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METALLIC NANOPARTICLES CHARACTERIZATION BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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1. Introduction

In the context of surface-enhanced Raman scattering (SERS) analyses, metallic nanoparticles (Nps) are used to enhance Raman signal. Most of the time, researchers synthesize themselves their own substrates to define the appropriate medium and to reduce the price. Given that physical properties such as Nps size or shape directly impact the Raman signal exaltation, a characterization is almost always required. Most of the time, an association of several techniques is used to obtain multiple information such as dynamic light scattering (DLS) or UV-Visible spectroscopy. This study aims to develop a method to rapidly and accurately characterize metallic Nps by an inductively coupled plasma mass spectrometry (ICP-MS) technique. Coupling with the single particle mode (spICP-MS), information about size, size distribution, Nps concentration and dissolved metallic content can be obtained. This is why, several suspensions of Nps made of gold or silver, the two most employed metals as SERS substrates, were prepared according to the largely used Lee and Meisel protocol. This process consisted to reduce a metallic salt by a trisodium citrate solution. These suspensions were then fully characterized by spICP-MS. This communication was focused on Nps size and presents a comparison with a reference technique (DLS) to confirm the measured size.

2. spICP-MS principle

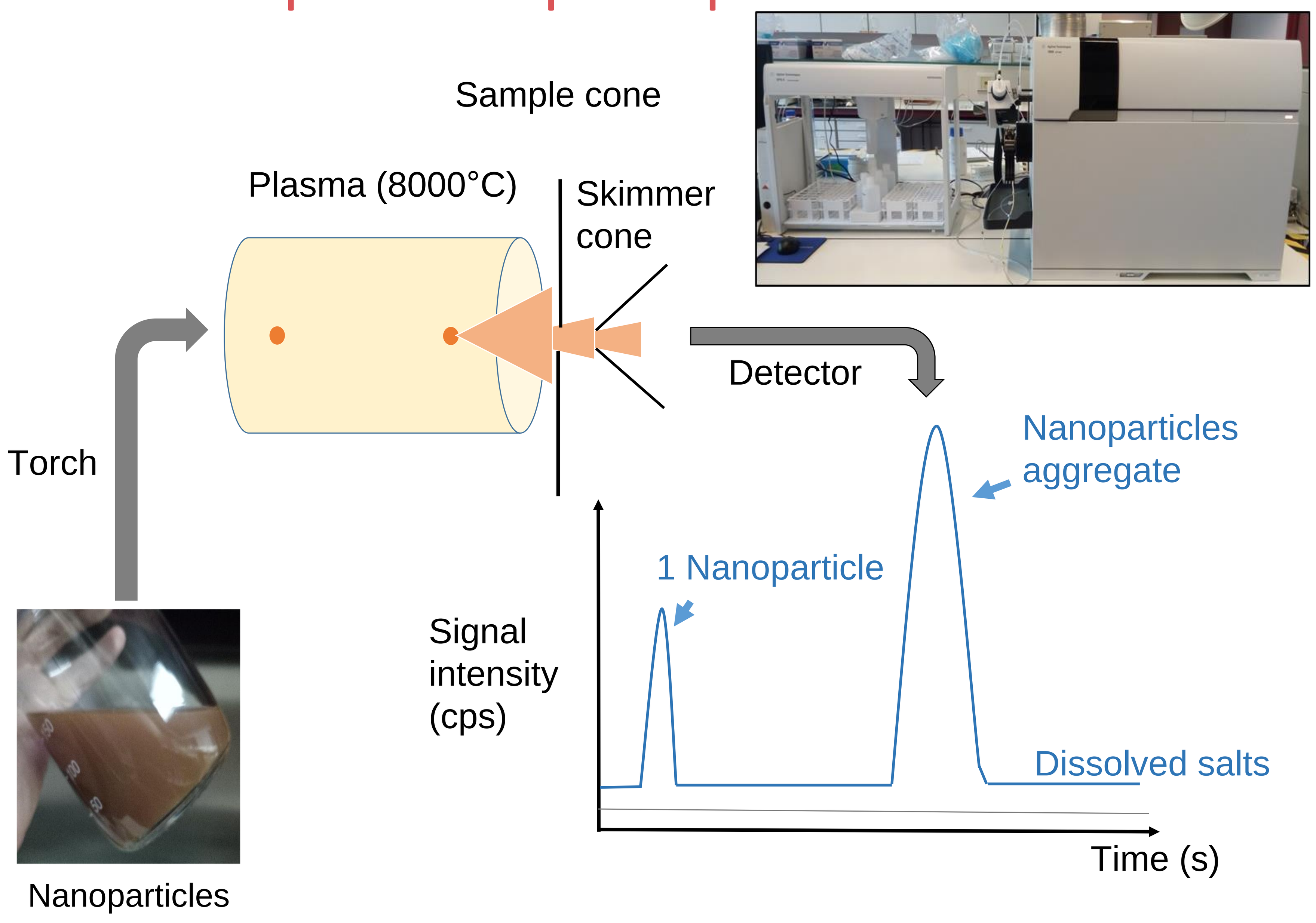

Figure 1: Principle of single particle inductively coupled plasma mass spectrometry (spICP-MS)

3. Material & Methods

3 syntheses of silver nanoparticles (AgNps)
3 syntheses of gold nanoparticles (AuNps) } Lee & Meisel process

DLS measurements:
Equipment: Zetasizer Nano ZS (Malvern Panalytical®)
Sample preparation: Suspension diluted 10 times with MilliQ water and sonicated 2 min before analysis.

spICP-MS analyses:
Equipment: ICP-MS 7800 (Agilent Technologies®)
Nebulizer gas flow rate: 0.85 L/min
Dwell time: 0.1 ms
Acquisition time: 60 s
For AuNps analyses:
Reference material (RM): AuNps 32.7 nm (LGC®) diluted 1 250 000 times.
QC: AuNps 60 nm (Sigma-Aldrich®) diluted 1 000 000 times.
Sample: AuNps dilution of 13 333 333 times.
For AgNps analyses:
RM: AgNps 60 nm (Sigma-Aldrich®) diluted 1 000 000 times.
QC: AgNps 80 nm (Sigma-Aldrich®) diluted 200 000 times.
Sample: AgNps dilution of 1 000 000 times.

All suspensions were sonicated before the dilutions. All preparations were made protected from light and extemporaneously.

4. Results & Discussion

Table 1: spICP-MS results for homemade AuNps

AuNps	Nps number	Size (nm)	Standard deviation (nm)	Concentration (particle/L)
	1324	26		6.7 x 10^7
Synthesis 1	1284	25	1.5	6.5 x 10^7
	1080	28		5.5 x 10^7
	1813	24		8.7 x 10^7
Synthesis 2	1748	24	0.0	8.4 x 10^7
	1805	24		8.7 x 10^7
	1748	24		8.8 x 10^7
Synthesis 3	1593	24	0.0	8.0 x 10^7
	1545	24		7.8 x 10^7

Table 2: spICP-MS results for homemade AgNps

AgNps	Nps number	Size (nm)	Standard deviation (nm)	Concentration (particle/L)
	1014	63		1.1 x 10^8
Synthesis 1	972	63	4.0	1.0 x 10^8
	1067	56		1.1 x 10^8
	708	65		7.4 x 10^7
Synthesis 2	730	65	1.0	7.6 x 10^7
	718	63		7.5 x 10^7
	1219	48		1.6 x 10^8
Synthesis 3	1342	47	1.0	1.7 x 10^8
	1460	46		1.9 x 10^8

Table 3: Sizes measured by DLS and spICP-MS

	DLS size (nm)	spICP-MS size (nm)
AuNps Synthesis 1	39	26
AuNps Synthesis 2	21	24
AuNps Synthesis 3	17	24
AgNps Synthesis 1	56	61
AgNps Synthesis 2	67	64
AgNps Synthesis 3	68	47

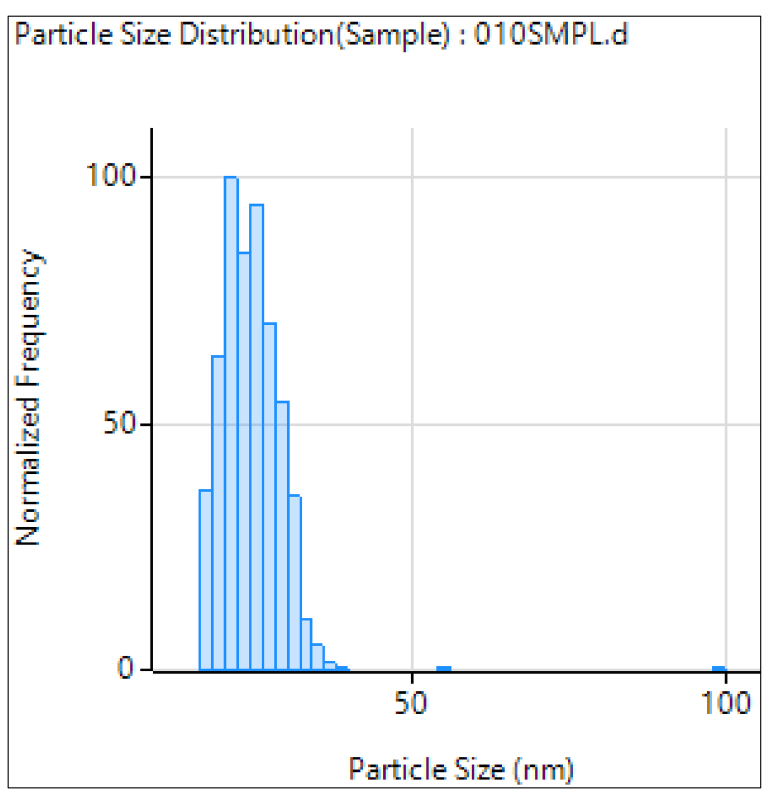

Figure 2: Size dispersion for AuNps 3

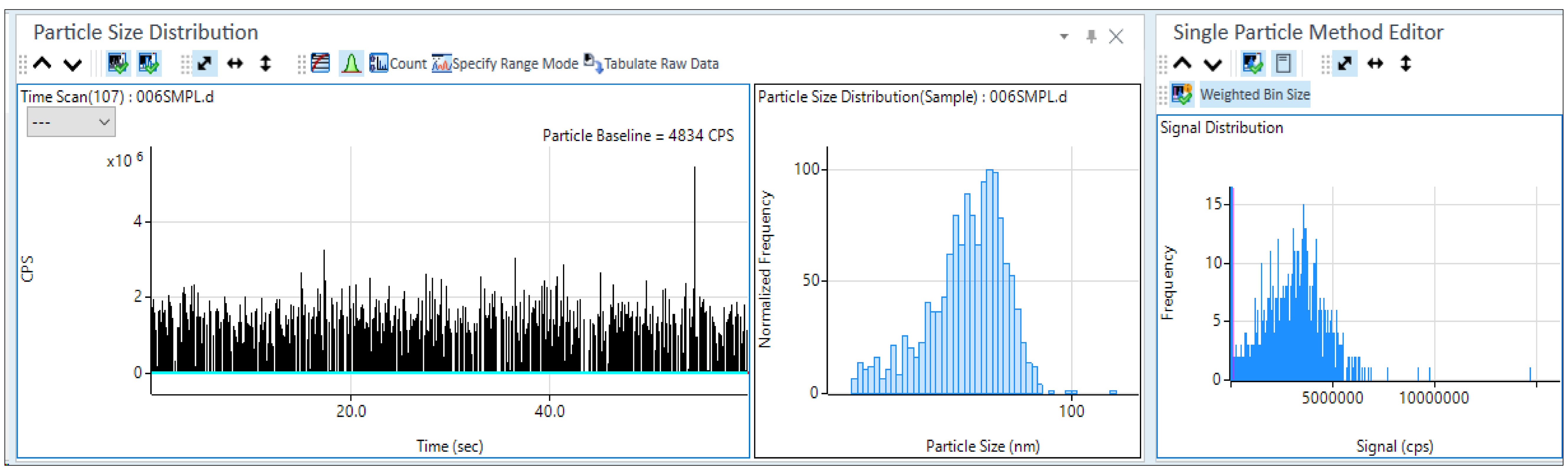

Figure 3: spICP-MS results for AgNps.

Acknowledgements

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8. Conclusion

- spICP-MS is a powerful technique to characterize SERS substrates.
- Size, size dispersion, Nps concentration can be obtained in a single analysis.
- spICP-MS sizes are closed to the DLS results (reference technique).

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