Theses of doctoral (Ph.D.) dissertation

Development of advanced laser-induced breakdown spectroscopy methodologies for elemental mapping and qualitative discrimination analysis

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1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) has developed rapidly over the past few decades and is now recognized as a versatile and powerful analytical technique for the quick analysis of solids, liquids, and gaseous samples. The widespread adoption of LIBS can largely be attributed to three key features: its relatively simple and robust instrument configuration, the ability to perform rapid analysis with little or no sample preparation, and its capacity to provide both qualitative and quantitative trace analytical information. Together, these features have made LIBS an increasingly important tool in both research laboratories and industrial applications.

In recent years, LIBS has progressively entered into the fields of life sciences (biology and medical science). It is being explored as a novel tool for detecting pathogens and disease markers, for mapping the spatial distribution of elements in biological tissues, and for the qualitative classification of complex biological samples. At the same time, advances in materials science have also created a strong demand for analytical techniques that are sensitive, versatile and have high spatial resolution. LIBS fits these requirements particularly well, especially for inorganic and composite materials. As an example, polymer nanocomposite thin films are used as functional materials, where the spatial distribution of embedded nanoparticles strongly influences material performance. Current methods capable for such analysis often suffer from limited sampling depth, small field of view, complex sample preparation, or restricted elemental coverage. LIBS can potentially provide a practical solution to this analytical challenge.

Enhancing the sensitivity of LIBS by exploiting plasmonic effects through nanoparticle-enhanced LIBS (NE-LIBS) approaches has emerged as an attractive strategy for extending the capabilities of the technique, particularly in terms of detection limits. Localized NE-LIBS experiments have demonstrated promising signal enhancements as high as two orders of magnitude. Its practical implementation in spatially resolved elemental mapping has not been done so far, due to several technical challenges. This includes that reliable mapping requires nanoparticle depositions that are homogeneous over large areas, reproducible between samples, and compatible with different substrate types. At the same time, the magnitude of signal enhancement is known to depend strongly on laser parameters and detection conditions, yet these dependencies are not fully understood in a mapping situation. In order to make NE-LIBS mapping a reliable and broadly applicable analytical approach, robust sample preparation strategies and systematic optimization of laser and detection conditions are required.

The laser source is one of the most critical components in LIBS. Traditional LIBS systems rely almost exclusively on Q-switched solid-state lasers with fixed nanosecond pulse durations and limited repetition rates, which constrains opportunities for tailoring plasma dynamics. Pulsed fiber lasers offer fundamentally different operating characteristics, including adjustable pulse shapes and very high repetition rates, suggesting that they could provide alternative laser-matter interaction regimes for LIBS. However, the consequences of these laser properties on plasma emission behavior, and analytical performance have not yet been systematically explored.

LIBS has become an important analytical technique in the agriculture and food sectors due to its capability for rapid and in situ analysis. Rapid and reliable detection of hazardous chemical residues such as organochlorine pesticides on agricultural products is an important analytical challenge, particularly when contaminants are present at trace levels and distributed heterogeneously on complex surfaces; which can significantly affect the quality and safety of agricultural products, with potential implications for human health. Although LIBS can rapidly generate chemical information from surfaces, it can also produce complex spectral backgrounds from the sample, hence the direct interpretation of LIBS spectra in such cases is often insufficient. Integrating LIBS with advanced data analysis and machine learning approaches has the potential to overcome these limitations, but the reliability of such strategies and the optimal measurement configurations require systematic investigation. In particular, the influence of sampling strategy, data preprocessing, and model selection on classification reliability must be understood.

The Laser and Plasma Spectroscopy Research Group led by Prof. Gábor Galbács has been active in LIBS-related research for more than 25 years, conducting a wide range of fundamental and applied spectroscopic studies. I joined Prof. Galbács’s group in 2021 and later continue into the Ph.D. in 2022. Within this research environment, my work has focused on the development of new strategies to enhance LIBS performance and on expanding the range of applications of laser-based spectroscopic methods.

2. OBJECTIVES

The plan for my research activities is based on former results of our research group and addresses key analytical challenges in modern LIBS, such as improving sensitivity, enabling reliable qualitative discrimination and expanding laser source options. Guided by these challenges, the following objectives were defined for my work:

1. Development and optimization of a sample preparation method and measurement conditions for the reliable use of nanoparticle signal enhancement in LIBS mapping.

2. Explore the potential of LIBS elemental mapping to quantitatively characterize nanoparticle distributions in polymer thin film nanocomposites.

3. Investigation of the applicability of fiber laser sources with tunable pulse shapes and high repetition rates to the improvement of LIBS analytical performance.

4. Assessment of the performance of machine learning evaluation of LIBS spectral data to solve qualitative discrimination analytical tasks relevant to the industry (e.g. identification of chemical contaminants on crops).

3. EXPERIMENTALS

Since each experiment required different instrumentation, the detailed descriptions of the devices and operating conditions are provided in the corresponding sections of my dissertation. Here, I only present a brief overview of the key instruments and their main characteristics.

For most LIBS experiments, a commercial J200 LIBS/LA tandem system (Applied Spectra, USA) was used. This is equipped with a Nd:YAG Ultra 100 laser (Quantel-Lumibird, France), operating at 266 nm via fourth harmonic generation, with a 6 ns pulse duration and a repetition rate up to 20 Hz, with an adjustable pulse energy up to 20 mJ by mean of an optical attenuator unit. The laser beam can be focused onto the sample surface to a directly adjustable spot size between 40 to 220 µm in diameter. Aiming and documentation is helped by dual CMOS cameras, for high magnification and wide-field viewing. The sample can be moved via a motorized XY-stage with a 0.2 µm resolution and a Z-stage with a 0.1 µm resolution. In this system, the spectra are recorded by a 6-channel CCD broadband spectrometer with a spectral window of 185-1050 nm and a resolution of 0.07 nm. An integrated pulse delay generator allows for gate delay adjustment in the 50 nsec to 1 msec range. Elemental maps recorded were evaluated by the ImageLab 3.20 (Epina GmbH, Austria) software.

In LIBS experiments performed at 532 nm and 1064 nm laser wavelengths, a stand-alone setup was employed, which included another Nd:YAG Ultra 100 Quantel laser source, but this unit is equipped with a frequency upconversion module. The laser light is focused on the sample by using a N-BK7 plano-convex quartz lens (f= 50 mm) and the plasma emission is collected at a 45° angle via a NA-matched quartz focusing lens. In experiments which required 532 nm or 1064 nm, or high-time resolution, an external spectrometer was used for the detection of LIBS emission. In such cases, we used a 400 µm core diameter optical fiber to connect the SMA905 fiber optic output ports of the LIBS setups to the 40 µm entrance slit of an Echelle spectrometer Aryelle 200 (LTB, Germany). This spectrometer is equipped with a gated ICCD detector-camera (iStar DH334T-18F-04, Andor Technology, Ireland), with a spectral range of 220-629 nm in the UV-NIR range and a spectral resolving power above 9000 and a resolution of 0.007 nm.

In experiments involving a fiber laser, a compact Trupulse Nano 5020 fiber laser (Trumpf, Germany) served as the laser source, with a maximum average output power of 200 W. It operates at a wavelength of 1062 nm and features 48 built-in temporal pulse profiles (waveforms), enabled by GTWave and PulseTune technology. These waveforms allow for adjustable pulse energies ranging from 0.35 to 4.96 mJ and pulse durations between 8 ns to 2000 ns. The system can reach pulse repetition rates of up to 4 MHz. Pulse temporal profiles were measured using a fast photodiode (DET10A, Thorlabs, USA) in combination with a digital oscilloscope (DS1102E, Rigol, China), detecting laser light reflected from a diffuser. Pulse energies were measured using a laser power meter (Gentec-EO, Canada). The laser output is collimated to a 10 mm diameter beam using the collimator head provided by the manufacturer. The beam exhibited multimode quality, with M^2 value around 4. The laser head was mounted vertically, and the beam was directed perpendicularly onto the sample surface using a 100 mm focal length plano-convex fused-silica lens (LA4380, Thorlabs, USA). In all standalone LIBS setups, a digital delay generator (TG5011, AIM-TTI, UK) was used to synchronize the spectrometer with the laser output.

Additional used softwares includes the open-source ImageJ and the open-source RStudio software package for chemometric data evaluation.

4. RESULTS

The main scientific results of the research are the following:

T1. I have shown that magnetron sputtering of gold followed by a thermal treatment at 550°C is an efficient, practical and highly controllable method to produce spheroid nanoparticle deposition on thermally stable solid samples suitable for the utilization of plasmonic signal enhancement in laser-induced breakdown spectroscopy (NE-LIBS). I have performed detailed optimization of the deposition conditions and studied the effect the laser fluence, laser spot size, laser wavelength and detection gating on the achievable signal enhancement. I found that the laser wavelength has only a small influence in the 266 to 1064 nm range, but there is an optimum for laser fluence and detection gate delay. The best signal enhancement achieved was 25-30, demonstrated for a glass sample. It was also established that the method can provide a spatial resolution of 100 to 200 µm, limited by the proportionality of the signal enhancement with the number of nanoparticles covered by the laser focal spot. The applicability of the method was demonstrated on glass, granite and paint samples in both quantitative and qualitative applications. The hyperspectral NE-LIBS mapping of a granite rock sample provided improved sensitivity for the study of elemental distributions (e.g. Li and Mg), and linear discriminant analysis of paints gave rise to a significantly improved accuracy of 98% as opposed to 84% without using nanoparticle enhancement [1, 2].

T2. I demonstrated that the nanoparticle distribution in polymer thin film nanocomposites can be assessed quantitatively with good accuracy and precision, with a spatial resolution of 100 µm using laser-induced breakdown spectroscopy elemental mapping. I optimized the measurement conditions and also studied the laser ablation behaviour of polymer thin films. A detailed application was described for polystyrene thin films containing spherical gold nanoparticles. I established that the method is applicable for films with a thickness of up to about 450 nm and for gold mass concentrations in the range of 3 to 700 $ng \cdot mm^{-2}$. Imaging of patterned samples containing gold nanoparticle concentration gradients was also successfully performed with 10% or less error. The method can also provide particle concentration distribution data in cases when the size of the nanoparticles is known and is especially useful for the mapping of fairly large areas (cm^2 or larger). It can be adapted to nanoparticles of any shape or composition [3].

T3. I experimentally proved that pulsed fiber lasers of the master oscillator power amplifier architecture can be advantageously employed in laser-induced breakdown spectroscopy, utilizing their configurable pulse profiles (from ns to µs duration) and ultra-high repetition rates (up to the MHz range). I studied the wavelength- and time-resolved light emission and temperature of the generated plasmas, as well as the ablation craters produced on stainless steel and silicon reference samples. The effect of the pulse shape on the emission intensities was also studied and it was concluded that the highest S/N LIBS spectra can be recorded when the largest possible fraction of the pulse energy is carried by the pulse head. Multi-pulse LIBS experiments were also carried out with up to 4 laser pulses with short interpulse delay times.

I demonstrated that even when using up to 100 µs interpulse delays, the second pulse always generates a significantly stronger emission than a single-pulse and that upwards from the second pulse, the signals generated by consecutive laser pulses show similar emission intensities. The integration of the emission signal across several consecutive laser pulses is beneficial and it is possible because the low energy (a few mJ) and relatively long laser pulses (several hundreds of ns) do not generate high background emission. I also demonstrated the improvement of quantitative analytical performance of multi-pulse fiber laser LIBS on steel samples for Cu, Ni and Cr elements [4, 5].

T4. I demonstrated that machine learning evaluation of laser-induced breakdown spectroscopy data is a sensitive and viable way of identifying hazardous (e.g. banned) organochlorine pesticides on the surface of crops. Five pesticides (chlorpyrifos, λ-cyhalothrin, acetamiprid, tebuconazole, and tefluthrin) were successfully classified, with 80%+ accuracy, on tomato fruits sprayed with solutions at as low as 100 ppm (0.01% m/v) in concentration. Three machine learners, namely linear discriminant analysis, classification tree and random forest, were applied to the LIBS data which were also subjected to advanced feature selection. Direct (on the fruit peel) and indirect (sampling-based) LIBS analytical approaches were both tested and a closed ablation cell assembly was also developed to provide safe conditions for the analysis. It was found that only direct LIBS analysis provides reliable data for the classification [6].

5. PUBLICATIONS

ID in the Hungarian Collection of Scientific Publications (MTMT): 10084886

Journal publications forming the basis of the dissertation:

[1] **Casian-Plaza, F.A.**; Janovszky, P. M.; Palásti, D. J.; Kohut, A.; Geretovszky, Zs.; Kopniczky, J.; Schubert, F.; Živković, S.; Galbács, Z.; Galbács, G. Comparison of three nanoparticle deposition techniques potentially applicable to elemental mapping by nanoparticle-enhanced laser-induced breakdown spectroscopy.
Applied Surface Science 2024, 657, 159844. **IF: 6.9 (Q1)**

[2] **Casian-Plaza, F.A.**; Palásti, D. J.; Schubert, F.; Galbács, G. Optimization of nanoparticle-enhanced laser-induced breakdown spectroscopy for the hyperspectral chemical mapping of solid samples.
Analytica Chimica Acta 2024, 1330, 343269. **IF: 6.0 (Q1)**

[3] **Casian-Plaza, F.A.**; Urbán, O.; Bélteki, Á.; Aladi, M.; Kedves, M.; Bonyár, A.; Kopniczky, J.; Veres, M.; Galbács, G. Quantitative characterization of the lateral distribution of gold nanoparticles in polystyrene nanocomposite thin films by laser-induced breakdown spectroscopy elemental mapping.
Applied Surface Science 2025, 700, 163276. **IF: 6.9 (Q1)**

[4] Palásti, D. J.; **Casian-Plaza, F.A.**; Bélteki, Á.; Kohut, A.; Makkos, L.; Galbács, G. Single-shot laser-induced breakdown spectroscopy using various duration pulses generated by a compact master oscillator power amplifier fiber laser.
Optics & Laser Technology 2025, 192, 114120. **IF: 5.0 (Q1)**

[5] Palásti, D. J.; **Casian-Plaza, F.A.**; Bélteki, Á.; Kohut, A.; Makkos, L.; B. Hopp; Galbács, G., Multi-pulse laser-induced breakdown spectroscopy signal enhancement using a MHz-repetition-rate pulsed fiber laser source
Spectrochimica Acta Part B 2026, *submitted for publication* **IF: 3.8 (Q2)**

[6] **Casian-Plaza, F.A.**; Bodó, B.; Palásti, D.; Lakatos, L.; Kolbert, Zs.; Galbács, G. Detection of organochlorine pesticide residues on tomato fruits by machine learning evaluation of laser-induced breakdown spectroscopy data
Food Chemistry 2026, *submitted for publication* **IF: 9.8 (Q1)**

Sum of impact factors for already published publications: **24.8**
Expected sum of impact factors for all publications: **38.4**

Additional journal publications:

[7] Palásti, D. J.; Urbán, O.; **Casian-Plaza, F.A.**; Kámán, J.; Rigó, I.; Szalóki, M.; Bonyár, A.; Chinh, N. Q.; Galbács, Z.; Veres, M.; Galbács, G. Improving the mechanical, spectroscopic and laser ablation characteristics of UDMA-MMA copolymers using a titanocene photoinitiator.
Polymer Testing 2024, 139, 108565.

IF: 6.0 (Q1)

[8] Palásti, D. J.; Villy, L.; Leits, B.; Kéri, A.; Kohut, A.; Bélteki, Á.; Kajner, G.; **Casian-Plaza, F.A.**; Kovács-Széles, É.; Ajtai, T.; Veres, M.; Geretovszky, Z.; Galbács, G. Detection and characterization of mono- and bimetallic nanoparticles produced by electrical discharge plasma generators using laser-induced breakdown spectroscopy.
Spectrochimica Acta Part B Atomic Spectroscopy 2023, 209, 106804.

IF: 3.2 (Q2)

[9] Jancsek, K.; **Casian-Plaza, F.A**.; Galbács, G.; Tóth, Tivadar M.; Laser-induced breakdown spectroscopy (LIBS) reveals lithium content in mórágy granite formation.
Geologica Carpathica 2025, *under revision.*

IF: 1.5 (Q2)

[10] Kondak, S.; Kondak, D.; Bodor, T.; Fejes, G.; Rónavári, A; Kónya, Z.; Szőllősi, R.; Kukri, A.; Gyenesei, A.; Urbán, P; Kun, J.; Gracheva, M.; Solti, A.; Pál, M.; Szalai, G.; Domonkos, I.; Szögi, T.; **Casian-Plaza, F.A.**; Galbács, G.; Kolbert, Z. Size-dependent zinc delivery and nanozyme-mediated stress alleviation by ZnO nanoparticles in zinc deficient tomato.
Environmental Science & Technology 2026, *submitted for publication*.

IF: 6.2 (Q1)

Book chapters and conference presentations:

1. Galbács, G., **Casian-Plaza, F.A**., Urbán, O., Rweyemamu, A.R., Kohut, A.: Nanoparticle detection and characterization by LIBS. In: Galbács, G. (eds) Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences. Springer (2025) Cham.

2. **Casian-Plaza, F.A.**, Janovszky, P., Kopniczky, J., Kéri, A., Tóth, T.M., Galbács, G.: Nanoparticle deposition by spray coating for enhanced elemental mapping of rock samples by laser-induced breakdown spectroscopy, *27th International Symposium on Analytical and Environmental Problems* (2021) Szeged

3. **Casian-Plaza, F.A.**, Janovszky, P., Kopniczky, J., Kéri, A., Tóth, T.M., Galbács, G.: Nanoparticle deposition by spray coating for enhanced elemental mapping of rock samples by laser-induced breakdown spectroscopy, *Colloquium Spectroscopicum Internationale CSI XLII* (2022) Gijón

4. **Casian-Plaza**, **F.A.**, Holub, D., Pořízka, P., Palásti, D.J., Villy, L., Kopniczky, J., Živković, S., Kaiser, J., Galbács, G.: Nanoparticle-enhanced discrimination analysis of polymers by laser induced breakdown and Raman spectroscopy, *European Winter Conference on Plasma Spectrochemistry* (2023) Ljubljana

5. Palásti, D.J., **Casian-Plaza**, **F.A.**, Janovszky, P., Bélteki, Á., Kohut, A., Geretovszky, Zs., Petrović, J., Radenković, M., Živković, S., Galbács, G.: A comparative study of NELIBS signal enhancement using ns and µs duration laser pulses, *XII World Conference on Laser Induced Breakdown Spectroscopy* (2022) Bari

6. **Casian-Plaza**, **F.A.**, Palásti, D.J., Balint, B., Fintor, K., Galbács, G.: Food safety-related qualitative discrimination analysis of herbs by LIBS and Raman spectroscopy, *12th Euro-Mediterranean Symposium on Laser-induced Breakdown Spectroscopy* (2023) Porto

7. **Casian-Plaza, F.A.**, Janovszky, P., Palásti, D.J., Kohut, A., Geretovszky, Zs., Kopniczky, J., Schubert, F., Živković, S., Galbács, Z., Galbács, G.: Optimalization of nanoparticle-enhanced laser-induced breakdown spectroscopy for the hyperspectral chemical mapping of solid samples, *63. Magyar Spektrokémiai Vándorgyűlés* (2024) Balatonszárszó

8. **Casian-Plaza**, **F.A.**, Palásti, D.J., Balint, B., Galbács, G.: Laser-induced breakdown spectroscopy method development for the qualitative discrimination analysis of plants, *63. Magyar Spektrokémiai Vándorgyűlés* (2024) Balatonszárszó

9. **Casian-Plaza, F.A.**, Janovszky, P., Palásti, D.J., Kondak, S., Kolbert, Z., Galbács, G.: Advanced laser-induced breakdown sepctroscopy-based qualitative analytical methodologies for food and plant-related applications, *30th International Symposium on Analytical and Environmental Problems* (2024) Szeged

10. **Casian-Plaza, F.A.**, Jancsek, K., Tóth, T.M., Galbács, G.: Lithium prospection in granitoid rocks from southern hungary by laser-induced breakdown spectroscopy elemental mapping, *9th International Symposium of Federation of European Societies of Trace Elements and Minerals* (2025) Timisoara

11. Urbán, O., **Casian-Plaza, F.A.**, Machlik, B., Gárdi, B., Palásti, D.J., Tóth, B., Mogyorósi, K., Galbács, G.: Identification of microplastic particles exposed to environmental and biological media based on their nanosecond and femtosecond LIBS spectra, *Euroanalysis* (2025) Barcelona

Statement (L1)

We, the undersigned, in connection with **Fernando A. Casian Plaza**'s doctoral thesis entitled "Development of advanced laser-induced breakdown spectroscopy methodologies for elemental mapping and qualitative discrimination analysis"

> Palásti, D. J.; Casian-Plaza, F.A.; Bélteki, Á.; Kohut, A.; Makkos, L.; Galbács, G.
> Single-shot laser-induced breakdown spectroscopy using various duration pulses generated by a compact master oscillator power amplifier fiber laser,
> Optics & Laser Technology 2025, 192, 114120.

co-authors declare that the candidate played a decisive role in achieving the results related to this publication and the candidate's T3 thesis point, and therefore we have not used these results to obtain a scientific degree and will not do so in the future.

....	....
Levente Makkos	Ádám Bélteki

January 27, 2026.

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> Palásti, D. J.; Casian-Plaza, F.A.; Bélteki, Á.; Kohut, A.; Makkos, L.; B. Hopp; Galbács, G., Multi-pulse laser-induced breakdown spectroscopy signal enhancement using a MHz-repetition-rate pulsed fiber laser source,
> *Spectrochimica Acta Part B 2026, submitted for publication*

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....	Bélteki Ádám ....
Levente Makkos	Ádám Bélteki

January 27, 2026.

Statement (L2)

I, the undersigned, as the doctoral supervisor of **Fernando A. Casian Plaza**, in connection with the doctoral thesis entitled "Development of advanced laser-induced breakdown spectroscopy methodologies for elemental mapping and qualitative discrimination analysis"

> Palásti, D. J.; Casian-Plaza, F.A.; Bélteki, Á.; Kohut, A.; Makkos, L.; Galbács, G.
> Single-shot laser-induced breakdown spectroscopy using various duration pulses generated by a compact master oscillator power amplifier fiber laser,
> *Optics & Laser Technology* 2025, 192, 114120.

with regard to the publication and the candidate's T3 thesis point, I hereby declare that the results used in the dissertation reflect the candidate's independent contribution.

....

Dr. Gábor Galbács

January 27, 2026.

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Dr. Gábor Galbács

January 27, 2026.