SIGNAL ENHANCEMENT OF GASEOUS SAMPLES IN THE PRESENCE OF NANOAEROSOLS GENERATED BY A SPARK DISCHARGE

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1. INTRODUCTION

Nanoparticle enhanced laser-induced breakdown spectroscopy (NE-LIBS), first described by de-Giacomo et al., is becoming a well-established signal enhancing technique in recent years [Dell'Angelo 2018]. Properly sized and distributed metallic nanoparticles (NPs) deposited on the surface of a solid sample proved to provide multiple orders of signal enhancement. In addition to solid samples, liquid samples were also described to be successfully analyzed sensitively by this approach [Palásti 2020]. The signal enhancement effect is generally described as being essentially caused by electron field emission. At the same time, gas samples, which generally have a 10-100 times higher breakdown threshold than solids and liquids, have not yet been attempted to be analyzed by the NE-LIBS approach.

Spark discharge nanoparticle generation is a promising physical technique for nanoparticle manufacturing. Similarly to other physical techniques, this method is able to avoid the use of reagents, precursors, or other chemical components therefore can provide a more environmentally friendly route of NP generation. In spark discharge generators (SDGs), high-voltage and high-current, microsecond-long spark discharges are created between two electrodes in a controlled gas flow at atmospheric pressure. Due to the sparking, the electrode material is eroded and a vapor plume is formed between the electrodes, which is then undergoes nucleation, condensation, coagulation, and aggregation [Tabrizi 2009].

In this study, we investigate the possibility of using the NE-LIBS approach to boost the sensitivity of the measurement of gases via mixing the gas with nanoparticles generated by an SDG.

2. EXPERIMENTAL

The central part of the spark discharge generator system is a vacuum chamber (Pfeiffer Vacuum GmbH.), in which the applied cylindrical, gold electrode (99.9% purity, Kurt J. Lesker Co.) pair was horizontally positioned and axially aligned whit 2.0 mm gap between the two electrodes.

The 5.0 standard litre per minute (slm) argon (99.996% purity, Messer Hungarogáz Ltd.) carrier gas flow, controlled by a mass flow controller (Model GFC16, Aalborg Inc.) was fed in the chamber via the down port (upward pointing "crossflow" with injector nozzle) [Kohut 2018]. All experiments were carried out at near atmospheric pressure, and the created gold NPs were lead through a 900 °C compaction furnace (EHA 12/300B, Carbolite Gero GmbH.). The concentration of the particles was controlled by the spark repetition rate and one or two dilution systems (VKL 10, Palas GmbH.). The size sorting and the number concentration measurement was done by a scanning mobility particle sizer (SMPS) system consisting of an electrostatic classifier (3082, TSI, USA), an ultrafine condensation particle counter (CPC, 3756, TSI, USA), and an aerosol charge neutralizer (Kr-85, NRD, USA).

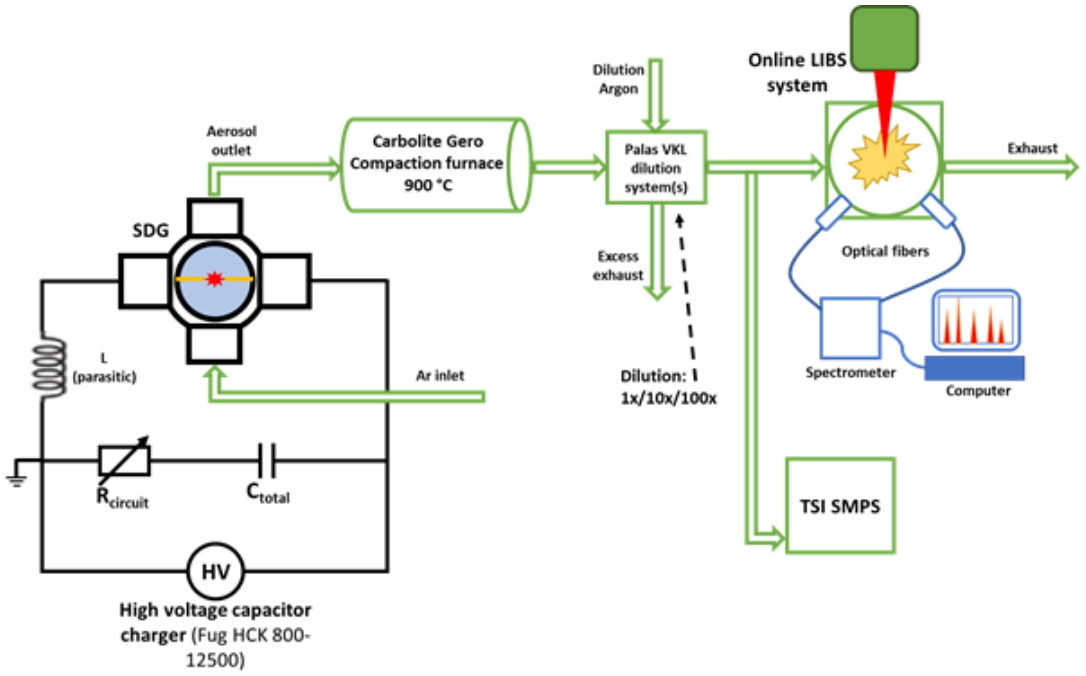

Figure 1. Schematic of the experimental setup.

The LIBS experiments were carried out in a flow-through, small volume measurement chamber constructed in-house for LIBS aerosol measurements [Palásti 2019]. The Nd:YAG laser provided 30 mJ pulses of 4 ns duration at the fundamental 1064 nm wavelength beam, which was focused into the chamber from above through a UV-grade fused silica window. The repetition rate of the plasma generating laser was set to a low value (ca. 0.25 Hz) thereby ensuring that the content of the chamber is completely renewed by the gas flow between laser shots. The LIBS

plasma was observed via two fused silica collimating lenses implemented in two ports located on the sides of the chamber (looking onto the same spot in the chamber in the horizontal direction, with 90° angle between the optical axes of the two lenses). The collected light was coupled into a two-channel fiber-optic CCD spectrometer (AvaSpec-FT2048, Avantes, NL) using optical fibers. The measurement chamber was mounted on a translation stage, which allowed bringing the laser focal spot inside the chamber in front of the light collection lenses.

Gating of the spectral data collection was achieved by the internal electronics of the spectrometer, which was triggered by the laser power supply unit and continuously monitored on a digital storage oscilloscope (TDS1002, Tektronix, USA). The minimum possible gate delay of 1 μs and gate width of 2 ms was set at the spectrometer. The double-channel spectrometer allowed the recording of the plasma emission in the 344–888 nm spectral ranges, with resolutions of 0.09 nm and 0.4 nm, respectively.

3. RESULTS AND DISCUSSION

The averaged spectra of 100 laser shots delivered into a clean argon gas and a gold nanoaerosol stream (in argon) are shown in **Figure 2**. It can be seen that the applied irradiance was not efficient to create a microplasma in the clean gas, but in the presence of nanoparticles it generated an intensive LIBS spectrum. The spectral lines can be assigned to Ar I and Ar II species and none of the intense gold spectral lines were noticeable. This indicates that the presence of Au NPs lowered the breakdown threshold of the argon gas, but their mass concentration was not sufficient to produce a gold spectrum of observable intensity. The Ar signal enhancement is nearly 5000-fold.

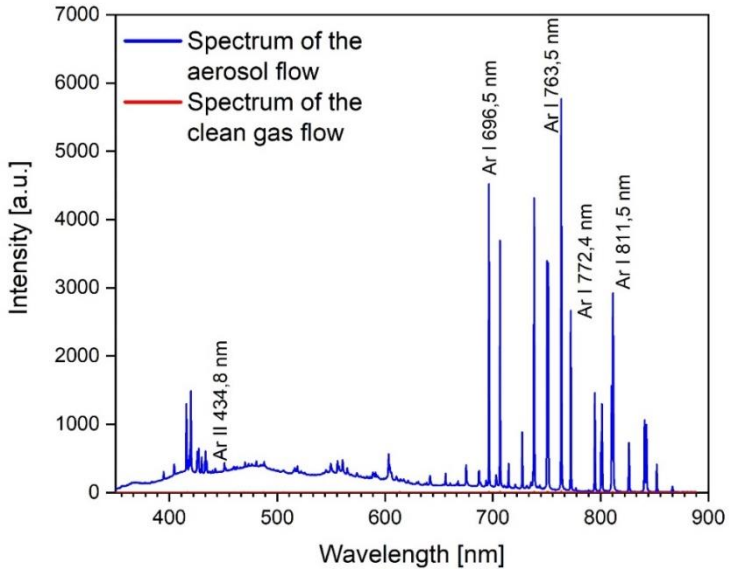

Figure 2. Average spectrum of 100 laser shots delivered into a clean Ar gas flow and an Au NP aerosol stream.

This latter finding is also illustrated on the left side of **Figure 3.**, which shows the monitoring of the net intensity of an Ar I and a Au I line during a 100-shot LIBS measurement session. Although the Ar line intensity may reach high values, but it shows a high variance. Sometimes it cannot even be separated from the background. Since the Ar I 736.5 nm was the most intensive line in our spectra, thus when this line could not be separated from the background, meant that, there was no plasma formation. During our measurements we noticed that if the number concentration of the aerosol was increased, then the frequency of the spectrum producing shots increased, and the shot-to-shot variance decreased at the same time. These trends are probably due to the more or less random distribution of NPs in the gas stream. When their concentration in the blast radius is too low, then no plasma formation is detected. However, a higher NP concentration results in the statistical increase of NPs presence in the blast radius. Due to the significant shot-to-shot variance in the intensities, the accumulation of several spectra is advised, especially if low aerosol concentration is used.

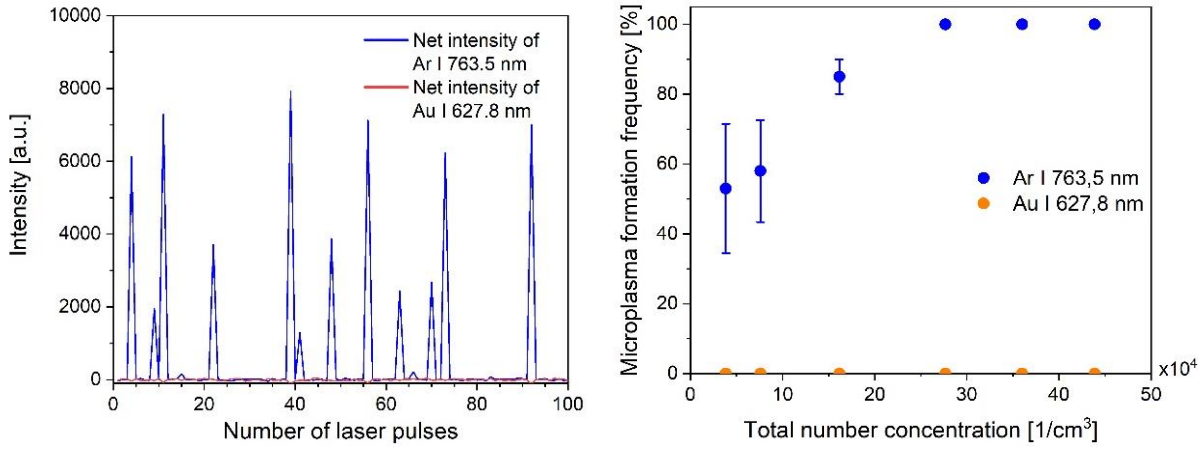

Figure 3. Net intensities of two spectral lines during 100 laser shots on the left, and the plasma formation frequency in the function of the total number concentration of the Au NPs in the aerosol flow on the right.

The effect of the aerosol number concentration and nanoparticle size to the signal enhancing phenomenon was investigated in detail, using similarly sized nanoparticles with different number concentrations and different sized nanoparticles with similar number concentration. Gas line intensities are shown in the **Figure 4.** in the dependence of the Au NP total number concentration. We investigated the effect of number concentration through c.a. two orders of magnitudes (it changed between $3.8 \cdot 10^3$ and $4.4 \cdot 10^5$). In the beginning of our concentration range, the signal grew linearly with the number concentration, but at higher concentrations, the signal started to reach a plato, where no significant change in the intensity of the spectra occurred. Due to instrumental limitations, we were able to investigate the aerosol of only three differently sized NPs, with diameters 20, 25 and 30 nm. Our findings suggest that larger NPs provide larger signal enhancement.

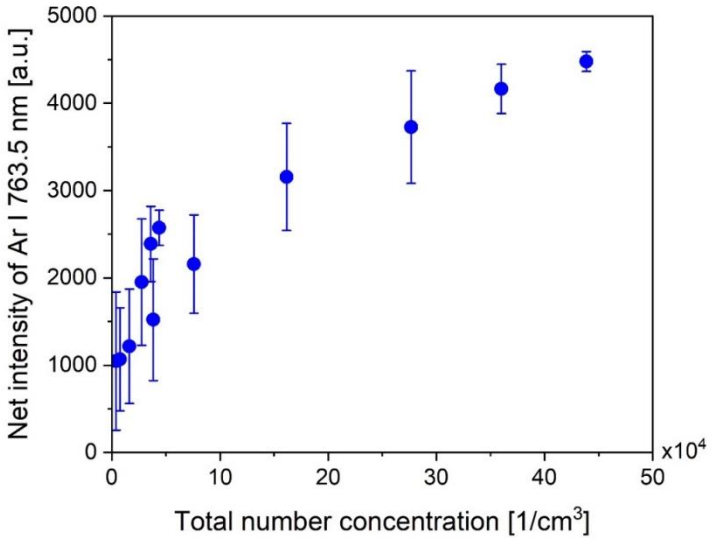

Figure 4. Net intensity of the Ar I 763.5 nm line as the function of the number concentration of Au NPs

Although the signal enhancement phenomenon still needs explanation, but we believe that electron field emission from the NPs causes a decrease in the breakdown threshold for the gas, which helps forming a microplasma. The frequency of plasma formation events seems to be correlated with the NP number concentration up to a level, therefore the use of a ca. $5 \cdot 10^5$ cm^{-3} concentration is advisable for maximizing the signal enhancement.

4. Conclusions

The mixing of nanoparticles into a gaseous sample is proved to be a potent signal enhancing technique. An approximately 5000-fold signal enhancement was achieved. In our opinion, NELIBS has a great potential for the trace gas analysis. Although at first the need for having an SDG attached to a LIBS system may not seem like a practical analytical setup, but in actuality, reasonably compact and portable SDGs (e.g. Palas model GFG 1000/3000) and LIBS instruments (e.g. Applied Spectra LIBScan 25+) are available on the market, thus their combination is not a far-fetched idea.

5. Acknowledgements

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