ASSESSMENT OF THE USEFULNESS OF LIBS AND ICP-MS FOR THE CHARACTERIZATION OF NANOPARTICLES IN INDUSTRIAL AND ENVIRONMENTAL SAMPLES

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Abstract
The need for analytical techniques capable for the detection and characterization of nanoparticles (NPs) in industrial and environmental matrices also grows along with the quickly expanding use of NPs in various products. Two candidate analytical techniques are laser induced breakdown spectroscopy (LIBS) and inductively coupled plasma mass spectrometry (ICP-MS). Both of these sensitive and versatile techniques provide elemental compositional information. Based on the success of the application of LIBS in aerosol analysis this technique can be expected to be similarly useful in NP monitoring applications, such as the detection of NPs in liquid or gaseous matrices, or for the monitoring of the properties of NPs produced by physical generation methods (e.g. electrical discharges or laser ablation). ICP-MS on the other hand has already proven itself useful in the literature, both in the solution or single particle analysis (spICP-MS) modes, for the characterization of nanoparticles. In recent years we also reported about the successful development of several ICP-MS based analytical methods for the compositional and dimensional analysis of NPs (e.g. [1, 2]).

In our study we assessed the potential of LIBS and ICP-MS for nanoparticle detection and characterization both in on-line (only for LIBS) or off-line (following collection on a filter) mode. Dispersions of various types of nanoparticles (e.g. monometallic, bimetallic, oxide) in simulated or real liquid and gaseous industrial and environmental matrices were measured. Some NPs were obtained commercially, while others were generated by in-laboratory developed electrical (spark or arc) discharge generators. Additional and reference characterization of the nanoparticles were performed by electron microscopy (SEM, TEM) and scanning mobility particle sizer (SMPS). Size and mass detection limits were also calculated for on-line LIBS detection of nanoaerosols and for spICP-MS detection of NPs in aqueous nanodispersions.

Introduction
Nanoparticles (NPs) can be the product of natural phenomenons or various industrial processes. Due to their favorable properties, their application has expanded to a wide range of industries, such as textiles, pharmaceuticals, food, construction electronics and so on. As their application shows an increasing trend, it is becoming necessary to detect them in both environmental and industrial samples. In our present study, we investigated the potential of

LIBS and ICP-MS for nanoparticle detection and characterization both in on-line (only for LIBS) or off-line (following collection on a filter) mode. Dispersions of various types of nanoparticles (e.g. monometallic, bimetallic, oxide, polymer) in simulated or real liquid and gaseous industrial and environmental matrices were measured.

Experimental

A quadrupole Agilent 7700X inductively coupled plasma mass spectrometer (ICP-MS), equipped with standard Agilent accessories, was used in our experiments. Sample introduction was performed by an Agilent I-AS autosampler and a Micro Mist pneumatic nebulizer equipped with a Peltier-cooled Scott-type spray chamber. The sample uptake rate was 400 µL/min. The ICP plasma and interface parameters were set up according to standard conditions (RF forward power: 1550 W, plasma gas flow rate: 15.0 L/min, carrier gas flow rate: 1.05 L/min, sampling depth: 10.0 mm). An in-house developed spark discharge generator (SDG) and an arc discharge generator (ADG) were used to generate well characterized gold and copper NPs, respectively. In the SDG, the operating time was kept constant and the spark repetition rate was changed between 50 and 250 Hz (this directly influences the numerical concentration of the produced nanoparticles). The nanoparticles were collected on a glass membrane filter in continuous Ar gas flow. The NPs were characterized by scanning mobility analyzer (SMPS) TSI model 3082 and transmission electron microscopy (TEM) FEI Tecnai G2 20 X-TWIN. In oue experiments LIBS spectra were recorded with a LIBSCAN 25+ instrument (λ=1064 nm, 50 mJ impulse energy). Commercially obtained NPs. Pt nanoparticles (46 nm , citrate stabilized, (NanoXact, NanoCompsix Inc.) and Ag nanoparticles (59 nm, Pelco NanoXact, Ted Pella Inc.)

Results

Nanoparticles may also be generated during the wear of the catalytic converters of cars, which is then released into the environment. In this simulation experiment, Pt nanoparticles were added to the collected environmental water matrix (Szeged, Vér tó). The sample was homogenized, filtered on a 0.22 µm pore-size PTFE membrane filter, diluted and measured by spICP-MS. The NPs can be detected in such a complex environmental matrix. Silver nanoparticles are widely used in textile industry because of their antimicrobial effects. In our experiment, we simulated the washing procedure of Ag NP coated textiles. The washing was simulated by vortexing the textile piece for 45 minutes in 0.4 g/L Na2CO3. The released washing water was diluted and measured with spICP-MS for the detection of silver nanoparticles. The Ag NPs were well detectable and barely degraded in size during the washing procedure. On-line measurement of nanoaerosols may be useful in the monitoring of ambient air samples or the production of nanoparticle synthesis in gases. These measurements can be carried out with a portable, robust equipment, in natural or industrial environment. In our experiments, we tested this using SDG and ADG produced Au and Cu NPs. We found that the SDG-generated Au nanoparticles (diameter of ca. 36 nm) did not contain sufficient amount of material to be detected in the on-line mode, but the ADG-produced Cu particles (with the diameter of around 236 nm) were well detectable.

Conclusion

In this work we successfully demonstrated that both LIBS and ICP-MS can be used to detect or characterize nanoparticles. The LIBS method was found to be suitable for particle detection with both on-line and off-line approaches in the case of sufficiently large nanoparticles. ICP-MS can provide accurate compositional and size information about NPs.

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