THE EFFECT OF THE PRESENCE OF GOLD NANOPARTICLES ON THE LASER INDUCED BREAKDOWN IN ARGON GAS

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Abstract
Noble metal nanoparticles can greatly affect the sensitivity and selectivity of many spectroscopic techniques, thus they are widely used in the analytical chemistry. In this current study we investigated the effects of the presence of gold nanoparticles on the formation of laser-induced breakdown plasmas in argon gas.

Introduction
Laser induced breakdown spectroscopy (LIBS) is a laser based elemental analytical technique, capable to deal with solid, liquid and gaseous samples as well with very little sample preparation [1,2]. However, gaseous samples require much higher pulse energy compared to the case of solid samples, thus the cost of instruments capable of measuring such samples is significantly higher, and at the same time the detection limits for gases are inferior [3].
Nanoparticle-enhanced laser-induced breakdown spectroscopy (NE-LIBS), first described by de-Giacomo et al., is becoming a widely tested signal enhancing technique in recent years [1]. Properly sized and distributed metallic nanoparticles (NPs) deposited on the surface of a solid sample under some conditions proved to provide multiple orders of signal enhancement. The effect is generally described as being essentially caused by electron field emission. This technique proved to be efficient to increase the signal not just for solid, but also for liquid samples, however gas samples, which generally have a 10-100 times higher breakdown thresholds 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. 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 then undergoes nucleation, condensation, coagulation, and aggregation [4].
In our study we used spark discharge generated nanoparticles to study whether the presence of nanoparticles in the gas medium is able to significantly lower the plasma formation threshold power density for the gas medium. Correlations between the magnitude of the effect and the size and number concentration of the nanoaerosol were investigated.

Experimental

The central part of the spark discharge generator system used here for the generation of gold nanoparticles is a vacuum chamber, in which the applied cylindrical, gold electrode pair was horizontally positioned and axially aligned with a 2.0 mm gap left between them (spark gap). The 5.0 standard liter per minute (slm) argon (99.996% purity) carrier gas flow, controlled by a mass flow controller was fed in the chamber via the bottom port of the chamber (upward pointing "crossflow" with injector nozzle) [5]. All experiments were carried out at near atmospheric pressure. A 8nF, monolithic, high voltage, pulse discharge capacitor (Model 450PM980, General Atomics) was connected to the spark gap and charged by a high voltage capacitor charging power supply (Model HCK 800–12500, FuG GmbH). The discharge of the capacitor between the electrodes commences when the voltage on the capacitor reaches the breakdown voltage in the electrode gap. The resulting spark discharge is a bipolar, oscillatory discharge. The repetition rate of the sparking, which affects the size distribution and number concentration of the generated aerosol, can be adjusted by controlling the charging current of the capacitor. The created gold NPs were lead through a 900 °C compaction furnace, so the attached primer particles are melted into solid particles. The concentration of the particles was controlled by a conventional (VKL 10, Palas GmbH) and/or a self-built dilution systems.

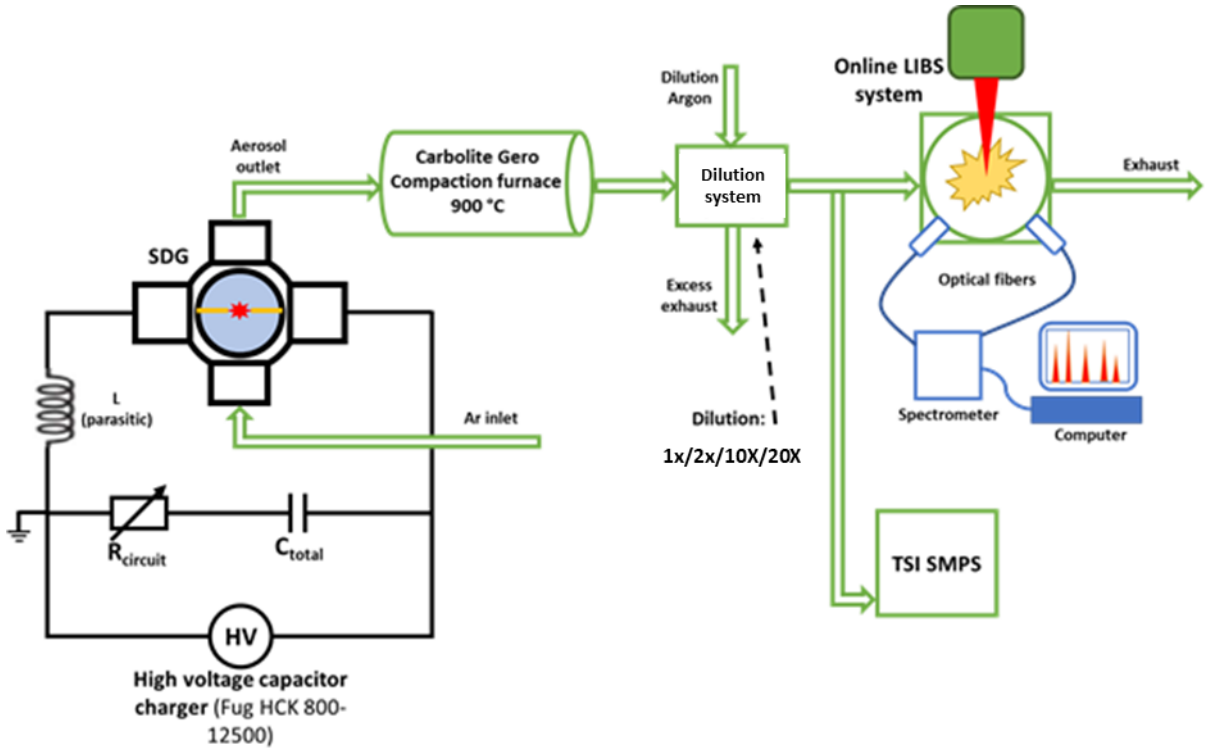

Figure 1. Schematic of the experimental setup

The LIBS experiments were carried out in a flow-through, small volume measurement chamber constructed in-house for LIBS aerosol measurements [6]. The Nd:YAG laser emitted of 10 ns long pulses at the fundamental 1064 nm wavelength, while the pulse energy was changed between 30 and 60 mJ. The beam 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. 1 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

Results and discussion
Our first exploratory results already proved the effect of nanoparticles, since their presence made it possible to generate laser induced plasma in the gas under conditions which resulted in no plasma when NPs were absent. Most of the intensive spectral lines observable in the LIBS sepctrum are argon atomic lines, while many of the less intensive lines were assigned to the Ar II species. However, none of the known strong gold spectral lines were noticeable in the spectra, which indicates that – according to the expectations - the small mass of gold in the blast radius must have been below the detection limit of our instrument. Although plasma formation was achieved at relatively low pulse energies already, but the plasma formation was found to have a random occurrence, thus the following data represents averaged data recorded for 100 laser pulses.

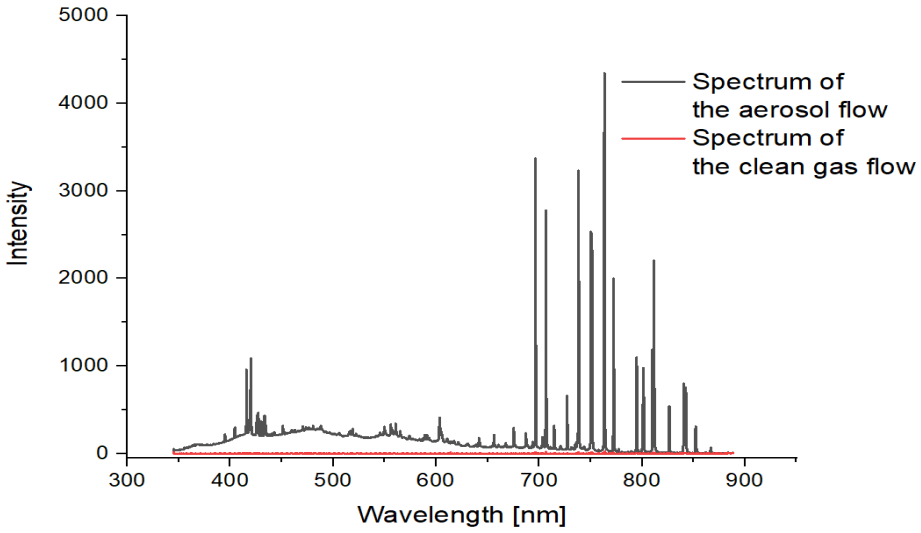

Figure 2. LIBS spectrum of clean argon gas and argon gas mixed with gold nanoparticles

Nanoaerosols with similar number concentration, but bigger mode of size distribution were found to produce microplasma at a similar frequency, but the average intensities were higher, meaning that the intensity of individual spectra increased. Using aerosols of the same size distribution, but with different number concentration, as well as in similar number concentration, but with different size distribution, the individual effect of the two aerosol parameters could be investigated. It was found that the increase in particle number concentration resulted in an increase of the average intensity on every pulse energy. The increased average intensity can be traced back to the increase of the plasma formation frequency and the higher intensities of the individual spectra as well.

By looking at the Figure 3. the differences in the intensity curves are also visible. The increasing aerosol number concentration makes the slopes of the intensity curves not just steadier, but it shifts them towards lower pulse energies as well. This can be clearly interpreted as a correlation between plasma ablation threshold and aerosol number concentration.

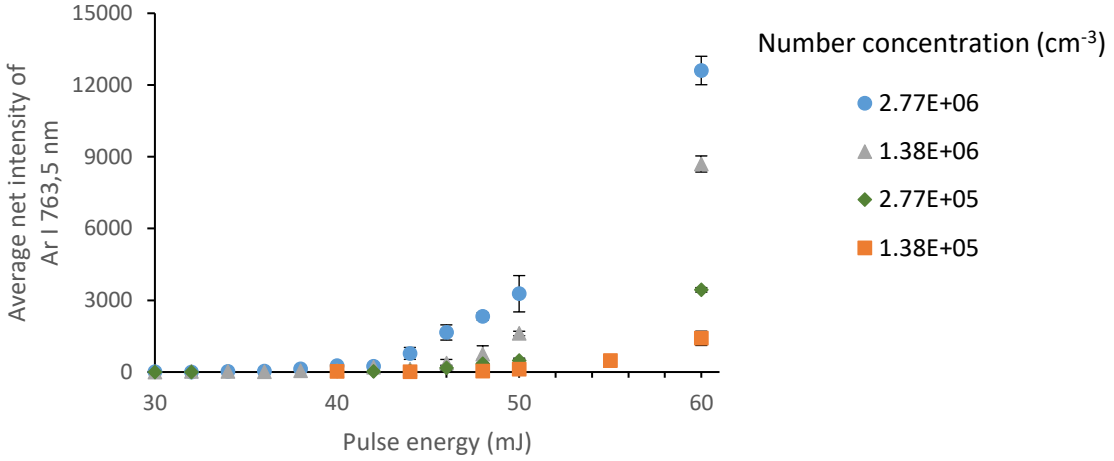

Figure 3. Intensity of a selected argon atomic line as a function of laser pulse energy on different aerosol number concentrations

In our opinion, the random occurance of plasma formation and its increase by the aerosol number concentration can be explained by the random distribution of the nanoparticles in the carrier gas. The nanoparticles are much easier to break down compared to gas, thus if a nanoparticle is present within the focal spot (or its close vicinity) of the laser beam, then they can provide electrons for the ignition of gas plasma. When sufficient number of nanoparticles are near enough to the focal point of the laser beam during the laser impulse, then the microplasma is formed. Thus, the increase in aerosol number concentration increases the probability of particles being in this volume, thus an increase in the plasma formation can be observed. If the number of nanoparticles present in this volume exceeds the minimum necessary for plasma formation, then above this threshold the number of the ejected electrons will be proportional to the total particle volume (mass), thus also with the particle size and number concentration.

Conclusion

The possibility of the plasma formation threshold lowering using dispersed nanoparticles were presented. The signal enhancing effect was proven to related to both the number concentration and size distribution of the applied aerosol. We also pointed out the dependence of the threshold lowering on the aerosol number concentration. Finally, a possible explanation for this phenomenon was suggested as well.

Acknowledgements
The first author thanks the support of the New National Excellence Program 2021 provided by the National Research, Development and Innovational Fund (NKFIH) of the Innovation and Technology Ministry of Hungary. The support from the NKFIH under project No. K_129063 is also kindly acknowledged.

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