Theses of doctoral (Ph.D.) dissertation

Development of performance-enhancing techniques and analytical methods in laser-induced breakdown spectroscopy

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1. INTRODUCTION

The laser-induced plasma spectroscopy (LIBS) is a dynamically developing laser elemental analytical method, which is based on the spectroscopic observation of a microplasma generated on the sample surface (in case of non- solid samples, it is generated inside the samples) by a high intensity, pulsed laser beam. The LIBS technique is capable of analyzing solid, liquid, gas and aerosol samples with little or no sample preparation. The measurements can provide data with high spatial resolution, and can be performed from a distance or even in the field. The detection limits for the majority of the elements are in the ppm range, and the dynamic range is usually a few orders of magnitude. Due to their line-rich character, LIBS spectra are quite characteristics of the samples, thus they can be well used for sample identification. Due to its many advantageous virtues, LIBS is getting more and more widespread in both academical and industrial circles.

In many countries of the world, intensive research is conducted in the field of LIBS – it is actually the most quickly developing branch of atomic analytical chemistry. One of the main goals of the researchers is to enhance the analytical performance of the method by investigating the details of the laser-matter interaction and the processes they initiate. An other sizeable part of the LIBS research and development aims at broadening its field of applications, which already includes many areas from the industry, through medical diagnostics and environmental protection till space exploration.

One of the performance enhancing methods described in the literature is nanoparticle enhanced LIBS (NELIBS). In the last decade many researchers demonstrated that metal nanoparticles deposited on the surface of a solid sample can increase the sensitivity of LIBS measurements by as much as two orders of magnitude. Due to the simple technicalities of the approach, NELIBS has become one of the most investigated signal enhancement technique for solid, conducting samples. However, the NELIBS analysis of liquids and gases are relatively new fields of research, which also present unique analytical challenges.

Spatial heterodyne spectrometers (SHS) are experimental interferometric instruments. Based on their advantageous characteristics predicted theoretically (high light throughput and resolution, a compact setup free from any moving parts, etc.) and demonstrated by several experiments, they appear to be a suitable alternative to charge coupled detector spectrometers widely used in analytical spectroscopy. The usefulness of SHS has been mainly demonstrated in remote and Raman measurements. Its use in the field of LIBS so far has been very rare, which is probably the result of the complicated and strict requirements (in terms of spectral bandpass, resolution, time resolution) of LIBS spectrometers. The interrelation of these characteristics with experimental conditions are also not fully known, which makes signal optimization tough.

A considerable research effort goes into the application of LIBS for discrimination analysis. The popularity of LIBS in this field is boosted by its short measurement time, microdestructiveness and easy to operate nature. Discrimination analysis based on the large and detail-rich LIBS datasets require the use of multivariable statistical algorithms. Although many such methods exist today, but their performance is greatly influenced by the characteristics of the investigated datasets, thus none of them can be universally applied. The selection of the most suitable chemometric method for a certain analytical task is still usually done on the trial and error base and it is the duty of researchers.

The laser and plasma spectroscopy research group of the Department of Inorganic and Analytical Chemistry led by Gábor Galbács has been active in the field of LIBS for over two decades. I joined the research group in 2013, and my PhD research started here in 2017.

2. OBJECTIVES

Similarly to the general trend of LIBS research, my research has also focused on its performance characteristics and the development of analytical methods. In search of better analytical performance, I have developed and optimized spectrometer arrangements and sample preparation methods. Within these fields, I mainly worked on the adaptation of spatial heterodyne spectrometers to LIBS and method development for the nanoparticle signal enhancement for liquid and gas samples.

Included in my goals was also the demonstration of the extension of LIBS discrimination analysis and data evaluation methods for sample types which are important from a practical point of view (e.g. industrial, environmental, forensic samples), but has not yet or rarely been investigated in the literature. Although I worked with many different sample types, but due to length limitations, I could only incorporate the results regarding coal and soot aerosol samples.

3. EXPERIMENTALS

Different experiments needed different instrumentation, thus the specific devices and conditions are specified in my dissertation. Here, I only give an overview of the most important tools and their properties.

In experiments, which required precision aiming were executed on an Applied Spectra (USA) J-200 instrument. The laser source of this system is capable of emitting 6 ns long pulses with up to 20 Hz frequency, and its pulse energy is variable between 0 and 17 mJ. The emitted 266 nm light can be focused onto 40 to 200 μm diameter spots on the sample surface. This instrument incorporates a six-channel spectrometer, which is capable of recording spectra between 190 and 1040 nm with an average resolution of 0.07 nm.

Experiments which required high pulse energy were carried out using a Quantel Ultra 100 (Lumibird, France) actively Q-switched Nd:YAG laser, which is capable of providing up to 100 mJ pulse energy. The laser head comes with a built-in polarization attenuator, which makes the applied energy freely variable. The 1064 wavelength emission has a duration of 10 ns, and the upper limit of the repetition rate is 20 Hz.

The LIBScan 25+ LIBS system, manufactured by Applied Optics Ltd. (Great Britain) was used during field compatible measurements. Its Nd:YAG laser source has a passive Q-Switch and can emit 4 ns long pulses with 50 mJ energy at 1064 nm. It has a fairly low repetition rate, ca. 1/3 Hz. It has a built-in four channel spectrometer, which records the spectrum in the ranges between 238-353, 360-455 and 492-907 nm. The minimum settable delay and integration times on the spectrometer are 1.27 μs and 1.1 ms, respectively.

In setups that required external light collection we used a two-channel, fast triggerable Avantes FT 2048 (Netherlands) spectrometer, which could record in the range of 198-318 and 345-888 nm using at least 2 ms integration time. Solarization-resistant fused silica fiber optics were used to guide the plasma emission to the spectrometer, via UV-COL (Avantes) collection lenses. For the synchronization of the individual instruments, signal generators (TTi TGP3152 and TTi TG5011, USA) and oscilloscopes (e.g. Tektronix TDS 1002, USA) were used. The optical setups were built using optomechanical parts manufactured mainly by Thorlabs (USA).

The computational models featured in my thesis were developed using Comsol Multiphysics, Matlab and R programming software.

4. RESULTS

1. I proved that the substrates intended for surface enhanced Raman specrtroscopy (glass slides with a thin layer of indium-tin oxide and covered with silver nanoparticles) can be easily modified for the purposes of nanoparticle enhanced LIBS of liquid samples. By systematically changing the surface coverage and size of the nanoparticles I determined that the smaller interparticle distances (without the contact of the particles) are more advantageous from the point of view of the signal enhancement factor. By optimizing the focal spot size and pulse energy I achieved a three times signal enhancement using a 266 nm laser [4].

2. I investigated the effect of gold nanoparticles in different number concentrations and size distributions on the laser-induced breakdown properties of argon gas in detail, and determined that
   a) the nanoparticles cause a significant, at least 50%, drop in the breakdown threshold of argon gas. This effect shows a correlation with the mass concentration of the aerosol. I proved that the electrons emitted from the nanoparticles via thermo- and field emission are the cause of this phenomena [6].
   b) the observed effect is suitable for not just the senitivity enhancement of the trace analysis of argon gas (and potentially other gas mixture), but also for the indirect analysis of the dispersed nanoparticles. It is possible to use the signal of the gas for the determination of the mass concentration of nanoparticles, even if they cannot be directly measured. The smallest aerosol concentration, which we were able to detect was in the fg/cm^3 range [6].

3. I built a unique, confocal spatial heterodyne Raman spectrometer using a diode pumped solid state laser for excitation, and characterized its performance. With the use of cyclohexane-isopropanol and glycerol-water sample mixtures and multivariable data evaluation approaches, I successfully demonstrated the feasibility of quantitative analysis by SH Raman spectrometers [3].

4. I constructed simulational models based on geometric optics and interferometric calculations for the study of the relationships between the experimental parameters and the spectroscopic performance of dual reflective grating SHS. I showed that the spectral range is mostly dependent on the pixel size of the imaging detector, while the resolution is mainly affected by the size of the detector (side length of the photosensor matrix) and the grating density of the optical gratings. I also revealed that however the spectral bandpass of the spectrometer can be easily shifted the rotating the gratings, but it also drastically changes the instrumental function, which is already dependent on many factors (sampling efficiency of the interferogram pattern, position and wavelength-dependent sensitivity of the detector, etc.). My simulations revealed that the temporal distortion occurring inside the spectrometer is significantly smaller than what occurs inside a typical fiber optic, and that an SHS can be used to record spectra with a better than ns time resolution [5].

5. I showed that coals with different quality and origin can be efficiently identified based on the chemometric evaluation of the visible range of their LIBS spectra. The change in coal quality can be detected even if no prior spectral information is available. Thus LIBS may applied in the energy industry as a new approach for online process and quality control. The performance of the method was demonstrated on six coal samples using three similarity functions and linear discriminant analysis. The accuracy of the classification was above 95% [1].

6. I worked out a method for the on-line LIBS analysis of soot aerosols.
   a) I determined that the frequency of the plasma formation correlates with the mass concentration of the aerosol. The detection limit for the soot particles was about 600 ng/cm^3, which means that the smallest individually detectable particle size was about 2.3 μm in diameter [2].
   b) I performed classification analysis of soot aerosols by testing three methods (linear discriminant analysis, quadratic discriminant analysis and classification tree), and established that the best classification accuracy (87.2%) can be reached by employing the classification tree method. I investigated the effect of data compression by multilinear curve resolution alternating least squares and data scaling on the accuracy and I found that dimension reduction worsens it, but scaling does not have any significant effect [2].

5. LIST OF PUBLICATIONS

My ID in the Hungarian Collection of Scientific Publications (MTMT) is 10062648

Journal publications forming the basis of my dissertation:

[1] A. Metzinger, **D.J. Palásti**, É. Kovács-Széles, T. Ajtai, Z. Bozóki, Z. Kónya, G. Galbács: Qualitative discrimination analysis of coals based on their laser-induced breakdown spectra
Energy and Fuels, 30 (2016) 10306-10313.

IF: 3.50 (Q1)

[2] **D.J. Palásti**, A. Metzinger, T. Ajtai, Z. Bozóki, B. Hopp, É. Kovács-Széles, G. Galbács: Qualitative discrimination of coal aerosols by using the statistical evaluation of laser-induced breakdown spectroscopy data
Spectrochimica Acta Part B: Atomic Spectroscopy, 153 (2019) 34-41.

IF: 3.24 (D1)

[3] A.B. Gojani, **D.J Palásti,** A. Paul, G. Galbács, I. B. Gornushkin: Analysis and classification of liquid samples using spatial heterodyne Raman spectroscopy
Applied Spectroscopy, 73 (2019) 1409-1419.

IF: 2.19 (Q2)

[4] **D.J. Palásti**, P. Albrycht, P. Janovszky, K. Paszkowska, Zs. Geretovszky, G. Galbács: Nanoparticle enhanced laser-induced breakdown spectroscopy of liquid samples by using modified surface-enhanced Raman scattering substrates
Spectrochimica Acta Part B: Atomic Spectroscopy, 166 (2020) 105793.

IF: 3.64 (D1)

[5] **D.J. Palásti**, M. Füle, M. Veres, G. Galbács: Optical modeling of the characteristics of dual reflective grating spatial heterodyne spectrometers for use in laser-induced breakdown spectroscopy
Spectrochimica Acta Part B: Atomic Spectroscopy, 183 (2021) 106236.

IF(2020):3.64 (D1)

[6] **D.J. Palásti**, L. Villy, A. Kohut, T. Ajtai, Geretovszky, G. Galbács:
Signal enhancement effect of gold nanoparticles suspended in argon gas with laser-induced breakdown spectroscopy,
Spectrochimica Acta Part B: Atomic Spectroscopy, 2022, accepted for publication

IF(2020): 3.64 (D1)

$\Sigma_{\text{impact factor}}$=19.85

Additional journal publications also related to the topic of the dissertation:

7. M. Pintér, T. Ajtai, G. Kiss-Albert, D. Kiss, N. Utry, P. Janovszky**,** **D.J. Palásti,** T. Smausz, A. Kohut. B. Hopp, G. Galbács, Á. Kukovecz, Z. Kónya, G. Szabó, Z. Bozóki, Thermo-optical properties of residential coals and combustion aerosols
*Atmospheric Enviroment,*178 (2018) 118-128.
IF:4.01(Q1)

8. P. Janovszky, K. Jancsek, **D.J. Palásti,** J. Kopniczky, B. Hopp, T.M. Tóth, G. Galbács, Classification of minerals and the assessment of lithium and beryllium content in granitoid rocks by laser-induced breakdown spectroscopy
Journal of Analytical Atomic Spectrometry, 36 (2021) 813-823.
IF(2020):4.02(Q1)

9. D.J. Palásti, J. Kopniczky, B. Hopp, A. Metzinger, G. Galbács: Qualitative analysis of glass microfragments using the combination of laser-induced breakdown spectroscopy and refractive index data
Sensors, 22 (2022) 3045
IF(2020): 3,58 (Q2)

$\Sigma\Sigma_{\text{impact factor}}$=31.46

Oral and poster presentationslated to the topic of dissertation:

1. **D.J. Palásti,** L.P. Villy, A. Kohut, Zs. Geretovszky, T. Ajtai, É. Kovács-Széles, G. Galbács: The effect of the presence of gold nanoparticles on the laser induced breakdown in argon gas
27th International Symposium on Analytical and Environmental Problems (2021) Szeged

2. P. Janovszky, A. Kéri, **D.J. Palásti**, J. Kaiser, M. Tóth, G. Galbács: Biológiai és geológiai minták nyomelem és nanorészecske eloszlásának tanulmányozása mikrométeres térbeli felbontású lézer indukált plazma spektroszkópiával
Az EFOP-3.6.2-16-2017-00005 „Ultragyors fizikai folyamatok atomokban, molekulákban, nanoszerkezetekben és biológiai rendszerekben" projekt zárókonferenciája (2021) Szeged

3. **D.J. Palásti,** P. Janovszky, L.P. Villy, A. Kohut, Zs. Geretovszky, M. Veres, G. Galbács: A lézer indukált plazma spektroszkópia érzékenységének javítása optikai és plazmonikai eszközökkel
Az EFOP-3.6.2-16-2017-00005 „Ultragyors fizikai folyamatok atomokban, molekulákban, nanoszerkezetekben ésbiológiai rendszerekben*" projekt zárókonferenciája* (2021) Szeged

4. Á. Bélteki, T. Biros, **D.J. Palásti,** L.P. Villy, B. Leits, A. Kéri, A. Kohut, É. Kovács-Széles, T. Ajtai, Zs. Geretovszky, G. Galbács: On-line and off-line LIBS detection of nanoaerosols generated by electrical discharges
International Workshop on Laser-Induced Breakdown Spectroscopy (2020) Szeged

5. **D.J. Palásti,** A. Metzinger, J. Kopniczky, B. Hopp, G. Galbács: LIBS-based approaches for the classification of glass microfragment samples
International Workshop on Laser-Induced Breakdown Spectroscopy (2020) Szeged

6. **D.J. Palásti,** P. Janovszky, Á. Bélteki, É. Kovács-Széles, M. Óvári, Cs. Tóbi, Zs. Varga, A. Berlizov, G. Galbács: Analysis of uranium-bearing materials by laser-induced breakdown spectroscopy
International Workshop on Laser-Induced Breakdown Spectroscopy (2020) Szeged

7. P. Janovszky, K. Jancsek, **D.J. Palásti,** J. Kopniczky, B. Hopp, T.M. Tóth, G. Galbács: Identification and Be, Li content assessment of minerals in granitoid rock samples by LIBS

International Workshop on Laser-Induced Breakdown Spectroscopy (2020) Szeged

8. **D.J. Palásti**, M. Veres, M. Füle, G. Galbács: Optical and numerical modeling of a spatial heterodyne laser-induced breakdown spectrometer
International Workshop on Laser-Induced Breakdown Spectroscopy (2020) Szeged

9. L.P. Villy, **D.J. Palásti,** G. Skoda, A. Kohut, Zs. Geretovszky, É. Kovács-Széles, G. Galbács: Signal enhancement of gaseous samples in the presence of nanoaerosols generated by a spark discharge
International Workshop on Laser-Induced Breakdown Spectroscopy (2020) Szeged

10. **D.J. Palásti**, M. Veres, M. Füle, Zs. Geretovszky, G. Galbács: Computational and experimental investigations on a tuneable spatial heterodyne spectrometer
26th International Symposium on Analytical and Environmental Problems (2020) Szeged

11. **D.J. Palásti,** Á. Bélteki, É. Kovács-Széles, A. Berlizov G. Galbács: Experimental optimization and assessment of the performance of laserinduced breakdown spectroscopy for the quantitative analysis of 20+ trace elements in uranium dioxide
European Winter Conference on Plasma Spectrochemistry (2019) Pau

12. **D.J. Palásti,** A. Gojani G. Galbács, I. Gornushkin: Quantitative and qualitative analysis of liquid samples by spatial heterodyne Raman spectroscopy
European Winter Conference on Plasma Spectrochemistry (2019) Pau

13. **D.J. Palásti,** M. Veres, I. Rigó; Zs. Geretovszky, É. Kovács-Széles, A. Gojani, I. Gornushkin, G. Galbács: Optimization and detailed spectroscopic characterization of an improved spatial heterodyne laser-induced breakdown spectroscopy setup
European Winter Conference on Plasma Spectrochemistry (2019) Pau

14. **D.J. Palásti,** P. Albrycht, K. Paszkowska, G. Galbács: Evaluation of silver nanoparticles on indium-tin-oxide (ITO) type SERS substrates for nanoparticle-enhanced LIBS analysis of liquid samples
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2019) Brno

15. **D.J. Palásti,** A. Kéri, L.P. Villy, T. Biros, Á. Bélteki, B. Leits, P.M. Janovszky, A. Kohut, É. Kovács-Széles, Zs. Geretovszky, G. Galbács:

Nanoparticle analysis by LIBS and ICP-MS in industrial and environmental samples
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2019) Brno

16. **D.J. Palásti,** A. Metzinger, A. Berlizov, É. Kovács-Széles, G. Galbács: Exploringthe potentional of LIBS for the in-field analysis of nuclear samples
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2019) Brno

17. **D. J. Palásti,** L. Himics, T. Váczi, M. Veres, I. Gornushkin, G. Galbács: Optical modelling of spectroscopic charactewristics of a dual-grating tunable spatial heterodyne LIBS spectrometer
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2019) Brno

18. N. Sushkov, P. Janovszky, **D.J. Palásti,** G. Galbács, T. Labutin, N. Lobus, K. Fintor: The use of laser spectroscopy techniques in studying zooplankton
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2019) Brno

19. **D.J. Palásti,** A. Metzinger, G. Galbács: Spectral fingerprint analysis of forensic glass microsamples by LIBS
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2019) Brno

20. **D.J. Palásti,** A. Metzinger, J. Kopniczky, G. Galbács: Üvegszemcsék LIBS spektroszkópiás megkülönböztethetőségének vizsgálata
62. Spektrokémiai Vándorgyűlés (2019) Balatonszárszó

21. **D.J. Palásti,** P. Albrycht, K. Paszkowska, P. Janovszky, G. Galbács: Az analitikai jel növelése lézer indukált plazma spektroszkópiában ezüst nanorészecskéket tartalmazó felület-erősített Raman spektroszkópiás szubsztrátok alkalmazásával
62. Spektrokémiai Vándorgyűlés (2019) Balatonszárszó

22. **D.J. Palásti,** G. Galbács, A. Gojani, I. Gornushkin: Folyadékminták Raman-analízise térbeli heterodin-spektroszkópiával
VIII. Eötvözet Konferencia (2019) Szeged

23. **D.J. Palásti,** T. Ajtai, Z. Bozóki, É. Kovács-Széles, G. Galbács: Qualitative discrimination of coal aerosols via multivariate statistical evaluation of LIBS spectra

XVI. Hungarian - Italian Symposium on Spectrochemistry (2018) Budapest

24. **D.J. Palásti,** A. Metzinger, É. Kovács-Széles, G. Galbács: Qualitative discrimination analysis of corn hybrids by laser-induced breakdown spectroscopy
European Winter Conference on Plasma Spectrochemistry (2017) Sankt Anton

25. **D.J. Palásti,** I. Rigó, M. Veres, G. Galbács: Construction and initial characterization of a spatially heterodyne LIBS spectrometer
Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (2017) Pisa

26. **D.J. Palásti,** É. Kovács-Széles, A. Berlizov, G. Galbács: Feasibility study of contaminants analysis in uranium-containing materials by LIBS spectroscopy
23rd International Symposium on Analytical and Environmental Problems (2017) Szeged

27. **D.J. Palásti,** M. Veres, G. Galbács: Térbeli heterodin lézer indukált plazma spektrométer építése és jellemzése
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28. **D.J. Palásti,** G. Galbács: Kukoricatermések lézer indukált plazma spektroszkópiás vizsgálata hibridek kemometriai azonosítása céljából
VI. Eötvözet Konferencia (2017) Szeged

29. **D.J. Palásti,** T. Ajtai, R. Rajkó, G. Galbács: Tüzelésre szánt szenek diszkriminációja tömbi és aeroszol fázisú LIBS spektrumaik alapján
V. Eötvözet Konferencia (2016) Szeged

30. Metzinger, **D.J. Palásti,** A. Nagy, A. Gáspár, É. Kovács-Széles, T. Ajtai, Z. Bozóki, G. Galbács: Analysis of liquid and aerosol sample by laser-induced breakdown spectroscopy
European Winter Conference on Plasma Spectrochemistry (2015) Münster

31. **D.J. Palásti,** A. Metzinger, R. Rajkó, T. Ajtai, É. Kovács-Széles, G. Galbács: Discriminant analysis of coal samples by laser-induced breakdown spectroscopy
21st International Symposium on Analytical and Enviromental Problems (2015) Szeged

32. **D.J. Palásti,** A. Metzinger, R. Rajkó, T. Ajtai, É. Kovács-Széles, G. Galbács: Szénminták és az ezekből lézeres ablációval keltett aeroszolok vizsgálata lézer indukált plazma spektroszkópiával