Single particle analysis of nanomaterials with agilent ICP-MS

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Introduction

Nanoparticles (NPs) are defined as ultrafine particles with one dimension between 1–100 nm [1]. Because of their small size, they have a very large surface area relative to their weight, so they often react quite differently from a bulk solid or dissolved material of the same composition. For this reason they may offer novel and interesting properties for a broad range of applications. But while their use is constantly increasing, questions and concerns have been raised about their safety and their health impact. For this reason, there is an urgent need to develop analytical methods that are suitable for the particular evaluation of NPs.

An interesting approach for the characterization of NPs has been developed by Degueldre et al. [2] based on elemental determination using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). If samples containing NPs are introduced at a low flow rate and the number of particles in the solution is sufficiently low, analysis using ICP-MS in time resolved mode makes it possible to collect the intensity for a single particle as it is vaporized and atomized in the plasma. Then, each measured data point can be correlated to the size and mass fraction of a unique NP. This method of NP characterization is called Single Particle ICP-MS (SP-ICP-MS) analysis.

In the present work the analysis of gold NPs has been carried out using the Agilent 7700x in SP-ICP-MS mode.

Standard and Sample preparation

Gold nanoparticle reference materials (RMs) NIST 8012 and NIST 8013, were purchased from NIST (Gaithersburg, MD, USA). Unknown gold NP samples with different sizes were provided by different NP producers. The nanoparticle samples were diluted with water using polypropylene vials. Sample dilution was performed on the day of the analysis in order to avoid sample degradation. Before dilution of the samples and prior to their analysis, all solutions were placed in an ultrasonic bath for 15 min to ensure that the samples were fully homogenized.

Experimental

Instrumentation

Measurements of NPs were performed using the Agilent 7700x ICP-MS. The samples were introduced directly into the ICP-MS system using the standard peristaltic pump with Tygon pump tubing and ASX-520 autosampler.

Analyses were performed in time resolved analysis (TRA) mode using an integration time of 3 ms for all measurements.

The general settings of the 7700x system are detailed in Table 1.

Table 1 - 7700x parameters for SP-ICP-MS analysis

Plasma power	1550 W
Carrier gas	1.05 l min^{-1}
Nebulizer pump	0.1 rps
Sample depth	8 mm
Integration time	3 ms
Acquisition time	60 s

Experimental

Data analysis

In the present work, a dedicated spread sheet developed by the National Institute of Food Safety in the Netherlands (RIKILT) was used for data conversion. The SP-ICP-MS analysis and custom spreadsheet calculations are able to determine the number of particles present in the sample, their size distribution, the median size of the NPs population and the mass concentration for the element that the NP is composed of.

Results and Discussion

The gold NP standard (NIST 8012), which has a reference diameter of around 30 nm, was used for the evaluation of the SP-ICP-MS method. A typical TRA acquisition for single NP measurement on the 7700x ICP-MS is shown in Figure 1.

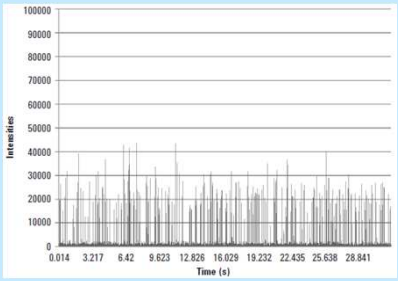

Figure 1. Measurement of 30 nm gold NP standard (NIST 8012) under SP-ICP-MS mode

From this raw data, the background signal was eliminated by the custom spreadsheet, and the remaining intensities were converted into particle size to give the distribution pattern shown in Figure 2. From this size distribution plot, the median size was calculated to be 26.9 nm. This measured size is in good agreement with the reference value shown on the investigation report, which is 24.9–28.4 nm, depending upon the technique used for the measurement. The three replicate analyses of this sample gave a relative standard deviation of 0.5%, demonstrating the good repeatability of the 7700x SP-ICP-MS method.

The particle number in the diluted sample was estimated at 1.6 x 10^7 particles/L and the mass concentration for Au was 3.2 ng/L.

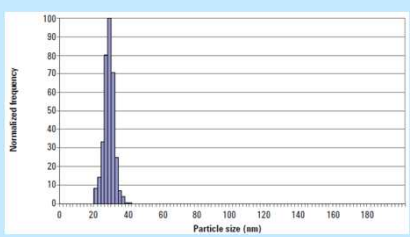

Figure 2. Particle size distribution for a 30 nm gold NP standard (NIST 8012)

It should be noted that the data in Figure 2 show that no NPs were detected at a higher size range than the expected group in the 30 nm region. In particular around the 38 nm region where the signal should appear if a particle containing a cluster of two NPs was measured, the number of events measured is less than 2% of the total number of NPs detected.

Results and Discussion

For a better evaluation of the developed method and to demonstrate that the method is able to discriminate NPs of a larger size, a mixture of gold NPs at 30 nm (NIST 8012) and 60 nm (NIST 8013) was also analyzed.

The result of this analysis is displayed in Figure 3. As can be seen, the method was clearly able to identify the presence of the two different NP sizes, with no overlap between the two different populations. The method has therefore been shown to have sufficient resolution to detect and discriminate between mixtures of different NP sizes within a single sample.

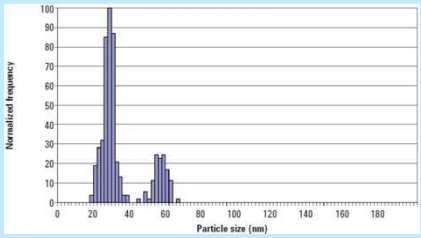

Figure 3. Particle size distribution for a mixture of 30 nm and 60 nm gold NP standards (NIST 8012 and 8013

Following the analysis of the NIST NP RMs, the remaining gold nanoparticle samples were measured as unknowns. Au NPs with a nominal particle size of 40 and 15 nm were analyzed as separate samples, and the median particle size was found to be 38 and 16 nm respectively. The results for the characterization of those samples can be seen in Table 2.

Table 2 - Results for the analysis of unknown gold NPs

Theoretical size	40 nm	15 nm
Experimental size	38 nm	16 nm
Particles number	5.5 x 10^7 particles/L	6.4 x 10^6 particles/L
Element concentration	3.7 ng/L	0.3 ng/L

Conclusions

The present work illustrates the suitability of the Agilent 7700x ICP-MS for the analysis of single nanoparticles. The method has been successfully applied to the analysis of gold NPs with sizes ranging from 15–60 nm. The SP-ICP-MS method provided the size distribution, median size, number of particles and the elemental concentration of a given NP sample.

For more information on the method, you can download the application note (5991-2929EN) on the Agilent website (www.agilent.com).

Acknowledgements

We acknowledge the contribution of RIKILT, who provided the Microsoft ® Excel® worksheet that was used in the present work to convert the raw SP-ICP-MS analysis data into NPs sizes.

References

1. ISO TS 80004-1:2010: Nanotechnologies - Vocabulary - Part 1: Core terms

2. Degueldre S., Favarger P.-Y., Bitea C., (2004) Analytical Chimicta Acta, 518: 137-142