On the Way to Routine Analysis of Nanoparticles Using spICP-MS and FFF-ICP-MS

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Overview

Purpose: Highlight the potential of FFF-ICP-MS and spICP-MS for the analysis of samples containing nanoparticles.

Methods: Samples containing different nanoparticles were analyzed directly using a Thermo Scientific™ iCAP Q™ ICP-MS. Data evaluation for spICP-MS was accomplished using the new npQuant evaluation module for the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Results: Different types of nanomaterials have been analyzed and the results show good agreement with the expected values.

Introduction

The analysis of Nanoparticles (NPs) has become one of the hot topics in analytical chemistry. Although many everyday products contain such material, detailed knowledge about potential risks or hazards is still unavailable. In order to leverage the potential of ICP-MS for the analysis of NPs, two approaches have been developed in recent years:

1. Hyphenation of an appropriate separation technique like Field-Flow-Fractionation (FFF), or,
2. Direct analysis of nanoparticles using spICP-MS.

Whereas the first technique is mostly used to fractionate a sample containing different nanoparticle sizes, the latter technique is a means to directly characterize nanoparticles in terms of size and particle number. Additionally, no peripheral devices are required as nanoparticle solutions can be aspired directly. Evaluation of the data is typically done using mathematical treatment of the measured signals obtained for signal particle events[1].

Methods

Sample Preparation

All measurements were conducted with NIST reference materials 8011, 8012 and 8013 (stabilized Au Nanoparticles of 10, 30 and 60 nm nominal diameter). All samples were sonicated before dilution in ultrapure water to an appropriate particle number concentration range.

Mass Spectrometry

The Thermo Scientific iCAP Qc ICP-MS was used for all experiments. All experimental parameters are summarized

FIGURE 1. The Thermo Scientific iCAP Q ICP-MS and the Wyatt Technology Eclipse FFF.

Field Flow Fractionation

A Wyatt Technology™ Eclipse® was coupled to the Thermo Scientific iCAP Qc ICP-MS (Fig. 1). A PES hollow fiber was used for separation (HF[5]). Mobile phase was delivered to the Eclipse chassis using a Thermo Scientific™ ICS-5000™ IC and injections were performed using the sample loop of the ICS-5000 AS-AP Autosampler.

TABLE 1. ICP-MS Instrument Operation Parameters.

Parameter	Value
Nebulizer	PFA-100 or PFA-ST
Nebulizer Gas Flow	1.06 L· min^{-1}
RF Power	1550 W
Interface	Ni Cones, High Sensitivity Skimmer Cone Insert

Data Analysis

Thermo Scientific Qtegra ISDS Software was used to operate the iCAP Q ICP-MS. The embedded plug-in for the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) was used to drive the Wyatt Eclipse and ICS-5000 IC in a single method.

All data handling to calculate particle size distributions and particle number concentration was carried out using the npQuant evaluation module for Qtegra ISDS Software.

Results FFF-ICP-MS

In order to completely characterize a sample and to judge potential hazards, a multidimensional approach including speciation and nanoparticle analysis may be required. Due to the complete integration of all required hardware devices seamless switching between Ion Chromatography (IC) and Field-Flow-Fractionation (FFF).

Figure 2 shows the Method Editor inside the Qtegra ISDS Software, which enables the analyst to completely control all devices within one software and one single sample list.

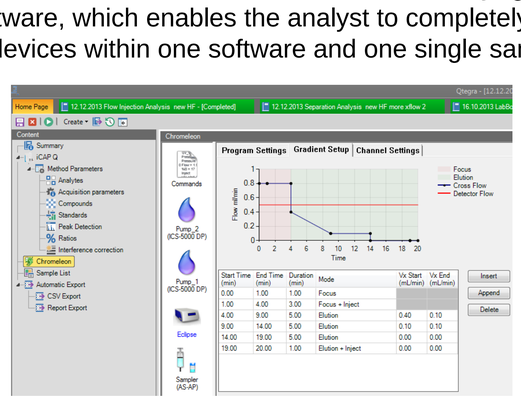


FIGURE 2.Screenshot of the Chromeleon CDS Method Editor inside the Qtegra ISDS software.

A typical fractogram can be observed in figure 3. In this example, AuNP´s with nominal diameters of 10 and 60 nm have been separated using HF[5] in 20 minutes.

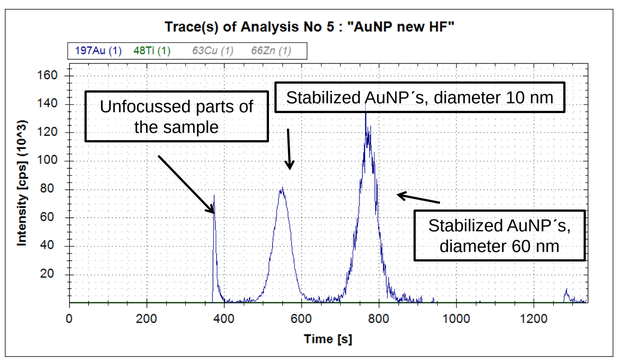


FIGURE 3. Fractogram showing the separation of two different nanoparticle fractions using HF[5]-ICP-MS.

Results spICP-MS

In contrast to conventional ICP-MS measurements, the evaluation of spICP-MS data is based on the individual treatment of discrete signals caused by the introduction and complete decomposition of particles in the plasma. The new npQuant evaluation module for the Qtegra ISDS Software allows to carry out all required calculation steps to generate the size distribution and number concentration for nanoparticles in a sample.

Determination of Particle Size Distribution and Number Concentration

To determine the particle size distribution and concentration from the acquired raw data, the following calculation steps and assumptions have to be made.

1. **Filter sp events from underground**
→ Signals above certain intensity threshold

2. **Calculate mass of element observed in every event**
→ ([CPS] x dwell time) / detection sensitivity x sample flow

3. **Calculate particle diameter**
→ spherical particles, density equal to solid material

4. **Evaluate size distribution and number of particles**
→ Sort individual particles in bins, evaluate abundance

In order to accurately calculate the size and the particle number concentration in a sample, the following experimental parameters have to be known in advance:

Sample Flow: Flow rate of sample to the plasma, can be determined using a flow meter or gravimetrically

Detection Sensitivity: Instrument response to the analyte of interest

Nebulization or **Transport efficiency**: Fraction of total sample material reaching the plasma

For routine analysis, simple and reliable determination of crucial measurement parameters is mandatory. The new npQuant module allows to automatically determine both parameters using a series of standards (both ionic as well as nanoparticle)[2].

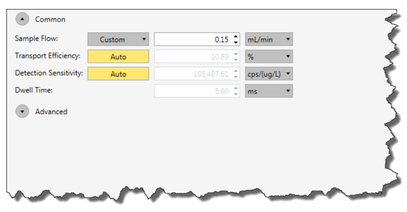


FIGURE 4. Automated determination of the transport efficiency using a particle standard.

Determination of Particle Derived Signals for Evaluation

Transforming the obtained data set from the time domain (CPS vs. measurement time) to the intensity domain (# of occurrences of signals vs. signal intensity) leads to a chart that allows to determine:

- Signals derived from background (instrumental or dissolved ionic species) with low signal intensity but high frequency
- Particle derived signals with high signal intensity but low frequency

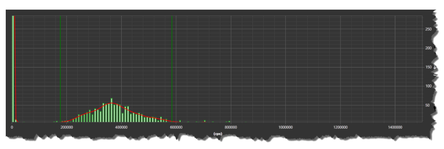
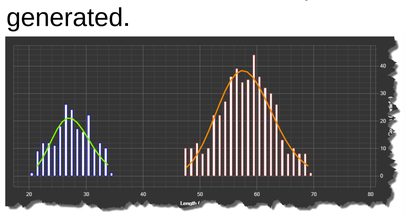


FIGURE 5. Signal distribution and selection of particle signals for evaluation.

Determination of Particle Size and Number

For every signal within the defined intensity window (Figure 5) for a given particle fraction, the corresponding particle size is calculated and the particle size distribution is generated.



Sample	Nominal Diamter	Determined
NIST 8011	10 nm	9.2 ± 3 nm
NIST 8012	30 nm	27.6 ± 3 nm
NIST 8013	60 nm	58.1 ± 5 nm

FIGURE 6. Particle Distribution and calculated particle size for NIST reference materials (Au nanoparticles).

Different particle fractions in one sample can be evaluated independently using dedicated intensity threshold values for each fraction.

Recognition and Elimination of Artefacts

The npQuant evaluation module for spICP-MS can help to recognize and minimize the most likely formed artefacts typically observed in spICP-MS, split particle events and multiple particle events, as highlighted in Figure 7.

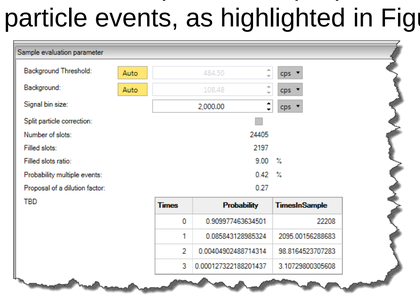


FIGURE 7. Tools for recognition and elimination of artefacts in spICP-MS.

Split Particle Correction: Sums up adjacent signals with intensities above background but below the lower particle threshold (similar to reference 3).

Multiple Particle Events: Based on the number of filled slots, the probability for double and higher multiple particle events is calculated and a dilution factor is proposed according to a user definable filled slots ratio (e.g. 10%).

Conclusion

- The analysis of nanoparticles is developing into an routine application since legislation is being defined.
- Intelligent software solutions can support the user in order to completely characterize a sample using different techniques with the shortest possible time.
- Potential errors and artefacts can be avoided using automated determination of key method parameters and statistical evaluation of the acquired raw data helping to assure data quality.

References

1. Laborda *et al.*, Anal. Chem. **86** (2014), 2270-2278
2. Pace *et al.*, Anal. Chem. **83** (2011), 9361-9369
3. Liu *et al.*, Anal. Chem. **86** (2014), 3405-3414

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