ON-LINE AND OFF-LINE LIBS DETECTION OF NANOAEROSOLS GENERATED BY ELECTRICAL DISCHARGES

Ádám Bélteki[1], Tira Biros[1], Dávid J. Palásti[1,2], Lajos P. Villy[2,3], Bálint Leits[2,3], Albert Kéri[1,2], Attila Kohut[2,3], Éva Kovács-Széles[4], Tibor Ajtai[3], Zsolt Geretovszky[2,3], Gábor Galbács[1,2]*

[1]Department of Inorganic and Analytical Chemistry, University of Szeged, 6720 Szeged, Dóm sq. 7, Hungary
[2]Department of Materials Science, Interdisciplinary Excellence Centre, University of Szeged, 6720 Szeged, Dugonics sq. 13, Hungary
[3]Department of Optics and Quantum Electronics, University of Szeged, 6720 Szeged, Dóm sq. 9, Hungary
[4] Nuclear Security Department, Centre for Energy Research, 1121 Budapest, Konkoly-Thege Miklós way 29-33, Hungary
**e-mail: galbx@chem.u-szeged.hu*

1. INTRODUCTION

With the increase of the intensity of production and industrial use of engineered nanoparticles comes a growing need for spectroscopic techniques that are capable of monitoring the characteristics of nanoaerosols (nanoparticles distributed in a gaseous medium). Such measurements are equally needed for industrial process control purposes as well as for environmental and health-related studies.

Laser induced breakdown spectroscopy (LIBS) is one of the laser-based spectroscopy techniques available for aerosol analysis. The appeal of LIBS in this field is that it is a robust, easy-to-set-up technique that even can be applied remotely. As it has been demonstrated, it has the potential of providing particle quality and concentration data, if the particle size (mass concentration) is large enough [Diaz 2020, Palásti 2019]. Particles in the micron and sub-micron range has been successfully detected by LIBS, either by on-line or off-line sampling. However, studies in the LIBS literature are very scarce that attempted the detection of nanoaerosols.

In the present work, we investigated the performance of LIBS for the analysis of nanoparticles (NPs) generated by electrical discharges, namely a spark discharge generator (SDG) and an arc discharge generator (ADG). The reason behind choosing these particle sources is that these devices are more and more often considered for industrial scale nanoparticle production in recent years, due to their productivity, energy efficiency, versatility and particle purity [Buonapart-e 2016]. They are also good model aerosol sources, as the particle properties can be relatively easily controlled. We tested both the on-line and off-line methodologies, and worked with not only monometallic, but also binary particles. Collecting detailed compositional information about the produced binary particles can also shed light on some of the particle formation and electrode erosion processes in these discharge generators that are not yet fully understood.

2. EXPERIMENTAL

There are important differences between the operation of the two types of electrical discharge generators. The SDG employs a high voltage, high AC current, oscillating electrical discharge plasma to erode/evaporate the material of two electrodes, whereas the ADG work in the low voltage, low DC current mode and utilizes a molten pool work electrode and a refractory counter electrode. Both generators have an inert gas flowing through their chambers, which cools, quenches the electrode material vapors and helps to form nanoparticles via condensation and aggregation. A quartz/ceramic tube sintering furnace is typically used in these generators for the post-processing of the particles, which helps to obtain uniform size, compact particles. The operating parameters of our SDG and ADG systems can be seen in **Table 1**. In the listed ranges of operating parameters, the particle diameter was 30-40 nm and 80-150 nm for the SDG and ADG, respectively.

Parameter	**SDG**		**ADG**	
	monometallic	bimetallic	monometallic	bimetallic
Carrier gas	Ar	Ar	N_2	Ar
Gas flow rate	5 slm		10 slm	
Gas pressure	1015 mbar			
Electrode material	Au - Au	Co - Ag	Cu/W	12, 42, 77 m/m% Sn-Cu alloy/W
Electrode distance	2 mm		~2 mm	
Repetition rate	50 - 250 Hz	100 Hz	continuous	
Impedance	1 Ohm	1 – 9 Ohm	not controlled	
Peak current	~825 A	~165 A	20 – 35 A	30 A

Table 1. The operating parameters of the experimental SDG and ADG systems.

The metallic electrodes used were made of 99.99% purity materials (Kurt J. lesker Co., USA), whereas the Sn-Cu alloy feedstock was prepared from analytical purity materials. For off-line measurements, the particles were collected on a glass fiber filter (Whatman 1822-047 GF/C Glass Microfiber Filter, 1.2 μm pore size, 47 mm diameter), which was later cut to segments and affixed onto microscope slides using double-sided adhesive tape for LIBS analysis. Some filters were dissolved in high purity acids and subjected to ICP-MS analysis (using an Agilent 7700x instrument) in order to obtain reference compositional data. Reference aerosol data were collected using a scanning mobility particle sizer (TSI, USA) and scanning electron microscopy (Hitachi S-4700, Japan). All gases used were 99.995% purity (Messer Hungarogáz).

LIBS measurements were carried out on an Applied Photonics LIBScan 25+ type portable instrument, using 1064 nm wavelength, 4 ns pulse length and 30 mJ pulse energy settings. In on-line experiments, 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 ablation 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 solarization resistant 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 gate delay was set to 1 μs and gate width to 2 ms. 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

We were particularly interested in the measurement of three aerosol parameters: a.) qualitative detection of the particles, b.) estimation of the particle number concentration (PNC), c.) estimation of particle composition (for binary particles).

3.1. Qualitative detection of nanoparticles

Although we tested both the on-line and off-line sampling methodology and found that the on-line approach only worked with the ADG, for which the particle size and PNC was significantly higher. We found that the on-line detection can only be successful, if the particle mass concentration is above a certain threshold, the value of which depends on the quality of the particles as well as the setup of the LIBS setup. For the metallic particles studied here, this threshold is such that a minimum of 60-70 nm particle diameter and 10^6 cm^{-3} PNC is required.

The qualitative detection of nanoparticles is demonstrated by selected spectra shown in **Figure 1.**; all particles, namely Cu, Au, Sn-Cu, Ag-Co could be detected by LIBS.

In the case of binary NPs, the detection of both component elements in all spectra indicated that alloy particles were formed and not alternating monometallic particles.

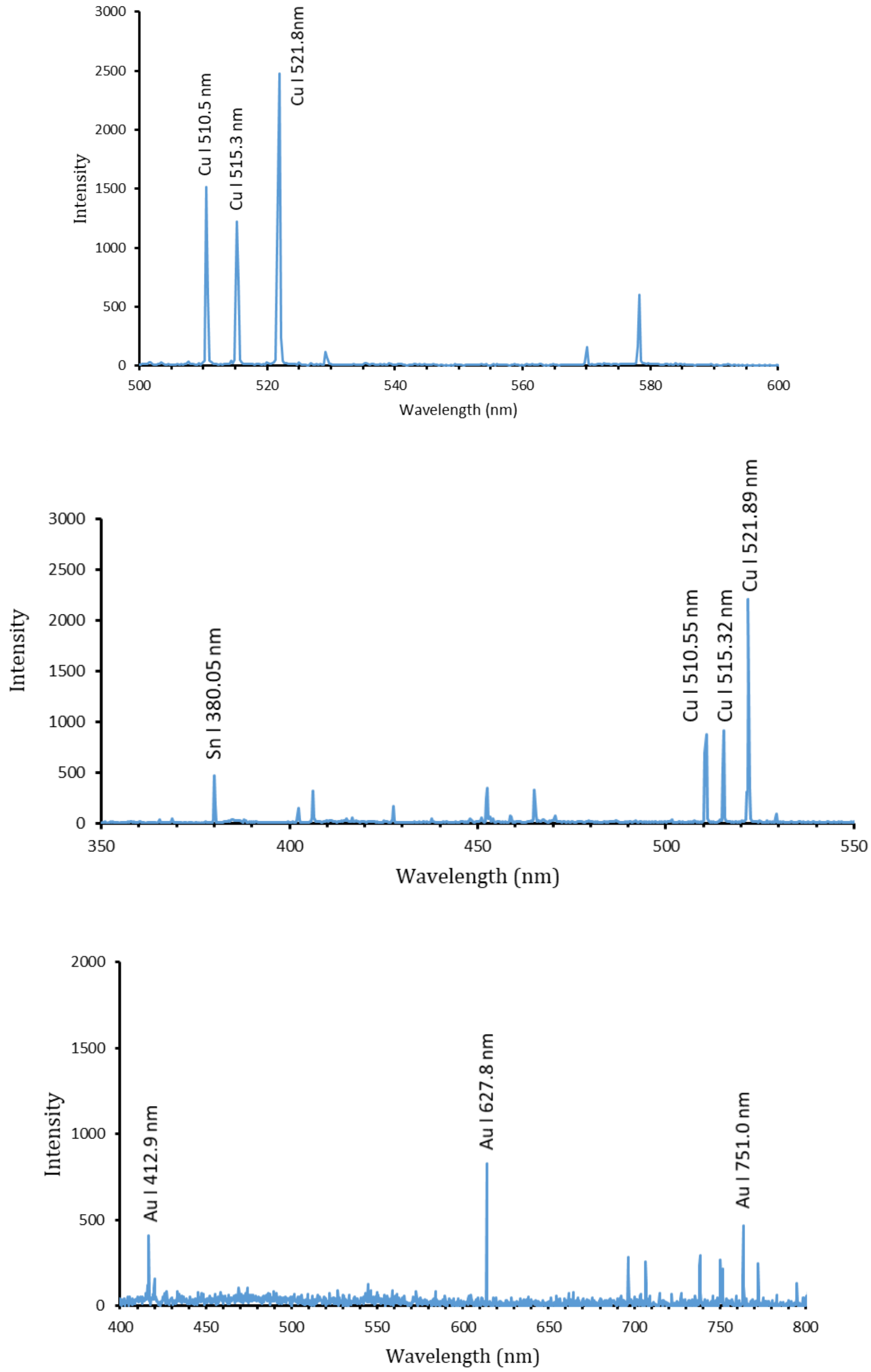

Figure 1. Selected LIBS spectra of some monometallic and binary nanoparticles studied. At the top: on-line detection with ADG; in the middle: on-line detection with ADG; at the bottom: off-line detection with SDG.

3.2. Estimation of the particle number concentration

In on-line mode, and by assuming a constant, calibrated ratio between the number of LIBS particle detection events and the particle number concentration, the latter can be principally estimated based on LIBS data. However, proportionality can be assumed only within a certain concentration range, which is limited at the bottom by the particle mass concentration detection limit and at the top by a „saturation" of the detection (when the PNC is so high that all laser shots result in a detection). **Figure 2.** illustrates such a proportionality curve for a copper ADG aerosol, where the time-integrated copper signal is shown as a function of PNC. The high signal scatter is a characteristic of ADG generation which has an uneven aerosol mass concentration output due to the strong thermal convection in the discharge chamber. Nevertheless, a reasonable estimate of PNC can be obtained for process control purposes.

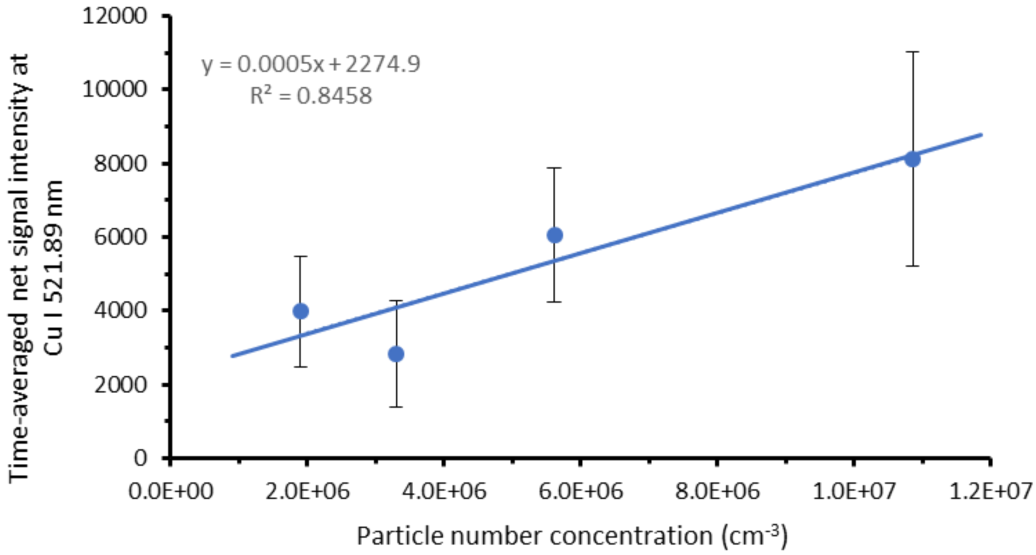

Figure 2. The correlation of the time integrated particle-specific on-line LIBS signal with the particle number concentration (ADG).

The off-line particle detection approach also produces a calibration plot, which shows proportionality between the PNC and the LIBS signal of the particle specific analyte signal, however the proportionality is not necessarily linear. As it is seen in **Figure 3.**, the plot shows a concave character and can be fitted reasonably well with an exponential function. This feature is related to the saturation of the filter on which the particles were collected. In the very low PNC range, the signal linearity holds – as long as there is a sufficient amount of analyte mass in the laser focal spot – as basically it is the filter material which gets ablated, along with some occasional particles. However, as the PNC increases, the particles will start to pile up on the filter (deposited particles will also decrease the effective pore size) and the laser ablation will mostly involve particle material. The LIBS signal in this regime will be determined by the packing density of the particles and above a certain thickness of deposited particles, the correlation between the signal and PNC will not hold. In the range shown in **Figure 3.**, the linear proportionality holds up to about $8.6 \cdot 10^5$ – $1.3 \cdot 10^6$, beyond that the signal increases stronger (filter saturation starts)

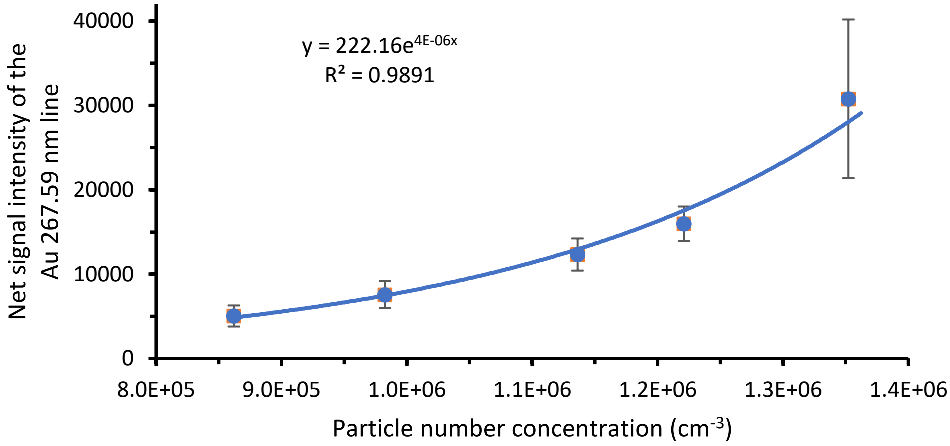

Figure 3. The correlation of the particle specific off-line LIBS signal with the particle number concentration (SDG).

3.3. Estimation of particle composition

In principle, binary particles (e.g. alloys) can be relatively easily produced by electrical discharge generators. For this to be achieved one needs to use different electrode materials (made of the component metals of the alloy) in the SDG, and mixture of metal powder (or alloy molten pool) in the ADG. LIBS in these cases can potentially provide elemental composition data about the particles.

We tested the SDG with a combination of Ag and Co electrodes. The particles were collected on a filter (off-line LIBS) and their reference composition was determined by ICP-MS analysis. As it can be seen in **Figure 4.**, the ratio of the detected LIBS elemental signals correlated reasonably well with the real composition. The signal scatter is large, probably due to the „looseness" of particles on the filter.

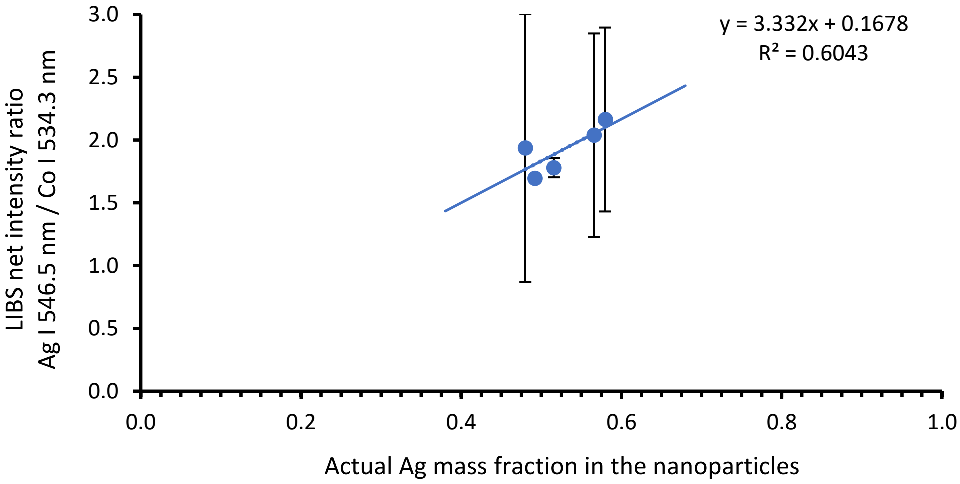

Figure 4. The correlation of the actual (determined by ICP-MS) and off-line LIBS detected particle composition of Ag-Co binary nanoparticles generated in an SDG.

In the on-line ADG experiments, we used a Sn-Cu alloy feedstock (with 12%, 42% and 77% mass fractions of Sn). As can be seen in **Figure 5.**, we found a linear proportionality between the composition of the working electrode and the detected particle composition. This is an important finding, as according to our knowledge, no previous results can be found in the literature on alloy particle production by an ADG. The results also suggest that the mixing in the molten pool fairly efficient and that there is no fractionation of the two metals during NP production, but this still needs to be checked by converting the LIBS intensity data to concentrations.

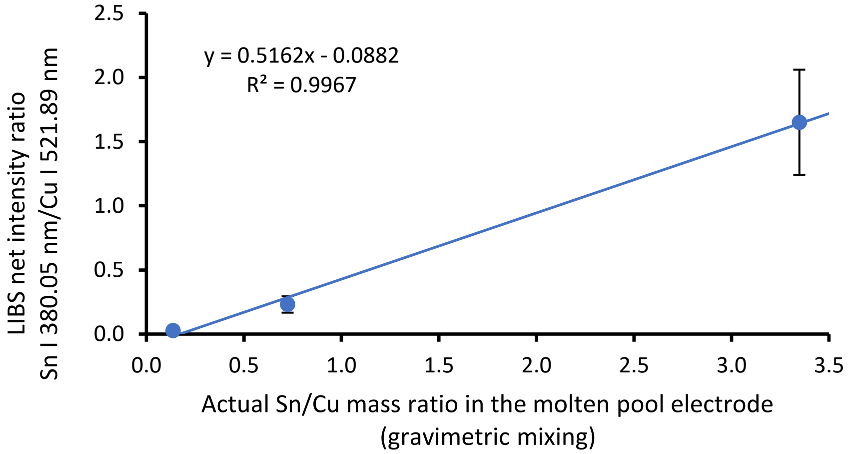

Figure 5. The correlation of the actual (based on gravimetric mixing) and on-line LIBS detected particle composition of Sn-Cu binary nanoparticles generated in an ADG.

4. Conclusions

Our experiments successfully demonstrated that the on-line and off-line LIBS analysis of nano aerosols is feasible. Electrical discharge generators were employed for the controllable production of the aerosols. It has been shown that particle detection, estimation of particle number concentrations and particle compositions (in the case of binary particles) are all possible. These preliminary results indicate that LIBS has a great potential for the monitoring of the operation of electrical discharge generators, but potentially also other nano aerosol sources.

5. Acknowledgements

The authors gratefully acknowledge the financial support from various sources including the National Research, Development and Innovation Office (through projects No. K_129063, EFOP-3.6.2-16-2017-00005 and TKP 2020 Thematic Excellence Programme 2020) of Hungary.

6. REFERENCES

[Diaz 2020] D. Diaz, D. W. Hahn, U. Panne: LIBS for aerosol analysis (Chapter 22) in: Laser-induced breakdown spectroscopy (ed.: J. P. Singh, S. N. Thakur), *Elsevier*, 2020.

[Palásti 2019] D. J. Palásti, A. Metzinger, T. Ajtai, Z. Bozóki, B. Hopp, É. Kovács-Széles, G. Galbács, *Spectrochim. Acta B*, 153 (2019) 34.

[Buonapart-e 2016] https://cordis.europa.eu/project/id/280765/reporting