Insights Into the Nanoworld – Analysis of Nanoparticles with ICP-MS

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Overview

Purpose: Demonstrate the potential of FFF-ICP-MS and sp-ICP-MS for the characterization of nanoparticles.

Methods: FFF was coupled to ICP-Q-MS, with liquid flows driven using an inert ion chromatography system. For sp-ICP-MS, samples were directly aspirated.

Results: FFF was shown to separate Au nanoparticles based on their diameters. sp-ICP-MS was used to determine the average diameter of Ag nanoparticles.

Introduction

The need for nanoparticle (NP) characterization has exploded in recent years due the ever increasing use of engineered nanoparticles (EN) in various industries and the consequent studies that investigate the environmental and consumer risk.

Of the methods developed with this goal in mind, Field Flow Fractionation (FFF) coupled to ICP-MS has proven to be one of the most promising. FFF has a separation principle based on the differing mobilities of different particle sizes in a laminar liquid flow. Smaller particles flow faster through the channel, enabling a separation based on size. FFF is compatible for particle sizes in the low nm to low μm range and is thus perfectly suited to NP separation.

Another promising approach for NP characterization is sp-ICP-MS. Through direct analysis of an appropriately diluted solution containing NPs, the NPs can be counted. If the NPs consist of just one element, the peak height is proportional to the size of the NP, and the frequency of individual signals can be used to determine the NP concentration.

Although both strategies benefit from the high sensitivity of ICP-MS detection, the single particle approach limit of particle size detection is actually governed by signal-to-noise ratio. The more sensitive an instrument, the smaller the particle it can detect.

Methods

Sample Preparation

In general NP standards were diluted in water and sonicated for 5 to 15 minutes just prior to analysis.

Field Flow Fractionation

A Wyatt Technology™ Eclipse® equipped with a short channel (SC) was coupled to the Thermo Scientific™ iCAP™ Qc ICP-MS (Fig. 1). Mobile phase was delivered to the Eclipse chassis using a Thermo Scientific™ ICS-5000™ HPIC System and injections were performed using the sample loop of the ICS-5000 AS-AP Autosampler. The Eclipse chassis splits the flow appropriately with a series of specially configured valves. The FFF membrane used and the separation parameters are shown in Table 1.

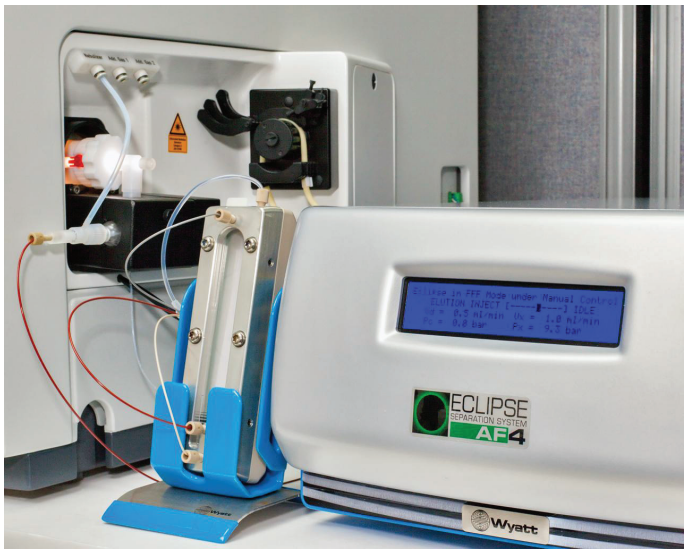

FIGURE 1. Wyatt Technology Eclipse AF4 with SC coupled to a Thermo Scientific iCAP Qc ICP-MS.

TABLE 1. Field Flow Fractionation Conditions.

	Gold NPs	
Membrane	10 kD RC*	
Mobile Phase	Water	
Injection vol. (µL)	20	
Detector flow (mL/min)	0.5	
Focus flow (mL/min)	1.5	
FFF protocol	**Time**	**Vx**
Elution	1	0
Inject	1	0
Focus and Inject	5	0
Focus	1	0
Elution	5	1.5
Elution	15	1.5
Elution	5	0.5
Elution and Inject	10	0

*RC – Regenerated Cellulose

sp-ICP-MS

An iCAP Qc ICP-MS was used for all sp-ICP-MS determinations. Ag NP of different sizes were prepared and analyzed. All solutions were prepared in 2 mmol L^{-1} ammonium citrate. A tap water sample was sourced locally, and diluted 3:1 in ammonium citrate before analysis.

Data Analysis

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used throughout for iCAP Qc ICP-MS control and all data acquisition. The embedded plug-in for the Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System Software was used to drive the Wyatt Eclipse and ICS-5000 HPIC system in a single method. Eclipse® ISIS software (Intelligent Separation Improvement Software) was used to optimize the FFF separation conditions.

Results

Field Flow Fractionation

Certified gold NPs with 30 nm (NIST 8012) and 60 nm (NIST 8013) diameters were used to evaluate the NP separation potential of FFF. Table 1 summarizes the channel, membrane and conditions used. Figure 2 shows elution profiles of 30 nm and 60 nm gold NPs.

Optimization of separation conditions based on detector flow (Vd), cross flow (Vx) and cross flow gradient were performed using ISIS, a dedicated software for predicting separation based on the input of flow-rates and channel geometry.

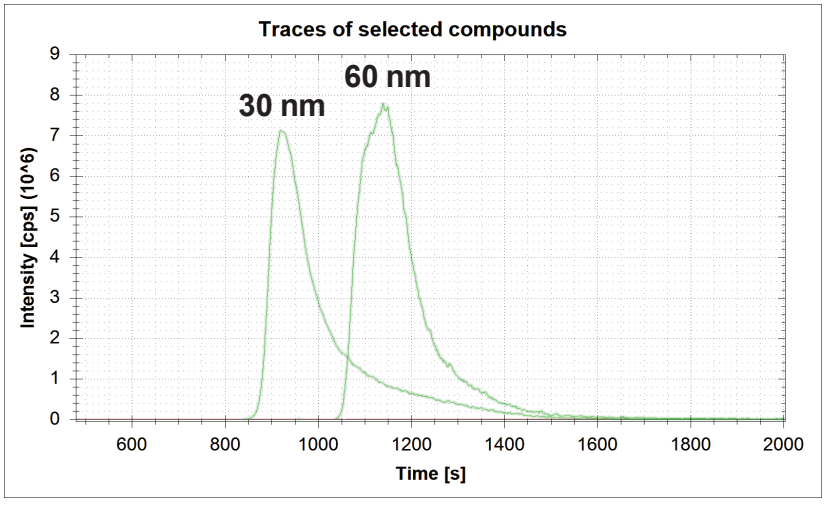

FIGURE 2. 197 Au FFF-ICP-MS fractograms of 30 nm and 60 nm gold NPs.

Single Particle ICP-MS

sp-ICP-MS requires the measurement of single particle events (SPE) in a time resolved analysis. The underlying principle of sp-ICP-MS lies in the fact that the size of the NP is directly proportional to the intensity of the SPE. This is presented in figure 4, where the smaller NPs (20 and 40 nm) generate lower intensity SPEs than the larger NPs (60 and 100 nm).

For sp-ICP-MS, the sample needs to be diluted so that only a suitable number of particles per volume is directly aspirated into the plasma. Data from fast scanning across a single isotope in a predetermined time window (e.g. 5 ms dwell time for 60 s) and is exported into a Microsoft® Office spreadsheet to calculate particle size and differentiate between actual NP´s and background signals.

The correlation between dwell time and particle events is illustrated in figure 3. A typical nanoparticle event has a duration of 300µs.

- Only one nanoparticle event should be monitored per data point (A).
- Short dwell times lead to incomplete registration of particle events (underestimation of particle size, B).
- Long dwell times lead to registration of two (or more) particle events (overestimation of particle size, C).

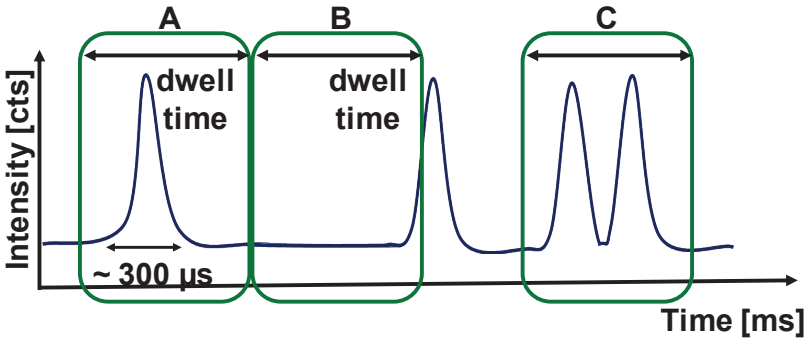

FIGURE 3: Relation between single particle event and dwell time.

For sp-ICP-MS, the instrumental detection limit is expressed as a nanoparticle size, that can no longer be discriminated against the instrumental background. It is therefore dependent on the instrument´s detection sensitivity, not on the dilution factor of the sample!

Figure 4 shows the resulting time resolved analysis for four different sized Ag nanoparticles, each solution containing the same total amount of Ag (5 ng kg^{-1}):

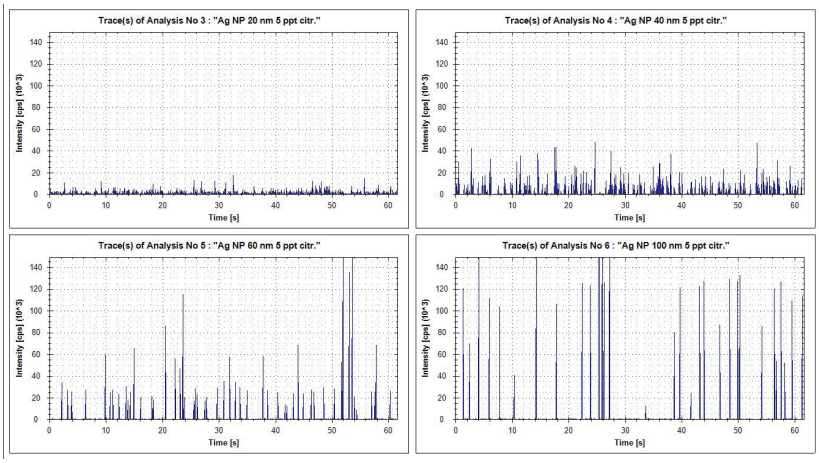

FIGURE 4. Time resolved measurements of Ag nanoparticles with size 20 nm, 40 nm, 60nm and 100 nm (top left to bottom right) @ total Ag amount of 5 ng kg^{-1}

The determined NP size is plotted against the theoretical value in Figure 5. Both values are in good agreement. The determined LoD is approximately 20 nm for Ag NP´s.

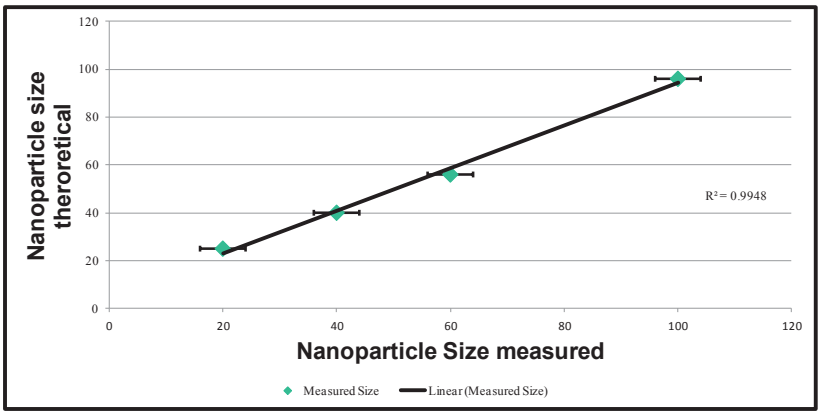

FIGURE 5: Correlation of theoretical and measured nanoparticle size for Ag NP´s.

As a final proof of the suitability of the method, locally sourced tap water was diluted 3:1 in 2 mmol L^{-1} ammonium citrate and was analyzed without and after addition of Ag NP´s (40 nm, 5 ng kg^{-1} total Ag), see figure 6.

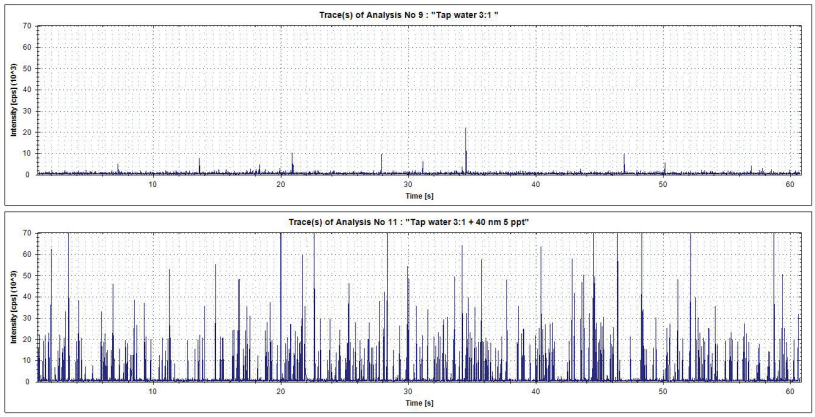

FIGURE 6. Analysis of unspiked tap water (top) and spiked tap water (bottom) with sp-ICP-MS.

The determined NP size in tap water was 41 ± 1 nm and is in excellent agreement with the expected value.

Conclusion

- Both FFF-ICP-MS and sp-ICP-MS bring analytical advantages to the characterization of NPs and act as complementary techniques.
- The integrated FFF-ICP-MS package is fully automated with bidirectional control and emergency shut-off features.
- The completely metal free FFF/IC system operates with a single pump and offers a switch option that allows the user to quickly change from FFF to IC.
- The high base sensitivity and low backgrounds of the iCAP Qc ICP-MS offer a particular advantage in sp-ICP-MS.

References

1. P. Krystek *et al.* J Anal. At. Spectrom. 26 (2011); 1701-1721.

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