25
Detection sensitivity	1.07 x 10^6 cps/(µg/L Ag)

Results

The time resolved intensities of a solution containing 1 ng/L of 20 nm silver nanoparticles are shown in Figure 1. The nanoparticle 'events' are significantly above the background noise caused by dissolved silver.

Figure 2 shows the histogram for the signal distribution which is calculated from the time resolved intensities. Calculations were done in a home made spreadsheet. A more comprehensive tool for single particle calculation was developed by RIKILT Wageningen UR [2, 3].

The nanoparticles (right side of Figure 2) are well separated from the ionic Ag signals (left side). The fact that there is a wide valley between the ionic Ag signal and the 20 nm Ag particles shows that even smaller than 20 nm nanoparticles would have been able to be detected. The threshold for particle detection was visually determined in this figure to be 5000 cps.

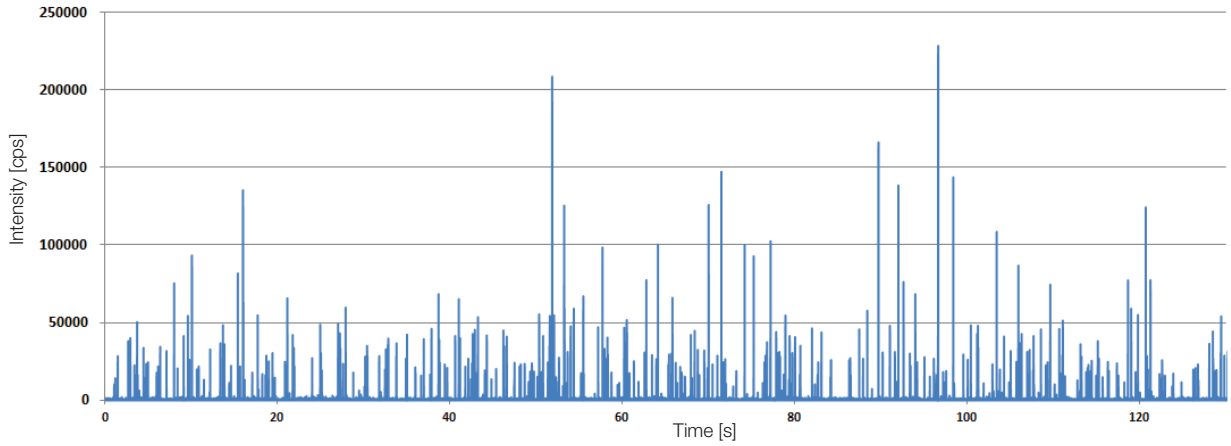

Figure 1. Time resolved intensities of 20 nm Ag nanoparticles (1 ng/L) Intensity

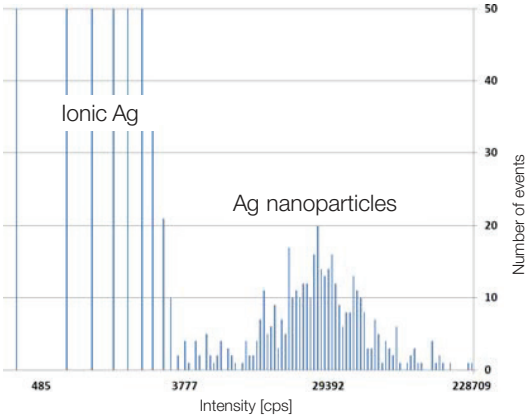

Figure 2. Signal distribution (20 nm Ag nanoparticles)

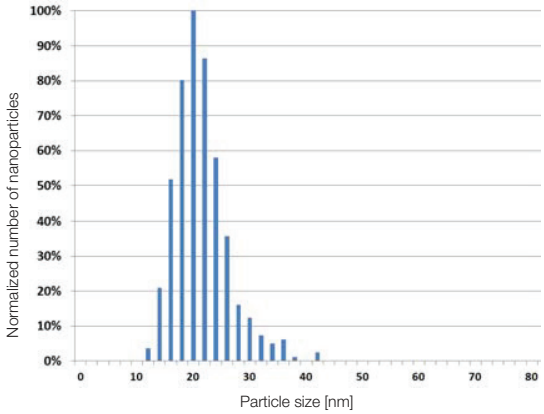

Figure 3. Calculated Ag nanoparticle size distribution

With this threshold of 5000 cps and the silver density of 10.49 g/mL the nanoparticle size distribution shown in Figure 3 was calculated. A 20 nm Ag particle equals 42 attogram silver, which results in an intensity of 26 000 cps. Within the 3 ms dwell time this means that 78 counts were registered at the detector within that time. A 10 nm particle would result in 1/8 of this count rate. The results calculated from this dataset are shown in Table 2. The calculated particle size and the concentration calculated agree well with the expected values.

Table 1. Element XR HR-ICP-MS parameters for Ag nanoparticle determination

Parameter	Value
Particle size	20 nm ± 5 nm
Number of particles detected	1.2 L/min
Particle number concentration	1.1 x 10^7 particles/L
Ag concentration of particles	1 ng/L

Conclusions and Outlook

- For the determination of small nanoparticles it is important to have an ICP-MS with the highest sensitivity.
- The high sensitivity of the Element 2 and Element XR HR-ICP-MS enables good detection of silver nanoparticles with 20 nm diameter and below.
- Hassellöv and coworkers have shown that 6.4 nm gold nanoparticles can be detected with the Element 2 using 0.1 ms time resolution [5].

References

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