Closing scientific report for NKFIH project No. K129063

„Construction and application of spatial heterodyne laser induced breakdown spectroscopy for the development of sensitive and selective trace analytical methods”

This project aimed at the development of new experimental arrangements and trace analytical methodology suitable for the improvement of the sensitivity and selectivity of laser induced breakdown spectroscopy measurements. Special attention was paid to the realization of a spatial heterodyne interferometric spectrometer (SHS) and the assessment of its figures of merit. The capabilities of the new analytical technologies developed were also successfully tested in a number of important application areas, like industry, environmental protection, geology, biology.

Challenges in time evolution of the project

The project team has not changed during the execution of the project. Carrying out the project, especially the experimental construction part, was hindered by the covid-19 pandemic, due to which we asked for a 3-month extension of the deadline (from August 31 to November 30, 2022), thus the total duration was 51 months. By the end we successfully reached all goals of the project, and in the area of the analytical methodology development we even significantly overfulfilled them. This is considered to be due the good project organization, the devoted work of the participating researchers and the efficiency of the national and international cooperation network revived by the project.

Summary of results within Task 1. (spatial heterodyne spectroscopy)

During the project, we successfully constructed, optimized and characterized two different spatial heterodyne spectrometers, both developed for the use of two reflective gratings. The first system was built, in cooperation with a German research group, for Raman spectroscopy, using a diode-pumped solid state laser source operating at 532 nm and microscope-based light collection. This system was tested to have a resolving power of 5000 which value compares well to the theoretically estimated value of 5400. The spectral range was 522–593 nm that allowed for the measurements of Raman shifts between 330 cm^{-1} and 1600 cm^{-1}. Detailed background correction and image analysis protocols were developed for the processing of the interferograms. For the first time in the literature, the analytical applicability and practicality of this SHS system was demonstrated in performing qualitative and quantitative analytical tasks on various liquid samples, such as solvents (cyclohexane, isopropanol, glycerol, water) and industrial oils (e.g. biodiesel, gasoline, heavy oil, lubricants, etc.) and the figures of merit were assessed. In quantitative tasks, two calibration strategies were employed: univariate calibration and multivariate partial least squares regression. Principal component analysis of the spectra allowed for the discrimination of oils.

Based on the experiences with the first system, we then set out to construct extensive numerical simulations (a combination of non-sequential ray tracing and numerical interferometric simulations) to study the effect of the most important optical and experimental parameters (e.g. grating density, grating rotation, interferometer arm length, camera pixel resolution, camera chip size, etc.) on the performance of spatial heterodyne interferometric spectrometers, relevant to their use in laser-induced breakdown spectroscopy (LIBS). We carried out detailed, numerical assessment of the

spectral bandpass, tuning characteristics, spectral resolution, sensitivity, and temporal gating achievable in such an instrument. The results showed that a compact (e.g. 75 mm arm length) arrangement with 25 mm gratings can achieve a spectral resolution (few pm) that is even adequate for isotope selective measurements. We also demonstrated that the spectral bandpass ranges from a few nm (for very high resolution) up to 100 nm (for a resolution still directly applicable in atomic spectroscopy) depending on the experimental conditions set. We also established that due to the compact size, the coherence length and the dispersion in the system allow for not only ns-LIBS, but also fs-LIBS application. In these simulations, we used the specifications of commercially available actual optical elements, therefore the results were directly used during the construction of our second SHS system, optimized for LIBS use. We built and then tested this system with different coherent and non-coherent light sources, intensified CCD and CMOS imaging detectors, imaging zoom objectives and various image processing algorithms.

The performance of the optimized SH-LIBS system was then compared to that of conventional LIBS systems equipped with a linear CCD spectrometer (known for its sensitivity) and an Echelle spectrometer (known for its resolution). It was found that the SHS, even with compromise settings, could achieve comparable resolution to that of the Echelle, and a sensitivity almost as good as that of the linear CCD. We demonstrated the analytical figures of merit with the analysis of gold alloys and hydrogen isotopes.

At present, we are testing the analytical capabilities of our compact SHS LIBS in demanding applications like hydrogen isotope analysis in liquid and solid samples.

Summary of results in Task 2. (LIBS analytical methodology)

Along the lines of our second major task, we carried our experimental and methodological developments for the performance enhancement of LIBS spectroscopy. We developed sample preparation and multivariate data evaluation protocols for various sample types and applications, and studied novel signal enhancement approaches (mainly based on the use of nanoparticles). These LIBS sub-projects were very diverse, but also highly successful. The following paragraphs provide an itemized list of results, organized according to our publications during the present project.

We performed a successful feasibility study of using modified surface enhanced Raman scattering substrates (Ag nanoparticles on indium-tin-oxide glass) for quantitative nanoparticle-enhanced laser induced breakdown spectroscopy (NELIBS) for the first time in the literature. In cooperation with a Polish research group, substrates were prepared with different surface coverage from various nanoparticle sizes, and their laser ablation behaviour was tested in detail. It was found that use of those combinations is most beneficial in terms of the signal enhancement factor, which provide the shortest interparticle distances. With the application of 266 nm laser wavelength, long (ms-range) gate width, and optimized laser pulse energy, the best NELIBS signal enhancement was found to be about a factor of three. By using liquid sample deposition by spraying, which was found to provide an even distribution of liquid samples on the substrate surface, successful calibration for Mn, Zn and Cr was performed. The NELIBS signal repeatability from five repeated measurements was found to be comparable to that of conventional LIBS, which results in an improvement of a factor of 2 to 3 in limits of detection. These results proved that the NELIBS signal enhancement approach can be used in quantitative analytical applications for liquid samples, if i) the substrate fabrication procedure has good repeatability, ii) surface coverage and nanoparticle size is tightly controlled, iii) a homogenous liquid sample deposition is achieved.

We also investigated the effect of the presence of nanoparticles (NPs) on the LIBS signal of gases. 10–20 nm diameter gold NPs were produced by a spark discharge nanoparticle generator, and dispersed in argon and nitrogen gas. The effect of particle size, number concentration and mass concentration, as well as laser pulse energy on the LIBS argon signal was systematically investigated. It was found that the breakdown threshold of the gas decreases considerably, facilitating the detection of gas emission at such laser fluences, which do not allow plasma formation without the presence of the NPs. Our observations persist even at aerosol mass concentrations that are too low to allow the direct detection of nanoparticles. We have shown that the effect is not a plasmonic effect, but can be attributed to electron thermo- and field emission induced by the high intensity laser pulse, and that it shows an asymptotically increasing magnitude with the aerosol mass concentration. The signal enhancement was found to be 10^2–10^4. We demonstrated that the effect is useful in trace gas analysis or for the indirect detection of NPs. The achievable indirect aerosol mass concentration detection limit was estimated to be in the ppt regime (as low as 50 $ng \cdot m^{-3}$), which is comparable to the best literature values reported for direct analysis.

We have also carried out extensive experiments to assess the applicability of nanoparticle signal enhancement for the LIBS elemental mapping and LIBS-based discrimination mapping of solid samples. We postulated that the challenge in this new approach is that i) it requires a very homogeneous NP deposition technique, and ii) the laser ablation of the deposited NPs has to be orderly, so that the spatial resolution of the mapping is not much compromised. We studied and optimized four different metal NP deposition techniques for this purpose: spray coating, droplet placement, spark discharge deposition, sputtering. The best results were obtained by using sputtering followed by thermal treatment of the metal NPs. We successfully demonstrated the feasibility of the approach with gold NPs on various patterned solid samples, such as rocks, polymers, glass, and painted steel. Signal enhancement of around a factor of three was found, which also improved the accuracy of material discrimination analysis by LDA.

We developed various LIBS sample preparation and data evaluation techniques for industrially relevant sample types. In two sub-projects, we studied the Li and Be content of granite rock types complemented with the automatic mineral grain type identification based on machine learning algorithms (e.g. RF, LDA, PCA, CT), in order to support prospecting/mining efforts for these technologically important elements. Another industrial sample type investigated was uranium oxide nuclear (fission) fuel. In this direction, we assessed the capability of LIBS for the in-field analysis of trace contaminants in this difficult matrix, in order to gauge the quality/purity of the fuel. It was established that LIBS is indeed capable of providing sensitive enough (ppm level, ASTM conform) detection limits for these sample types.

The third sample type (of industrial origin) targeted was glass; the particular context of this LIBS analysis effort was to help forensic investigations in the identification of the source of glass microfragments by classifying them. We have shown that it is possible to carry out such classification with 90%+ accuracy based on the LIBS measurement data complemented with refractive index measurements on the sub-mm samples even within the most difficult soda-lime glass group. The fourth industrial sample type for which we contributed to with LIBS methodology developments was cement, in which chlorine analysis (a culprit of cement erosion) was performed. We have shown that an accuracy and precision adequate for such engineering applications can be done by quick LIBS measurements performed using the emission at the CaCl recombination molecular band.

Finally, the fifth industrial sample type investigated was coal aerosol. In this environmentally oriented study, we generated aerosol from five commercial coal samples (lignite, anthracite, Pécs-vasas brown coal, Polish brown coal, Czech brown coal) by laser ablation and the features of the

aerosol LIBS spectra were characterized. We showed that for the successful detection of individual coal aerosol particles, their diameter should be over 2.3 μm. The possibilities for coal classification based on the statistical evaluation of the LIBS spectra of the aerosols was also investigated in detail by using simple comparative functions (overlapping integrals, sum of squared deviations, linear correlation) as well as multivariate methods (classification tree, linear and quadratic discrimination analysis). The best performance was showed by the classification tree method (without data compression), which had a good overall accuracy of 87.2% with a repeatability value of 2.2%,

In addition to the above sample types, we also contributed to the qualitative and quantitative analysis of biological samples by developing LIBS-based analytical methods. For example, within the frameworks of a cooperation with Russian scientists, we contributed to the qualitative discrimination of different zooplankton types with the help of data fusion from LIBS and Raman spectroscopy. These small marine organisms are interesting also because they were found to accumulate a substantial amount of lithium in their body. The results, obtained by using four chemometric data evaluation methods, revealed that LIBS spectra are more sensitive towards taxonometric differences than Raman spectra. It has been showed that a semi-automatic classification of marine zooplankton animals without the visual inspection of whole organisms.

In another study, done in cooperation with plant biologists, we developed sample preparation, measurement and visualization protocols for the elemental LIBS mapping of crop plant material (*Brassica napus*). The study was aimed at assessing the response of the plant to a limited Zn supply. The LIBS elemental maps provided information about the distribution of various minor and trace elements (Zn, K, Ca, Mg, Fe, Mo) in the plant leaves, and revealed that the decreased Zn content of the nutrient solution caused reduced tissue Zn concentrations and reduced K, Ca, Mg levels, whereas for Ca, Zn, Fe and Mo inhomogeneous distribution was induced. Further, similarly oriented LIBS plant studies have also been started in our laboratory.

Finally, we completed a study in cooperation with an Austrian research group, in which we developed LIBS quantitative elemental and qualitative discrimination mapping methodologies for biological tissues (seven different swine tissue types). In this study, we successfully demonstrated that matrix-matched external calibration is necessary for the conversion of intensity maps to concentration maps. We also proved that tissue types can be accurately recognized by their LIBS spectra, therefore an automatic selection of matrix type (and hence, calibration samples) is possible.

Summary of results in Task 3. (dissemination)

This formal task was dedicated to the dissemination of our results in scientific papers, book chapters, dissertations and on international conferences.

Two PhD dissertations, by project participants Dávid J. Palásti és Patrick M. Janovszky, were prepared directly based on the results of the present LIBS research. Dávid J. Palásti already defended his dissertation in the summer of 2022, whereas the dissertation of Patrick M. Janovszky is now under submission and will be defended in the early Spring of 2023.

During the course of the four-year project, we published our results in a total of 12 papers in high prestige international scientific journals (all with the acknowledgement of the NKFIH support). Two additional journal papers have already been submitted, and further five papers are under submission to various international scientific journals.

Our results also formed the basis for three accepted book chapters that we wrote for two current, international scientific LIBS books. These books are published by Springer and Wiley at the end of this year.

In spite of the hindrance caused by the covid pandemic, our research team also managed to present the project results at several international conferences (e.g. EMSLIBS 2019 (Brno), EWCPS 2019 (Pau), 2022 World Conference on LIBS (Bari), ESAS 2022 (Brno), CSI 2022 (Gijon), IHSS 2018 (Budapest)) and just submitted several further contributions to the EWCPS 2023 (Ljubljana). In total, we delivered over 20 presentations. In addition, our research group also organized a successful small online LIBS scientific conference in 2020, during the pandemic, with 29 presentations from ten countries around the world.

It is also worth mentioning that the project allowed us to strengthen our existing LIBS-based international cooperations and extend them towards further research groups. During the four years, we opened up new mobility projects with foreign research groups in Austria, Germany, Czech Republic and Serbia. Between 2018 and 2022, the research group carried out four, multi-month international student mobilities with our partners. We also successfully continued and expanded our cooperations with Hungarian research groups in search for further challenging applications of our LIBS technologies.

Please note that the following list of publications only contains the main publication types (journal papers, books, dissertations). The “complete” publication list included in the online form additonally also contain some of the conference contributions, but not all of them (e.g. those conference contributions were excluded the material of which were later published in journal papers).

List of main project publications

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