EMSLIBS 2023

PORTO, PORTUGAL

12TH

EURO-MEDITERRANEAN SYMPOSIUM ON LASER-INDUCED BREAKDOWN SPECTROSCOPY

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DAY 1

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C Derrick Quarles Jr. Elemental Scientific
Arif Demir, System Technik
Thomas März. INNOLAS
Giedrius Kudaba, EKSPLA
Florian Trichard, Ablatom

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DAY 3

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SESSION 1

Processing & Chemometrics

Chemometrics as the Swiss Army Knife of LIBS

L. Duponchel[1,a], V. Motto-Ros[2]

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Laser-Induced Breakdown Spectroscopy has gained popularity as an analytical technique for the analysis of complex samples due to its rapid and high sensitivity nature. However, navigating and interpreting the vast quantities of data generated by this technique can be challenging. Chemometrics, a field of analytical chemistry that uses statistical and mathematical methods to extract information from chemical data, offers a solution to this challenge. Chemometrics has been successfully applied to LIBS spectroscopy to extract useful information from the spectra, including identifying elements, quantifying the concentration of analytes, and even predicting sample classes. We are all familiar with the methods commonly applied in this context, such as exploration methods (PCA, …), clustering methods (k-means,…), classification methods (SVM, PLS-DA, SIMCA, k-NN,...), regression methods (PLS, SVR, ANN,…), and unmixing ones (MCR-ALS, ICA, MNF,…). The presentation will explore the versatility of chemometrics in the context of LIBS spectroscopy and showcase its aptitude as a "Swiss Army Knife" for this technique, by tackling challenges that are outside the usual scope of the field.

Firstly, we will discuss the statistical significance of the predictive models that we construct in LIBS (regressions and classifications). Indeed, we mistakenly believe that the best model is the one with the smallest prediction error or the highest rate of correct classification. Therefore, we will propose a statistical methodology to address this question. The second challenge we wish to address in this presentation concerns LIBS imaging, specifically the issue of spectral interference. The generation of a representative elemental distribution map from LIBS spectra is based on selecting a specific wavelength from the spectral domain. This hypothesis of ‘spectral purity’ is all the stronger because nobody can claim to know all the elements present in a potentially unknown sample. We will thus propose a method capable of diagnosing the presence of such interference, as well as correcting it if it is present, to retrieve an image consistent with the analytical reality of the sample.

Extraction of chemical features from complex LIBS matrices

Z. Gajarska[1,a)], H. Lohninger[1], E. Képeš[2], P. Pořízka[2], J. Kaiser[2], A. Limbeck[1]

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Although modern LIBS instruments allow for a rapid mapping of complex data matrices, a universal approach to the retrieval of element-specific information from the resulting data seems to be still lacking. The deep learning methods show a great potential [1], nevertheless, these tools are not accessible to many LIBS practitioners heavily relying on manual data processing. Combining the LIBS expertise, long-term experience in data processing, and modern statistical and information-retrieval tools [2], we aim to fill this gap by providing the community with a feature-extraction algorithm (Fig. 1) enabling rapid extraction of element-specific information from the LIBS spectra as a pre-step to common analytical tasks such as classification, quantification, and imaging.

The talk will outline the algorithm's nuts and bolts, the challenges faced during its development, as well as its current state of the art demonstrated on various use-case scenarios and data matrices (geological samples, technological materials, biological tissues) collected within the LIBS community.

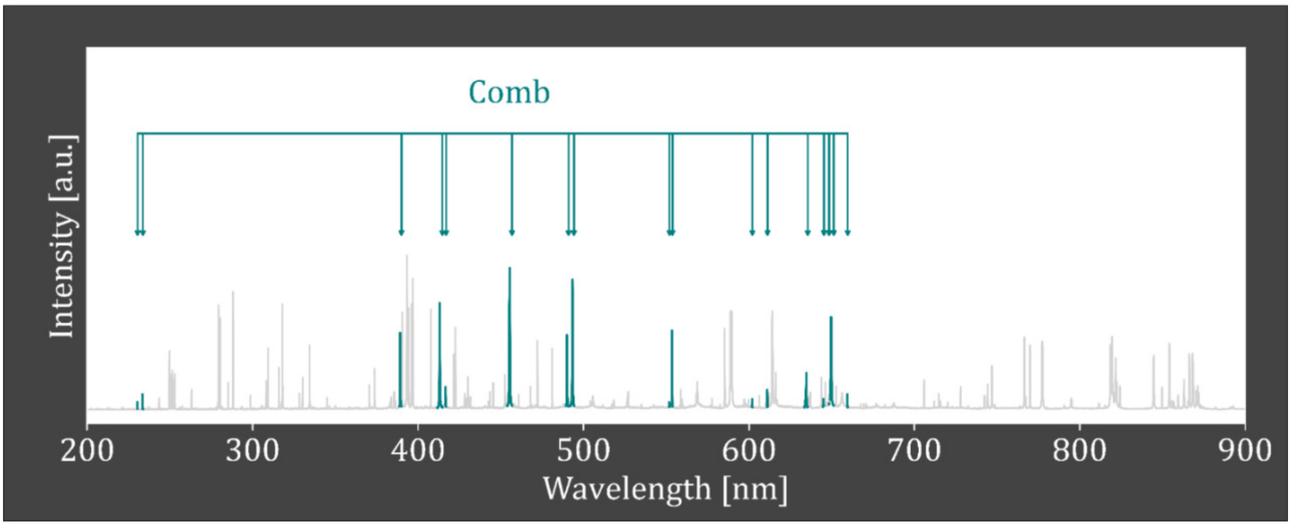

Fig 1. Use of comb algorithm to retrieve element-specific information from LIBS spectrum.

ACKNOWLEDGEMENTS

The authors greatly acknowledge the financial support of the TU Wien through the Grant for diploma and PhD theses and specialist courses abroad.

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Study of matrix effects at micrometer scale

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Materials characterization at micrometer scale is of great interest to many sectors of activity. Quantitative measurement at this scale is not as easy to achieve as at macroscopic scale.

The LIBS (Laser Induced Breakdown Spectroscopy) technique allows access to this information. However, when spatial resolution at the micrometer scale is required, it is difficult to make these measurements quantitative because at these scales the materials are no longer homogeneous. Locally the interaction with matter is different considering laser shot-to-shot because of the nature of the grains forming the material.

This work focuses on matrix effects study encountered at the 3µm interaction scale. Ablation characterization is crucial for µLIBS analysis. These quantities have been measured for different matrices. The matrix effects is characterize with different calibration curves obtained on different metallic materials at this spatial scale. The statistical study of shot-to-shot signal also shows behavior differences between the different materials. The sources of experimental noise have been studied and the part of signal fluctuation coming from inhomogeneity of the sample has been evaluated.

The use of two different experimental setups allows to determine the contribution coming from the setup itself or from physical effects related to the laser-matter interaction.

LIBS classification and regression techniques for waste sorting

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In recent years, the development of Laser-Induced Breakdown Spectroscopy (LIBS) applications for waste characterization and sorting has accelerated. The advantages of LIBS are its potential for rapid material identification, high classification accuracy and ability to characterize materials that are problematic for more traditional sorting methods. The presented work summarizes the results that have been achieved in the EU-funded AUSOM project (Automatic Sorting of mixed scrap Metals: https://www.ausomproject.eu). In this project, several methodologies have been investigated to use LIBS for sorting post-consumer aluminum scrap.

Firstly, a Deep Learning classifier was developed to sort mixed aluminum scrap into three alloy groups: one class of cast alloys and two classes of wrought alloys [1]. Proving that wrought alloys can be separated from a mix of aluminum scrap in a real-time industrial system was of high relevance, because it is a critical step towards enabling more wrought-to-wrought aluminum recycling. Currently, a downcycling approach is dominant for aluminum post-consumer scrap.

Secondly, a Deep Learning regression method was developed for quantitative LIBS analysis [2]. It was demonstrated that the method is able to estimate the alloying element concentrations of aluminum scrap samples with a Mean Average Error (MAE) of just 100 ppm. By integrating this method in a sorting system, the operator can choose and adapt the definition of the output classes by selecting thresholds on the alloying element concentrations for each class. This allows more flexible sorting strategies.

Thirdly, the possibility was investigated to classify aluminum scrap samples based only on the acoustic waves generated during Laser-Induced Breakdown. The experiments demonstrated that the acoustic signal can indeed be used to some extent for the classification between cast and wrought alloys, albeit with a lower accuracy than the usual LIBS approach or computer vision techniques that are especially developed to make this distinction.

Currently, the authors are exploring how similar LIBS methods can be developed to classify polymers in Waste of Electrical and Electronic Equipment (WEEE) in the context of the Horizon Europe INCREACE project (https://increace-project.eu). The goals are to distinguish between different polymer types and to estimate the concentrations of potentially hazardous additives such as bromine.

ACKNOWLEDGEMENTS

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under Horizon 2020, the EU Framework Programmes for Research and Innovation (project name: AUtomatic SOrting of mixed scrap Metals (AUSOM project – www.ausomproject.eu), project number: 19294).

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under Horizon Europe, the EU Framework Programmes for Research and Innovation (project name: INCREACE (https://increace-project.eu), project number: 101058487).

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SESSION 2

Fundamentals

Laser induced high-density plasma evolution and optical emission efficiency

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One of the most crucial issues for improving the detection of elements with LIBS is the yield of atomization and excitation of the ablated matter, because this directly affect the intensity of the emission spectra. In this frame the ablated matter during the laser irradiation as well in the first tens of nanoseconds after the laser pulse play a key role [1]. At this stage the ablated matter consists in a high-density plasma and its characteristics can be interpreted as the ones of WDM (warm dense matter) and, in the case of metals, can be investigated with the Fermi Dirac distribution [2]. The evolution of laser induced WDM [3] that allows the formation of the ideal plasma, also include the formation of different kind of particles ranging from tens of nanometers to micrometre scale. In this lecture within the discussion on fundamental aspects, the factors that improve the yield of atomization and in turn of plasma emissivity, will be discussed with a new point of view on the ablation mechanisms and particle formation.

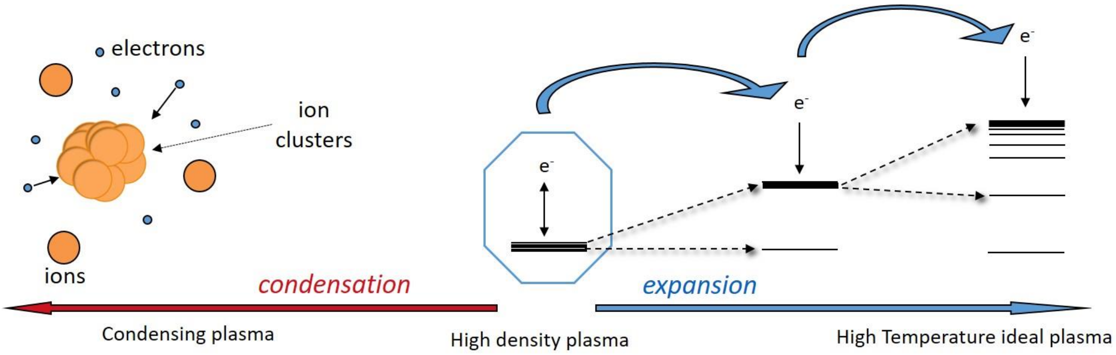

Fig. 1. Sketch of high-density plasma evolution.

ACKNOWLEDGEMENTS

The authors are grateful to Vincent Motto Ros and Igor Gornushkin for the support in the scientific discussion.

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[4] A. B. Author, *Thesis Title* (Ph.D. Thesis, A University 1998).

Non-analytical Applications of Laser-Induced Breakdown Spectrometry

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Laser-induced breakdown spectrometry is typically utilized for qualitative or quantitative analysis of a sample. Over the last two decades, there has been a marked increase in the number of publications devoted to utilizing the technique for analytical purposes. Besides this, there are numerous areas where the emission of laser-induced plasma (LIP) can be employed to address particular problems. Our primary focus is on such non-analytical applications, including fundamental studies of laser plasma itself, determination of atomic line parameters, and laboratory modeling of emission from cosmic objects.

To accurately determine fundamental parameters, it is essential to accurately study the plasma source. Consequently, considerable effort has been directed towards evaluating the presence of equilibrium through comparison of translational, excitation, vibrational, and rotational temperatures at various pressures as well as studying the particle distribution in laser plasmas, including employing probing techniques.

Among the non-analytical applications of laser plasma, it is primarily desirable to begin with the determination of Stark parameters due to the relatively straightforward operations with LIP. Generating a long plasma (“long spark”) instead of a spherical plasma can provide a significant improvement in Stark parameter measurements, allowing for accurate estimation of ion broadening, the impact of hyperfine splitting on profile shapes, and measuring Stark broadening parameters even for resonance lines.

A significant challenge in studying the processes related to the entry of celestial bodies into the upper layers of the Earth's atmosphere is the interpretation of molecular bands, particularly FeO (its theoretical modeling is impossible). Laser plasma has proven to be a beneficial source for laboratory modeling of these processes. Specifically, laboratory spectra have been found to be considerably more accurate than chemiluminescent spectra when compared against meteor event data. Additionally, we discovered substantial discrepancies between laser plasma spectra and the spectra of the Beneshev bolide obtained at corresponding pressures: a similar profile is formed at pressures that are 7-10 times higher than the corresponding height during a bolide's atmospheric passage. Thus, laboratory modeling can be employed to assess pressure during various events in atmosphere accompanied by plasma formation.

Another pressure-depending effect was that the intensity of the CaO band rapidly increases with growing pressure, while the intensity of the FeO band is practically independent of pressure. This leads us to believe that CaO formation in plasma primarily occurs using atmospheric oxygen, while FeO originates from the target material and we can conclude that laser plasma may be also useful for revealing of meteor burning mechanisms.

ACKNOWLEDGEMENTS

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MULTIPLE IONIC PEAK ANALYSIS OF LASER INDUCED PLASMA OF RUBY TARGET USING LANGMUIR PROBE

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Irradiance of a material via a high intensity pulsed laser produces a high temperature and high-density transient plasma plume termed as laser induced plasma (LIP) which expands in the surrounding medium. In order to understand the dynamics of such rapid LIP, various diagnostics probes viz; optical emission spectroscopy, Faraday cup, Langmuir probe (Lp) etc. have been explored successfully by various research groups. Langmuir probe technique [1] is one of the simplest plasma diagnostic tools. It is widely used in the determination of plasma temperature, ion velocities, electron and ion densities. In the present paper, multiple peak structure in LIP of Ruby via Lp has been studied. The electron and ion densities were estimated by analysing the time of flight (TOF) signals. The LIP of Ruby was produced by launching a focused beam of high power Q switched Nd:YAG laser on to a solid Ruby pellet. The dynamics of LIP of Ruby was monitored via a Langmuir probe placed perpendicular to the direction of plume expansion. The detailed experimental arrangement is described elsewhere [2]. The TOF signals at a distance of 4 cm from the target are shown in Figure 1. Both ion as well as electron signals show multiple peak behaviour. The I-V characteristics obtained from TOF signals is shown in Figure 2 and temporal evolution of ion density is shown in Figure 3. The deconvoluted velocity distribution of various ionic peaks are displayed in Figure 4. The details will be presented during the conference.

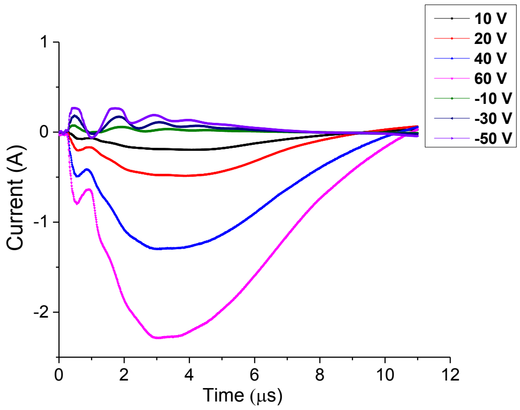

Fig. 1. Ion and Electron signals at various bias.

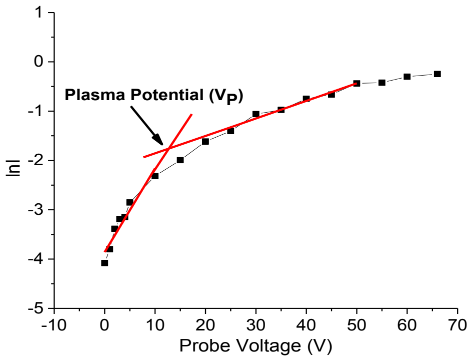

Fig. 2. Semi-logarithmic plot of I-V curve at 10 µs

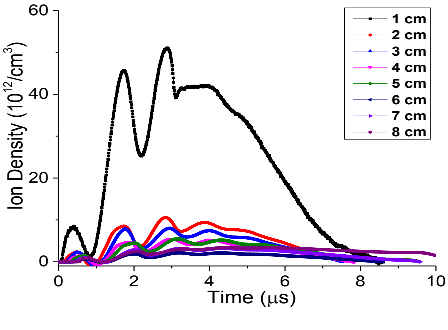

Fig. 3. Temporal evolution of ion density as a function of distance from the target.

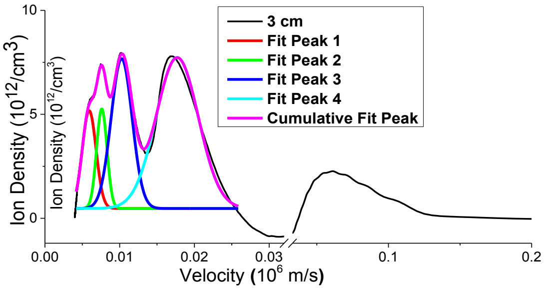

Fig. 4. Deconvoluted peaks of ion density at a distance of 3 cm from the target.

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Importance of Spectral Resolution for Accurate Plasma Diagnostics with Implications for Calibration-Free LIBS

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In the LIBS literature, almost every second article reports the determination of the plasma temperature using the Boltzmann plot method or the determination of the electron density using the Stark line broadening relation. The first requires the measurement of the integrated intensities of the spectral lines, and the second requires the measurement of the linewidth, under the same assumption of optical thinness. It is taken for granted that this can be easily done either by working with the raw spectra or by fitting an appropriate function to the observed spectral lines. As a rule, reported data are not verified either by an alternative method (e.g., Thomson scattering) or by computer simulations using synthetic spectra.

However, the question of how to extract the necessary information from the raw spectral data is not as simple as it might seem. The quality of such an extraction will depend critically on the type of spectral instrument used, its resolution, and the noise superimposed on the data. The problem is that we do not see the spectrum emitted by the plasma, but the spectrum distorted by the measurement; an exaggerated example of such a distortion is shown in Fig. 1. The elimination of this distortion belongs to the class of inverse problems, the so-called ill-posed problems, whose successful solution crucially depends on the quality of the information available. When it comes to spectroscopy, quality of information primarily means high spectral resolution and low noise. Not all spectrometers used in LIBS can provide the quality needed to solve the inverse problem; this casts doubt on many published plasma measurements.

The current presentation will be devoted to general shortcomings in the processing of spectral data and inaccuracies in the determination of plasma parameters resulting from these shortcomings. The analysis is based on the use of synthetic spectra produced by plasma with known characteristics, i.e., temperature, species densities, and electron density. The estimation of errors caused by inadequate processing of spectral data is made by comparing the initial and reconstructed plasma parameters. Recipes will be given for which the analytic function best approximates the observed spectral lines, and how data processing errors affect accuracy of calibration-free LIBS will be discussed. These issues were only partially covered in previously published works, for example [1, 2, 3].

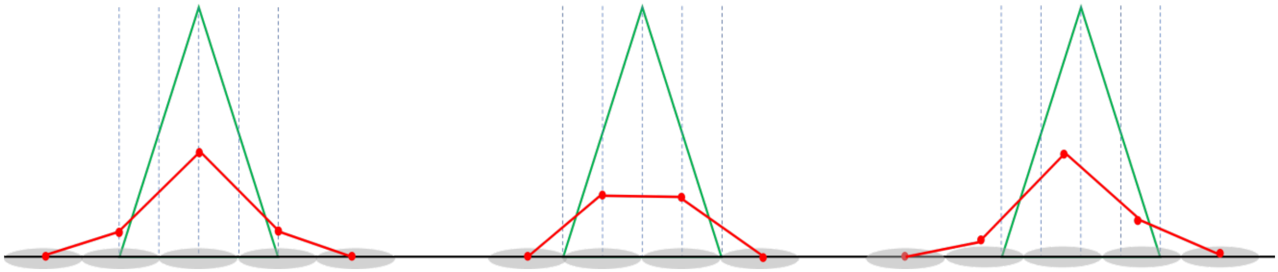

Fig. 1. Distortion of the triangular signal (green) by piecewise integration over detector pixels (grey) for three different pixel positions relative to the signal center. The red dots are the per-pixel integrated signal values, and the red profiles are the distorted signals. Neither the height of the peak of the original triangle, nor its width, nor even the position of the line center can be determined from the distorted signal.

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Laser-induced Fluorescence and Thomson Scattering for Spatially Resolved Plasma Diagnostics

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Laser-induced plasma plays a very important role in the study and modeling of various low-temperature plasma sourses. The modern state of research requires knowledge not only of cumulative properties of plasma, but also the study of its static and dynamic structure and composition. Probing methods, such as laser-induced fluorescence (LIF) and Thomson scattering (TS), are the most promising approaches for spatially and temporary resolved diagnostics of laser-induced plasma. These approaches outperform methods based on analysis of plasma emission spectra since they are not influenced by self-absorption or plasma inhomogeneity. However, their implementation is undoubtedly complicated due to highly sophisticated equipment, low signal-to-noise ratio (in case of TS) and high requirements on reproducibility. Therefore, in the present work, we aimed to develop and implement approaches for spatially resolved plasma diagnostics by LIF and TS, including selection of excitation and emission schemes for atomic and molecular species as well as signal processing routines.

We proposed the schemes for atomic and molecular fluorescence of Ca, Fe, CaO and FeO species in laser-induced plasma. Spatial distribution of these species was studied under low pressure (10 to 100 Torr) using pellets of pure $CaCO_3$ and Fe_3O_4 as targets. Spectra of TS were obtained for air breakdown and plasma induced on a solid sample under atmospheric pressure. We used the 2nd harmonic of a Q-Switched Nd:YAG laser for ablation in all cases, while a tunable Ti:Sapphire laser and another Nd:YAG laser were used to probe the plasma to study LIF or TS, respectively.

Investigation of the spatial distribution (0.2 mm resolution) of atomic and molecular species demonstrated that monoxides are primarily formed from the ablated material. However, in the outer regions of plasma, recombination and reactions with oxygen from surrounding atmosphere make a significant contribution to the formation of monoxides. Moreover, we suggested a scheme for simultaneous LIF of CaO and Fe due to agreement between their excitation wavelengths. At the same time, observation of TS with and without installation of a notch filter coupled with a novel approach of wavelet spectra denoising allowed the determination of plasma temperature and electron number density with high spatial resolution. This approach has also enabled a comparison of plasma diagnostics results with distributions of atoms and molecules in plasma plume.

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In-situ LIBS study of temperature induced processes in material analysis

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The thermal behaviour of solid materials is an important feature in a lot of high-end industry applications. To study temperature-induced or temperature-dependent processes, ex-situ analysis is state of the art but introduces the risk of sample contamination or alteration during storage. Additionally, as sample treatment and measurement are separated, inconsistent ambient conditions or temperature related processes due to cooling might induce changes in the final material properties. Hence, in-situ analysis is indispensable for concerning applications in material chemistry.

Since Laser Induced Breakdown Spectroscopy (LIBS) is a universal technique for direct solid analysis offering fast measurement times, broad elemental coverage as well as spatially- and depth-resolved investigations, we have implemented a heating chamber for our commercially available LIBS instrument for in-situ experiments. In this work, we present the development and application of our custom-made heating stage, facilitating temperatures up to 1000°C and different atmospheres. The versatile applicability is demonstrated for different industry-relevant use cases. First, the scaling of copper was monitored at different temperatures by measuring the oxygen signal of the growing oxide layer. Second, the imidization reaction of a precursor polyimide film was monitored exploiting LIBS molecular emission signals, e.g. C2 and CN as well as elemental lines from the polymeric substance. Finally, the interdiffusion of metals in layered systems was investigated using depth-resolved analysis.

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SESSION 3

Mapping

The Tortuous Issues of Imaging Rocks by LIBS

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LIBS elemental imaging has made significant advancements in the past decade and has now reached a mature stage. It is widely applied across various fields such as biology, medicine, industry, and especially geology. What sets LIBS imaging apart is its unique capability to image a large majority of elements from the periodic table with impressive levels of sensitivity (~ parts per million), resolution (~ 10 µm), and speed (ranging from 100Hz to kilohertz). Moreover, it can be seamlessly integrated with conventional microscopy systems, making it a highly versatile tabletop instrumentation [1,2]. For instance, the ability to image extensive surfaces of samples (> 50 cm²) is particularly appealing for geological samples. This feature allows the macroscopic imaging of samples while retaining information at the microscopic scale with a high level of sensitivity. LIBS imaging is one of the few techniques that can be routinely employed for this type of analysis (figure 1).

Nevertheless, there are notable challenges associated with implementing such analyses for rocks. Due to the nature such samples, generally rich and heterogeneous, the spectral data is highly complex, and the volume of generated data is immense, resulting in time-consuming and arduous processing steps. The size of these datasets varies based on the spatial resolution employed, but it is not uncommon to generate tens of gigabytes of data for a single sample. The abundance of spectra to be processed, coupled with their intricate and noisy nature (due to single shot analysis), leads to recurring issues that can compromise the quality of the resulting images. These issues may include incorrect extraction due to spectral interference or potential loss of information.

In this presentation, we will utilize examples to demonstrate the common obstacles encountered during the analysis of rocks. Subsequently, we will propose various methods for constructing elemental images from the spectral dataset, ranging from "basic" line intensity extraction to the use of artificial intelligence.

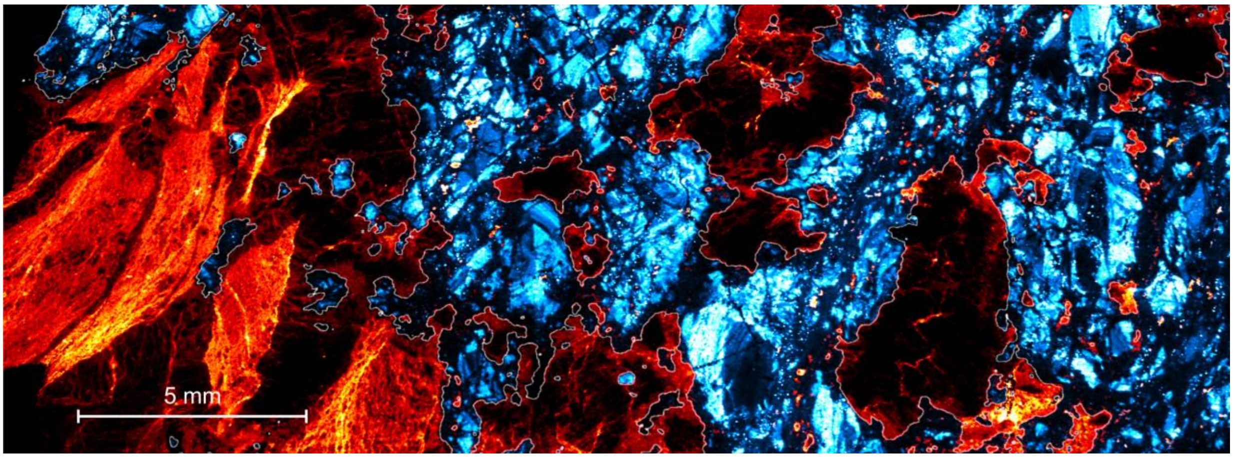

Fig. 1. Example of LIBS imaging of rocks: distribution of Germanium in sphalerite (blue) and quartz (red).

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Rock classification utilizing correlative imaging of large-scale geological samples using LIBS and EDX

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Mapping the distribution of light elements (Li, Be, B, F) and trace elements in large geological samples poses an analytical challenge. The growing interest in rare-element deposits, particularly those containing Li, has highlighted the need for reliable detection and mapping of these elements, which can be difficult with traditional analytical techniques. Laser-induced breakdown spectroscopy (LIBS) combined with advanced data processing has emerged as a promising solution to this problem [1], [2].

In this work, we analyze four large-scale samples (up to 8x8 cm) using LIBS in combination with energy-dispersive X-ray spectrometry (EDX) [3]. Utilizing the LIBS we observe space-resolved distributions of selected elements (major, trace, and light) within the whole samples as well as the impact of natural processes resulting in qualitative changes in the spatial elemental distribution. Thanks to the sensitivity of the LIBS, we can acquire spatial distribution of light elements as well, such as Li or Be, which are out of the reach of the EDX.

Since the samples are composite of various matrices, the k-means clustering algorithm was applied to the acquired hyper-spectral images to determine different minerals and their transitions within the samples.

The LIBS analysis was extended by EDX due to its extensive libraries for minerals providing exact mineral information on the whole samples. The combination of these two methods reaps the benefits of speed, multi-elemental acquisition, and detection of light elements for the LIBS, and accuracy and precision in the mineral determination of EDX. The acquired space-resolved results from these methods are combined in the form of cross-correlation for the purpose of detecting specific minerals as well as natural processes that were forming the rock samples.

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LIBS imaging for high throughput screening in thin-film materials

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High throughput screening (HTS) of materials is developing as an efficient approach to accelerate the discovery of new compounds and to identify the best candidates related to a specific functional property. In the case of thin film materials, magnetron co-sputtering is a convenient way to conduct combinatorial synthesis, and to prepare libraries of materials with different compositions in a single experiment on a single substrate. The next steps of the HTS approach consist in the application of a combination of spatially-resolved, fast and automated characterization techniques aimed at mapping composition, structure, thickness, … and functional properties of the sample set.

The present study, reporting the first demonstration of thin film characterization by LIBS imaging was carried out in the context of HTS of amorphous lithium-conducting materials. LIBS is ideal to achieve fast and quantitative analyses of these materials containing mainly light elements, and particularly lithium. In order to assess the methodology, lithium phosphorus oxynitride, which is a solid electrolyte widely used in all-solid-state thin-film microbatteries, have been deposited on silicon wafers by off-axis reactive magnetron sputtering from a single Li_3PO_4 target. The continuous film was patterned as a set of 3x3mm squares thanks to a shadow mask. The film thickness ranges between 10 and 700 nm depending on the target-to-substrate distance, and consequently on the position on the substrate and the process duration, the other process parameters being fixed. A typical material processed in such a way is shown in Fig.1.

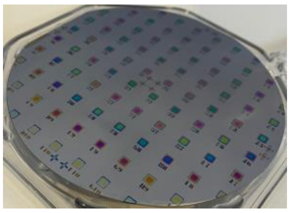

Fig. 1. Square-shaped layers of Lithium phosphate thin-films deposited on a silicon wafer.

The LIBS setup has been described in [1]. Briefly, a 1064nm-8ns-0.8mJ laser beam is focused onto the sample surface on a about10 μm-diameter spot size. A single shot per location is set. The > 5μm-depth ablation craters are much deeper than the film thickness. Different spectrometers enable to detect and analyze emission lines related to Li, P, O, Si and H. XY-translation stage enables to scan the sample surface with a 35μm-spacing. Fig.2 shows a LIBS map of lithium (323nm) resulting from 4 scans of 1250x1050 pixels each covering 20x4 plots with thickness varying from 700 to few tens of nm of LiPO material.

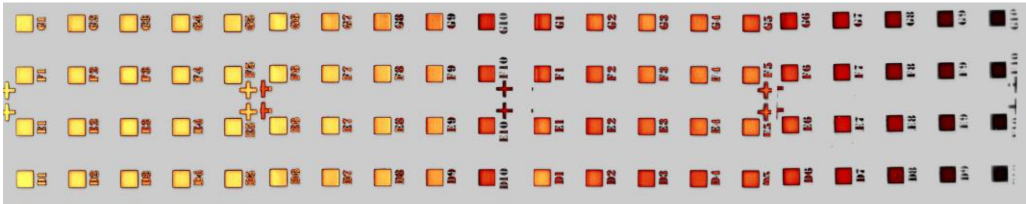

Fig. 2. LIBS map of lithium (323nm) related to samples prepared as in Fig.1; yellow: strong signal; dark: low signal. The half-left series corresponds to 6-hour deposition and the half-right one to 2-hour.

We will present the LIBS spectra and the characteristics of different spectral features driving to variable selection and data extraction. We will also discuss sample homogeneity and demonstrate the relevance of LIBS for future high throughput screening in thin film materials.

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Characterization of lithium isotopes in innovative materials for energy-related applications using elemental mapping based on LIBS analysis

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Lithium is an element of interest in various fields such as geochemistry, archaeology, biochemistry and energy [1]. In this latter field, the increasing demand for lithium induces competition for imports between different countries due to its categorization as a critical raw material [2]. Moreover, its electrochemistry is still being studied to develop innovative materials for future generation batteries. As one of the most sensitive elements in optical spectrometry, lithium is well suited for characterization using LIBS-based techniques. In this work, we introduce the use of this technique to characterize Li-containing materials used for the two applications described below related to the energy field.

The first one is part of the research performed on new materials for lithium extraction from brines. In order to characterize the mechanisms and extraction efficiency of these materials, LIBS imaging can be successfully used. Particularly, localization of the selective adsorption sites of lithium in hierarchical materials by LIBS with a lateral resolution of 8 µm will be presented. The results will be compared with other ones obtained by time of flight secondary ion mass spectrometry (ToF-SIMS).

The second application focuses on lithium batteries, particularly on lithium isotopic labelling in hybrid electrolyte materials constituted by an ionic conductive ceramic in polymer matrix dedicated to solid-state batteries [3]. Thus, we aim at characterizing the mobility of lithium ions and at better understanding its behavior at interfaces in the electrochemical system. For that purpose, we developed Laser-Induced Breakdown Self-Reversal Isotopic Spectrometry (LIBRIS). Based on the same instrumentation as LIBS, the LIBRIS technique aims to overcome the low spectral shift between lines of ^{6}Li and ^{7}Li isotopes using the self-reversal phenomenon. Self-reversal is an extreme case of self-absorption, i.e. absorption by the outer layers of the plasma of photons emitted by the plasma core, for which an absorption dip appears in the center of the emission line. The analytical method is based on the correlation between the wavelength of the absorption dip and the isotopic abundance. We will present experiments on LIBRIS analysis in model stack electrochemical systems (^{7}Li electrode/electrolyte/^{6}Li electrode). Lithium isotopes analysis is developed in depth-profiling mode, and by mapping the lithium isotopic abundance at high lateral resolution over a transverse section of the system. This characterization is performed on samples of variable complexity, from pristine material to hybrid materials used as solid-state electrolytes in Li-ion batteries. This approach aims at providing insight on transport mechanisms of lithium in such materials, with the objective of their optimization to enhance batteries performances.

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Determination of elemental composition and mapping of plastic pellets by LIBS – an interesting tool for plastics recycling

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In recent decades, the use of plastics has drastically increased in almost every aspects of modern life. Mainly produced from exhaustible fossil resources, their recycling has become an increasingly important issue and is one of the main challenges of the energy transition. Plastics are widely used in many fields (automotive, packaging, and housing) and generate a huge quantity of waste, then high-order recycling of plastic plays an important role for a sustainable use of resources. Recycling is beneficial if the resource recovery can be made into profitable industry. **Consequently, efficient identification and classification of plastics are the key for profitable recycling.** Chemical recycling (dissolution, depolymerization or conversion) is needed to develop a circular economy, in which purified monomers and/or polymers can be used in similar applications as the virgin material, which is produced from fossil fuels. In addition, during the chemical recycling of plastics, there is a risk of degrading certain pigments and other additives present in the plastic and generating new organic and inorganic chemical compounds. The most precise organic and inorganic characterization possible of plastic matrix is therefore essential today and in the future, the final chemical recycled product will have to fulfill specifications depending on each application.

To make clear progress in the field of the rapid identification and quantification of polymers and their contaminants, this abstract proposes to use laser induced breakdown spectroscopy (LIBS). LIBS might be able to bring elemental composition over a whole batch of plastic pellets (several tens of pellets) in less than 3 hours providing around 5 M elemental spectra revealing simultaneously about fifteen elemental mapping to compare both batch heterogeneity as well as individual information on each pellet. LIBS technique is also compatible with multi-elemental mapping of the cross section of a pellet in order to quantify the repartition of the elements over a wide dynamic range to the %w up to the ppm that are not clearly evidenced using conventional techniques[1]. Such procedures were developed and are optimised in our institute with high performance LIBS imager (ELM-XS-I, Ablatom) operating under ambient atmosphere on various type of plastics (PET, PP and PE) containing various number of inorganic additives. Mapping of trace elements were observed over pellets (Figure 1) and these results will be shown to emphasize promising perspectives of such a rapid and efficient tool.

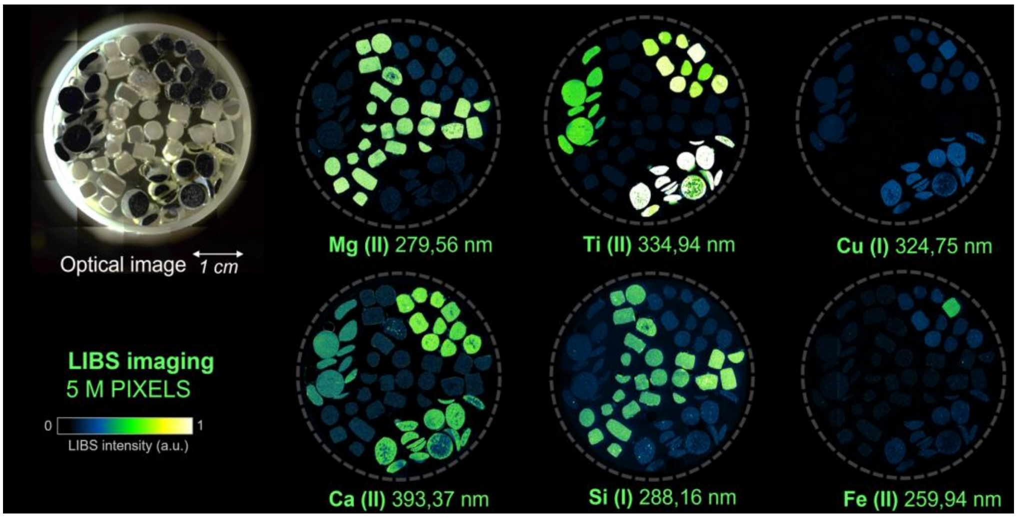

Fig. 1. Optical image and corresponding elemental LIBS images of plastics pellets.

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SESSION 4

Multimodal

Harnessing Multimodal Spectral Imaging: from sensor fusion to autonomous supervisors

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Spectral imaging is a promising technology that leverages the use of spatially referenced spectral signatures to create informative visual maps of sample surfaces that can go beyond what traditional RGB-visual images can offer. Indeed, even distinct spectroscopy modalities may offer distinct information regarding the same sample: for example, Laser-Induced Breakdown Spectroscopy (LIBS) imaging[1] can be used to identify the presence of specific elements on the surface while Hyperspectral Imaging (HSI) [2] may provide valuable information regarding its molecular contents, being both capable to positively impact in multiple industry processes from quality control to material sorting [3,4].

In the path from science to technology, the increasing accessibility to such solutions and the strong market pull has open a window of opportunity for innovative multimodal imaging solutions, where information from distinct sources is set to be combined in order to enhance the capabilities of the single modality system[5]. Yet, in spite of its theoretical potential, the effective harnessing of the power of multimodal spectral imaging is yet to be achieved.

In this presentation, we will overview the current major methodologies utilized for in the context of multimodal spectral imaging, dividing the most common approaches into two large groups: i)hyphenated approaches, where one technique is utilized as a coarser analyzer, followed by the second technique and ii)data fusion approaches, where data from both systems are collected at the same point and combined in complimentary manners. Then, we present an innovative approach to multimodal spectral imaging techniques, that tries to explores the combination of two techniques to capitalize on their individual strengths. In specific, we propose a knowledge distillation framework, utilizing one technique as an autonomous supervisor for the other, leveraging the higher degree of interpretability of one of the techniques to increase the performance and transparency of the other. We present some example scenarios with LIBS and HSI and Raman spectroscopy and LIBS, discussing the impact of this new approach for scientific and technological applications.

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Elemental and mineralogical imaging of Cu-mineralized rocks by coupling μ-LIBS@HSI

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Nowadays there is an increasing global demand for strategic elements, which are required as driving force materials of the transition to clean energy sources and technologies [1, 2]. The decarbonization of energy sources and electromobility depend on the efficient production of Cu-based materials. A fast and detailed instrumental analysis of mineral species in copper rocks is a need in the modern mining industry, but it remains as an analytical challenge. However, conventional techniques have important limitation, e.g., time-consuming, costly, use of toxic reagent, specialized infrastructure and technicians [3]. In this research we address a detailed mineralogical characterization by the combination of micro-Laser-induced breakdown spectroscopy (μ-LIBS), Hyperspectral imaging (HSI) and machine learning (ML) in three different Cu-mineralized rocks. Based on the complementary information obtained by μ-LIBS and HSI we characterized the distribution of valuables element such as copper (Cu), iron (Fe), sulfur (S), among others; and mineral species such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), quartz (SiO_2) and others. Even, in this kind of samples we identified minor elements such as gold (Au), silver (Ag), arsenic (As) and antimony (Sb), which bring valuable information for the valorization and penalization of the copper concentrate at worldwide. The results demonstrate that the elemental and mineralogical characterization of Cu-mineralized rocks can be carried out by the complementary use of both techniques and simple chemometric methods. For the first time in those kinds of samples, a detailed mineralogical distribution was assessed from elemental imaging.

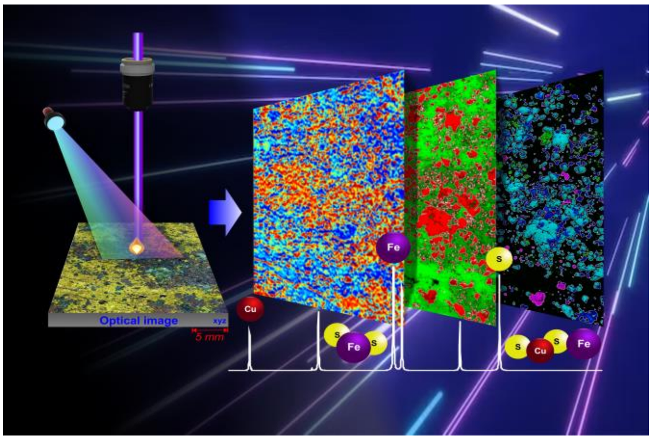

Fig. 1. Elemental and Mineralogical imaging based on μ-LIBS@HSI.

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What can we learn about lithium-ion battery materials from the combination of LIBS and Raman?

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Lithium-ion batteries have become the dominant technology for storing electrical energy in recent decades. For quality control, development of new materials and recycling it is very important to get information about the initial structure and elemental composition but also to understand the processes of aging and degradation of the materials. Therefore, a demand for analytical methods for the investigation of those materials arises. Due to the fact that changes during aging and degradation can occur very locally[1] chemical imaging methods are preferred over bulk analysis methods.

The combination of LIBS and Raman is very promising in this context because LIBS delivers information about the elemental composition and with Raman structural and chemical information about the metal ions, degradation products and the graphite layer can be obtained. From the structure of the graphite layer information about the intercalation of the metal ions into the graphite layer can be derived.[2]

We will present first results on the combination of LIBS and Raman for the investigation of different lithium-ion battery materials, among others lithium nickel manganese cobalt oxide (NMC), lithium cobalt oxide (LCO) and lithium iron phosphate (LFP). This includes the development of models for the quantification of metal content, investigations on the correlation of metal ion content and the graphite structure as well as the investigation of the degradation processes on cathode foils in air.

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A combination of LIBS and LUS for quality control of WAAM components

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In this talk we present the combination of Laser Induced Breakdown Spectroscopy (LIBS) and Laser-Ultrasound (LUS), two non-contact photonic measurement methods suitable for offline and online quality control of Wire Arc Additive Manufacturing (WAAM) components.

In 1925 a novel technology named Wire and Arc Additive Manufacturing (WAAM) was introduced. WAAM also known as Shape Metal Deposition (SMD), Shape Welding (SW) and Shape Melting (SM) belongs to Directed Energy Deposition (DED) based methods in ASTM F2792-12a. It uses arc welding technologies, such as Gas Metal Arc Welding (GMAW), Gas Tungsten Arc Welding (GTAW) and Plasma Arc Welding (PAW), and wire materials to manufacture near net shape metallic components via a layer-by-layer deposition approach. The difference between WAAM and welding are the geometry of the component and resultant effects on the temperature distribution. Due to large progresses in computer aided design (CAD), automated and robotized welding, rather complex components can be produced by WAAM. This is assumed to be one of the most promising additive manufacturing techniques in various branches, such as the aerospace, space and marine industries, owing to its demand for manufacturing complex and large components, high deposition rate and reduced waste material and lead time to reduce costs.

Laser-Ultrasound (LUS) is a contactless method which can be used to detect internal defects and material properties. A short intense pulse of an excitation laser is used to heat up a small spot or even ablate a thin layer of the sample surface. Due to the thermal expansion and/or the rebound effect an ultrasound wave is generated which propagates through the material. At a defect or a delamination, the wave is reflected back to the surface. A laser vibrometer is used to pick up the echos reaching the surface again, which allows us to detect defects and their position.

When we ablate thin layers of the surface for strong LUS-signals as mentioned above, the generated plasma can be used to measure the chemical composition of the material by common LIBS analysis.

Combining both methods simultaneously, shortly after the deposition process, leads to early detectability of various inconsistences like pores, cracks, change in chemical composition due to erroneous gasses or gas flows and changes in the wire alloy. This provides the possibility to quickly adapt process parameters or even trigger a stop. Additionally, the combination of both methods can be used offline in the lab for a more precise quality control of the produced WAAM parts.

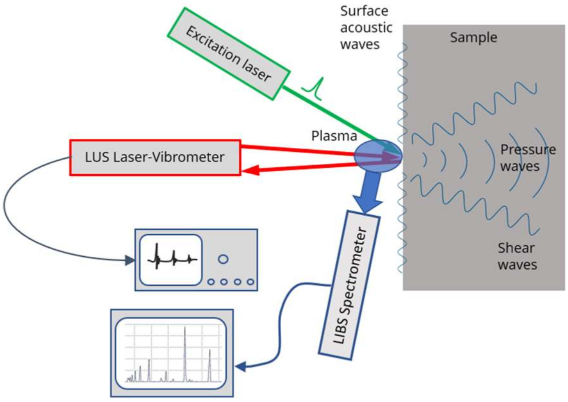

Fig. 1. Combined LIBS-LUS-setup

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ISOTOPE DETECTION BY MICROWAVE-ASSISTED LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Laser-Induced Breakdown Spectroscopy (LIBS) is a well-established online elemental detection technique that highly benefits from minimal requirement for sample preparation, applicability to solid, liquid, and gaseous samples, and robust experimental arrangement [1]. Due to the substantial broadening of the atomic emission lines in the dense and hot plasma, the isotopic shifts in atomic emission lines cannot typically be resolved. Laser Ablation Molecular Isotopic Spectrometry (LAMIS) utilizes the isotopic shift in the molecular emission observed in the cooling laser-induced plasma plume [2]. However, as the plasma plume expands and cools down rapidly in the ambient atmospheric conditions, the time window for detection of the molecular emission in the laser-induced plasma is short and/or high energy ablating pulse is required, thus, limiting the sensitivity and/or applicability of the method.

In this work, microwave radiation is used to extend the plasma emission lifetime and, consequently, extend the time window to observe the molecular emission. The experimental arrangement is shown in Fig. 1a. Microwave-Assisted LIBS (MW-LIBS) [3] can extend the plasma emission lifetime from the typical ~20 μs in conventional LIBS to several milliseconds in MW-LIBS. The plasma conditions in the microwave-maintained plasma plume are similar to the late conventional plasma plume with temperature of ~5000 K and electron density of ~10^{16} cm^{-3} creating suitable environment for the formation of molecules in the excited electronic states. The MW-LIBS approach is utilized for the detection of $^{11}B/^{10}B$ fraction. Emission from diatomic and triatomic molecules, namely ^{10}BO, ^{11}BO, $^{10}BO_2$ and $^{11}BO_2$ have been observed. The isotopic detection is based on the isotopic shift recorded in the molecular emission from BO and BO_2 molecules. Fig. 1b shows the spectra of ^{11}BO and ^{10}BO $B^2\Sigma^+$-$X^2\Sigma^+$ system's (0-2) band at 255.2 nm and at 255.9 nm, respectively. The spectra are obtained from separate solid boric acid samples containing ^{11}B and ^{10}B isotopes. Similarly, the Fig. 1c demonstrates the isotopic shift in BO_2 $A^2\Pi_u$ - $X^2\Pi_g$ transition's (200-000) band.

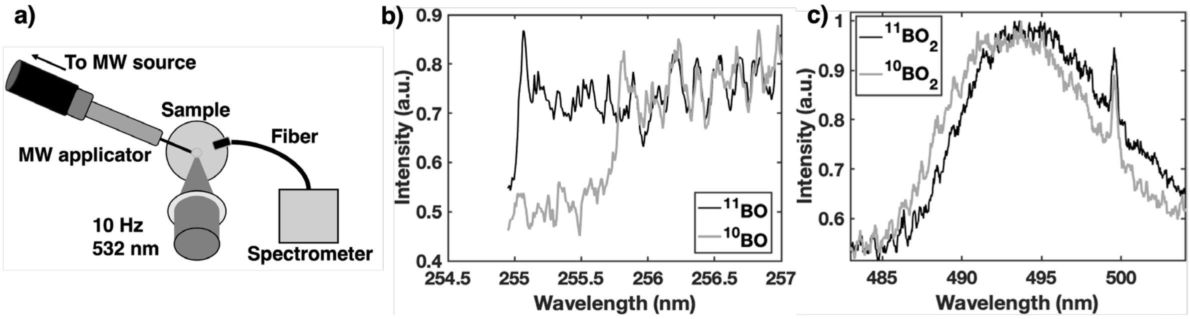

Fig. 1: a) The experimental arrangement, b) an example spectrum from ^{11}BO and ^{10}BO, and c) the isotopic shift in BO_2 200-000 band obtained with MW-LIBS. The gate delay from the ablation laser pulse is 10 ms and the gate width is 900 ms. Laser ablation energy is 12 mJ and microwave power is 540 W.

Use of MW-LIBS reduced substantially the need of averaging over laser pulses and required lower ablation energy than previously demonstrated with LAMIS technique enabling future development of more compact and cost-efficient isotope detection arrangements for online applications. The applicability of the method is further studied for different elemental isotope fractions and molecules, such as $^{35}Cl/^{37}Cl$ fraction using emission from CaCl molecule.

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SESSION 5

Instrumental & Industry

Towards universal calibration libraries for LIBS payloads

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The exploration of near celestial bodies, such as Mars, Moon, and asteroids, requires accurate elemental analysis of their surfaces. Laser-Induced Breakdown Spectroscopy (LIBS) has proven to be a convenient approach for this purpose, but it is influenced by various experimental parameters and sample matrix effects. Understanding the laser ablation processes and plasma formation under different ambient conditions on celestial bodies is crucial for reliable LIBS analysis. We propose a transfer-learning approach to address calibration challenges in Moon-like and Martian conditions. A calibration dataset will be collected at feasible pressures, and numerical modeling will extend it to lower pressures. A deep learning model will then transform the calibration dataset to the chosen ambient conditions.

This project aims to elucidate the LIBS signal's dependence on measurement and instrumental parameters, using a unique dataset. The transformation functions between source and target datasets will be established, enabling accurate LIBS data prediction for distinct systems on near celestial bodies. In this talk, we will present our recent advances in transfer learning when improving regression models based on ChemCam and SuperCam datasets. [1, 2] Moreover, we strive to formulate new goals that will challenge the LIBS community and set a platform for cooperation.

ACKNOWLEDGEMENTS

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LIBS APPLICATIONS OF ONLINE MONITORING AND 2D/3D MAPPINGS FOR ADVANCED CONTROL OF INDUSTRIAL PROCESSES

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Advanced monitoring and control methods are significant in the industrial processes. Laser-induced breakdown spectroscopy (LIBS) is an analytical detection technique based on atomic emission spectroscopy to measure the elemental composition, which has been widely applied in various fields [1]. In this study, LIBS applications of online monitoring and 2D/3D mappings were demonstrated for advanced control of industrial processes.

A collinear long and short DP-LIBS method (LS-DP-LIBS) was developed to improve the detection ability and measurement accuracy by the control of the plasma cooling process using the long pulse-width laser irradiation [2]. The plasma generated by the short pulse-width laser is stabilized and maintained at high temperature during the plasma cooling process by long pulse-width laser radiation. C, Al, Si, S, Ti, Cr, Ni, Cu, Nb, Mo, Mn, B, and P concentration measurements in molten steel samples were performed using LS-DP-LIBS(Fig. 1). It demonstrates the feasibility of multi-element concentration measurements in iron and steel making processes and this will lead to the advanced monitoring and control methods in these processes.

The analysis of elemental composition distribution is indispensable to ensure the quality of various materials production. In this regard, 2D/3D mapping techniques using LIBS are widely used in various fields. In many LIBS studies, lasers with ns pulse widths are used, and the spatial resolution of 2D LIBS mapping is usually several to several tens of micrometers. In this study, a spatial resolution of 1 µm was achieved by using a laser with a pulse width of 9 ps. This LIBS mapping system consists of a picosecond laser, lens, spectrometer, ICMOS camera, and XYZ stage. The LIBS system was applied to steel and Li-ion battery electrodes for 2D elemental distribution analysis. The steel sample has a structure with Zn coating around the steel at the µm level, and this LIBS mapping system was able to detect the Zn distribution around the steel at the µm level. This result was in good agreement with the SEM-EDS measurement. LIBS has the advantage of elemental composition mapping without the need for high vacuum conditions and has many advantages when applied to industrial processes. In the future, the LIBS analysis speed is improved to 1 kHz and the LIBS system is utilized for elemental composition mapping in industrial processes.

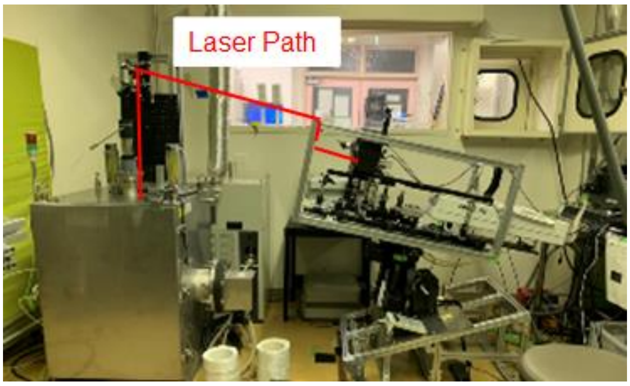

Fig. 1. Experimental setup for remote LP-DP-LIBS.

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LIBS and LA-SD-OES for the discrimination of technical polymers

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Spark optical emission spectroscopy (spark OES) and Laser-induced breakdown spectroscopy (LIBS) are advanced element analysis methods that are widely used in the metal industry (spark OES) and in many different industry branches (LIBS [1]). While spark OES requires samples that are electrically conductive, LIBS can be employed to nearly all kinds of materials. However, LIBS is suffering from the matrix effect, i.e. the sensitivity and limits of detection depend on the structure and composition of the sample matrix. We combine electric spark discharge and laser ablation for the excitation of analytical plasma and optical emission spectroscopy (Laser Ablation Spark Discharge OES, LA-SD-OES). This combination has been shown to overcome the matrix effect for high alloyed steel samples [2]. Here, we report on further advancements of the LA-SD-OES method to measure also non-conductive samples. A low-to-mid energy laser pulse is applied to the sample inducing a faint plasma that triggers an electric spark discharge between two electrodes. The optical emission of the laser-induced/spark plasma is measured (Fig. 1).

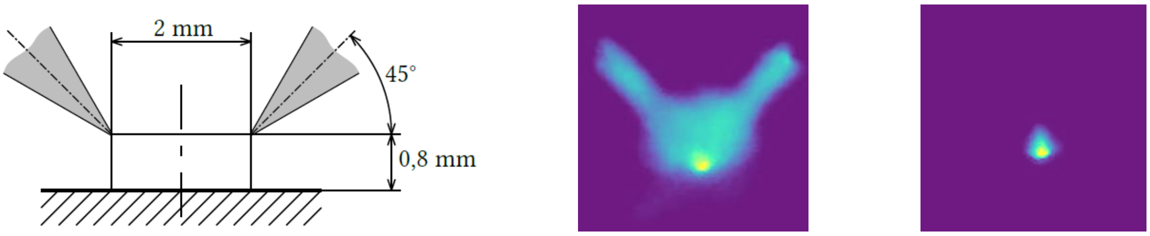

Fig. 1. Electrode tips close to an electrically non-conductive sample (left). Photographs of LA-SD-OES plasma (center) and LIBS plasma (right). Laser pulse energy 4 mJ and spark discharge energy 50 mJ.

Different technical polymers (PA6, PC, PE-HD, PET, PMMA, POM, PP, PS, PTFE, PVC, UHMWPE, etc.) are measured by LIBS and LA-SD-OES aiming to distinguish the materials by distinct spectral features. Molecular emission bands of CN and C_2 as well as atomic lines of O, N, H, and of some specific elements are measured and the correlation of intensities is used for materials discrimination. For polymers containing halogens LA-SD-OES outperforms LIBS. Measurements for flame retardant and UV-resistant additives are ongoing. The damage of the polymer sample surfaces stays minimal as the electric spark discharge does not contribute to the ablation process.

ACKNOWLEDGEMENTS

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Conversion of an industrial single-pulse LIBS system to double-pulse operation to improve sulfur detection in rubber-based parts

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The detection of sulfur as an elementary component of the crosslinking system of rubber compounds is difficult in LIBS single-pulse operation [1; 2] due to the usually low concentration and the poor response behavior of the analyte. However, reliable proof of the distribution quality of sulfur in the compound is a decisive quality criterion for the homogeneity of the crosslinking density achievable during vulcanization, which is important for the uniform performance of an elastomeric article, especially under dynamic load.

Therefore a commercially available industrial LIBS system, (1064 nm Nd:YAG solid state laser, 100 mJ, 20 Hz) is extended with a 266 nm laser (Nd:YAG solid state laser, 50 mJ, 20 Hz) to combine an UV-based initial excitation (for increased ablation) followed by an IR-pulse (to realize highest plasma heating) to improve sulfur detection in rubber based compounds and parts. [3; 4] Optimization of the system parameters are investigated to improve the ablation efficiency and to increase the measured signal intensity/signal-to-noise-ratio of the analyte. The VUV sulfur lines at 180.658 nm, 181.956 nm, and 182.561 nm and the NIR sulfur lines at 921.298 nm, 922.823 nm, and 923.751 nm are under investigation. [5]

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30 years of LIBS in civil engineering – A transfer from the laboratory to practice

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LIBS as a versatile tool has been presented for many different applications in the scientific community. In the last 30 years, LIBS has been explored for the use in civil engineering to detect harmful species like chlorides, sulfates, and alkalis [1,2]. While using a scanning procedure the multi-phase structure (heterogeneity) caused by the binding matrix and the aggregates, can be determined and therefore the ingress of these harmful species into the porous structure is considered to the binding matrix only. Standard methods in civil engineering (e.g. wet chemistry) cannot provide that.

Currently, it is primarily used in research institutions and but the interest of the industry like building materials laboratories is increasing. Optimized commercial devices have also been developed, which greatly simplify the application due to the high degree of automation. A prototype of a mobile LIBS systems allows an on-site application as well. A limiting factor for the use of LIBS in the commercial sector, is the lack of norms and standards. Therefore, within the framework of a project funded by the German government, a leaflet on quantitative chlorine determination in concrete has been prepared, which will be published this year (2023). In interlaboratory comparisons the robustness and accuracy for the practical application was demonstrated.

During the presentation, the story as well as the state of the art of LIBS in civil engineering will be presented and future challenges will be outlined.

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Advances in LIBS Direct Analysis of Particle Flow: From Plasma Characteristics to Practical Applications

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Laser-induced breakdown spectroscopy (LIBS) direct analysis of particle flow has emerged as an adaptive measurement scheme for process industries [1], including additive manufacturing, power generation, and raw material production. However, it encounters bottlenecks in signal uncertainty, resulting in less precise quantitative analysis. Considering the complex interactions between laser and particles, we investigated plasma morphology fluctuations of four plasma patterns arising from stochastic particle ablation in particle flow analysis. With the understanding of plasma excitation instability, plasma modulation methods were proposed, such as metal target-assisted excitation, optics optimization, and spark-induced plasma excitation. We also devised a spectra identification method based on the standard deviation of characteristic peak intensities. By incorporating plasma modulation methods and spectra identification, the measurement repeatability of particle flow analysis became comparable to bulk sample analysis. To address practical applications, such as coal-fired unit operation control and carbon emission verification, we developed a fly ash analyzer for in-situ, real-time analysis of unburned carbon content and a rapid coal quality analyzer for proximate and elemental analysis, both fulfilling the performance capability required for industrial applications.

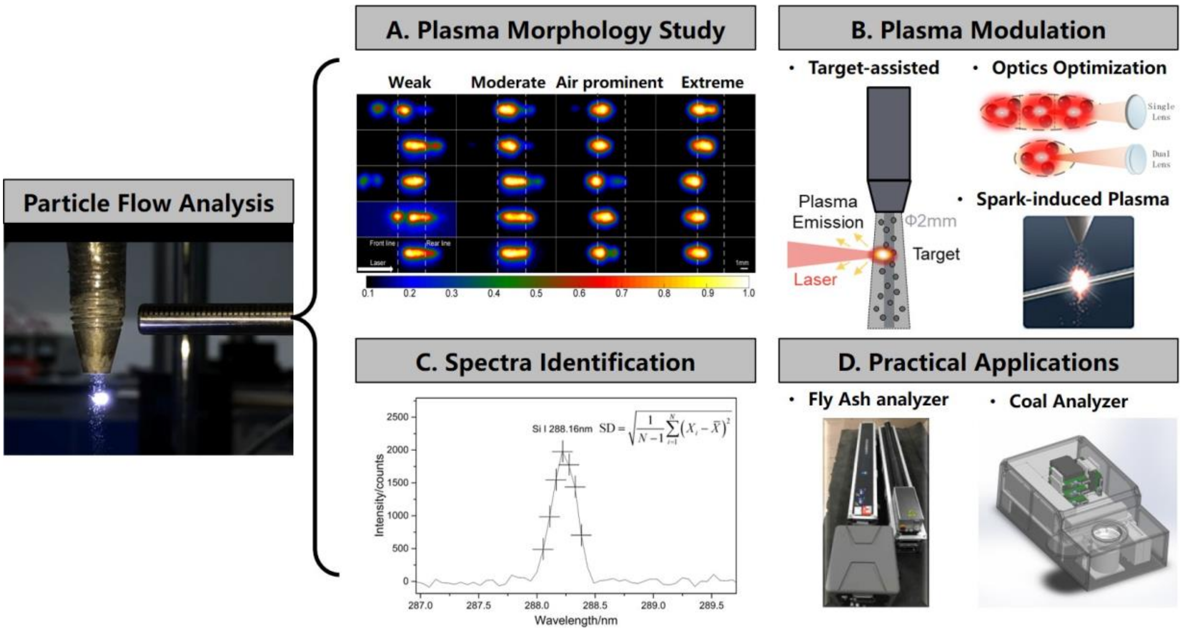

Fig. 1. Overview of advances in LIBS direct analysis of particle flow.

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SESSION 6

Industry

Opening up industrial applications for inline analysis with LIBS

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The main motivation for inline chemical analysis in industrial applications is to measure the composition of the materials to be processed quickly and consistently to adjust the process control to it on time or to take fast decisions about subsequent processing steps. The goal is to achieve well-defined, reproducible final compositions of refined and sorted materials, semi-finished and finished products, while the chemical composition of the input streams or process variations cause permanently changes.

In most cases, the information about the chemical composition of the input materials is based on company know-how, information from the suppliers, and random measurements with laboratory-based analytical methods for which samples have to be taken from the process line. However, there are significant time intervals between these spot tests. Often they do not keep pace with the dynamics of process inherent compositional fluctuations. Feedback actions are delayed and respond not adequately to these changes. A fast inline analysis with 1 to 1000 measurements per second can overcome this drawback, allowing for a real-time monitoring of the compositional variations to follow the dynamic behaviour and trends in the respective process line. However, based on their experience with laboratory methods, users often expect the analytical performance of inline methods to be equal to that of laboratory methods.

This ignores the fact that for laboratory analytical methods, the sample often has to go through various preparation steps before it is analyzed in a defined measurement environment. This preparation itself is prone to so-called sample preparation errors. Established standards, calibration and recalibration methods exist for these procedures. The accuracy of the analyses can thus be evaluated. For inline analysis, the challenge is to perform measurements in the typical process environment - characterized by different atmospheric conditions, dust loads, vibrations, surface contamination of the sample, state of motion of the sample. In general, standards are not available and calibration, as well as recalibration procedures, can not simply be transferred from offline to inline analysis.

The basic suitability of LIBS for inline analysis is well known. Successful implementation for industrial applications requires the elaboration of procedures for optical access to the measuring object, control of environmental conditions, mitigation of the influence of interfering factors, and tailored calibration and recalibration procedures. The latter is mandatory, especially with regard to traceability to established standards.

An overview of LIBS systems already routinely used in the industry and LIBS systems currently under development is given. These comprise stationary and mobile systems. The approaches taken to enable inline measurements are highlighted exemplarily.

ACKNOWLEDGEMENTS

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Inline-LIBS for the metal recycling industry

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The industrial production of crude metals relies to an increasing degree on recycling. The remelting of scrap is reducing the consumption of natural resources such as ore minerals and energy, and thereby also carbon dioxide emissions in comparison to primary metal production. The intention to increase the fraction of secondary metal production implies the use of an input material feedstock with higher variability. Scrap grades of lower quality due to a mix of material composition and contaminations are to be treated by the plant without reduction of output material quality. The control of the material feedstock is an important measure for process and quality control.

In this work, a LIBS sensor was developed for the monitoring of scrap metal feed batches. The sensor is designed for retrofitting into existing metal recycling plants and their material handling processes. Individual material batches as delivered to the plants or transported internally are analysed to determine their average composition. For this purpose, the LIBS system uses a 3D laser beam scanning in order to achieve a full representation of the inspected material. Its operation is based on a geometry inspection of the material surface using laser line section technology. In addition to plasma excitation on the individual scrap pieces, the single ND:YAG laser beam source is also employed for the removal of surface contaminations on the metal.

The presentation comprises the experience of field trials of the LIBS sensor in different industry installations. Each application implies its own challenges, ranging from drill chips with lubricants, material from thermal pre-treatment, dirty shredder scrap, and material including metallics and non-metallic chemical compounds. Trials are performed on-site in plants for aluminium, steel and lead metal recycling.

Fig. 1. Continuous flow of aluminium metal chips inspection by scanning LIBS sensor.

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New developments on LIBS technologies for the Cu-industry

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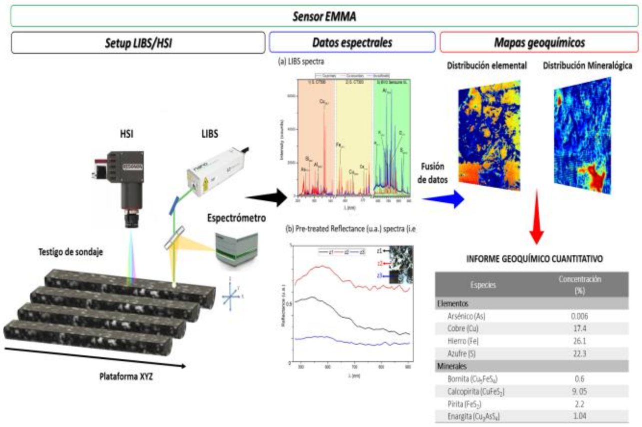
The global decarbonization of energy sources depends on the production of raw materials like copper. The demand for copper will grow a 20.7% by the year 2030, mainly supported by the transition to green energy sources, electromobility, and new electrical networks. Thus, copper production requires overcoming the problems of traditional atomic spectroscopy and moving to new online sensors to obtain rapid analytical information. In this sense, "Eleminerals SpA" is a new startup born in the Universidad de Concepción-Chile that aims the development of new customized analytics for the copper industry based on Laser-Induced Breakdown Spectroscopy (LIBS), Hyperspectral Imaging (HSI), Diffuse reflectance spectroscopy (DRS) and Machine Learning (ML). In this presentation we show new LIBS based developments for online elemental and mineralogical determination at different stages of the copper production, such as exploration and metallurgical processes. In this sense, we have developed different setups for quantitative determination of valuable elements, manly Cu, Mo, Ag, Au, and toxic one like As, Pb, Zn, S, Fe, with a simultaneous mineralogical determination of species such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covellite (CuS), chalcocite (Cu_2S), Bornite (Cu_5FeS_4), pyrite (FeS_2), enargite (Cu_3AsS_4), among others [1-2] in samples like copper ores, rocks and drilling cores. Furthermore, LIBS-based sensors for mineralogical 2D mapping in rocks and drilling core is presented. Also, stand-off LIBS for monitoring of Cu, O and S in molten phase along the desulfurization process is described [3]. These laser-based sensors present a great potential for improving the analytical assessment in the copper production avoiding tedious, contaminant, time consuming and costly analytical classical techniques.



Especies	Concentración (%)
Elementos	
Arsénico (As)	0.006
Cobre (Cu)	17.4
Hierro (Fe)	26.1
Azufre (S)	22.3
Minerales	
Bornita (Cu_5FeS_4)	0.6
Calcopirita ($CuFeS_2$)	9.05
Pirita (FeS_2)	2.2
Enargita (Cu_3AsS_4)	1.04

Fig. 1. 3D-design for EMMA: Elemental and Mineralogical analyzer based on LIBS@HSI.

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LIBS In situ Chemical Analysis in Duplex Stainless Steel Welding

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The high corrosion resistance and good mechanical properties of duplex stainless steel (DSS) are due to its special chemical composition, which is a balanced phase ratio of ferrite (α) and austenite (γ). Many industrial applications require the integration of DSS components. For this, tungsten inert gas welding (TIG) is an excellent choice, as it allows an automated operation with high reproducibility. However, when the weld pool solidifies, critical ratios of α- and γ-phases can occur, which leads to solidification cracking, increased susceptibility to corrosion, and a decrease in ductility and critical strength. Previous studies have shown that these defects can be caused by the accumulation of manganese and chromium in the heat affected zone (HAZ), and this accumulation can be detected using LIBS [1, 2].

Unlike conventional LIBS analyses, which requires reference samples to generate a calibration curve, calibration-free LIBS (CF-LIBS) can determine the chemical composition solely from the emission spectrum of the plasma. Numerous publications [3, 4] show that CF-LIBS is a fast and efficient analytical method for quantitative analysis of metal samples.

We present the results of in situ CF-LIBS analysis during TIG DSS welding. Using a new approach, it is possible to quantitatively determine the chemical composition of the weld metal directly in the welding process. The results of the CF-LIBS analysis are compared with the results of the calibration-based PLS analysis and reasonable agreement is found. Thus, the CF-LIBS method offers the significant advantage of quickly measuring in situ the concentrations of the main alloying elements that prevent the formation of welding defects, without the tedious calibration procedure.

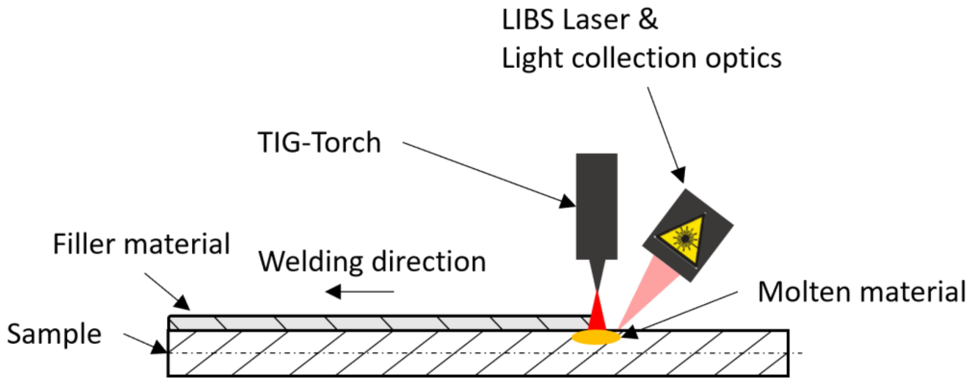

Fig. 1. Principal sketch of the experimental set-up of the TIG welding and in situ LIBS measurement.

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Deployment of LIBS Analyzers in the Aluminum Industry

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We will review the commercial deployment of LIBS-based liquid-metal analyzers in the aluminum industry. DTE's elemental analyzers are currently being used in primary aluminum production plants as well as in secondary production of aluminum alloys and in aluminum recycling. Each industrial segment has different requirements in terms of measured elements, concentration ranges, and accuracy. We will discuss the trade-offs in hardware design that are necessary to meet the different requirements, as well as the need for automation or portability [1-3].

Measuring chemical composition of metals or alloys directly in their liquid state introduces certain challenges but also presents unique advantages. We will describe how LIBS measurements can reveal metallurgical information that cannot be derived from conventional elemental analysis on solid samples. One such example is the capability to study the behavior of highly volatile alloying or trace elements in the melt [4]. Another example is the ability to monitor in-situ the formation and dissolution of native solid phases in liquid binary alloys on a time scale of seconds [5]. This presents new opportunities for the application of LIBS in metallurgical research.

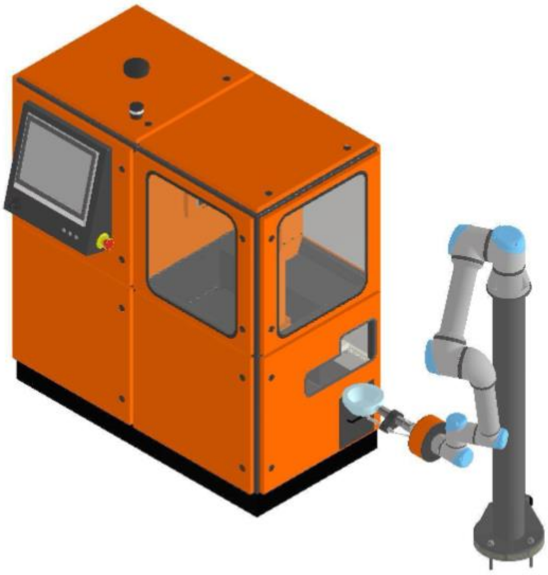

Fig. 1. Automated LIBS analyzer for liquid metal.

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In-situ Chemical Composition Analysis of Molten Aluminum Alloys in Industrial Furnaces by LIBS

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Fast and accurate determination of chemical composition of the molten aluminum during the production of standard alloys plays a critical role in aluminum industry. Laser Induced Breakdown Spectroscopy (LIBS) is a fast analysis technique used for measuring the chemical composition without any sample preparation with ppm level precision [1]. Furthermore, it eliminates operator-related errors and reduces the time of sampling preparation from molten aluminum. In this study, in-situ measurements of elements in molten aluminum in industrial furnace were carried out with LIBS. For measurements, diode pumped Nd:YAG with 100 mJ energy, 4.4 ns pulse length, 10 Hz repetition frequency and a Czerny Turner type spectrometer with a 0.1 nm resolution were integrated to the ST LIBS system. The laser pulses were focused with a 50 cm focal length lens into molten aluminum at 700°C with a special tube. Spectral measurements were performed through the molten aluminum under argon gas pressure in the furnace. The photons emitted from the plasma were collimated by a parabolic mirror with a focal length of 4 inches and transferred to the slit of the spectrometer with optical fiber. Elements such as Mg, Si, Cu, Fe in molten Al were measured qualitatively and quantitatively and alloys were classed. Principle Component Analysis (PCA) technique was used for classification of aluminum alloy types. Fig.1. illustrates the ST LIBS system setup for molten aluminum analysis.

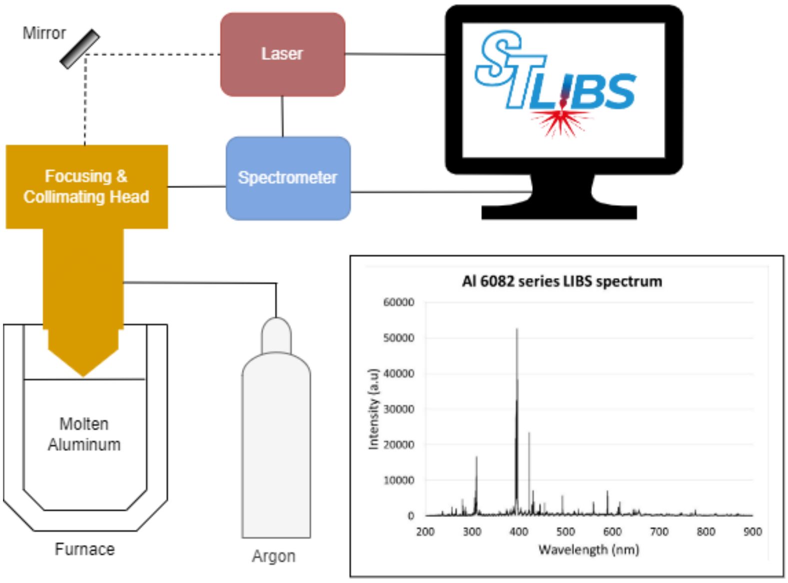

Fig .1. ST LIBS system setup for molten aluminum analysis

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SESSION 7

Mining and Geological applications

The Laser-Induced Breakdown Spectroscopy Assisted with Laser-Induced Fluorescence (LIBS-LIF) advantage and drawbacks for mining and energy applications

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Laser-induced breakdown spectroscopy (LIBS) has seen significant advances and expanded adoption in recent years. In particular, LIBS is being implemented in industrial applications, where it can provide important advantages over other techniques. In mining applications, exploration of precious metals is very challenging, because the cutoff grade continues to decrease as the value of metals increases. So, the mining industry is on the lookout for new technologies that meet their cost reduction needs and decarbonization of their process. One of these innovative technologies, the development of which would be a major breakthrough, is the measurement of precious metal concentrations in ore, in real time and on site, during various stages of exploration and mining.

During the last three decades, in order to fulfil some industrial needs in terms of sensitivity, extensive research has been carried out to improve LIBS sensitivity and performances by several approaches such double pulse mode, combining LIBS with laser-induced fluorescence (LIF) among others etc. The approach of LIBS combined with LIF (LIBS-LIF) is an emerging analytical tool that has the potential to analyze rapidly and in situ with little or no sample preparation any kind of materials. It is a good candidate to fulfil the needs for real time analysis in mining, environment and clean energy applications.

LIBS-LIF approach uses a first conventional laser to ablate the sample and generate a plasma. Then, a second tunable laser (based on an optical parametric oscillator (OPO)) selectively excites the plasma ablation and thus enhances the emission of spectral lines of interest. Different combinations of excitation/fluorescence lines as well as plasma generation creation conditions were studied to optimize the performance of the LIBS-LIF for spectrochemical analysis in our laboratory and elsewhere.

In this presentation, we will highlight the most significant research contributions for improving the quantitative analysis by LIBS-LIF in terms of sensitivity and accuracy for environmental, agriculture and mining applications. We will present some novel approaches aimed at the improvement of the analytical figure of merit of LIBS-LIF. Finally, a viewpoint on the LIBS and LIBS-LIF combination and their future will be given.

Dedicated LIBS tools for characterizing geomaterials

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Following the phase of interpretations, experimental developments, and demonstrations, laser spectroscopy techniques such as LIBS, Raman, and other are gradually moving towards widespread use to solve a variety of on-site compositional characterization problems encountered in various fields. In several cases, such a valorization step cannot be properly addressed using off the shelf technologies and then further efforts are needed to develop dedicate devices, application methodologies, and software, according to the well known "problem led approach". During the last decade, our group has had the opportunity to gain experience on investigating characterization problems concerning geomaterials, which were successfully solved through the development of novel laser setups and measurement protocols. In particular, fruitful collaborations were established and promising advances have been achieved within the upscaling and networking projects of the KIC-Raw Materials, such as InSITE "*Insitu ore grading system using LIBS in harsh environments*", InnoLOG "*Innovative geophysical logging tools for mineral exploration*", PIMAS "*Portable Instant Mineral Analysis Systems*", and related R&D services. Here, we discuss the basic ideas of the systems prototyped along with associated application procedures and results. These show that despite the rapid and impressive market evolution of the portable laser spectroscopy techniques, there is still room for further instrumental improvements and significant extension of the application domain of the laser spectroscopy.

ACKNOWLEDGEMENTS

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When LIBS can help the geologist

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If there's one main question geologists ask themselves when examining their samples, it's "where are my trace elements? ". In fact, where are the invisible elements present in my rock, hidden in which mineral phases? We generally carry out bulk analyses to determine the content of elements of interest, as the economic aspect is now paramount in view of the increasing demand for certain critical elements. Our Geology & Ressources team is focused on several topics related to the research of critical elements such as the light and critical elements or Rare Earth Elements (Y, La, Ce …).

The global demand of light elements (lithium and beryllium) that are hardly detected by common analytical methods (SEM, EMPA), is currently increasing due to their use in the manufacturing of batteries, connector components or even used in so-called green energy technologies. We will see in several case studies that the portable LIBS tool can be used to determine lithium content directly [1, 2], in order to better select sampling or to help drill follow-up at the mine site. Access to µLIBS imaging is an essential step in constraining Li distribution in micas, as Li content is generally only obtained by stoichiometric calculation with major elements.

We recently studied several metamorphic rock samples from the Sanandaj-Sirjan area in Iran, where deposits of Rare Earth Elements are located. µLIBS imaging was undertaken with a spatial resolution of 15 µm, allowing the identification of rutiles, zircons and pyrites in addition to classic paragenesis minerals. But in this case, µLIBS imaging highlighted the Yttrium enrichment of the garnets and the presence of numerous La-Ce-Y minerals dispersed in the matrix. Luminescence bands observed in some LIBS spectra suggest the presence of other REEs (Dy or Gd).

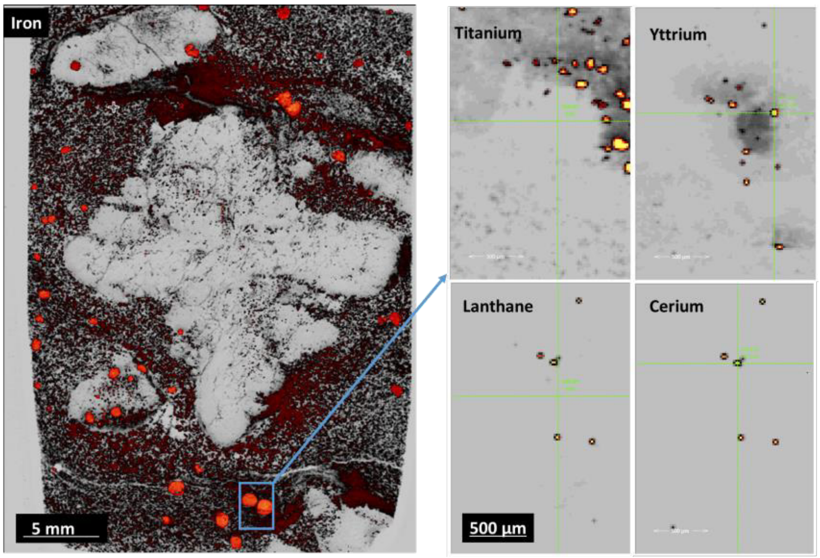

Fig. 1. µLIBS imaging on rock thin section displaying garnets enriched in yttrium and numerous microscopic Y-La-Ce minerals

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LIBS profiles of sedimentary sections: a new tool for paleoclimatic and paleoenvironmental reconstructions?

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Reconstructing climates and/or environments of the past requires analysis of sedimentary sections based on profiles of various geological data (geochemistry, sedimentology, mineralogy, paleontology, ...). LIBS analysis can be carried out with a fast acquisition rate on minimally-prepared samples, allowing measurement of large geological sample sets such as sedimentary sections.

Here we show preliminary results obtained from a field and a core section to illustrate the potential of LIBS for paleoclimatic and paleoenvironmental studies.

The studied field section consisted in 6 m thick Devonian siliciclastics with varying carbonate content used as a reference for cyclostratigraphy (New York State, USA [1]). 300 samples were analyzed manually in less than two days and the results showed very good match with the XRF measurements previously used for astrochronology, including productivity (Ca) and detrital (Ti, Al, etc.) proxies. Therefore, astronomically-forced climatic cycles could be analyzed based on LIBS data as it is reliably done with XRF.

The studied core section, which consists of 150 m of Ypresian to Bartonian formations (Le Tillet borehole, France) was more challenging for LIBS measurement as it consists of both soft siliciclastic sediments and consolidated carbonate rocks [2]. Therefore, the 157 selected samples were powdered and fixed onto double-sided adhesive and automatically analyzed with the LIBS within about 1 hour. The obtained data, still under interpretation, showed that some elemental ratios such as Cs/k and Li/k exhibit interesting correlations with mineralogical and environmental data (Fig. 1).

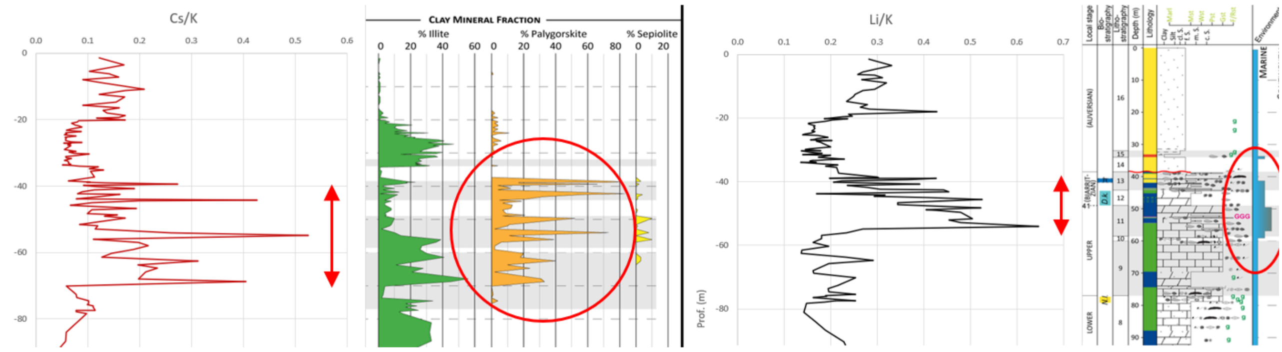

Fig. 1. Elemental ratio profiles Cs/K and Li/K measured by LIBS on Le Tillet borehole (Upper Lutetian, Paris Basin).

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Analysis of palladium in rock ore by Laser-Induced Breakdown Spectroscopy (LIBS) and characterization of the morphology of laser-produced craters

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The mining industry is looking for ways to improve the energy efficiency and reducing GHG emission through innovative technologies enabling real time analysis in their process. In particular, geologists are interested in the rapid characterization and measurement of the concentration of Platinum Group Elements (PGE, which include Pt, Pd, Rh, Ru, Ir, Os) in rocks at mine sites. LIBS is an emerging technique in geochemistry that allows rapid in situ analysis of the elemental and mineralogical composition as well as the measurement of the concentration of targeted elements [1]. This work demonstrates the analytical applicability of LIBS as an analyzer for assessing the palladium content in different types of ore.

Three types of palladium-bearing ore with different mineralogy were analyzed by LIBS: two with high Ni-Cu-(PGE) and Fe content (36% and 22.5% of iron), namely one from the Sudbury mine (Ontario, Canada) and one from the Raglan mine (Québec, Canada), and the third type from the Si-rich deposit with low iron content (~5% of iron) from the Lac des Îles palladium mine (Ontario, Canada). To calibrate the LIBS instrument, we used three sets of certified reference materials in the form of compressed powders with a quasi-homogeneous concentration of palladium ranging from around one part per million (ppm) to 500 ppm. The palladium concentration was determined by LIBS using the Pd line at 348.115 nm and the average Pd concentration was compared to that obtained by conventional chemical analysis. In addition, using optical coherence tomography (OCT) and scattering electron microscopy (SEM), we investigated the crater morphology in the three major phases of a palladium ore fragment from the Lac des Îles mine (see **Fig. 1**), namely plagioclase feldspar, amphibole, and sulfides, as determined by µ-XRF analysis. For plasma characterization, the electron temperature and electron number density of the plasma during crater formation in the three phases were also determined using emission spectroscopy standard methods.

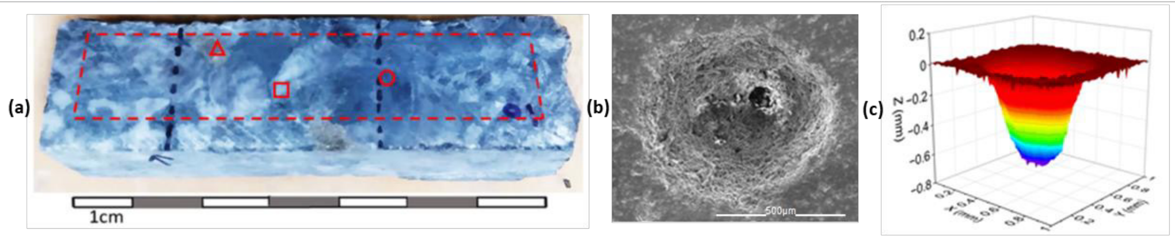

Fig. 1. (a) Photograph of one fragment of a drill core from the Lac des Îles mine with enhanced contrast before laser scanning, (b) SEM images at 300X of craters produced by laser ablation in the plagioclase phases for 1000 laser shots, and (c) OCT image of the ablation crater for the same phase.

ACKNOWLEDGEMENTS

We are grateful to Impala Canada for providing us with quarter drill cores from the Lac des Îles mine and their laboratory analysis, as well as for their financial support. This work was primarily supported by the National Science and Engineering Council of Canada (NSERC).

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High-Throughput micro LIBS imaging on geological applications

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LIBS has shown the potential to be a "Swiss Army Knife" for elemental geological analysis.[1] The development of the technique has allowed it to be implemented for geological characterization either inside a backpack[2] or on board a rover on the Martian surface. [3] Furthermore, the on-laboratory measurements have also demonstrated their great practical value. In particular, the significant evolution shown by LIBS in imaging applications has provided new functionality to this technique. [4]

Nevertheless, the compromise between resolution (considering the distance between 2 sampling zones) and speed of analysis is one of the significant challenges to be faced because of the total analysis time per sample. In many cases, it can be overcome when the sample size is relatively compact; however, this is not always possible. y incorporating a kHz-laser [5], it is possible to analyze larger regions without compromising image resolution.

We present a compilation of geological applications of interest, showing the potential and relevance of LIBS imaging in this field. In particular, we have selected a panel of applications for kHz-LIBS imaging, including the detection of light elements (e.g., Li, Be), the potential LIBS for the detection of elements with potentially high economic interest, such as rare earth elements (e.g., Y, La) or Polymetallic nodules (mineral concretions on the seabed containing valuable metals); and, additionally, imaging of thus elements considered as "non-friendly" for LIBS, such as Sulfur.

Finally, we will present the challenges concerning the data processing associated with using kHz-LIBS, as well as a critical perspective on the future of kHz-LIBS imaging in the geological field.

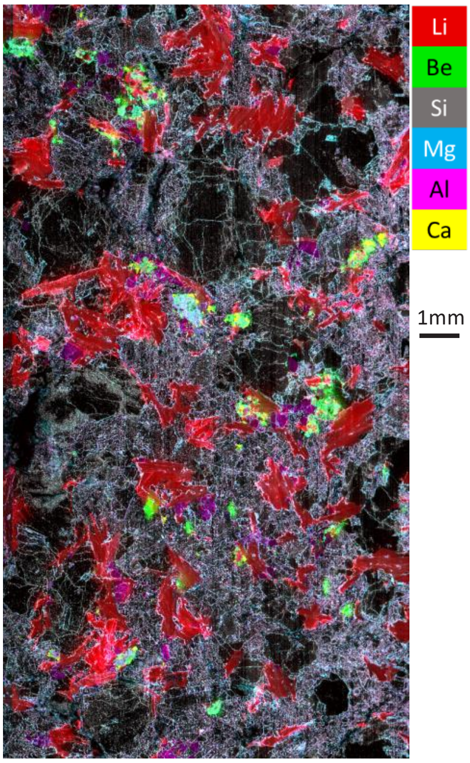

Fig. 1. kHz-LIBS imaging containing 900 000 spectra, showing presence of light elements (Li, Be).

ACKNOWLEDGEMENTS

The Research is produced with the financial support of the *Agence Nationale de la Recherche* under the «France Relance» plan ILM/Ablatom and the French government "France 2030" initiative, under the DIADEM program managed by the "*Agence Nationale de la Recherche*" (ANR-22-PEXD-0014, "Libelul").

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SESSION 8

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SESSION 9

Nuclear

Application of laser-based surface analysis techniques in magnetically confined nuclear fusion research

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Magnetically confined plasmas are at the border from short-pulse discharges in the seconds range to long-pulse discharges in the range of minutes or hours and operation over multiple years. At the same time the transfer to operation with tritium, like in JET and ITER, and associated neutron production is imposing new restrictions to the access of first wall components and their analysis. Fusion-relevant first wall materials like tungsten, graphite, molybdenum, and beryllium are undergoing a permanent bombardment by energetic plasma particles (~10^{25}ions/sm^2) like hydrogenic species (H,D,T) and impurities (Ar, Ne, He etc.) causing material erosion, mixing, and deposition as well as helium and tritium retention in the plasma-facing materials at different locations of the reactor chamber. Theses processes are potentially critical for the most relevant material W as they can limit the duty cycle of a reactor by e.g. tritium retention, causing challenges to fulfill the tritium cycle conditions, and they are safety relevant as they can reduce the power handing capabilities of the armour material by erosion [1]. As the plasma-facing components are actively cooled, it is very challenging to obtain in-situ information about the state of the materials, the retention of fuel or about the residual thickness of the armour. Ex-situ analysis is for specific questions a viable way in the research phase of devices like the tokamak JET or the stellarator W7-X, but not an option for a nuclear facility like ITER or beyond. Therefore, a high effort is made in the plasma-wall interaction and diagnostics community related to nuclear fusion research to develop and qualify laser-based techniques like LIBS, LIA-QMS, LIDS etc. for in-situ analysis of plasma-facing components [2,3].

A large part of current research is still ex-situ after extraction of tiles exposed in tokamaks or linear devices to the harsh plasma conditions expected in a reactor. These studies are done a) to optimise the technique, e,g, to enhance the sensitivity to detect T in W or Be, and b) but to study physics process like global material migration in fusion devices and benchmark plasma-wall interaction codes used for reactor studies. Exemplary results of such studies from TEXTOR, JET, W7-X and EAST will be presented indicating the specific challenges and optimisations applied [2, 4, 5, 6,7]. The second part of research is the actual application of those techniques installed in fusion devices by either fixed arrangement like in TEXTOR, JET or EAST or embedded on remote handling arms during maintenance phases of devices like WEST and FTU [8,9]. Here results of recent investigations in JET with LID-QMS and in EAST with LIBS and plans including ITER will be presented to the LIBS community. Finally, a few outstanding results regarding in-operando application during plasma operation in linear plasma devices will be presented showing the capabilities to study fundamental processes of plasma-wall interaction and the dynamic behaviour. The later is focussing on the hydrogen fuel cycle in a reactor and the retention of hydrogenic fuel in materials and how this can be released under a controlled way [10].

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Recent advances in developing LIBS as a fuel monitoring tool for nuclear fusion applications in Europe

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Laser-Induced Breakdown Spectroscopy (LIBS) is one of the most promising methods for quantitative in-situ determination of fuel retention in Plasma-Facing Components (PFCs) of magnetically confined fusion devices. Within the framework of EUROfusion, a research programme was set up to study the physics involved for LIBS, but also to address the main requirements for ITER, i.e. quantification of fuel retained in different plasma-facing surfaces with high sensitivity.

In order to validate LIBS as a tool for quantitative determination of the elemental composition of ITER-like deposits, LIBS analysis was successfully performed on W and Be (or Al, being the non-toxic alternative) layers and their mixtures, with the inclusion of O and other species, all being proxies to layers expected in ITER or already observed on operating fusion test facilities like JET. Deuterium (D) was used as a substitute for tritium. D surface densities below 10^{16} D/cm^2 could be measured with an accuracy of ~30% (depth resolution ranging from 50 up to 250 nm per laser pulse), complying to the required high detection sensitivity in ITER.

The performance of different LIBS systems based on single pulse and double pulse lasers with different pulse durations were explored. It was shown that ps-based LIBS is currently the most mature method for measuring D retention, because surface modification (for instance melting), outgassing and diffusion of retained D are minimized.

To improve the distinguishability of spectral lines of hydrogen isotopes for LIBS at atmospheric pressure, two different time delays will be applied after each laser pulse. Furthermore, the spectral line brightness of hydrogen and isotopes could be enhanced and the contribution of hydrogen from the ambient air could be reduced by using a flow of Ar or He at the LIBS spot. Double pulse LIBS could potentially also lead to improved distinguishability of the spectral lines, but further systematic research is required.

To provide a key stepping stone from LIBS in laboratory experiments to application as a remote handling tool in JET or ITER, a compact remotely controlled LIBS system was mounted on the multipurpose deployer of the Frascati-Tokamak-Upgrade (FTU) enabling successful measurement of the composition of the deposits in the FTU vessel.

The current state of understanding and an outlook for LIBS application in fusion reactors will be reported.

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LIBS as diagnostics of analytical chemistry for surface mapping of complex mixed samples simulating debris inside the TEPCO's Fukushima Daiichi Nuclear Power Plant (FDNPS) reactor cores.

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The Nuclear Energy Agency (NEA) launched the Nuclear Education, Skills and Technology (NEST) Framework to pursue careers in the nuclear field, by exposing researcher working on these topics to international challenging project of real-world issue and by transferring the knowledge and expertise accumulated in the current generation to them through hands-on training.

In this framework the 2022 edition of the NEST project offered a training educational period at the Collaborative Laboratories for Advanced Decommissioning (CLADS), located at Tomioka, Futaba District, in the Fukushima prefecture (Japan).

Among the research sectors active at CLADS there is the application of the LIBS technique as diagnostics of analytical chemistry, aiming at characterizing the debris inside the Tokyo Electric Power Company (TEPCO)'s FDNPS reactor cores after the tsunami of March 2011, which destroyed three of the six reactors of the plant. These debris need to be characterized with techniques suitable for compact and remote devices, due to the residual radioactivity. The present study will partly show the results of a LIBS characterization and surface mapping of samples simulating these debris, in the form of compressed tablets of mixed oxides with a complex surface distribution and concentration. The results allowed creating a detailed chemical surface map of the samples, with spatial resolution of 0.5 mm and an excellent correspondence between the real spatial distribution of the materials and that reconstructed by LIBS.

The results also showed a good correspondence between the nominal concentration of the materials and the concentration estimated from the LIBS surface maps.

Finally, a brief overview of the activities carried out daily at FDNPS by TEPCO, to completely decommission the plant, will be discussed.

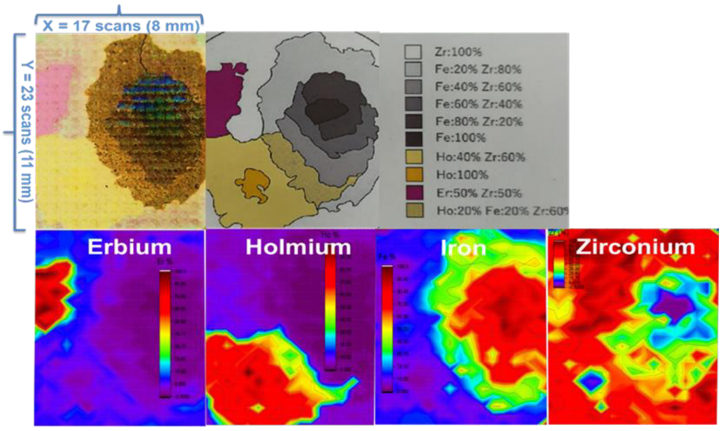

Fig. 1. LIBS surface maps of different mixed oxides. Red areas identify high concentration zones, blue-violet areas identify low concentration zones.

ACKNOWLEDGEMENTS

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Laser ablation – laser absorption spectroscopy for isotopic analysis

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Isotopic analysis can be difficult with LIBS as it requires large and expensive high resolution spectrometers. In this approach we probe the laser ablation plasma with a tunable diode laser and measure the absorption spectra at the same time as the emission spectra with traditional LIBS. In this case the high spectral resolution comes from the narrow laser linewidth instead of a spectrometer. This hyphenated technique is termed laser ablation – tunable diode laser absorption spectroscopy (LA-TDLAS). We have demonstrated the approach for isotopic measurements of ^{6}Li and ^{7}Li [1] as well as ^{235}U and ^{238}U [2]. Figure 1 shows the LA-TDLAS measurements of ^{6}Li and ^{7}Li. The tunable diode laser was a home-built external cavity diode laser with a single mode output and wavelength tunable across absorption features from different isotopes. For the uranium measurements a second diode laser at a fixed wavelength away from the absorption features was used for background subtraction. Measuring the LIBS spectra simultaneously enabled plasma temperatures and electron densities to be calculated. The latest results will be presented along with future prospects for the combined techniques.

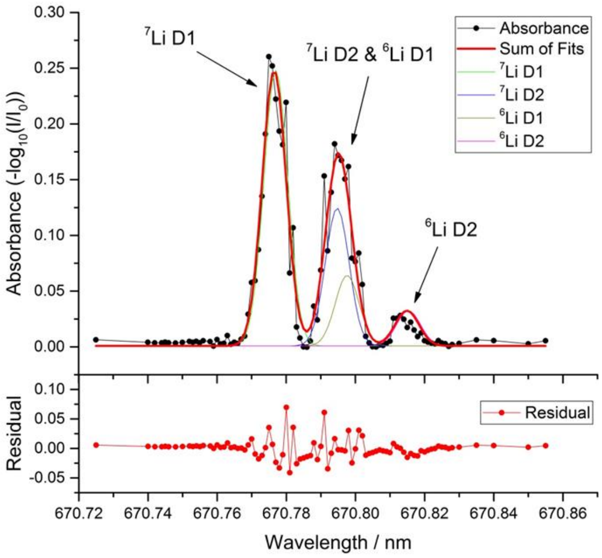

Fig. 1. LA-TDLAS measurements of ^{6}Li and ^{7}Li around 670 nm [1]

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Depth Analysis of WTa-D/Mo sample by Resonant-Laser Induced Breakdown Spectroscopy

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Laser- Induced Breakdown Spectroscopy has gained widespread popularity due its ability to perform depth profiling. Depth profiling is a procedure used to ascertain the interfaces between various materials in a layered sample at different depths. This is realised by ablating the material under study using successive laser pulses and capturing the Laser-Induced Plasma generated by each laser pulse. The precision of depth analysis is heavily influenced by the depth resolution and ablation rate which are the determining factor. The primary factor that affects the resolution of the depth profile is the non-uniform distribution of laser pulse energy in the radial direction[1]. This work is dedicated to enhancing the depth resolution during depth profiling by implementing Resonance- Laser Induced Breakdown Spectroscopy (RLIBS). In this technique, a single tuneable laser is used to ablate the material from the sample based on Resonant Laser Ablation (RLA) coupled with Optical Emission Spectroscopy (OES)[2]. In this work Calibration-Free Laser Induced Breakdown Spectroscopy (CF-LIBS) along with RLIBS too is used to examine the depth profiles of a WTa-D mixed coating. The samples are mainly pertinent to fusion and depth analysis uncovers the fuel retention or erosion/deposition in plasma facing components (PFC) in fusion reactors [3]. The coating has a thickness of 5 µm and contains varying amounts of Ta and D, up to 20%. To ablate the material, a laser beam from a tuneable ns Optical Parametric Oscillator (OPO) (Ekspla NT342C, a tuneable nanosecond laser, 210 - 2200 nm) is utilized. The ablation laser wavelength chosen is associated with W excitation levels at 255.135 nm for resonance conditions and 222.75 nm for non-resonance conditions. Measurements are performed at atmospheric pressure, with OES signals from 100 consecutive laser shots recorded by an Echelle spectrometer (Mechelle ME5000, Andor Technology) equipped with an iCCD camera (iStar DH734, Andor Technology, and temporal resolution 5 ns. The gate delay is set at varying intervals to achieve optimum plasma conditions. In RLIBS, only one laser beam is employed for both ablation and simultaneous excitation of the plasma, making it a simpler experimental setup compared to RELIBS. Resonant conditions have been found to yield better depth resolution than non-resonant conditions the former results in a slower ablation rate yet produces nearly equivalent spectral intensity. The spectra recorded are divided by sensitivity curve, and the peaks are assigned according to the data available in NIST and Harvard databases. The signal enhancement in resonant versus non-resonant conditions are compared and CF-LIBS analysis is performed. The results are also compared to those obtained from TOF-ERDA and GDOES primarily for the quantification of deuterium in sample.

ACKNOWLEDGEMENTS

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Utilization of LIBS for rapid elemental mapping of surrogate TRISO particles - an alternative for nuclear fuel

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Laser induced breakdown spectroscopy (LIBS) has become a popular tool for measuring and determining elemental distributions within a given sample. Here LIBS was employed to characterize coatings on surrogate fuel particles. Tri-structural isotropic (TRISO) particles are a proposed nuclear fuel alternative for high temperature reactors. These particles are constructed of a central U-bearing fuel kernel, surrounded by a carbon buffer and inner pyrolytic carbon layer. An outer carbide layer is then used as a barrier to fission products. These particles are embedded within a graphite compact and housed within the fuel core enclosure. Simply put, due to its robust nature, performing elemental analysis of these particles poses a challenge.

Here we perform elemental mapping and depth profiling of surrogate fuel particles (ZrO_2/C/ZrC layers) utilizing a 193 nm ArF laser in combination with a multi-channel CMOS detector. LIBS was successfully used for discerning small (50 µm) carbon layers, detecting the location of carbon and oxygen layers, providing fast 2-D mapping (<5 min/particle) and rapid depth profiling (10 sec/particle). The laser material interaction with the 193 nm wavelength provided ablation rates for the depth profiles that were in the 75-150 nm/pulse range.

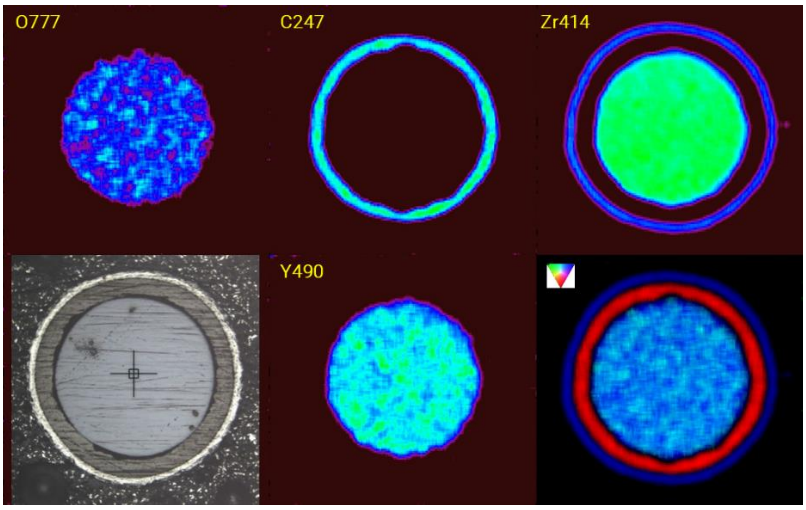

Figure 1. Elemental images of a single TRISO particle, displaying O 777 nm, C 247 nm, Zr 414 nm, Y 490 nm, and a red-green-blue overlay of C, Zr, and O.

SESSION 10

Biomedical applications

LIBS for direct and indirect detection of bioindicators in human clinical samples

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Bio-applications of Laser-Induced Breakdown Spectroscopy (LIBS) elucidate how individual diseases cause significant changes in the chemical composition of bodily fluids and tissues. [1] The focus is on localizing these chemical variations and correlating them with cell changes and degradation. The spectroscopic community aims to provide chemical information with cell-level resolution, which can greatly impact our understanding of disease initiation and tissue proliferation.

In this study, we restrict our investigation to soft and hard/calcified tissues, and we discuss the potential of imaging the distribution of elements in other biological tissues. The direct, label-free detection of biomarkers within tissues is achieved by bioimaging endogenous elements, including trace and macro elements. We also explore the detection of exogenous elements, which involves studying artificially administered metallic NPs within an organism and detecting foreign metals due to environmental pollution or unhealthy lifestyle. LIBS proves to be a suitable technique for bioimaging endogenous and exogenous elements. It finds applications in bioaccumulation studies of metals, medical/clinical use [2], and immunochemistry [3]. Despite some limitations related to sample preparation and laser-tissue interaction, LIBS demonstrates sufficient detection limits for NPs, beneficially used in tumor radiotherapy enhancement and specific protein marking within tissues. The utilization of nanometallic labels also makes LIBS a promising alternative to standard immunochemistry techniques.

In summary, our study explores the potential of LIBS for chemical imaging of endogenous and exogenous elements in biological tissues, presenting opportunities for various applications, particularly in medical and clinical research.

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LIBS imaging for medical applications: overview and case studies

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Several feasibility studies in LIBS have been conducted on biological or medical samples. These studies have shown that LIBS can bring useful information in regard of other analytical technique [1-2]. Currently, the LIBS imaging technique is progressively moving to the clinic. Thanks to international partnerships, the Institut Lumière Matière in Lyon was able to perform LIBS imaging on human lung specimens as a part of a registered clinical trial [3], for investigating medical needs for elemental identification of large-sized biopsies. Initiated with with the CHU of Grenoble, several specimens from different hospitals over France were recently collected and analysed. In addition, biopsies from Belgian patients with lung diseases were also analyzed with LIBS imaging.

Along with the interest given to idiopathic lung diseases, our group was also involved in several medical projects. In this work, a summary of the methodology applied for analyzing medical specimens with LIBS imaging is presented. We will present several case reports showing different medical applications: from the sarcoidosis clinical trial to more punctual studies, such as elemental segregation in thyroid cancers, or trace analysis in femoral lymph node in the case of podoconiosis, a neglected tropical disease.

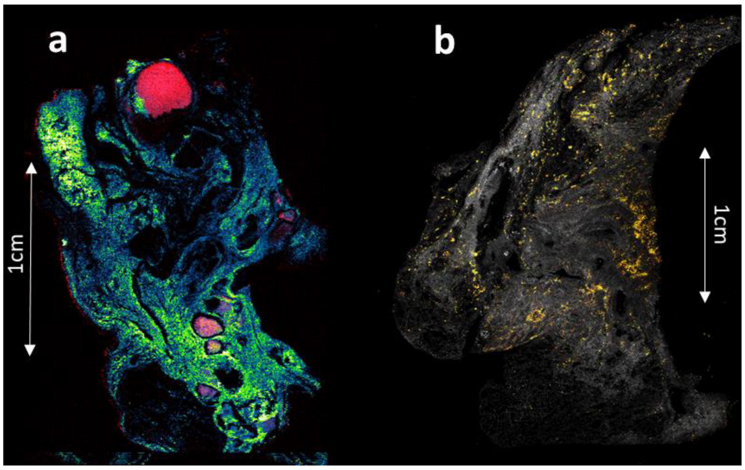

Fig1. (a) Elemental imaging of a thyroidal tumor: phosphorous is represented in green-blue, copper in red. (b) Lung biopsy imaging: P displayed in grey, Al and Si merged in yellow

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Screening ovarian cancers using patient plasmas with LIBS and Raman: separated and fused data analysis with machine learning

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Early screening of ovarian cancer is critical to enhance the patient survival rate [1]. Conventional detections with imagery and antigen test are insufficient in terms of sensitivity and specificity. Laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy applied to blood analysis have shown a great potential as means for rapid, minimally-invasive, and cost-effective detection of cancer [2,3]. In this study, we collected a substantial set of 176 blood plasma samples from female patients within a clinical environment, including 63 ovarian cancer cases, 39 ovarian cyst cases, and 79 normal controls. The samples were prepared as a thin film coating on a graphite substrate. LIBS and then Raman measurements were performed for these samples. Data visualization with a dimension reduction algorithm showed merging between the clusters of data with different labels, particularly with the data of the intermediate cyst case. Supervised classification models were therefore developed for a ternary classification realized with two successive steps of binary classifications using a back-propagation neural network for the LIBS and the Raman data respectively. The classification of independent test samples with the LIBS model shows a sensitivity and a specificity of 71.4% and 86.5% for cancer diagnosis [4]. These performance metrics become respectively 81.0% and 97.3% with the Raman model [5]. A close look on the features important for classification, we find emission lines from the elements involved in the body electrolysis, K, Na, Mg, and Ca, for the LIBS model, and molecular vibration bands of amino acids and proteins for the Raman model.

Fusion of LIBS and Raman spectral data can be realized by spectral channel concatenation (Fig. 1 a) or feature combination. In the case of spectral concatenation, a feature selection algorithm selects channels from the both LIBS and Raman spectra as shown in Fig. 1 (a), where we can see that the channels of the Raman spectrum are most probably selected, while the LIBS spectrum appears sparser. In addition, elemental and molecular features important respectively for the separated LIBS and Raman models are included in the features important for the fused LIBS-Raman model. And the both types of features received equivalent scores (Fig. 1 b), indicating coherent and equilibrium information brought by the both types of the features. A direct ternary classification model was trained. The classification of independent test samples shows a sensitivity and a specificity of 95.0% and 94.6% for cancer diagnostics, which is significantly improved compared to the performances of the LIBS or Raman separated models.

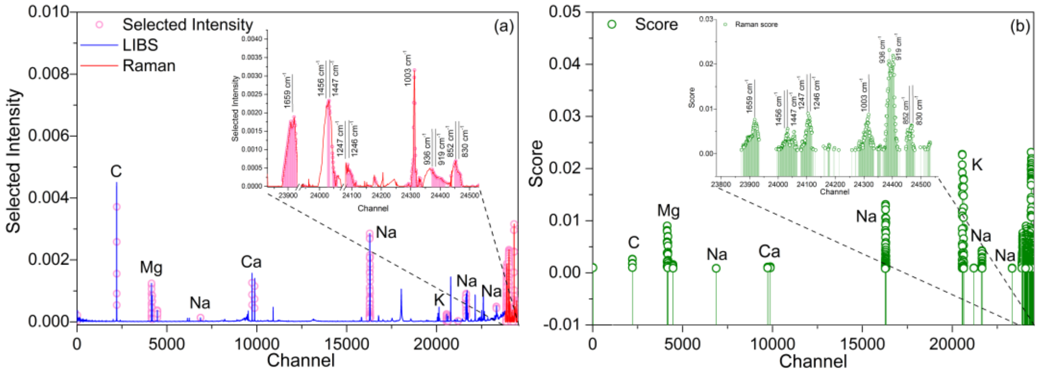

Fig. 1. (a) Direct spectral concatenation between the LIBS and the Raman spectra of a sample, together with the indications of the selected spectral channels; (b) scores of the 500 selected features.

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Comparative study of human teeth decalcification by LIBS

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Teeth are the hardest parts of the human body due to their inorganic composition. To study them on a microscopic level, it is necessary to create ground sections. This process is crucial in histological studies of hard dental tissues and pulp for diagnosing developmental disorders, pulp pathologies, and forensic odontology. However, the teeth' hardness makes their preparation very difficult. Thus, dental tissue decalcification is an essential step in the preparation process, during which the inorganic content of dental hard tissues is removed. The most commonly used decalcifying method is chemical agents [1].

This comparative study investigated the sufficiency of five commercially available decalcifying agents by Laser-Induced Breakdown Spectroscopy (LIBS) analysis to evaluate the most efficient one. A total of 22 analyzed human teeth samples were provided by our long-term collaborators at the University Hospital Ostrava and the Czech Academy of Sciences. Decalcifying agents were 5% nitric acid, 8% formic acid, Microdecfast, Löwy agent, and decalcifier DC1 (mixture of formic acid and formaldehyde). Their effectiveness was assessed by analyzing the spectra lines of biogenic elements (calcium, magnesium, and phosphorus).

The results showed that the most sufficient decalcification was obtained by decalcifier DC1. All teeth decalcified by this agent showed extremely low signals of all calcium lines visible in the measured spectral range (245–410 nm), magnesium was detected only in two of four samples, and phosphorus was not detected in any of them. The worst decalcifying agent was Löwy's agent, which had a comparable signal to a non-decalcified tooth.

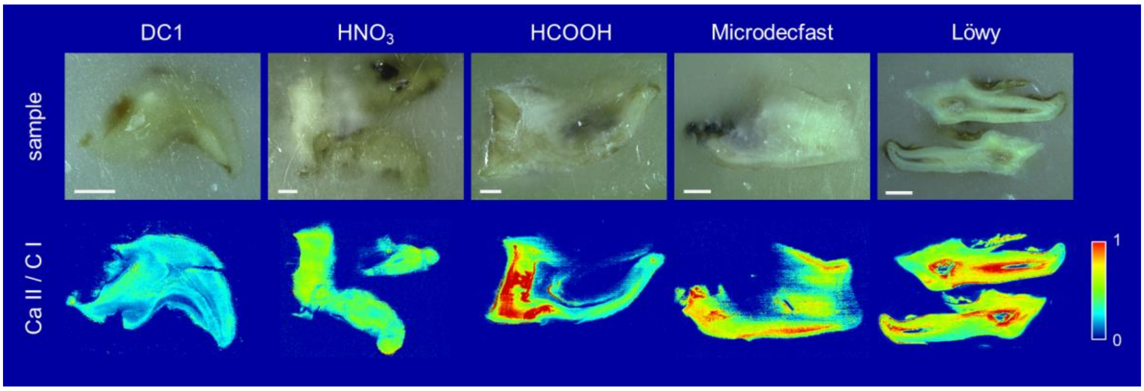

Fig. 1. LIBS elemental maps of Ca II 396.85 nm line for comparison of used decalcifying agents. The Löwy agent's color scale maximum is 10× higher due to high intensities. Scale bars are 2 mm.

ACKNOWLEDGEMENTS

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Laser-Induced Breakdown Spectroscopy for the Identification of Bacterial Pathogens in Blood and Urine

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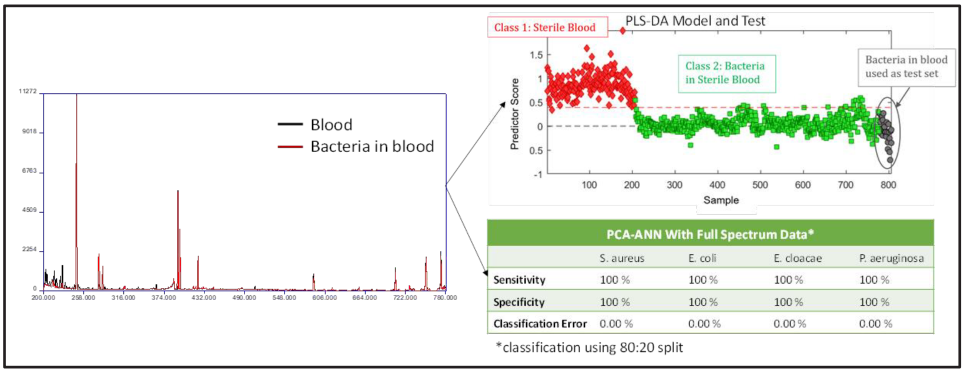
Our group has recently demonstrated the ability to utilize laser-induced breakdown spectroscopy to detect and classify bacterial cells in arbitrary fluid specimens using a simple centrifugation device to deposit cells on disposable nitrocellulose filters [1]. Bacterial concentrations of approximately 11,000 CFU per laser shot were detectable using 8 mJ pulses from a 1064 nm, 9 ns Nd:YAG laser with a spot size 75 μm in diameter [2].

A partial least squares discriminant analysis of LIBS spectra obtained from specimens of blood and urine spiked with known bacterial pathogens possessed a 98.9% sensitivity and 100% specificity for the detection of bacteria in urine and a 96.3% sensitivity and 98.6% specificity for the detection of bacteria in blood. An artificial neural network analysis with principle component analysis pre-processing of the LIBS spectrum from 200 nm – 600 nm was used to discriminate and classify the bacteria in the clinically-obtained biofluids. Use of an 80:20 split cross-validation resulted in an average sensitivity and specificity of 97.2% and 98.6%, respectively, for the discrimination of three species of bacteria in urine. External validation performed on 16 filters gave an average sensitivity of 77.5%. Applying PCA-ANN using an 80:20 split cross-validation for the discrimination of four species of bacteria in blood resulted in 100% sensitivity and 100 % specificity, shown in Fig. 1. External validation of 19 filters of bacteria in blood yielded an average sensitivity of 82.3% [3]. These results indicate the potential usefulness of LIBS in the clinical setting.



PCA-ANN With Full Spectrum Data*				
	S. aureus	E. coli	E. cloacae	P. aeruginosa
Sensitivity	100 %	100 %	100 %	100 %
Specificity	100 %	100 %	100 %	100 %
Classification Error	0.00 %	0.00 %	0.00 %	0.00 %

*classification using 80:20 split

Fig. 1. A LIBS spectrum of bacteria in blood and the results of the detection of four species of bacteria in blood with a PLS-DA analysis utilizing ratios of peak intensities and a PCA-ANN classification utilizing the entire LIBS spectrum.

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Laser-induced breakdown spectroscopy for the *in vitro* bioequivalence determination of generic drugs with BCS-class II, III and IV active pharmaceutical ingredients

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Bioequivalence studies of generic drugs are an essential technical-scientific requirement for the sanitary registration of these types of drugs worldwide [1]. Regardless of the type of analytical procedure used, the demonstration of the bioequivalence of a generic drug is based on the similarity of the pharmacokinetic performance of the generic drug with respect to a reference drug[2-5]. The qualitative and quantitative similarity of the composition or formula of both drugs will give this similarity.

Since Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical technique that is capable of discerning differences and similarities in the composition of substances and materials[6], through the generation of atomic emission spectra that constitute a unique "fingerprint" of the sample[7]; this is a strategic technique for studying the similarity between drugs formulations and, from this, inferring their potential in vitro bioequivalence, given the intrinsic relationship between the drug formulation and its pharmacokinetic performance.

In this work, we have successfully used the LIBS technique for the determination of the *in vitro* bioequivalence of generic drugs in oral dosage forms, specifically coated tablets and immediate release capsules, whose APIs belong to BCS categories II, III and IV, based on the study of the similarity of the formulations between the generic and reference drug, using the same algorithms for the quantitative determination of similarity and differentiation in *vitro* bioequivalence studies. The results obtained in the study demonstrate the great analytical potential of the LIBS technique for the determination of in vitro bioequivalence, based on the direct comparison of the chemical composition of two drugs through their LIBS spectra.

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SESSION 11

Extreme Environments

Deep-UV laser-induced breakdown spectrometry and laser-ionization mass spectrometry for astrochemistry studies.

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The recent ambitions of different national space agencies to return to the Moon and to potentially set up a permanent moon base soon, have triggered the interest to adapt different analysis techniques to the conditions of our satellite. The Moon has virtually no atmosphere, with a vacuum level in the range of the pico mbar. Under such conditions, and after the formation of a laser-induced plasma, the possibility of direct recording of LIBS spectra below 200 nm (DUV/VUV LIBS) or performing mass spectrometry out of the generated ions (LIMS) can be done without the use of pumping system.

This communication will show the results obtained in the laboratory under ultra-high vacuum conditions monitoring the photons and ions of solid samples of interest in astrochemical research. For LIBS, a flat-field XUV spectrometer was used, with capability to cover a spectral range from 30-250 nm. Such region, very unexplored in conventional LIBS offers several advantages as reduced interferences and a higher emission intensity from elements of interest in astrochemistry as CHNOPS. For LIMS, a reflectron-type time-of-flight mass spectrometer was used, allowing the simultaneous recording of mass spectra in the 1-1000 range.

A deep discussion on the two experimental configurations will be provided, detailing the experimental parameters affecting the signal in both cases. Different examples will be shown, with special emphasis in non-consolidated matter that can be assimilated to the moon regoliths.

In-situ LIBS measurements in Utopia Planitia Mars by the Zhurong Rover

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On May 15, 2021, the first Chinese Mars exploration mission Tianwen-1 successively landed its Zhurong rover in southern Utopia Planitia (Fig. 1), announcing a new era of Mars exploration with the Chinese contribution of a third rover currently in activity on Mars [1]. A common feature of these rovers, two American and one Chinese, is their use of laser-induced breakdown spectroscopy (LIBS) for detections and analyses of Mars surface geological materials. Such specificity becomes the main asset for Zhurong rover, since the LIBS payload represents the unique instrument on board capable of material composition analysis. The successive landing of the Chinese mission permitted its rover to investigate this area virgin of human exploration. During its first 110 sols of travel, 32 scientific targets, including igneous rocks, duricrusts, sands and soils, have been aimed by the scientists operating the MarSCoDe instrument [2] (Fig. 1). The 32 corresponding LIBS spectra carry therefore the first compositional information of the explored area, assumed to compose of volatile-rich sediments since late Hesperian. The analysis of these data appeared thus crucial to confirm the hypothesis and to constrain the geological evolution model. In this paper, we will present the spectral data produced by the Key Laboratory of Lunar and Deep Space Exploration, National Astronomical Observatories, Chinese Academy of Sciences [3], visualize the data structure with a dimension reduction algorithm, determine the method for their normalization, and perform the regressions for predictions of the contents of major elements as well as water in the scientific targets, which allows an observation on the past and present aqueous activities in the landing zone of Zhurong rover [4].

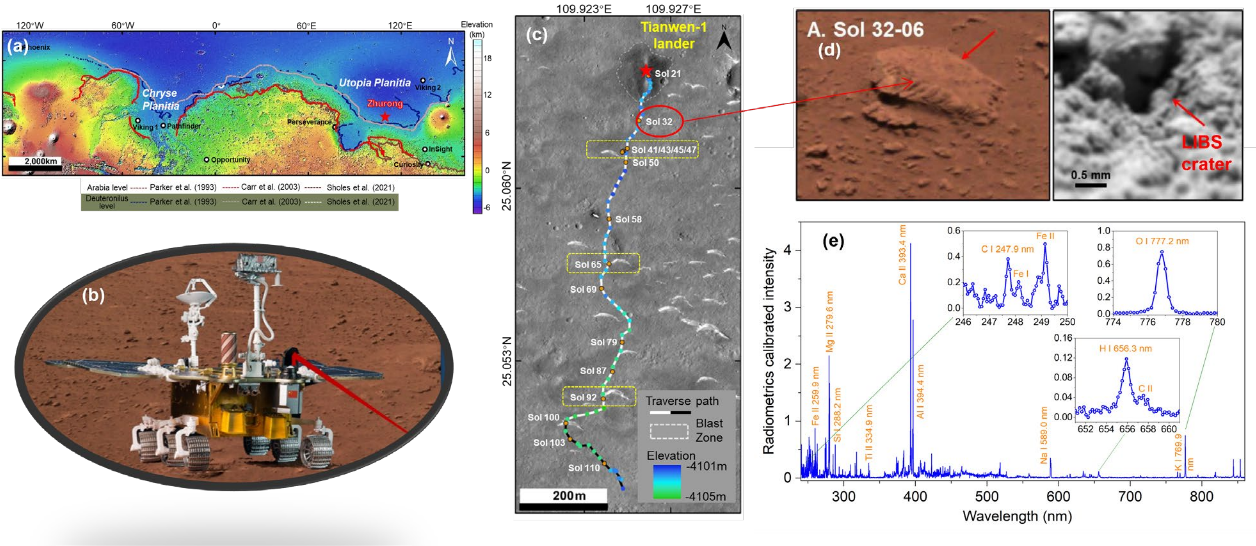

Fig. 1. The landing site (a) of Zhurong rover (b), its trajectory during the first 110 sols of the exploration (c), a cemented duricrust encountered and LIBS-analysed on sol 32 together with the LIBS crater on it (d), and the LIBS spectrum with emission lines from major metallic elements and some non-metal elements (e).

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Detection of kerogens in sedimentary rocks by LIBS. Implications for the search for biosignatures on Mars.

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Oil shale is a sedimentary rock that naturally contains organic matter. In its chemical composition presents a wide range of inorganic minerals including carbonates, silicates, etc. and kerogens – a mixture of fossil hydrocarbons. Kerogen is insoluble in normal organic solvents, being the most abundant source of organic matter on Earth [1,2]. Chemical composition of a particular kerogen differs as a function of the source microrganisms that participated to the sediment and may be classified into three categories [3]. Type I kerogen, produced by algae or eventually bacteria and is the less abundant; type II, derived from other aquatic organisms (phytoplankton and zooplankton); the most common on Earth is type III, generated from organic plant matter.

To the best of our knowledge, this work demonstrates for the first time the detection of natural organic matter in different rock of oil shales with a total organic carbon content between (2.78 % and 15.06 %) using LIBS under Martian conditions. A linear correlation was found between the net CN intensity and the concentration of total organic material of the samples under CO_2 and Martian atmosphere.

The fact that natural organic matter can be detected and characterized by LIBS in this kind of sedimentary rock – known for suggesting the existence ancient life - through its emitting species such as CN or C_2 is of great relevance in astrobiology. Results presented here, may provide essential understanding on the search for biosignatures on Mars and for the development of planetary exploration strategies.

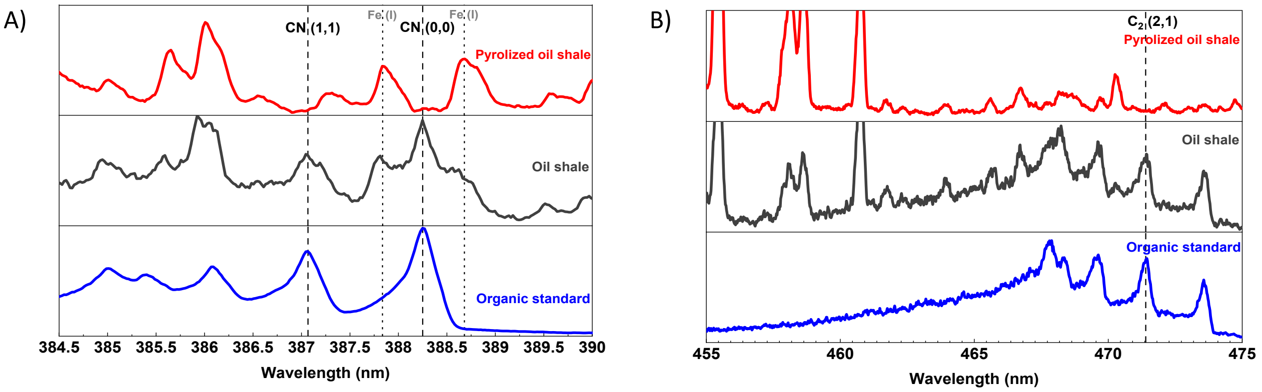

Figure 1. LIBS emission for A) CN molecular band (B2Σ+-X2Σ+, Δv=0) and B) for C2 molecular system (D3Πg-A3Πu, Δv=+1). For better identification of the bands, a polystyrene standard was used.

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Hyphenated acoustic/optical emission spectroscopic data from laser-induced sparks to geological material characterisation

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The acoustic emission accompanying laser-induced plasmas have been used for decades for multiple purposes as a monitoring signal of the ablation process, as a correction/normalisation factor of shot-to-shot plasma inherent instabilities, to characterise the focal position, to elucidate essential parameters during the inspection of surfaces and as an observable capable of detecting and recognising a material [1]. In this context, the recent integration of a microphone synchronised to the LIBS laser in the Perseverance rover deployed as part of the NASA mission Mars 2020 has re-kindle the motivation towards comprehending the acoustic sound waves from the laser-generated sparks, mainly to be exploited as a new characterising tool complementary to the optical emission response of plasmas.

In this research, the multiple factors that may be conditioning acoustic from laser-induced plasmas have been evaluated, from the sample-related traits (physical properties like dimensions, colour, porosity, ...), to the boundary conditions governing the workspace where the inspected sample may be placed (the nature of the terrain over which the sound propagates, the presence of the obstacles ...) without neglecting the coordinates that locate the sender (the plasma) and the receiver (the mic). Furthermore, the influence of the instrumentation (laser wavelength, type of microphone, ...) on the ensuing acoustic waveform has also been investigated. With all this, possibilities of combining simultaneous acoustic and optical data from plasmas from laser ablation scanning of the surface of a geological material through a dual mapping have been evaluated to develop a methodology that allows multidimensional micro-scale characterisation of mineral phases. For the first time, hyphenated acoustic/optical emission spectroscopic data resulting from micro plasmas induced by short laser pulses may suppose a synergy on exploration at the microscopic level of solid bodies in the Solar System to help a better interpretation past geological conditions and the possible processes that have occurred, and for ascertaining the putative presence of evidence of life, if any.

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Impact of high pressure on underwater laser-induced breakdown spectroscopy

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Underwater laser-induced breakdown spectroscopy (LIBS) has been proven to be an attractive technique for in-situ oceanic applications, with the advantages of multi-elemental and stand-off analysis capabilities [1]. However when applying LIBS into the deep-sea, the pressure effect caused by different ocean depths (e.g., 2000 m depth corresponds to ~20 MPa) is inescapable, and could have great impact on the characteristics of laser-induced plasma and then on the LIBS signals. In this work, we built a high-pressure chamber in the laboratory and investigated the temporal evolution of laser-induced plasma and cavitation bubble in water at high pressures, by using the fast imaging, shadowgraph, and spectroscopic techniques [2,3]. As shown in Fig. 1, the high pressure has a great impact on the dynamics of the plasma and the bubble. As the pressure increases, both the size and the oscillation period of the bubble decreases dramatically as a consequence of faster dynamics. The plasma can gain energy from the bubble collapse phase to maintain the plasma emission, but it will quench immediately after bubble collapse which leads to a sharp reduction in the plasma emission persistence. This indicates a strong plasma-bubble interaction at high pressure conditions and it explains well the observed spectral features of ionic, atomic and molecular emission lines. The evolution of the spectral line broadening shows a good consistency with the bubble internal pressure deduced from the Gilmore model of cavitation bubble dynamics. In this presentation, we will also show our recent works on underwater LIBS instrumentation and the obtained results from in-situ deep sea trials.

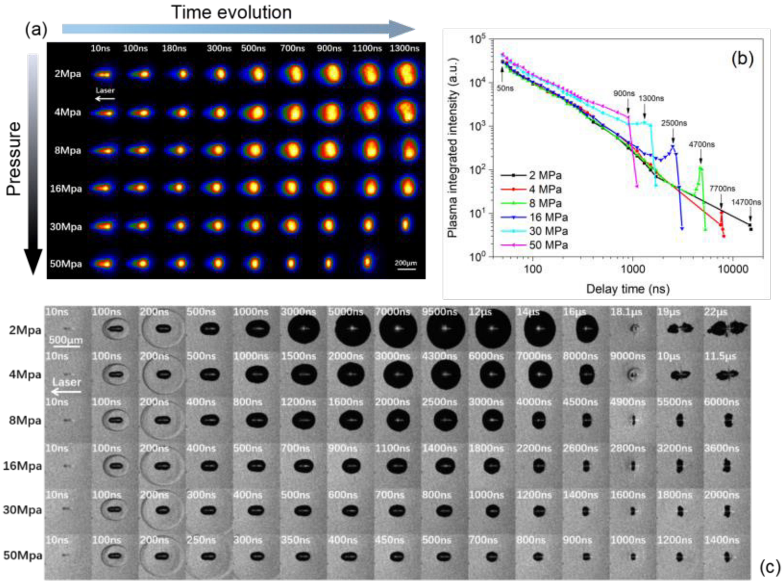

Fig. 1. Temporal evolution of laser-induced plasma and cavitation bubble in water at different pressures of 2, 4, 8, 16, 30, and 50 MPa: (a) normalized plasma emission images; (b) integrated plasma emission intensities; (c) bubble shadowgraph images.

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SESSION 12

Agro-food & Environment

LIBS Applications for Food Safety and Quality

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Food safety and food quality are important parameters for human health and quality of life, from the production to consumption in food industry. Due to that, producers have an attention on rapid and reliable, eco-friendly technologies to follow the food processes and final products. Also, consumers demand to be informed about the composition, origin and quality of food and they should choose their diet according to this information. However, food fraud is a worldwide problem due to economic gain. Detection of fraud require analytical tools to investigate the food quality and authenticity. In this respect, different analytical methods have been developed for monitoring food safety and quality which have main technological challenges. Majority of them depends on DNA, proteomics and isotopic analysis. Which are time-consuming, lab-scale methods and require certain hazardous chemicals, rigorous pre-processes and specialized person. Despite that, rapid, basic and practical on-line analysis in food industry gain popularity by the development in the spectroscopic analysis. From these methods; LIBS has the ability to determine elemental composition with high potential for rapid food analysis. In our research group, it was shown that potential usage of LIBS for analysis of quality parameters and determination of food adulteration. In this context, it was shown that applicability of LIBS in identification of meat species, determination of whey adulterated milk powder, determination of ash and protein contents of cereals and NaCl analysis in bakery products. In addition to the promising results of LIBS on food applications, future prospects of these methods and ongoing studies for food safety and quality are discussed.

KEY WORDS: LIBS, rapid analysis, spectroscopy, food safety

Limits of detection in LIBS analysis of food

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The growing demand for quality control of foodstuff generated a strongly increasing need to qualify and quantify the food composition in terms of nutritional and salutary income [1,2]. Beside the evaluation of protein, carbohydrate, lipid, and vitamin content, the quantification of minerals and toxic elements is challenging, as it involves measurements of traces at very low concentrations [3]. The standard techniques for these measurements are inductively coupled plasma atomic emission- or mass spectrometry (ICP-AES/MS), atomic absorption spectrometry (AAS), and more recently X-ray fluorescence spectrometry (XRF) [4]. Except XRF spectrometry, these techniques are time- and cost-expensive as they require extensive sample preparation and the use of hazardous chemicals, incompatible with routine measurements in the innumerable sites of food production and distribution [3,5].

Laser-induced breakdown spectroscopy is an emerging technique for fast elemental analyses. To evaluate its capability for food quality control, we determine the limits of detection for 82 elements that may alter the nutritional value of food, or present sanitary risks. Therefore, LIBS spectra of dried food samples were recorded with an echelle spectrometer and analyzed with a sensitivity-improved calibration-free approach [6,7]. Validated for several minerals, the approach provides limits of detection not only for the observed elements, but for all elements for which the available spectroscopic data enable the calculation of the element-specific emission spectrum. Comparing the deduced limits of detection with the typical content of minerals and the upper limits of toxic elements recommended by food safety regulations, we establish a list of elements compatible with food quality monitoring via LIBS. Moreover, we demonstrate that almost all elements can be monitored if the spectra were acquired with a LIBS apparatus of optimized detection efficiency.

ACKNOWLEDGEMENTS

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Optimization of Spark Discharge-LIBS parameters to measure soil total organic carbon

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The measurement of soil total organic carbon (TOC) content is essential in the production of soil carbon stock maps. The traditional analytical techniques utilized for evaluating TOC in soil typically require sample preparation and chemical reagents for analysis and are time-consuming, costly and susceptible to errors resulting from sample handling, and generate chemical waste. Spark Discharge assisted Laser-Induced Breakdown Spectroscopy (SD-LIBS) is a powerful analytical technique that satisfies the requirements of high analytical speed, sensitivity and accuracy while minimizing the generation of waste. LIBS has been applied for determination of soil total carbon content, including both organic and inorganic carbon and although applications for TOC has been reported they are based on indirect measurements [1-2]. In this exploratory work, 15 soil samples with different TOC contents were analyzed with the aim of evaluating the LIBS molecular bands of C2 and CN originating from soil organic compounds to quantify directly soil TOC content. In particular, twenty SD-LIBS spectra were acquired on pellets of each homogenized soil sample using various SD values, i.e., 7800, 1530, 3600, and 4000 V, and argon flows, i.e., 0, 3, 5, and 10 L/min, in order to achieve spectral signals of superior quality and clarity, while keeping the delay time fixed at 0.5 µs, which was found to yield more intense spectra without the use of SD. Due to the significant impact of fluctuations on the spectral regions of CN and C2, three spectral processing approaches, i.e., baseline adjustment, first derivative and second derivative, were evaluated based on the values of the corresponding linear correlation coefficients (R) between spectral signal intensities and TOC. Results showed that the intensity and definition of the molecular bands of interest were higher applying a higher electrical discharge and the use of argon flow, although no significant difference was observed among the three flow values. Thus, the operating parameters were fixed at a flow rate of 5 L/min of argon and a discharge of 4000 V. Spectra processed by the first derivative method yielded 44 variables with R-values$\geq$0.5, while the second derivative process yielded 20 variables, and baseline adjustment 11 variables. Thus, the highest R-values were achieved by processing the spectra using the first and second derivative methods. In particular, the variables featuring R-values ≥ 0.5 in the first derivative spectra were 43% from the CN violet system ($\Delta v = 0$) and 45% from the C2 SWAN system ($\Delta v = +1 \; and \; \Delta v = -1$), whereas in the second derivative spectra, 55% were associated with the CN violet system emission ($\Delta v = 0$) and 45% to the C2 SWAN system. The findings of this work suggest that the appropriate spectral processing of C2 and CN LIBS molecular bands for measuring soil TOC is essential to minimize fluctuations, background and matrix effects, and to obtain the expected proportionality between LIBS spectral signal intensity and soil TOC concentration.

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Development of a Field-Capable LIBS System for Rapid Soil Elemental Monitoring

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In the context of global environmental management soil plays an important role and its dynamic and versatile nature makes its investigation a challenging task. The existing laboratory-based techniques (e.g., dry combustion) for obtaining soil parameters and composition are laborious and time-consuming. In order to investigate a wide range of soil types and matrices, a method capable of extensive, rapid, and on-site monitoring is essential. Due to its simplicity, as well as its ability to offer rapid and multi-elemental analysis, laser-induced breakdown spectroscopy (LIBS) has the potential to become an increasingly popular analytical technique [1-2].

In the present work, we have developed a compact, durable, and field-capable LIBS device for on-site soil elemental monitoring. It comprises a Q-switched Nd:YAG laser (1064 nm, 8 ns) for plasma generation, a set of USB-connected spectrometers (Ibsen Photonics, covering 173-830 nm wavelength range), a 3-axis motorized stage (Thorlabs), and various optical and opto-mechanical components. Fig. 1(a) illustrates battery powered LIBS device that is controlled using self-built LabView based interface. Laboratory-based testing and optimization of the device have already been performed, and it is fully prepared for field deployment in the coming days. In our recent studies, the measurements have been performed on the soil samples (total 175) from the twenty-eight different locations and various depths (up to 1 m) of a test agriculture field (area 6.3 ha) located in Maaninka region in eastern Finland. The measurements were carried out under optimized parameters, such as a laser energy of 28 mJ/pulse, gate delay of 600 ns, and exposure time of 12 µs. Spectral signatures of constituent elements (e.g., C, Fe, Si, Ca, Mg, etc.) were evident in the LIBS spectrum. the calibration and validation of LIBS carbon line intensities at 193.1 nm against dry combustion (LECO)-based carbon content measurements enabled us to determine the spatial distribution of carbon content throughout the field. Fig. 1(b) shows an example of the carbon map of the topmost layer (0-10 cm) of the test field. Moreover, chemometric methods have been also used to visualize LIBS spectra and extract meaningful insights. The results demonstrate the potential of our device for fast and on-site spatial elemental monitoring in soil, and improvements in the accuracy of soil models.

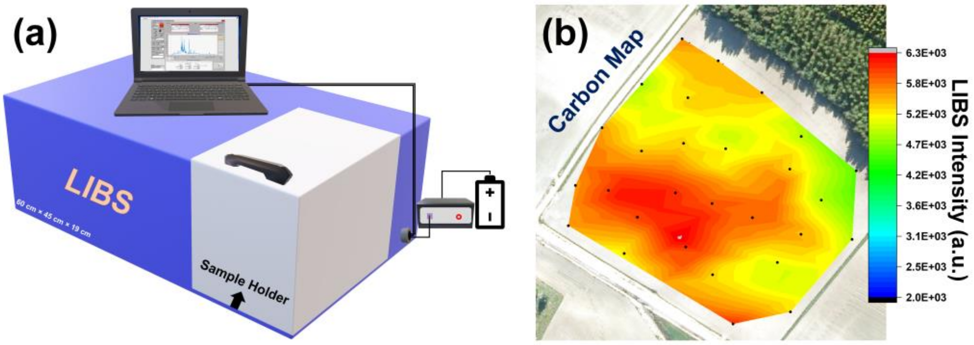

Fig. 1. (a) Field-Capable LIBS System for Soil monitoring, (b) an example of carbon map of the topmost layer (0-10 cm) of the test field.

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Scalable solution for the carbon credit market in agricultural soils using laser-induced breakdown spectroscopy

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Soil organic carbon (SOC) determination is the present and future focus of international negotiations and treaties related to global climate change, as it allows assessing the capacity of agricultural systems to sequester carbon in the soil and, in addition, presents economic advantages to farmers due to the growing carbon credit market. Looking for faster and cheaper techniques, recently, Verra a leader of greenhouse gas crediting programs recognized four techniques as emerging technologies to determine SOC content [1]. Among which laser-induced breakdown spectroscopy (LIBS) stands out because it requires minimal sample preparation, relative simplicity to operate, highly analytical, and relatively low maintenance cost. LIBS is a spectroanalytical technique that employs microsampling by laser ablation and subsequent excitation of the species present in the microplasma during and/or immediately after ablation [2].

Logiag Inc. (Canada) has developed LaserAg-Quantum, a novel method to analyse agri-environmental samples employing LIBS. This technology allows a significant reduction in SOC laboratory analysis costs and improves logistics. The LaserAg process for determining SOC ranges from sample collection to the SOC concentration value determined by our algorithm. Samples are collected in special cups, homogenized, dried, grinded, compressed, then placed on a carrousel in the Laserag-Quantum analyzer. LIBS measurements are taken over the course of a minute and the data is sent to our servers and processed within seconds. Then the results are accessible from an information management software.

The LaserAg method has shown good predictive ability for SOC across 14 different soil textures found throughout the province of Quebec with a linear working range of 0.80% to 10.00% of SOC. In addition, our method has a supervisory method that is able to preemptively flag samples that cannot be quantified by the predictive model. The analysis of a validation set composed of 333 samples showed a coefficient of determination of 0.82, root mean square errors of prediction of 0.38 and accuracy of 91% (relative error less than 30%).

The LaserAg process can be applied to determine SOC in soils from different regions as long as it is combined with a calibration set that represents the soils to be analyzed. Currently, Logiag has three commercial machines in operation, two in Canada and one in Zambia, one of which is in production in partnership with Eurofins-EnvironeX to analyze SOC and support farmers in the carbon credit market in Quebec.

Fig. 1. LaserAg® Quantum developed by Logiag Inc.

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SESSION 13

Heritage

The LIBS Heritage: a brief history of the first 40 years of LIBS, with some considerations on its future perspectives

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Preexisting knowledge of flame and plasma spectroscopy is the foundation of the principles of the Laser-Induced Breakdown Spectroscopy technique. Following the introduction of the laser, techniques akin to LIBS were proposed, commencing from the frequently cited 1962 Brech and Cross paper [1].

Nonetheless, the acronym LIBS were initially introduced in the two pivotal publications authored by Radziemski and Loree in 1981 [2,3], which can be regarded as the inception date of contemporary LIBS.

This communication will retrace the story of the first 40 years of the technique, with a special focus on the successes (and, above all, the failures) that have shaped the way we intend LIBS today and traced the path for its foreseeable evolution.

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µLIBS imaging for the characterization of heterogeneous archaeological materials

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In archaeology, studying of building materials such as mortar or architectural ceramic provides an important insight into the technological choices and skill, as well as the supply dynamics of construction sites and the construction phasing [1][2]. This is especially their heterogeneity and complexity in phases, mainly regarding the mineral filler, that are rich in information. The study of those heterogeneous materials is commonly lead by observation with binocular magnifier, but for broader interpretation, mineral identification and fine analysis, an examination under polarized light microscope is necessary. Preparation of thin sections for such studies is time consuming and classic petrography is limited with regard to images treatment .

In this work, we will show that µLIBS imaging brings a new dimension to the study of this kind of material, both in terms of sample requirements and phases identification [3][4]. The technique allows to conduct analysis on a simple polished section and to carry out geochemical identifications on phases present in heterogeneous materials, even for the smallest grains thanks to a high resolution of about 15 µm. In addition, LIBS offers the possibility to work on large samples, which has significant benefits for granulometric and morphological studies where acquiring good statistics is essential. The elemental data provided by LIBS (especially minor and trace elements) can thus provide an effective means of comparing phases between different samples. Furthermore, we use an AI system (artificial neural network) for the classification of spectral data, which enables us to identify the components of archaeological materials in an effective way while allowing for a fast and automated analysis.

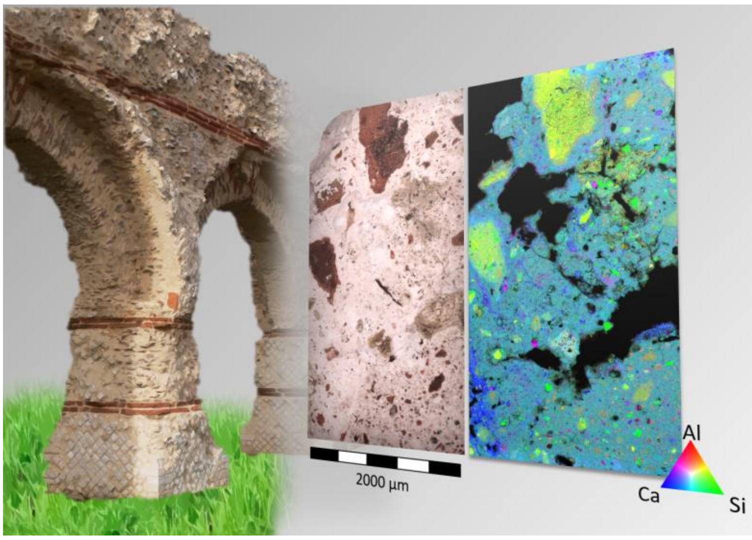

Fig. 1. LIBS merged imaging of archaeological mortar.

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Laser induced breakdown spectroscopy (LIBS) for identification and classification of archaeological bones

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An important discovery was made in October 2015 in the Albufera of Mar Chiquita district of Buenos Aires province where two teachers found human remains, including a jawbone, a skull, and several limbs. A research group led by Dr. Verónica Aldazabal was able to determine that the remains belonged to one adult and two sub-adults based on their fusion states and relative dimensions. However, another set of remains could not be individualized, making it unclear whether they belonged to another individual.

To further study these important archaeological samples, non-destructive tests or tests that only slightly alter the samples are sought. Caceres et al. demonstrated the use of laser-induced breakdown spectroscopy (LIBS) in combination with neural networks to classify and discriminate human bones and tooth fragments. This methodology could be useful in identifying disaster victims. The LIBS system provides a unique opportunity to train professionals in a cutting-edge technology that has the potential to revolutionize the field of archaeology.

A measurement protocol was established and three groups of archaeological samples were correctly classified with LIBS measurements. Individuals were classified with a spectral correlation greater than 97% using neural networks, SVM, and discriminant analysis, regardless of the type of bone or dental sample analyzed. Different methods of features selection were implemented to improve model performance and establish the most relevant features to prevent over fitting, reduce model size, improve interpretability, and reduce noise error.

The combination of ancient bones knowledge and LIBS technology has the potential to make significant contributions to the LIBS field and contribute to a better understanding of our past.

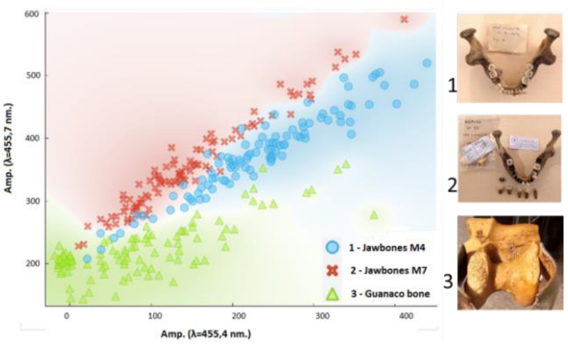

Fig. 1. Discrimination of the bone samples (1,2 and 3) taking the 2 most relevant variables

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LIBS stratigraphy in the aid of revealing the hidden layers of a post-byzantine icon

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The icon depicting the Holy Great Martyr Theodore the Tyron is part of a set of eight double-faced high artistic value panel painted icons delimiting the narthex of The Episcopal Church from Curtea de Argeș - built by Neagoe Basarab in 1517 [1]. The icons are representative for the proficiency of the Romanian 15-16th century post-Byzantine Wallachian iconography, and now they are part of the collection of the Cozia Monastery. The one under study is severely deteriorated and presents lacks of the pictorial composition on more than 25% of its surface. The remaining artistic composition, as well as the support, were subjected to a multi-analytical investigation using Hyperspectral Imaging (HSI), UV Fluorescence Imaging, X-Ray radiography (XRR), X-Ray Fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy and Laser Induced Breakdown Spectroscopy (LIBS) in order to characterize the constituent materials and the state of conservation [2-5]. Based on the imagistic techniques results (HSI and XRR) it is clear that the icon was fully repainted, some of the original motifs and decorations being lost underway. The spectroscopic analyses helped identify the materials (traces of gold leaf, lead pigments, earth pigments, cinnabar, traces of copper-based pigments and several blue pigments, protein binder, varnish, natural resin, as well as degradation products on the pictorial layer: lead-based carboxylates and calcium oxalates. LIBS was performed on several interest areas, using 20 pulses stratigraphy, and correlated to HSI helped differentiate the painting layers attributed to different historical and stylistic representations.

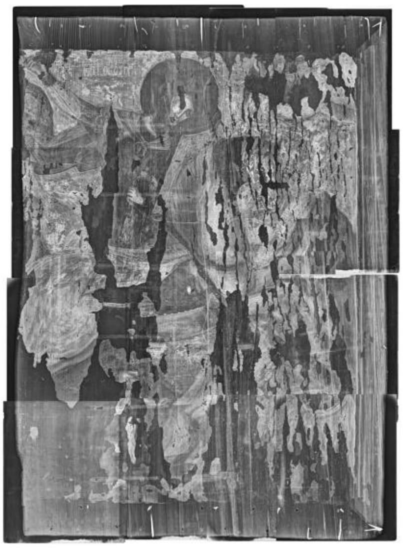

Fig. 1. Digital X-Ray image of the icon

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Implementation of a laser-induced breakdown spectroscopy (LIBS) solution for controlling safe analysis of cultural heritage materials under intensive radiation beams

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The impact of intense radiation beams employed to investigate heritage materials in large scientific facilities and mobile instrument platforms, such as particle and laser beams (Raman, CARS, SHG, THG), is gaining an increasing attention both from the point of view of non-destructiveness and the improvement of analytical protocols. The issue of the long-term integrity of works of art and archaeological artifacts should be considered for the investigations under these intense beams.

Safe analytical protocols for the study of cultural heritage collections using high-energy beams, such as the ion beam of the particle accelerator AGLAE (Accélérateur Grand Louvre pour l'Analyse Élémentaire) located in the C2RMF (Centre for Research and Restoration of Museums of France) are being developed in order to avoid introducing bias in the analytical results or inducing delayed effects resulting from slow kinetic processes. An unexpected modification of the target material should be alerted as soon as possible by real-time monitoring methods during the analysis. We propose to exploit the laser-induced breakdown spectroscopy (LIBS) technique to monitor the impact of the ion beam on the materials in real-time to prevent the onset of damage by detecting the desorption of gases by the paint materials, for example, lead white, one of the most sensitive pigments to irradiation. [1-2] The pigments and binding media are susceptible to release a small volume of gases under proton irradiation as a consequence of the energy transfer process between the beam and the target. The identification and quantification of the gas release during or shortly after the irradiation allows to understand and follow the evolution of its composition according to the experimental time of the tested sample. In this work, we will present and demonstrate the feasibility of this novel approach using LIBS and its specific capability to detect light elements in gases such as hydrogen. [3-4] The results show that the LIBS method has allowed us to successfully quantify the hydrogen emission of lead-white containing paint layers exposed to 10 to 40 μC/cm^2 of protons of 3 MeV in a sealed cell specially designed and filled with pure helium gas, which corresponds to standard PIXE (Particle Induced X-Ray Emission) analysis conditions. After irradiation by the ion beam, the ratio between the intensity of the line of hydrogen at 656.2 nm and that of helium was found to increases progressively with the irradiation dose, which indicates the implementation of a progressive desorption kinetics of hydrogenated gases under beam.

ACKNOWLEDGEMENTS

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SESSION 14

Molecular and Nanoparticles

Metallic and alloy nanoparticles: their detection and application to signal enhancement in LIBS

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Due to their several advantageous properties, metallic and alloy nanoparticles (NPs) are already widely utilized in the industry and science. Analytical laser and plasma spectroscopy not only uses these materials, but also contributes to or provides inspiration for the development of new ones. Spectroscopy techniques are also crucial to the characterization of NPs, as well as to the monitoring of nanostructures either during controlled synthesis or when released in the environment [1].

In this presentation, we provide an overview of our recent results related to the detection and application of NPs in laser induced breakdown spectroscopy (LIBS). In the latter category, our interest was focused on novel methodologies for the application of the nanoparticle enhanced-LIBS (NELIBS) approach [2]. Three particular fields are addressed in our contribution. First, we demonstrate the realization of signal enhancement in the liquid and gas LIBS analysis with the application of modified silver NP-decorated surface enhanced Raman spectroscopy substrates [3] and dispersing gold NPs in the gaseous samples [4], respectively. Second, we describe our efforts and results in obtaining a homogeneous and controlled NP coverage on solid sample surfaces for the purpose of enhancing LIBS elemental maps, useful for both in quantitative or qualitative applications. Last, but not least, we will also present our experimental observations related to the on-line and off-line detection of metallic and alloy nanoparticles generated by electrical discharge plasma generators, useful also for the monitoring of the NP production of these generators, e.g. in industrial settings [5].

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Ultrafast laser excitation in atmospheric pressure optical traps for studying attogram mass nanoparticles

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Owing to the exceedingly small mass involved, complete elemental characterization of single nanoparticles demands a highly precise control of signal background and noise sources. LIBS has demonstrated remarkable merits for this task, providing a unique tool for multielemental analysis of particles in the attogram-picogram mass scale [1-3]. Despite this outstanding sensitivity, the air plasma acting as heat source for particle dissociation and excitation is a meddling agent, often limiting the acquisition of an accurate sample signature [4]. Although thermal effects associated with ultrashort laser pulses are known to be reduced when compared to the widely used nanosecond pulse duration regime, attempts to improve nanoinspection performance using ultrafast excitation have remained largely unexplored. Herein, picosecond (*ps*-) laser pulses are used for the first time as a plasma excitation source for the elemental characterization of single nanoparticles isolated within optical traps in air at atmospheric pressure (Figure 1). Results for *ps*- excitation of copper particles lead to a mass detection limit of 27 attogram, equivalent to single particles of 18 nm in diameter. Temporal and wavelength-resolved plasma imaging reveals unique traits in the mechanism of atomic excitation in the picosecond regime, leading to a deeper understanding of interaction in single nanoparticle spectroscopy [5].

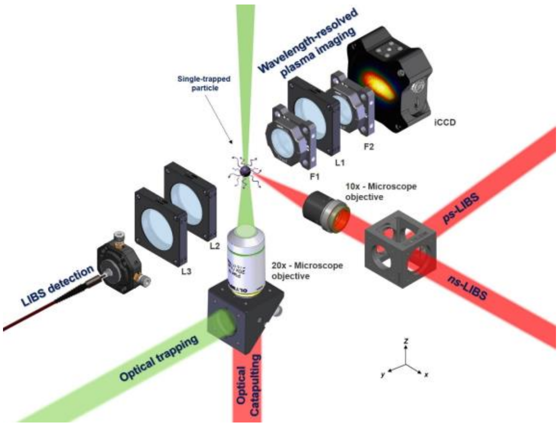

Fig. 1. Experimental setup illustrating the different excitation and detection lines comprising the λP-OC-OT-LIBS instrument.

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TiO_2 as a Modifier of a Bentonite/Sepiolite Substrate for Signal Intensification in LIBS Molecular Analysis of Organic Liquids

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Laser Induced-Breakdown Spectroscopy (LIBS) is an analytical technique for direct analyses of solid, liquid and gas samples, capable of performing elemental, molecular and isotopic characterizations [1]. However, analysis of liquids by LIBS is considered a major challenge, due to physical properties of the liquid and instrumental limitations [2]. In this work, it is described a solid substrate consisting of a Bentonite/Sepiolite composite enriched with titanium dioxide (TiO_2) for signal intensification in molecular analysis of organic, volatile and flammable liquids by LIBS spectroscopy. TiO_2 anatase is a well-known photocatalyst, which has a bandgap with energy equivalent to a 380-400 nm photon [3]. The substrate was prepared by calcination of a mixture of bentonite/sepiolite (70:30 %wt) at 800°C for 4h to remove organic matter. Then, the mixture was enriched with 2 %wt TiO_2, dispersed in water (10g / 50mL) and leave under reflux for 24h, according to the procedure described by Eslamipanah *et al.*[4], filtered and dried in an oven at 60°C for 24h. Pellet substrate was obtained with 300 mg of the composite submitted under pressure of 9.0 tons for 3 min (12.7-mm diameter, 8-mm height). Pellets of bentonite/sepiolite without and with 2 %wt TiO_2 were also prepared. Pellets are capable of ab-adsorbing up to 100 µL of solvent, avoiding its splash. A pulsed Nd:YAG laser (1064 nm, 5 ns, 80 mJ/pulse, 20 Hz) was focused on the pellet with a 10 cm focal length lens and the emitted radiation was focused on a 105-µm diameter optical fiber with a 5-cm focal length lens. An iCCD detector (iStar DH 734, Andor Technology) was employed for spectral acquisition (gate delay 3.0 µs and gate width 20 µs). Pellet was placed on a rotating device, allowing to integrated 30 laser shots focalised on different points of the pellet to obtain a spectrum. Figure 1 shows images of the substrate and energy dispersive spectroscopy (EDS) measurements that indicate the distribution of TiO_2 particles in Bentonite/Sepiolite pellets, specifically in a homogeneous way in the composite, as well as emissions of CH, CN and CC radicals for toluene embedded in the pellets, demonstrating the photocatalytic effect of TiO_2 [3]. The performance is further improved with the composite, as the intensity and the repeatability of the measurements are enhanced. As laser emits at 1064 nm, it is believed the continuum radiation of the plasma excites the TiO_2, promoting the photocatalysis reaction, increasing the emission signals.

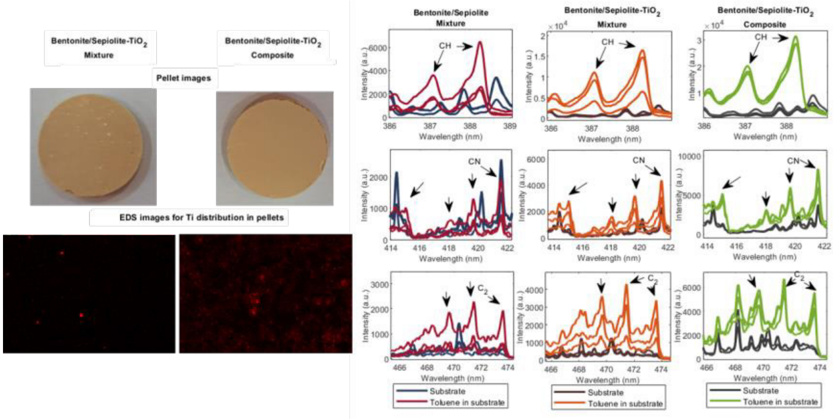

Fig. 1. Pellets of bentonite/sepiolite-TiO_2 mixture and composite, with respective EDS images and emission spectra for toluene embedded in these substrates (estimated irradiance of $2.9 \cdot 10^{12}$ W · cm^{-2}).

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Simultaneous UV/Visible/NIR + LWIR Laser Induced Breakdown Spectroscopy of Organic Isomers

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Recent studies of midwave- to longwave- IR (MWIR to LWIR) emissions (2- 12 µm) from laser-induced plasmas discovered various intact target molecules existed in the vicinity of the plasma [1]. Those molecular gas in the vicinity of the vapor-plasma plume were thermally excited by the hot plasma and emitted vibration-rotation spectral signatures in the mid-IR which could be utilized for molecular identification. Based on those discoveries, an innovative LWIR LIBS spectroscopy was recently developed [2]. One of the greatest advantages of this new spectroscopy is its simplicity to pair with a UV/Vis/NIR LIBS spectrometer. Placing side-by-side, UV/Vis/NIR LIBS spectrometer captures the ionic, and atomic emissions of a laser-induced plasma generated on the target surface in the UV to NIR region while the LWIR LIBS spectrometer acquires the molecular emissions of the same plasma plume in the MWIR to LWIR region simultaneously.

Isomers are compounds that contain the same elemental compositions but differ from each other by the way in which the atoms are arranged. Isomers are widely presented in organic materials and of particular importance in numerous biological chemistry applications. Among organic isomers, carbohydrates (Fig. 1a) represent a main class of compounds in biological systems and play a key role in numerous processes essential to life. Currently, the main techniques used in the analysis and identification of isomers are nuclear magnetic resonance, mass spectrometry, colorimetric analysis, and fluorescent responses [3]. All these techniques require complex sample preparation and cannot achieve real-time monitoring. LIBS, on the other hand, has the ability of in situ and real-time detection without sample preparations. Based on these advantages, LIBS has a wide range of field applications. However, using LIBS in UV/Vis/NIR spectral range (Fig. 1b) to identify one organic isomer from the others remains a great challenge for isomers sharing identical elemental compositions [3]. On the other hand, LIBS in LWIR range may be a complementary candidate for more rapid and robust identifications and differentiation of isomers. LWIR LIBS measurements (Fig. 1c) of solid monosaccharide samples revealed and identified spectral signatures of atomic, molecular breakdown products, and intact monosaccharide molecules in the vapor-plasma plume. The temporal evolutions of the LWIR LIBS spectra of monosaccharide isomers also reveal possible conformation shifts of the hot sugar molecules around the laser-induced plasma.

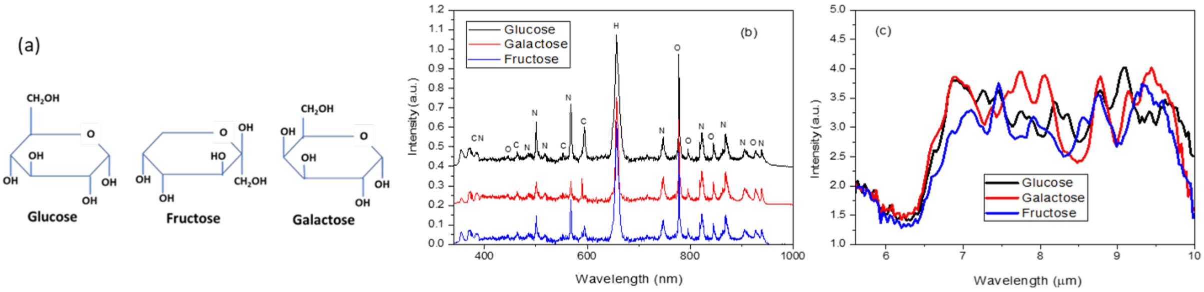

Fig. 1. (a) Monosaccharide isomers and (b) UV/Visible/NIR + (c) LWIR LIBS spectra of monosaccharide isomers.

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Isotopes Detection of GdO in Laser-Induced Plasma by Demon High Spectral Resolution Double Echelle Monochromator

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Isotopic shifts in GdO molecular emission were previously studied by Arc Induced Plasma (AIP) [1]. The spectrum was first photographed on a 1.5 m Bausch and Lomb concave grating spectrograph and the bands in the region 445.0-515.0 nm have been recorded on the high resolution 10.6 m concave grating spectrograph in first order with a reciprocal dispersion of 0.74 Å/mm. A large number of sequences of red degraded bands have been observed including A(1-0) transition with six heads at 446.40, 446.42, 446.45, 446.47, 446.54, and 446.60 nm. The five isotopic molecules, viz. ^{155}GdO, ^{156}GdO, ^{157}GdO, ^{158}GdO, and ^{160}GdO, are expected to contribute significantly to the spectrum. The calculated isotopic shifts with reference to the most abundant (^{158}GdO molecule) for the A(1, 0) transition have the values -0.62 (^{155}GdO), -0.41 (^{156}GdO), -0.019 (^{157}GdO), and +0.42 (^{160}GdO) cm^{-1}.

Figures 1a-b present the A(1-0) emission band in Laser-Induced Plasma (LIP) received with different spectral resolutions. With spectral resolution of 0.02 nm, we detect 3-4 heads, but the isotopic shifts are absolutely out of range. Figures 1c-d present the comparison of natural GdO and GdO enriched by ^{158}Gd. The enriched sample exhibits much higher emission intensity and a lot of new lines appear which may be ascribed to different isotopes in the spectral range of 22391.24-22400.92 cm^{-1} [1]. Besides, several evidently rotational bands in the spectral range of 22363.33-223712.31 cm^{-1} become relatively more intensive. Interpretation of each specific line is presently difficult because we do not know exactly the isotopic composition of the enriched sample. But it may be concluded that Demon monochromator has spectral resolution which is adequate to the task of isotopic shift analysis of molecular REE emission.

Data will be presented on several Gd isotopes spectroscopy and also the effect of Molecular Laser-Induced fluorescence combination with LIBS.

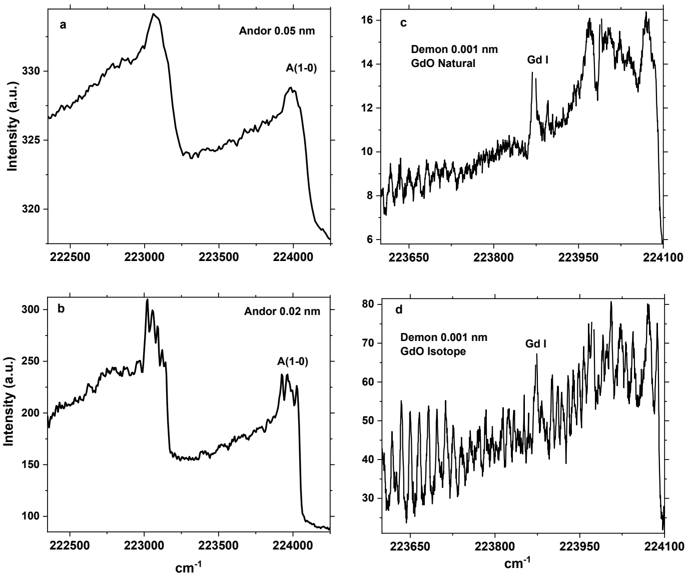

Fig. 1. A(1-0) GdO emission spectra with different spectral resolutions: a- 0.05 nm; b- 0.02 nm; c- 0.001 nm of natural GdO; d- 0.001 nm of ^{158}GdO enriched

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LIBS Analysis of Surface Homogeneity of Deposited Nanocomposite Films for Sensor Applications

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In the last few decades, technologies based on laser ablation in liquid [1] have become increasingly important in the synthesis of advanced nanomaterials and their application in different fields including development of efficient electroanalytical sensors for the determination of selected analytes. For sensor fabrication of optimal performance it is extremely important a uniform deposition of the colloidal nanoparticles (NPs) on the electrode surface. Laser-induced plasma spectroscopy (LIBS) can be an effective tool for spatial mapping of the concentration of deposited NPs as a confirmation of their successful immobilization at the surface. In this work we will discuss the results of LIBS application for the analysis of spatial homogeneity of the CuO/ZnO nanostructured surface after their deposition on carbon electrodes.

For preparation of composite CuO/ZnO nanostructures a novel method based on laser ablation in liquid in the external electric field was developed. A series of studies has been performed to explore the structure, morphology and composition of as-synthesized nanocomposites.

The LIBS experiments were carried out by using a Nd:YAG laser (LOTIS TII, LS2134D) for ablation, operating in a double-pulse mode at 1064 nm (energy 80 mJ/pulse, pulse duration 10-12 ns, optimal delay between the laser pulses 2 µs). Plasma emission spectra were detected using a grating spectrometer equipped with CCD linear array in the spectral range of 200–1060 nm. The spectrometer entrance slit was set perpendicularly to the ablation plume axis (Figure 1a). Such configuration allows selecting the emission of the plume at the 2-mm distance from the sample surface, thus eliminating most of the bremsstrahlung radiation and increasing the signal/noise ratio.

The obtained LIBS spectra revealed that NPs can be identified and that the LIBS technique can be used to determine the NPs elemental composition (Figure 1b). In the case of compound NPs, the control of their stoichiometry can be achieved using the comparative analysis of spectral line intensities related to the particles components and calculating the elemental composition of the NPs. The results of LIBS analysis of CuO/ZnO NPs composition were in a good correlation with the data obtained by the energy dispersive X-ray analysis. The main advantages of using LIBS for spatial mapping of the concentration of deposited NPs consist in its simplicity, speed, reliability and possibility of multi-elemental both qualitative and quantitative analysis that make LIBS a particularly well adapted tool to analyze the elemental composition of nanomaterials.

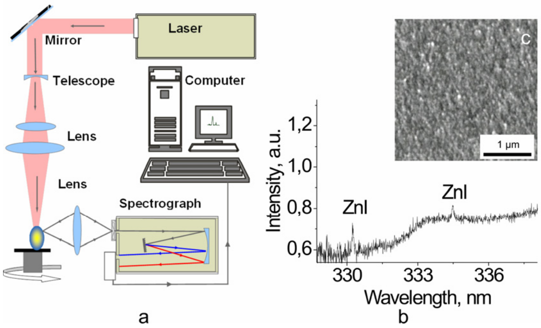

Fig. 1. Experimental set-up (a) and typical LIBS spectrum (b) of the deposited zinc oxide film (c).

ACKNOWLEDGEMENTS

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POSTERS

A design proposal for an unmanned LIBS system for the detection of bioagents in aerosols

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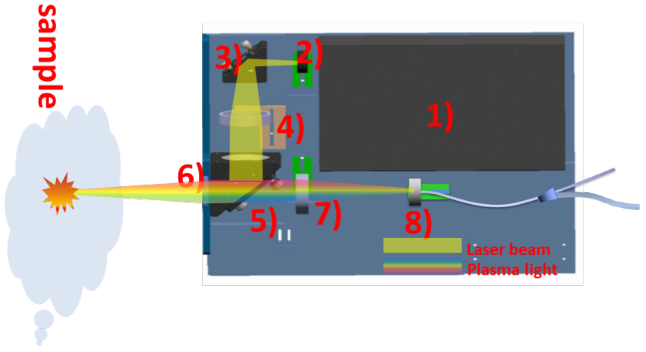
Recent accidental and terroristic events have, once again, demonstrated as bioagents can easily spread through the population: they can be transmitted by aerosol, via the water or the food supply, or by person-to-person contact.

To quickly identify these threats Laser-Induced Breakdown Spectroscopy (LIBS) has been attracted a growing interest in recent years due to its high capability in the identification of chemical species. The LIBS technique has been used in many applications, including the compositional analysis of rocks and soils, detection of explosives, sorting of metals, and trace element detection in aerosols, liquids, and solids. [1–2] Most recently, LIBS has also been investigated as a tool for detecting and identifying biological material [3]. In the framework of the EU Mosaic (Real-time monitoring and sampling of CBRN threats for improved dynamic mapping of threats, vulnerabilities, and response capacities) project, it is foreseen the development of a compact LIBS device for operation onboard UGVs and for stand-off detection of biological warfare agents in aerosols and on surfaces. In this contribution we present the system set-up of the device, that will be designed being capable to discriminate against interferents and different substrates and provided with processing algorithm to reduce false positive/negatives. The device will be based on a double pulse ns-laser and on a compact telescope. Chemometric techniques (principal component analysis, partial least square regression, or others) will be applied to analyze the signals. Finally, the device will be compact and autonomous for operation onboard robotic UGVs.



	Description
1)	DP – laser (λ = 1064 nm)
2)	1’’ dia. lens
3)	1’’ dia. HR-IR 45° mirror (45°)
4)	2’’ dia. lens
5)	2’’ dia. HR-IR HT-VIS dielectric mirror (45°)
6)	2’’ dia. lens
7)	2’’ dia . Lens collecting the LIBS light on the optical fiber
8)	Bifurcated optical fiber

Fig. 1. (left) Scheme of the LIBS head. (right) definition of the main optical components.

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Compositional analysis and classification of rocks with calibration-free standoff laser-induced breakdown spectroscopy (LIBS) and Principal component analysis (PCA)

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Standoff laser-induced breakdown spectroscopy was used to remotely analyze the geological samples, such as rocks, collected from various mines in the Baluchistan province of Pakistan. The laser-induced plasma was produced on the surface of rock samples at a standoff distance of 2 meters, and the plasma emissions were collected using a Newtonian telescope and LIBS2500+ spectrometer. The qualitative analysis of the emission spectra identified Ba, Na, Mg, Si, K, Ca, Fe, Cu, and Mn in almost all three rock samples, whereas the quantitative analysis of the detected elements with calibration-free LIBS (CF-LIBS) technique [1-2], the plasma temperature and electron number density were determined using Saha Boltzmann plot method and Stark broadening technique [3]. The compositional analyses revealed that iron is a major constituent, followed by copper, sulfur, and lead, but their concentration varies from sample to sample. These rocks were classified using principal component analysis (PCA). The CF-LIBS results were validated with the XRF analysis, which shows close agreement. This work will be extended toward the LIBS sensor for deployment in mines and fields.

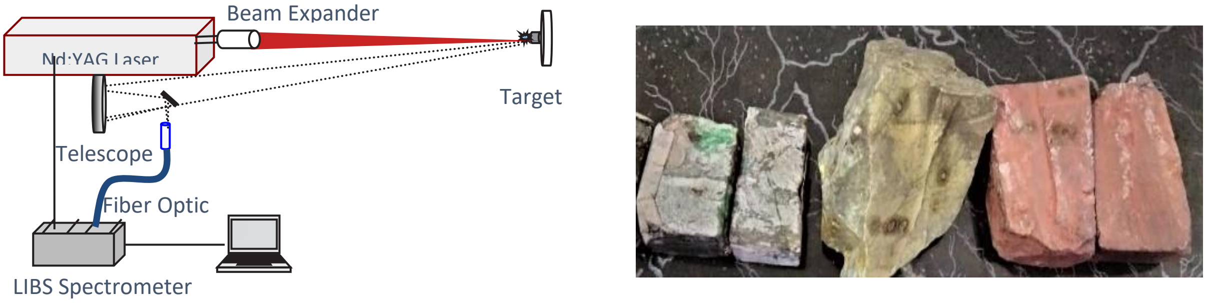

Fig. 1. The schematic of standoff LIBS setup and photograph of rock samples

ACKNOWLEDGEMENTS

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AlN Plasma Emission Behavior in Nitrogen and Argon Atmospheres

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A comparative study of plasma emission during Nd-YAG laser ablation of AlN target in N_2 and Ar ambiances has been performed at different pressures and different laser fluences, using optical emission spectroscopy diagnostics. Into nitrogen ambience the emission spectra are dominated by lines of Al, Al^+, Al^{2+}, N, N^+, N^{2+} and molecular bands of N_2 and N_2^+ species distinguished by their prompt emission. In addition to atomics and ions lines detected in nitrogen, in argon gas the emission lines of Ar, Ar^+ and Ar^{2+} were observed (fig 1a). For both gases, no emission of AlN molecules was detected with experimental conditions using in this work. To follow the kinetic of plasma species, we investigated space and time resolved of their emission spectral lines at 1.5 mbar of N_2 and Ar pressures. Then, the temporal profile of principal emission lines was reproduced. Comparatively to the temporal profile of Al in ambient nitrogen, which showed triple components starting to appear at greater distances (d ≥5.5mm), in argon atmosphere an evolution of a multiple structure appeared from 2mm (fig 1b). Into nitrogen ambience, the plasma components were forward peaked, whereas in argon, the particular components moved backward undergoing reflected shocks. Further, we found that the fast components observed for each ambient gases follows the fast component observed into vacuum. Our results are of particular interest in view of selecting the optimal regime of AlN target ablation and plasma composition-emission affected by laser fluences for each ambient gas pressure for AlN thin films deposition.

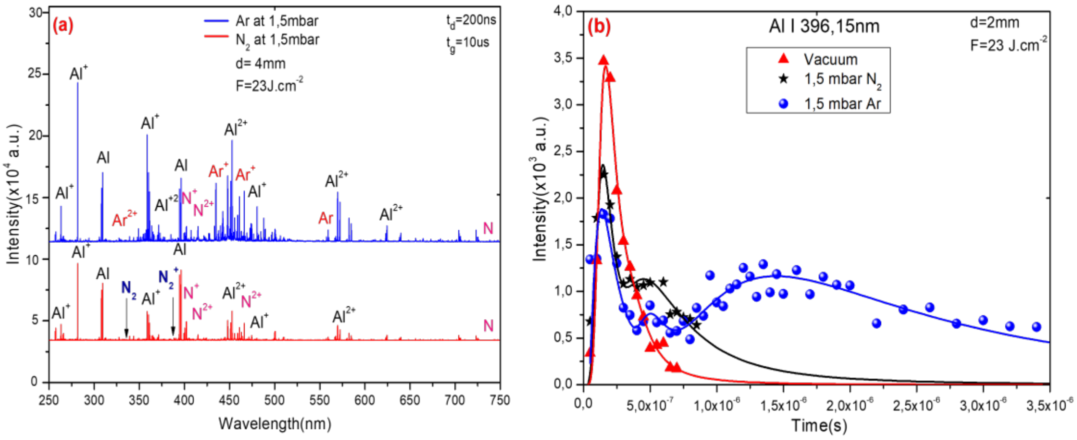

Fig. 1. (a) Emission spectra from 250 to 750nm of all emitting species of AlN plasma at 1.5mbar of N_2 and Ar pressures. (b) The temporal profile of Al into vacuum and at 1.5 mbar of N_2 and Ar pressures recorded at 2mm.

Keywords: Laser Induced Plasma; Laser Ablation; Optical Emission Spectroscopy, Aluminum Nitride.

Expanding the Elemental Coverage by Combining LIBS with ICP-TOF-MS for High-Speed Imaging

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The use of laser ablation-inductively coupled plasma-time of flight-mass spectrometry (LA-ICP-TOF-MS) has become an intriguing option for the analysis of materials due to the ability to capture the entire mass spectrum with each laser pulse. However, a few hurdles still exist: the speed of analysis must be precisely synced with the laser ablation system, the difficulty of measuring light elements with a TOF, and the data treatment of very large data sets when performing large mapping experiments, to name a few. The work presented here will discuss some of these hurdles while providing pathways to address them.

The speed of analysis, including the syncing of the LA system (TOF sync) will be displayed using a two-volume laser ablation chamber (TwoVol3) in combination with a dual concentric injector (DCI) to provide ultra-fast washouts with speeds up to 1,000 Hz (in this example the max laser repetition rate was set to 200 Hz). To address the difficulty of detecting light elements, laser-induced breakdown spectroscopy (LIBS) is coupled to the LA system to provide coverage to elements such as Li, Be, C, Na, Mg, K, and Ca that may be difficult or impossible with the TOF-MS. LIBS also provides the unique ability to measure H, N, O, and F at the same time when the LA chamber is purged with a inert gas, which is the case when performing LA experiments (e.g. helium is almost always used). Lastly, the entire data processing of the TOF and LIBS data will be conducted in iolite V4, providing a complete, single software platform capable of handling large data sets.

In this work, a sample of finchite and carnotite, strontium and potassium uranyl vanadate minerals, respectively, are analyzed using LIBS and LA-ICP-TOF-MS to better understand the isotopic and chemical composition. Of interest is the isotopic ratio of ^{235}U/ ^{238}U and ^{206}Pb/^{207}Pb, and the distribution of U and O within the mineral. As finchite and carnotite are alteration phases of primary uranium ores, with their limited solubility making them important immobilization species for environmental U(VI), understanding the paragenesis of these phases in the context of spatially resolved isotopic information is essential towards understanding the environmental behavior of uranium. Further, this effort provides valuable insight into the potential of analyzing radiological material with high spatial resolution for other environmental, mineralogical, and nuclear nonproliferation applications.

Study of intensity enhancement by a ns-laser focused on slow or fast component of a fs-LIP

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Femtosecond lasers have been more commonly used in LIBS set-ups in the last decade. These lasers, which are technologically more complex than their ns-counterparts, deposit pulse energy in a time frame shorter than the electron-lattice relaxation time. As a consequence, the ablation mechanism does not involve extensive thermal effects, ensuring confinement of heat-damage within a small region (improving lateral resolution) and avoiding fractionation (unequal ablation of the matrix elements) [1]. However, the fs-laser-induced plasma (fs-LIP) does not interact with the laser pulse, therefore losing a mechanism of excitation of the ablated matter as compared to typical ns-LIBS.

To overcome this drawback, a strategy is to re-excite the plume with a second laser shot in a double-pulse scheme. There are various geometrical configurations, most typically collinear (both pulses normal to the sample) and orthogonal (second pulse parallel to the sample, as depicted in **Fig. 1**) [2]. In order to avoid further damage of the sample, an orthogonal configuration is chosen in this work. Previous studies carried out by our group have characterized the impact of the reheating laser focusing spot position with respect of the fs-LIP, both in terms of height (distance to the sample surface) and lateral displacement with respect of the vertical axis of symmetry of the plume. In particular, the structure of the fs-LIP plays a fundamental role in the optimization of the fs/ns-LIBS scheme; the plume is divided in two components: a slow one that remains close to the sample surface and a fast one that quickly displaces away from it. Characterizing the fs-LIP is then very important prior to the positioning of the ns-laser. In this work, a comparison is made when selectively focusing onto the slow or the fast components at different interpulse delay times, collecting broad-range spectra to carry out a study with multielement information for both fundamental diagnostics and analytical enhancement evaluation, for which a time-integrated spectrometer is utilized.

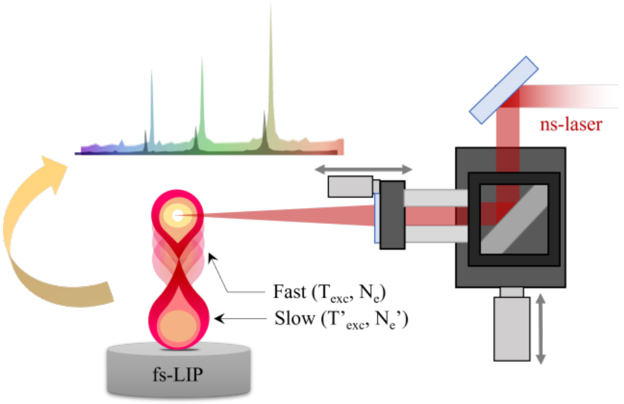

Fig. 1. Schematic representation of the focusing scheme. Depending on interpulse delay time, the ns-laser can be focused onto distinct fast and slow fs-LIP components.

ACKNOWLEDGEMENTS

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Self-calibrated LIBS approach for space exploration and volcanic hazards assessment

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Among all the analytical techniques, LIBS is the one that can more easily adapted to advanced application for the space exploration as well as to extreme environment in the Earth. This is not only because the instrumentation can be compacted and automatized, but especially because self-calibrating spectroscopic approaches can be used for developing robust analytical methodologies for employing LIBS in advanced missions[1,2].

On previous investigations on LIBS for asteroid exploration, it has been shown for the first time, that the all instrumentation could be calibrated on the emission spectrum itself, allowing a decrease of the potential payload of the LIBS instrumentation and increasing the robustness of the elemental analysis with calibration free (CF) methods[3] and opening the way to compact on-flight instrument for asteroid classification and space exploration. Recently the same methodology has been extended for volcanic Investigation in combination with gas sensors. In particular, volcanic plumes are rich in fine juvenile ash, representing magma fragments expelled from the crater during explosive eruptions. The composition of fine ash is of primary importance for volcano monitoring and hazard assessment, but not much effort has been put until now to build portable instrumentation allowing real-time measurements. A laboratory experiment is carried out to build and test an apparatus based on Calibration-Free Laser Induced Breakdown Spectroscopy (CF-LIBS)[4]. This methodology is extremely promising because it does not require any standard calibration strategies (no calibration curve and no instrumental calibration) and the elemental composition is directly obtained by the laser-induced breakdown optical emission. In the experiment, volcanic ash samples are suspended in the air by a laser-induced shockwave in a dedicated chamber, as to mimic the conditions of a volcanic plume, and contemporaneously the laser-induced plasma (LIP) spectrum is analyzed. Based on the result of this experiment, the feasibility of the construction of a portable instrument to be used in the field for the monitoring of active volcanoes is discussed..

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Correlation of Surface Hardness and Plasma Temperature in LIBS Measurements of Low-Alloy Carbon Steel

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Conventional tactile methods determine the surface hardness of materials such as metals mechanically by comparing abrasions or indentations on the material surface. This mechanical process is time-consuming and the surface of the sample is severely affected by small craters. With classic hardness testing methods (Brinell, Rockwell, Knoop, Vickers) it is almost impossible to map an inhomogeneous distribution of the material hardness. However, in industry the visualization of differently hardened areas of components would be of great interest.

A promising alternative could be an optical, i.e., non-contact and almost non-destructive, fast test method with laser-induced breakdown spectroscopy (LIBS). Recent publications have reported a correlation of material hardness and the ratio of ionic to atomic spectral line intensities [1-2]. In our measurements we found a correlation of the surface hardness and the intensity ratio of the Fe II (263.1 nm) and the Fe I (358.1 nm) emission lines. A drawback of these methods may be the dependence of the derived hardness values on the selected spectral lines. In order to consider several emission lines simultaneously, we measured the correlation of plasma temperature and surface hardness (Fig. 1). Since both the hardness and the ablation of atoms and ions depend on the microscopic structure of the surface of the sample a correlation can be expected.

We used samples of 80CrV2 steel with a surface hardness gradient obtained by a special heat-treating and tempering process. After determining the different hardnesses using the conventional tactile Brinell method, we obtained spatially resolved maps of the plasma temperature through LIBS measurements. Of course, the spatial resolution of the classic destructive methods is quite low, but a correlation of surface hardness and plasma temperature is obvious.

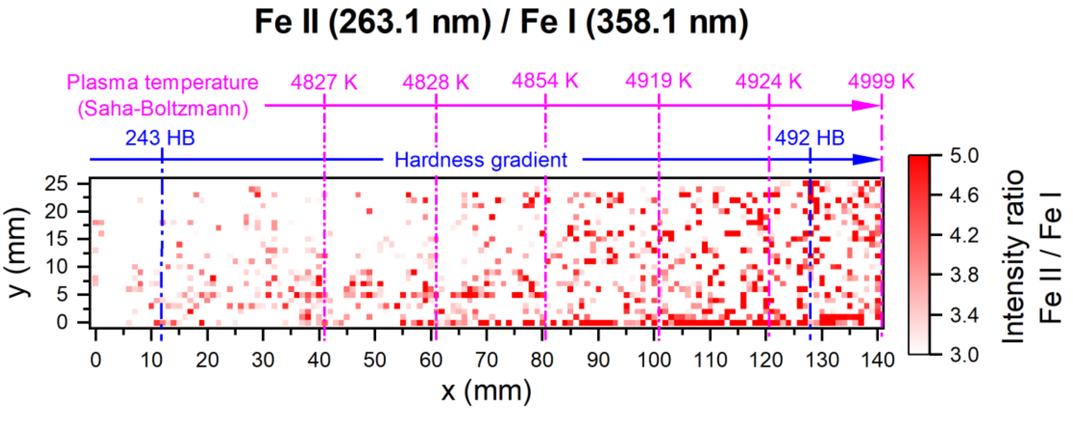

Fig. 1. Imaging of the trend of the surface hardness of low-alloy carbon steel (80CrV2) using LIBS mapping with a spatial resolution of 1 mm² in comparison to the measured Brinell hardness (HB) gradient and the simultaneous increase in plasma temperature from left to right. The stated plasma temperatures represent an average of values in the y-direction.

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LIBS of uranium in eye-safe area

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Uranium has numerous geochemical forms of presence in rocks, forms separate minerals or is isomorphically present in other minerals. It can therefore enter the environment natural way, i.e. directly from uranium minerals like uraninite or secondary forms, potentially by weathering and leaching of rocks, or by anthropogenic manner associated for example with ore processing. In the Czech Republic, mining is currently subdued, but there are several areas rich in uranium. Besides, there is local pollution associated with mining and processing of uranium ore.

Determining the presence of uranium in geological structures is important for both geological exploration or for determining possible ways of migration, given that uranium is very soluble in the aqueous environment and therefore passes well into underground and surface water sources.

LIBS analysis, enabling the determination of the uranium occurrence in minerals and other rock components is very fast, robust and efficient, it can be performed both in situ and in laboratory conditions. However, in the places with people fluctuation, LIBS in-situ measurement is difficult because of the risk of damage to the human eye by the randomly reflected laser beam. That is the main motivation we tested LIBS using lasers from the eye safe spectral region, therefore the emission wavelengths close to 1.4 μm or longer. Results achieved using following wavelengths will be presented: 1.54 μm (Er: Glas), 1. 64 μm (Er:YAG), 2.01 μm (Tm:YAG), 2.12 μm (Ho:YAG), possibly also 1.34 μm (microchip laser) and their comparison with the wavelength 1.06 μm (Nd:YAG laser).

At the same time, we dealt with the problem of possible respiratory exposure to vaporized sample containing uranium in laboratory conditions or places with limited air exchange.

This study has a significant practical impact for the implementation of the detection of the uranium presence in different types of rocks with regard to the minimization of health risks. This can be possibly utilized in a variety of research applications for rapid determination of total concentration of uranium in environmental samples, including screening of areas of interest for mining, subsequent analysis of trace isotopes like ^{236}U and others.

ACKNOWLEDGEMENTS

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Validation of Laser-Induced Breakdown Spectroscopy assisted by Laser-Induced Fluorescence (LIBS-LIF) for the measurements of platinum and palladium in solid ore

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The determination of precious metal concentrations in solid ore samples is a critical step in the mining industry. Laser-induced breakdown spectroscopy (LIBS) has been used for this purpose, but its detection limit is often too high to measure precious metals in ores. In this study, we investigated the LIBS-LIF technique to improve the detection limit of platinum and palladium in solid ore samples.

Calibration curves were established using certified reference materials from the Lac des Îles palladium mine, and the LIBS-LIF technique resulted in a platinum detection limit of 0.15 ppm over an average of 200 laser shots, two orders of magnitude lower than the LIBS technique. The palladium detection limit is around ten times lower than platinum due to the more efficient excitation-fluorescence scheme. The LIBS-LIF method was used to estimate palladium [1] and platinum concentrations in six quarter core fragments from the Lac des Îles palladium mine ore. The technique provides concentrations similar to those obtained by conventional chemical analysis for solid surface and pulverized rock analyses, with two exceptions where palladium appeared to be very inhomogeneously distributed in the ore.

The results of this study demonstrate the potential of the LIBS-LIF technique for determining precious metal concentrations in solid ore samples.

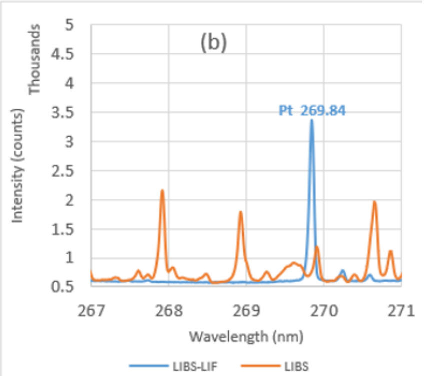

Fig. (b) LIBS (orange curve) and LIBS-LIF (blue curve) spectra of platinum analytical line Pt 269.84 nm.

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We are grateful to Impala Canada for providing us with quarter drill cores from the Lac des Îles mine and their laboratory analysis, as well as for their financial support. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) [grant number STPGP 521608-18].

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Double-pulse LIBS in water with up to 600 bar hydrostatic pressure and up to 400 millijoule each pulse

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Double-pulse LIBS is a promising technique for deep-sea exploration [1]. However, high pressures in the deep sea will have an impact on the plasma and its emission [1, 2]. Therefore, LIBS measurements in water with up to 600 bar and 400 mJ each pulse were done to select laser parameters which promote optimized spectral line emission from plasma even at elevated pressures, where line broadening until loss of the most spectral information can occurs. Optical emission spectroscopy, using a Czerny-Turner spectrometer, has been applied to study the plasma and its emission for different laser parameters. For this purpose, the ratio between continuous and line radiation as well as the line broadening were examined.

Contrary to previous observations in shallow water [3], it could be observed that an increase in the laser pulse energy can lead to larger line broadening and a higher continuum-to-line ratio in case of a reduced delay time between the laser pulses, as are required at high pressures in water due to the reduced cavity and plasma lifetime. For a more detailed study of the dependence of continuum-to-line ratio and line broadening on the laser pulse energies and the hydrostatic pressure, spectra were measured for a variety of laser pulse energies of up to 400 mJ.

These comparative spectra with different laser parameters and hydrostatic pressures are shown in this contribution. Thereby, it has been found, that higher laser pulse energies, especially with high hydrostatic pressure, can also have an adverse effect on the measured spectrum. Finally, conclusions for the later application in elevated hydrostatic pressure were made.

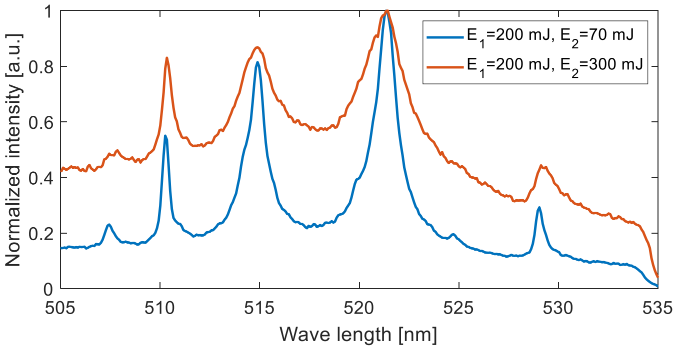

Fig. 1. Two spectra of a plasma, *generated by* double-pulse LIBS on a brass surface in shallow water for different energies of the second laser pulse *and a pulse delay of 10 µs*. Copper lines at 510 nm, 515 nm, 522 nm and 529 nm.

ACKNOWLEDGEMENTS

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Laser-Induced Plasma Lasers: Polarization properties.

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We demonstrate that stimulated emission and lasing occur under appropriate resonant and **linearly polarized** optical pumping of a pre-formed laser-induced plasma (LIP) plume. It manifests as the emission of intense, collimated, and **polarized** beams. We call this effect Laser-Induced Plasma Lasers (LIPLs). Lasing was found in LIP on atoms from the 13th and 14th periodic table groups and in *Na, Ca, Ti, Zr, Fe, Mg, Cu,* and *V.* The polarization properties of the lasing light are studied, finding that the Degree Of Polarization (DOP) varies depending on the pumping transition chosen. DOP can be reliably controlled by applying a relatively weak ($\leq$0.3 T) external magnetic field $\boldsymbol{B_{ext}}$ [1-5].

LIP on atoms from the 13th group (except Tl) generates according to the 3-level generation scheme [1-3]. A model explaining polarization and effects of the external magnetic field in LIPLs of the 13th group is based on considering optical transitions between magnetic sublevels involved in the pumping–generation cycle.

Most LIPLs on the 14th group and on other elements generate according to the quasi-tree generation scheme, which we nominate as a Direct Generation (**DG**) scheme because generation occurs directly from the pumped level. A typical example is Ti LIPLs. The modified Hanle effect may explain DG LIPLs polarized generation and $\boldsymbol{B_{ext}}$ effects.[5]. Pumping the same generation line from ground levels with ($\Delta J=\pm1$) leads to a change in the sign of the DOP of the generation line. The same changes in the sign of the DOP occur for generation lines, with common upper level but lower levels differ on $\Delta J=\pm 1$ (different generation lines wavelengths). Examples of such generation are presented in Fig. 1 for V LIPL; The same effects are observed on other DG LIPLs. These effects need additional theoretical consideration. Still, it may be supposed that density matrix formalism has to be used to explain these effects.

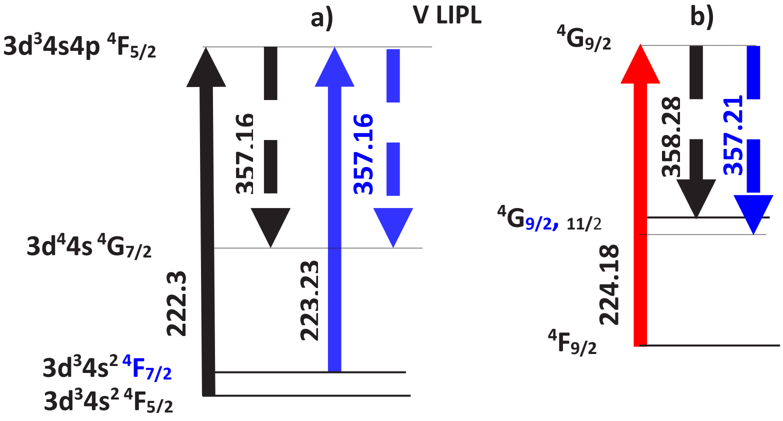

Fig.1 Examples of the V LIPL transition schemes for ground manifold (a) and for lower generation levels manifold (b) with $\Delta J=1$. The numbers along the arrows are pumping and generation wavelength. Black and blue arrows down are generation transitions with negative and positive DOP, respectively. Energy level lines are not located accordingly to scale for more clarity.

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Diagnostic Insights into Cancer and Malaria Utilizing Machine Learning Peak-Free LIBS

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LIBS has remarkable potential towards point-of-care disease diagnostics as the spectra are chemically rich. However biometal spectra from body tissues and fluids are subtle (peak-free) and hardly discernible against the background, making single shot trace LIBS in air and atmospheric pressure a challenge: the plasma are dense and inhomogeneous. As the spectra are multivariate, leveraging LIBS with machine learning enables to detect, extract and analyze biometal signatures and to give diagnostic insight on the physiological state of the body from which the fluids and tissue originate.

Single-shot peak-free LIBS realizes rapid but accurate trace analysis and speciation of Cu, Zn, Fe, Mg, Mn in malarial blood; and Cu, Fe, Mg, Zn in model tissue (HEp-2 and Lewis carcinoma); and in human liver, breast and abdominal tissue biopsies utilizing ANN calibration strategies. The method utilizes only one standard - to delineate the trace biometal spectral regions of interest for feature selection toward multivariate modeling, and for method validation.

Blood Cu, Fe, Zn, Mn, Mg and Cu/Zn ratio alter empirically and predictably during malaria pathogenesis. Peripheral finger blood drops dried directly on Nucleopore filters and analyzed by peak-free LIBS is discriminated by PCA as malaria-infected or healthy; and the morphological evolution of *Plasmodium falciparum* is accurately predicted. Liver, breast, and abdominal biopsies group up into malignant or benign stages in agreement with their histopathological state. Utilizing SVM modelling Hep2 and Lewis tissues get segregated into early, benign and malignant based on the speciation of Mn, Cu, Fe.

Pathogenesis of cancer and malaria are found to depend critically on the correlative concentration (and speciation) of trace Mn, Fe, Zn Mg, Co and Cu (as the disease biomarkers) in body tissues and blood as well as on their sequential alterations and multivariate correlations. Machine learning-based peak-free LIBS shows potential to inform the etiology of both cancer and malaria at the biochemical level (trace biometals are intrinsic to cellular biochemistry). Mn, Fe, Zn and Cu are the most suitable trace metal biomarkers to detect, characterize and perform early diagnosis of cancer and malaria.

Fig. 1. (a) PCA score plot for cultured blood (b) PCA cclassification of liver, breast and abdominal tissue biopsies.

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Improving the sensitivity and resolution of LIBS by laser technology

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Since its birth, laser-induced breakdown spectroscopy (LIBS) has been concerned as one of element analysis techniques with great potential. However, the application of LIBS is restricted by its relatively weak sensitivity and resolution. Therefore, it is urgent to develop new methods of LIBS to improve its sensitivity and resolution. In our team, different laser sources were developed to improve the sensitivity and resolution of LIBS. The femtosecond supercontinuum (SC) light can be generated by nonlinear effects of femtosecond laser propagating in medium, which has an extremely wide spectral range (shown in Fig.1a) and a high peak power. A femtosecond SC light source was produced in our lab by a femtosecond Ti:sapphire laser. Then the SC light was used to excite the plasma plume at different delay time. The experimental results show that the signals of multiple lines for multiple elements can be enhanced obviously. Relative low resolution is also a problem of LIBS. Normally, it is hard to analyse the isotope by LIBS directly except using a spectrometer with very high resolution. However, the expensive cost and low sensitivity of high-resolution spectrometer limits the application of it on isotope analysis. To overcome these problems, a nanosecond Ti:sapphire laser with narrow linewidth and widely tunable range was developed in our lab for isotope analysis. With the help of resonance-enhanced LIBS (RELIBS) and laser ablation absorption spectroscopy (LAAS) technology, a high spectral resolution and high sensitivity could be achieved. To promote the application of LIBS, a portable nanosecond laser (shown in Fig.1b) with high peak power was developed [2], which has been used to analyse the electrolytes in human blood serum. The prediction accuracies for three ions of electrolytes analysis can be smaller than 4% [3]. In summary, we have developed different type of lasers for LIBS to improve its sensitivity and resolution.

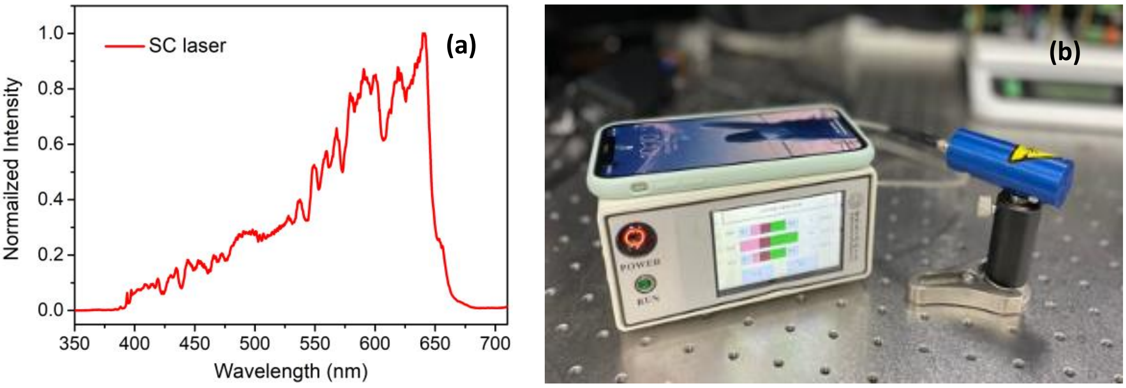

Fig. 1. Laser sources for LIBS measurement (a)the spectrum of femtosecond SC laser, (b) a portable **laser.**

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Quantification of solid metallic nanoparticles on glass functionalized surfaces by Laser-Induced Breakdown Spectroscopy

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For decades, nanomaterials have demonstrated a diversity of properties that constitute them as a strategic support for the development of highly sensitive and selective detection systems for an important variety of analytes[1]. A wide range of detection modes, such as absorption, fluorescence and surface enhanced Raman scattering, have been used during the progress of nanoparticle-based detection systems. These systems have demonstrated that metal nanoparticles are an interesting prototype for developing rapid, sensitive, selective and low-cost detection systems for the quantification of various analytes in many types of samples, but especially environmental[2] and biological[3] samples.

In this study, we have successfully applied the LIBS technique for the identification and quantification of solid metallic nanoparticles of Au and Ag on glass surfaces previously functionalized with thiol groups. The results show that the LIBS technique offers high selectivity for the identification of Au and Ag nanoparticles immobilized on functionalized glass surface, and conveniently low detection limits for the quantification of the nanoparticles of interest, among other analytical advantages over techniques conventionally used in sensor systems based on solid metallic nanoparticles; paving the way for the use of LIBS as an emerging technique in the field of metallic nanoparticle-based sensors and biosensors.

ACKNOWLEDGEMENTS

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Clever data treatment procedure for spectrochemical analysis with laser-induced breakdown spectroscopy spectral data

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Thanks to its many analytical advantages, such as direct sample analysis without any pre-treatments[1], the LIBS technique has been successfully employed in the spectrochemical analysis of a wide range of samples[2]. However, the treatment of LIBS spectral data is still a major analytical challenge that must be approached in a very specialised way[3] so that 1) aberrant spectra that are generated in the analysis are easily identified and eliminated, 2) the effects of instrumental problems (the variation of laser pulse energy) on the results of the analysis using the spectra are minimised, and 3) a comparison of spectral similarities and differences is made from a quantitative point of view; so that a spectrochemical study of high confidence and reproducibility can be carried out.

In that sense, this work highlights a simple but clever approach for LIBS spectral data processing to perform spectrochemical studies based on the quantitative establishment of the similarity and differentiation of two LIBS spectra from the same or different samples. The data processing method is based on three parts: 1) the statistical study of Pearson's linear correlation coefficient for individual spectra relative to a mean spectrum, 2) fitting the correlation with a probability distribution function and establishing a confidence level for the selection of suitable and aberrant spectra and 3) quantitative establishment of spectral similarity by determining the statistical differentiation (f1) and similarity (f2) factors. The obtained results not only evidence the suitability of the proposed method to serve as a basis for comparative spectrochemical studies based on reliable and reproducible LIBS spectral data but also provide a simplified perspective for the path towards the generation of LIBS libraries.

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TOTAL SOIL PHOSPHORUS DETECTION USING LASER-INDUCED FLUORESCENCE-ASSISTED LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Quantification and monitoring of phosphorus in soil plays a critical role in environmentally friendly agriculture, especially in mitigation of phosphorus leakages to water systems and subsequent risk for eutrophication. On the other hand, deficiency in phosphorus would lead problems in development and growth of cultivated crops. Therefore, monitoring and quantification of phosphorus status in soil is essential.

Laser-Induced Breakdown Spectroscopy (LIBS) is a well-established online elemental detection technique that highly benefits from minimal requirement for sample preparation, applicability to solid, liquid, and gaseous samples, and robust experimental arrangement. It is extensively used in different fields of science and industry for elemental quantification utilizing the atomic emission from the plasma plume produced on the sample with a laser pulse [1]. However, LIBS suffers from relatively poor limit of detection (LoD) for elements that require high plasma temperature for thermal, excitation as the high temperature plasma is available only for a short time and, on the other hand, this is the time when the background continuum radiation is high and most other elements are excited as well with substantially temperature broadened lines causing spectral interferences.

In this work, Laser-Induced Fluorescence (LIF) is applied to the conventional LIBS setup (LIBS-LIF) for sensitive and selective phosphorus detection. The plasma plume is overlapped with another laser pulse that is produced with a wavelength tunable OPO laser unit. The OPO laser pulse is tuned to 253.6 nm that is resonant to the atomic phosphorus transition to re-excite the phosphorus atoms produced in the plasma plume. The experimental arrangement is shown in Fig. 1a. The resulting phosphorus fluorescence is observed at 213.6 nm as shown in Fig. 1b. The LIBS-LIF approach improved the LoD of soil phosphorus detection up to 31-fold compared to phosphorus-optimized conventional LIBS measurement enabling studies in soils containing low amounts of phosphorus. It is demonstrated that calibration curve can be generalised to cover same soil types from different geographical location, thus, improving the applicability and efficiency of the method. As LIF arrangement can be added to any LIBS setup, providing that a suitable light source is available, LIBS-LIF can be utilized in analysis of phosphorus in various environmental samples, such as water reservoirs, that are in the need of more sensitive phosphorus detection schemes with high sample throughput.

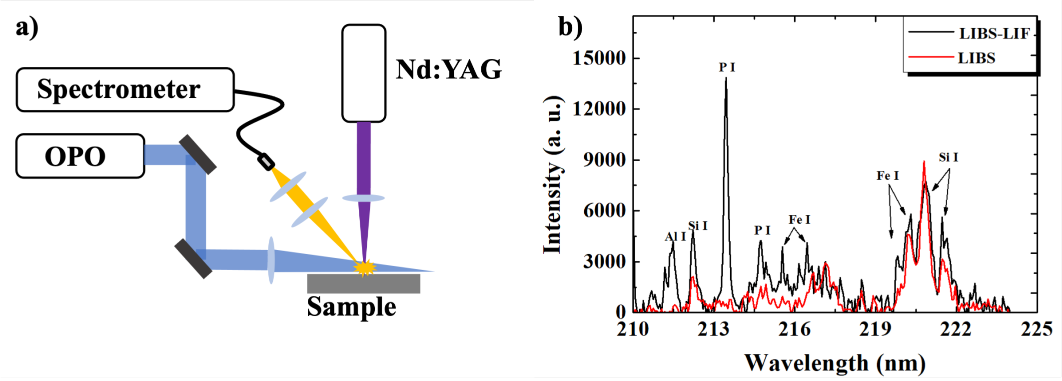

Fig. 1: a) The experimental arrangement, b) the observed phosphorus fluorescence at 213.6 nm with LIBS-LIF on a soil sample containing 2.2 mg/kg of soluble phosphorus.

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LIBS detection of organic biosignatures in carbonate and sulphate substrates under a Mars simulated atmosphere

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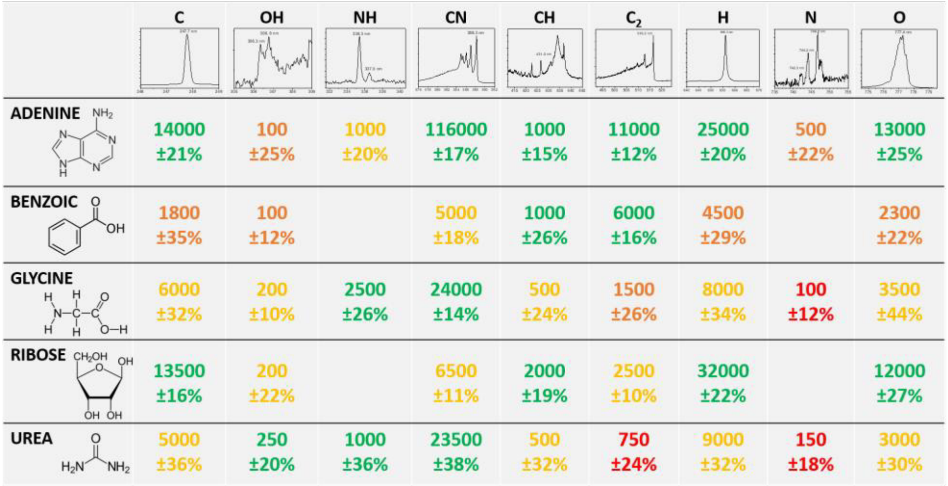
This work's main aim is to detect organic biosignatures in doped substrates under Martian-like atmosphere. The results presented here attempted to demonstrate the capability of LIBS as a valuable technique for detecting and interpreting past life evidence in organic biosignatures for future space missions [1-3].

Limits of detection (LOD) were estimated in conditions similar to those used in the SuperCam module of the Perseverance rover. For LIBS analysis, two types of inorganic matrices were used as substrates (present on the Martian surface and whose formation could be associated with a past biogenic origin). However, these matrices interfered with the molecular signals, making detecting organic signals an analytical challenge. This study analyzed organic compounds of interest in astrobiology in association with carbonates and sulphates under laboratory simulations of Martian conditions. Finally, in order to identify and classify groups with similar organic structures and a priori, the same spectral fingerprint, a chemometric study was achieved using discriminant function analysis (DFA). From LIBS spectra, atomic and molecular signals were used for DFA analysis.

Results may contribute to establishing the optimal experimental conditions for the observation of organic carbon species in laser-induced plasmas and the basis for the subsequent detection of carbon biosignatures in geological samples of interest as potential Mars analogues.



	C	OH	NH	CN	CH	C_2	H	N	O
ADENINE	14000 ±21%	100 ±25%	1000 ±20%	116000 ±17%	1000 ±15%	11000 ±12%	25000 ±20%	500 ±22%	13000 ±25%
BENZOIC	1800 ±35%	100 ±12%		5000 ±18%	1000 ±26%	6000 ±16%	4500 ±29%		2300 ±22%
GLYCINE	6000 ±32%	200 ±10%	2500 ±26%	24000 ±14%	500 ±24%	1500 ±26%	8000 ±34%	100 ±12%	3500 ±44%
RIBOSE	13500 ±16%	200 ±22%		6500 ±11%	2000 ±19%	2500 ±10%	32000 ±22%		12000 ±27%
UREA	5000 ±36%	250 ±20%	1000 ±36%	23500 ±38%	500 ±32%	750 ±24%	9000 ±32%	150 ±18%	3000 ±30%

Fig. 1. Mean intensities of organic emission signals detected for each analyzed molecule in a simulated Mars atmosphere. An example type spectrum of each atomic line/molecular band is also shown.

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Use of the LIBS technique in archaeological contexts for the re-association of human remains.

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Over the last 30 years, osteological studies applied in archaeology have increased the understanding of past populations, from health-related contexts to food practices, diseases, social relations, identity, etc. [1, 2]. Despite the advances that have emerged in this field of knowledge, there currently needs to be more opinions about the limitations of this type of research. One of these limitations, which significantly affects collective burial contexts, is the problem of re-association of commingled[3], disarticulated and even decontextualised bone remains, an issue aggravated by human variability[4].

Laser-induced ablation spectroscopy (LIBS), by the nature of its technical foundation, is a widely used analytical technique in spectrochemical applications for the identification/classification of a wide variety of materials[5] and archaeological samples[6]. Its ability to quickly and easily generate characteristic atomic emission line spectra that serve as fingerprints of analysed materials constitute a strategic analytical approach for its application in osteological re-individualization remains. In this work, we present a new application of the LIBS technique for the re-individualization of bone remains from the graves of the archaeological site of El Castillo Viejo de Ponferrada, León, Spain. Based on the spectrochemical identification of the fingerprint of the elements that compose the bone tissue of each individual and its subsequent classification through advanced classification algorithms such as artificial neural networks (ANN). The results demonstrate the analytical convenience and feasibility of the LIBS technique for studying archaeological bone remains and the significant spectrochemical specificity offered by LIBS spectral data for archaeological and cultural heritage-related studies.

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Investigation of Nail Samples Using Laser-Induced Breakdown Spectroscopy and Energy Dispersive X-ray Spectroscopy

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Renal stone diseases are extremely painful and affect people worldwide. Given the importance of the role of elements in their formation and the fact that the growth and genesis of renal stones are imprinted in their morphology, the aetiology of lithiasis could be studied with relevant analytical tools. Renal diseases also greatly affect the calcified tissues such as teeth, bone, hairs and nails of humans. The prime objective of this investigation is to investigate the effect of renal disease on human nails. We have employed laser-induced breakdown spectroscopy (LIBS) for the study of nails samples of healthy person and renal patients with tobacco and smoking habits. The elements detected in the nail samples were calcium, magnesium, silicon, iron, sodium, phosphorous, strontium, titanium, zinc, and cadmium. Significant changes in the level of these elements were observed. We have also used the partial least squares discriminant analysis (PLS-DA) method to distinguish the different nail samples of different categories. Our results revealed the potential use and usefulness of LIBS techniques to study nail samples.

ACKNOWLEDGEMENTS

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Investigations of matrix effects on steel samples with LIBS and LA-SD-OES (Laser Ablation-Spark Discharge-Optical Emission Spectroscopy)

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Laser-Induced Breakdown Spectroscopy (LIBS) is an element analysis technique that can be applied to nearly all kinds of materials and many applications even under harsh conditions [1]. However, the appearance of unfavourable matrix effects between samples with different composition is well known. In our research, we use a combination of laser ablation and an electric spark discharge for plasma formation and optical emission spectroscopy, a technique introduced as LA-SD-OES [2], [3]. The electric discharge appears between one tungsten electrode and the conductive and grounded steel samples. The discharge is triggered by the laser pulse. The energy is provided by a 25 nF capacitor on which a high voltage of up to 3 kV is applied. Strong matrix effects with LIBS emerged during experiments on around 50 steel samples with a Fe concentration any higher than 94 wt% and a lot of different minor and trace elements. However, it was only observed with LIBS under typical conditions (ns, 1064 nm, 55 mJ) and not with LA-SD-OES [4]. Further investigations showed drastically lower Fe spectral line intensities (Figure 1) and bigger crater volumes for Si content higher than about 2 wt%. To find the physical mechanisms causing these effects observed in LIBS, the steel properties such as the Vickers hardness, the steel phase and the grain sizes were investigated.

Moreover, in our ongoing LIBS measurements we investigate this matrix effect in steel in further detail by using a double-pulse (DP) LIBS system with 532 nm laser wavelength and a femtosecond (fs) LIBS system with 1040 nm wavelength.

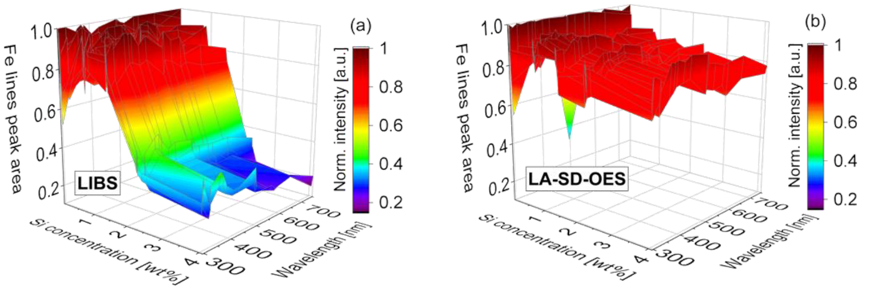

Fig. 1. Intensities of 20 Fe emission lines in 36 steel samples of different Si concentration (0–4 wt%) measured by LIBS (a) and by LA-SD-OES (b).

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Go-on-target in art

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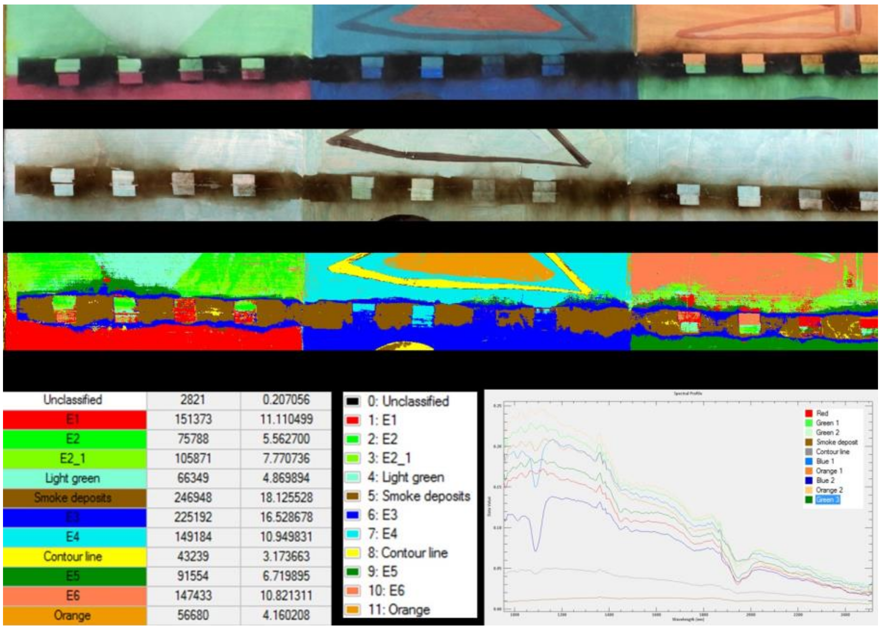
Go-on-target in art (GoT) is an exploratory research project focused on developing an original remote setup for investigation and diagnosis of cultural assets, providing valuable results that will improve the characterization and discrimination of materials (mapping) for preservation, restoration, evaluation of interventions or authentication of heritage.

GoT correlates 3 extremely versatile methods of investigation, with high sensitivity and precision: Hyperspectral Imaging, Laser Induced Breakdown Spectroscopy and Raman Spectroscopy in a hybrid system for *in situ* analyses of cultural heritage (no sampling) that generates a complete stratigraphic profile of the object, guiding the restorer and the investigator in the micro/nanoscopic universe of the hidden layers and providing information about the original material, the degradation mechanisms, hidden defects, hidden layers, repainting, previous interventions, painting technique, new (contemporary) or historical materials validation etc. [1]

The hyperspectral analysis digitally "decomposes" the layers of the artwork and reveals the particularities of the technique specific to an artist or a school, and by associating spectroscopic analyses at atomic/ionic and molecular level provides a synergistic effect for the complex identification of unknown samples, complex information on degradation mechanisms, hidden defects, hidden base layers, overpainting, restorations, artist's painting technique, validation of new (contemporary) or historical painting materials, authentication of works of art, thus providing a valuable tool for authentication of works of art, the anti-fraud fight and art trafficking.



Unclassified	2821	0.207056
E1	151373	11.110499
E2	75788	5.562700
E2_1	105871	7.770736
Light green	66349	4.869894
Smoke deposits	246948	18.125528
E3	225192	16.528678
E4	149184	10.949831
Contour line	43239	3.173663
E5	91554	6.719895
E6	147433	10.821311
Orange	56680	4.160208

Fig. 1. HSI analysis of a polychrome mural painting

ACKNOWLEDGEMENTS

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High - resolution imaging of Li-ion electrodes by micro-LIBS

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The improvement of Li-ion batteries is a major challenge for the decarbonization of individual means of transport. Their behavior and performance mainly differs by the nature of their electrode materials, some of which are still in development. In order to fit with electrochemical models, the elemental distribution of lithium in electrodes needs to be measured at micrometric resolution. Nowadays, few techniques (e.g. MRI (Magnetic Resonance Imaging)) are able to characterize lithium. These techniques are generally time consuming and are difficult to apply in routine due to technical constraints. Furthermore, other approaches such as SEM (Scanning Electron Microscopy) or TEM (Transmission Electron Microscopy) combined to EDS (Energy Dispersive Spectroscopy) can image most of the elements with a high spatial resolution (~ µm) [1, 2] but cannot detect lithium with enough sensitivity due to its low atomic number. In this work we propose to apply the micro LIBS-based imaging approach for the characterization of the lithium distribution in various types of electrodes. Thanks to its high sensitivity for light elements and the possibility to focus the laser beam on very small surfaces, LIBS is very promising for this application [3-5]. However, there are several major obstacles to overcome. Firstly, the measurement resolution must be comparable to that of SEM – EDS (~ 1 µm). Achieving this resolution is indeed essential to observe properly lithium grains of a few micrometers in size. Secondly, given the small amount of material ablated per shot (~ pg), it is essential to work with a high sensitivity and optimized detection system. In this presentation, we will describe an original LIBS microscope using a high numerical aperture objective (×50 magnification), a UV laser beam (266 nm) shaped to achieve an M^2 close to 1, and a detection system optimized for measurement in the visible range. With this instrument, the lithium distribution has been imaged with a resolution of 3 µm (cf. figure 1), as well as other elements of interest, such as C, Co, Ni, Cu and Al. Charged and discharged NMC type electrodes with different lithiation states will be shown. To the best of our knowledge, this is the first time that such type of LIBS analysis is performed.

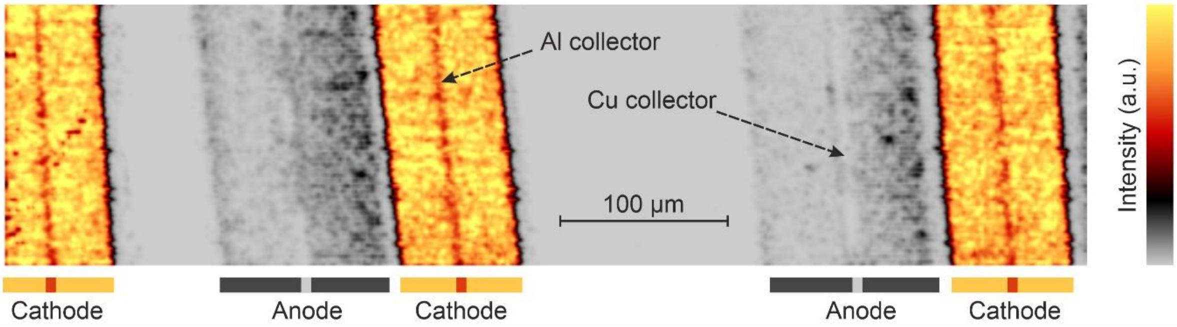

Figure 1 : Lithium image at 3 µm spatial resolution on a sample composed of a formed and discharged NMC type commercial battery.

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An Experimental Study of Colliding (Ultrafast) Laser Plasma Plumes Using Time Resolved Imaging and Spectroscopy

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We report preliminary results from single and colliding plasma plumes created using femtosecond (<100 fs) laser pulses. The experiments are designed to observe the evolution of lateral colliding plasmas, along with plasma plumes created on V-shaped targets. This work is intended to serve as a comparison with earlier nanosecond-pulsed colliding plasma experiments.[1-3] Preliminary results from these experiments will include temporally resolved and/or spectrally filtered images as well as spectra (e.g., figure 1, LHS). The objective is to track the evolution and elucidate the behaviour of colliding plasmas in a regime where differences in the nature of the ablation process and the subsequent features/characteristics of the individual or 'seed' ultrafast laser plasma plumes themselves, and stagnation layer formed at their collision front, can be examined.

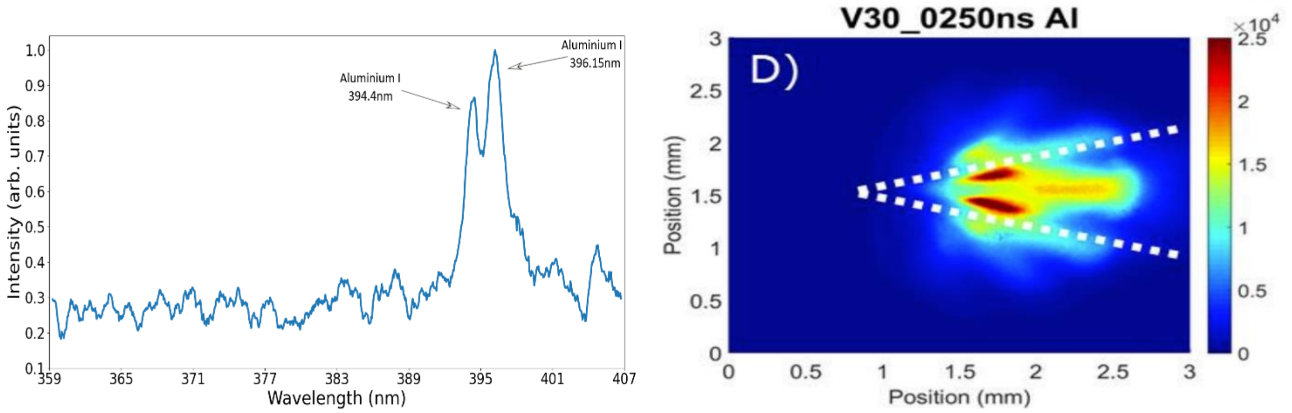

Fig. 1. (LHS) Time Integrated Spectrum – femtosecond laser produced plasma formed on a flat aluminium target showing the Al I doublet at 394.4nm and 396.15nm (This work). (RHS) Nanosecond laser produced colliding aluminium plasmas at a time delay 250ns from plasma ignition (10ns ICCD gate width). The image is spectrally filtered to isolate the Al I 394.4nm and 396.15nm transitions.[4]

ACKNOWLEDGEMENTS

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Long-short double pulse laser-induced breakdown spectroscopy for carbon detection in steel samples

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Long-short double pulse laser-induced breakdown spectroscopy (LS-DP-LIBS) employed to detect the carbon element in solid and liquid steel samples. The important issues for the industrial application of LIBS are investigated in this work, which include the carbon excitation in steel, the influences of CO2, the quantitative analysis and the escape phenomenon of carbon [1]. It is found that the CO2 in air can also be involved to the plasma generation and emits the carbon specific spectral lines. The strong emission line at C I 193.091 nm can be observed when the sample is placed in the gas atmosphere with CO2. CO2 in atmosphere has shown significantly influences on LIBS signal. The laser beam excites the sample material as well as the gas molecules in atmosphere. Thus the CO2 in air can also be involved in the plasma generation and emits the carbon specific spectral lines. The study indicates that the ignoring of CO2 influences may cause an error for quantitative analysis of carbon, especially in the case of minor carbon measurement on steel production line.

It is also found that the carbon signal generated from liquid steel is continuously decreasing after the sample is molten, as shown in Fig. 1. Through the real-time monitoring of liquid steel using LS-DP-LIBS, it is found that the carbon signal is continuously decreasing after melting, which has been known as carbon escape phenomenon. The investigation on the O2 effect has demonstrated that the redox reaction is an important reason for this phenomenon. The carbon escape phenomenon should be fully considered for the quantitative analysis of carbon element in liquid steel. The experimental investigation demonstrates that the influences of O2 cause the carbon escape phenomenon in liquid steel, which should be fully considered for the industrial application of LIBS.

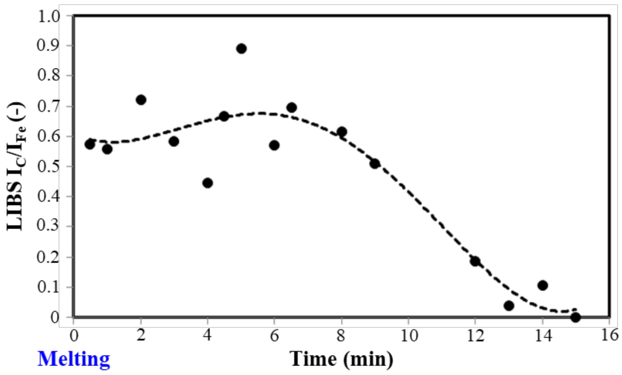

Fig. 1. Monitoring of carbon element in liquid steel sample using UV LS-DP-LIBS.

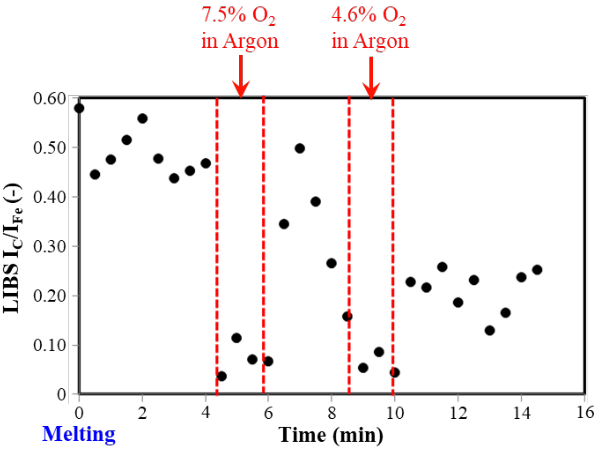

Fig. 2. Carbon escape phenomenon in liquid steel sample

ACKNOWLEDGEMENTS

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Deep learning-based laser induced breakdown spectroscopy for inline process monitoring

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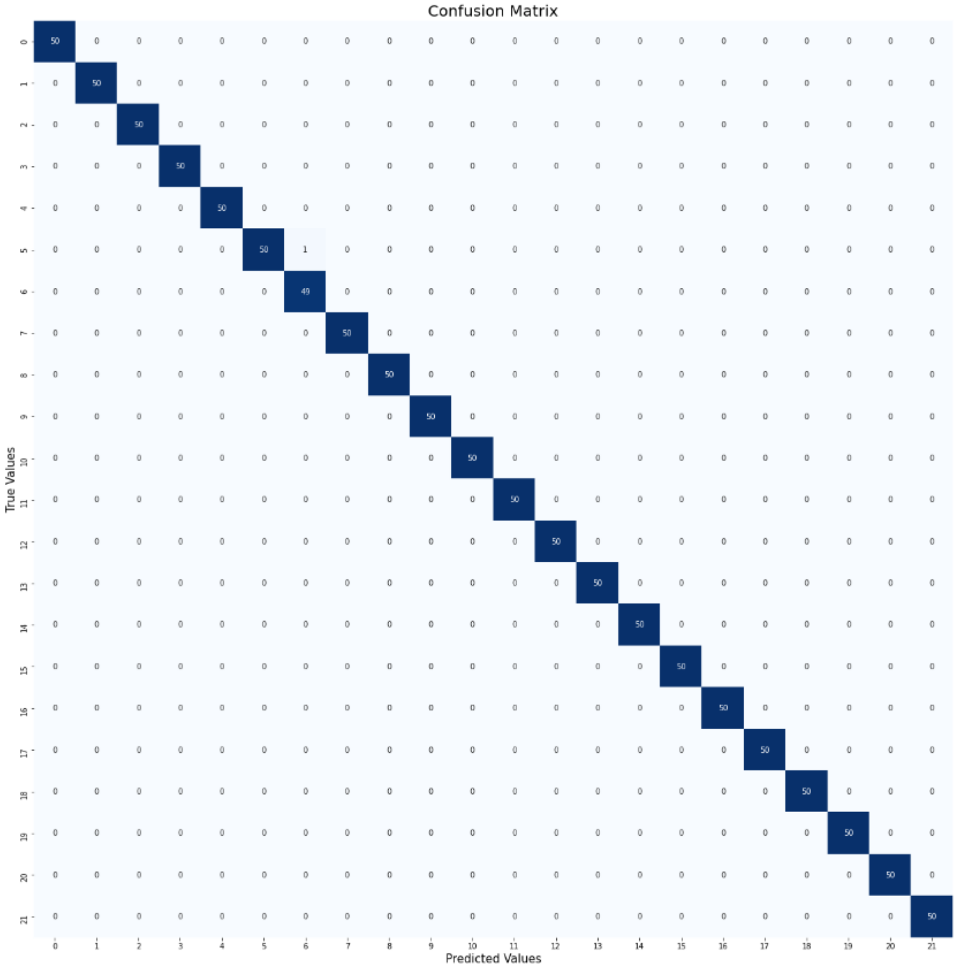
Real-time quality evaluation by artificial intelligence is being studied for the purpose of smart laser processing devices. In this study, we develop an on-site laser processing quality evaluation algorithm based on the Convolution Neural Network (CNN). By developing a CNN-based quality evaluation algorithm, analysis time of the laser spectral data was reduced to less than 10 millisecond with the 96% accuracy. The results verify the possibility of real-time quality evaluation in the industrial field by artificial intelligence.



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17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	50	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	50	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	50	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	50	0
21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	50

Fig. 1. Confusion matrix of CNN model

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Scanning laser induced breakdown spectroscopy for depth resolved elemental analysis

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Laser induced breakdown spectroscopy (LIBS) has been applied to material analysis successfully, especially in post mortem analysis for several fusion device [1, 2]. Quantitative and qualitative results of erosion and retention information in different plasma facing material (PFM) were obtained [3, 4]. However, the high roughness value of ablation crater, the ablated material in the crater edge (not belongs to the layer to be analysed), the thermal effect of laser and the difficulty for detecting elements with low concentration are still challenging [5]. To solve these problems or decrease the influence of these problems, a scanning LIBS system is developed.

In this system, scan mirror and ultrafast fiber laser with high frequency (50 kHz) are implemented. With scan mirror and high frequency laser, flexible ablation rate (depth resolution), ablation area (crater edge effect) and accumulated laser number (sensitivity) can be modulated by changing the scan speed and scan length. For W analysis, a depth resolution (ablation rate) around 7 nm/pulse is obtained, while the surface fluctuation of the ablated bottom can reach 42 nm, as shown in Fig. 1, and the depth resolution is tunable from 7 to hundred nm/pulse by changing the scanning speed without changing the ablation energy, which makes the results comparable in different depth resolutions. By adjusting the ablation laser energy density, we find a threshold around 2 J/cm^2 to excite the H atom in plasma, when the laser energy density higher than the threshold, H retention analysis become achievable. Therefore, with a smaller focused laser spot, H line can be observed in air in W and Fe samples.

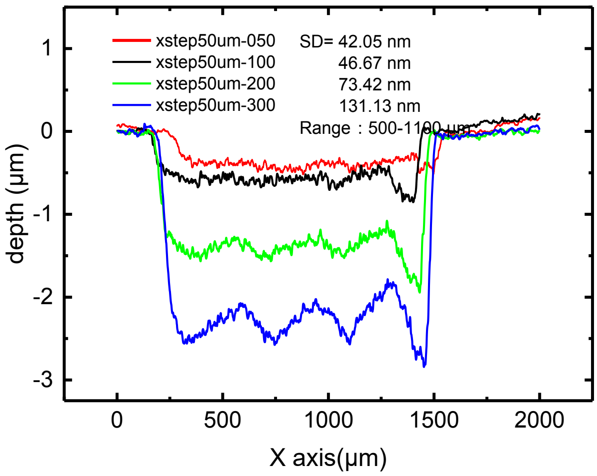

Fig. 1. The profile of ablated W spmple after different scan times(from 50 to 300 times).

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Analyzing the Catalyst Particles in the Vertically-Aligned Carbon Nanotubes using Laser Induced Breakdown Spectroscopy Method

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Vertically aligned carbon nanotubes (VACNTs) have been received much attention in last decades for many applications including polymer nanocomposites (PNCs) [1], nano-porous membranes [2], supercapacitor electrodes [3] etc. However, the use of VACNTs in demanding applications such as electronics, supercapacitor and/or sensors is still limited within their low quality in batch production [4]. For many applications, fast detection of impurities and their content is the critical issue before the large-scale synthesis of VACNTs for applications. However, characterization methods such as the X-Ray diffraction method are unable to detect the catalyst particles due to the low amount of them in the composition (<5% wt.)

In this study, laser induced breakdown spectroscopy was utilized to identify the catalyst particles in the VACNTs. LIBS measurements were performed using a high resolution Mechelle type spectrometer and a 4.4 ns pulsed Nd:YAG laser. The laser pulses were focused on the target with a 200 mm lens. The photons emitted from the VACNTs materials were transferred to the spectrometer with a 150 mm focal parabolic mirror and a 200 micrometer diameter optical fiber. Line spectra of carbon, iron and Si substrate in VACNT between 200 and 900 nm wavelength were recorded and analyzed.

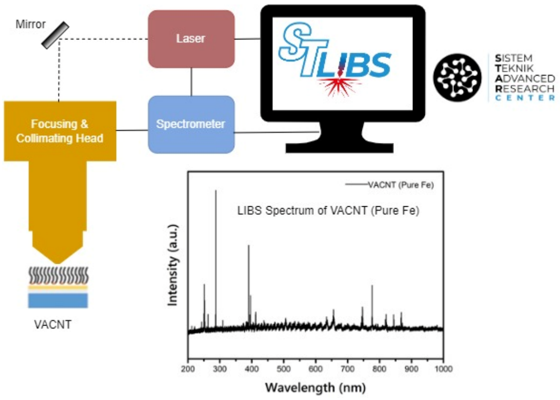

Fig. 1. LIBS spectrum of synthesized VACNT onto pure Fe catalyst particles.

ACKNOWLEDGEMENTS

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Femtosecond filament-induced breakdown spectroscopy for quantitative analysis of remote targets

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Composition analysis of a remote target corresponds to an important application in industry, in homeland defense, or in Mars exploration. The use of laser-induced breakdown spectroscopy (LIBS) based on a nanosecond laser is limited in the operation range by the diffraction which affects the linear propagation of a nanosecond laser pulse, leading to a linear increase of the focused beam size with the detection distance. The operation of a nanosecond laser-based remote LIBS system is usually limited within a distance of about 30 m [1]. The optical Kerr effect corresponds to a nonlinear refractive index effect, which causes an intense laser beam to self focus in such way to balance the diffraction, leading to the formation of a filament. Since its first observation with a chirped-pulse-amplification (CPA) femtosecond laser in 1995 [2], femtosecond laser filamentation has been extensively studied in the atmospheric scale, especially by the Teramobile team, for the development of a series of innovative applications [3], among which one can remark remote filament-induced breakdown spectroscopy (R-FIBS). Experimental works carried out by the Teramobile team demonstrated the feasibility of R-FIBS, and in particular, pushed the operation distance up to 180 m [4]. The subsequent developments have concentrated on the control and optimization of filamentation, as well as the enhancement of FIBS signal. Quantitative analysis with R-FIBS remains however much less explored, while at the same time, quantitative analysis with conventional nanosecond LIBS experienced a substantial improvement of its quantitative analysis capability especially thanks to the introduction of machine learning method for LIBS spectral data processing [5].

In this work, we studied the process of quantitative analysis of a solid target at a remote distance by FIBS, using a set of certified reference materials in aluminum alloy. A CPA laser operating at 800 nm, 10 Hz, and delivering pulses of 30 mJ with 35 fs pulse duration, was used to generate filaments at the surface of a target placed at a distance of 13 m from the laser (Fig. 1 a), with the help of a telescopic beam expender able to adjust the starting position of the filaments. The LIBS emission was detected using a telescope with a 10-inch primary mirror, coupled to an echelle spectrometer equipped with an ICCD camera. A typical LIBS spectrum is shown in Fig. 1 (b) with the indications of detected major and minor elements. For the quantitative analysis purpose, a univariate model for Cu based on the Cu 324.75 nm line normalized with the Al I 256.25 nm line is shown in Fig. 1 (c). For a further improvement of the analytical performances of R-FIBS, a multivariate model based on machine learning has been developed. In addition, the influence of an inclination of the sample with respect to the filaments was studied to simulate a real measurement scenario, where the posture of the target is uncontrollable. We will present the detailed results in the conference.

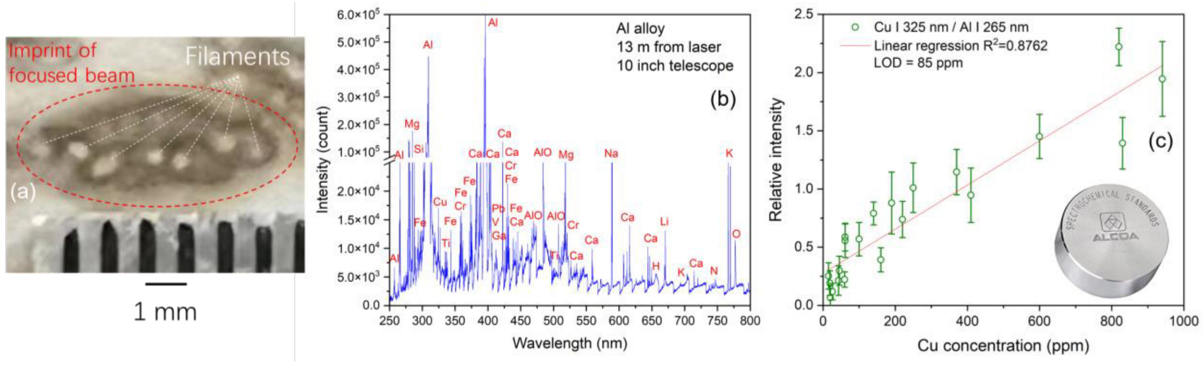

Fig. 1. (a) Imprint of a focused femtosecond pulse on an aluminum sample at a distance of 13 m from the laser, together with filaments formed inside; (b) Typical filament-induced breakdown spectrum with indications of lines from some major and minor elements; (c) Univariate regression model for Cu.

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Comparison of analytical methods for determination of scaling ions in oilfield produced water

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The deposition of ions in pipelines used in oil exploration at marine platforms is one of the main causes of productivity reduction of the oil industry due to the high concentration of alkaline-earth metals in produced water [1]. In the present work, two different methods for the determination of scaling ions in produced water by LIBS were compared. The determination of Mg(II), Ca(II), Sr(II) and Ba(II) ions was performed using filter paper for phase conversion, while underwater measurements allowed the determination of Ca(II) and Sr(II) ions. A Q-switched Nd:YAG laser (Brilliant Quantel B, 1064 nm, 20 Hz) was employed for the method using phase conversion (Figure 1a). Liquid samples were deposited on a quantitative filter paper (Whatman 40) and dried in an oven before LIBS analysis. A Quantel Brio laser source, 1064 nm, 10 Hz was employed for underwater measurements, whose laser beam was expanded by a concave and a convex lens, reflected by a lens combination and focused into a cuvette filled with sample (Figure 1b). It was only possible to detect Ca(II) and Sr(II) ions with this setup. With optimized conditions and data normalization in the phase conversion method, it was possible to obtain LOD from 1.0 to 11.4 mg L^{-1}, with a linear range from 20 to 80 mg L^{-1} for Mg(II), Ca(II), Sr(II) and Ba(II). For underwater measurements, limits of detection of 0.58 mg L^{-1} for Ca(II) and 0.85 mg L^{-1} for Sr(II) were obtained. Both methods were applied to oilfield produced water samples and the spectral examples for each method is shown in Figure 1 (c, d). The scaling ions determination by both methods provided results that do not significantly differ from those obtained by ICP OES at a confidence level of 95%. It was demonstrated that the two methods can be used as an analytical tool to help prevent scale in the oil industry.

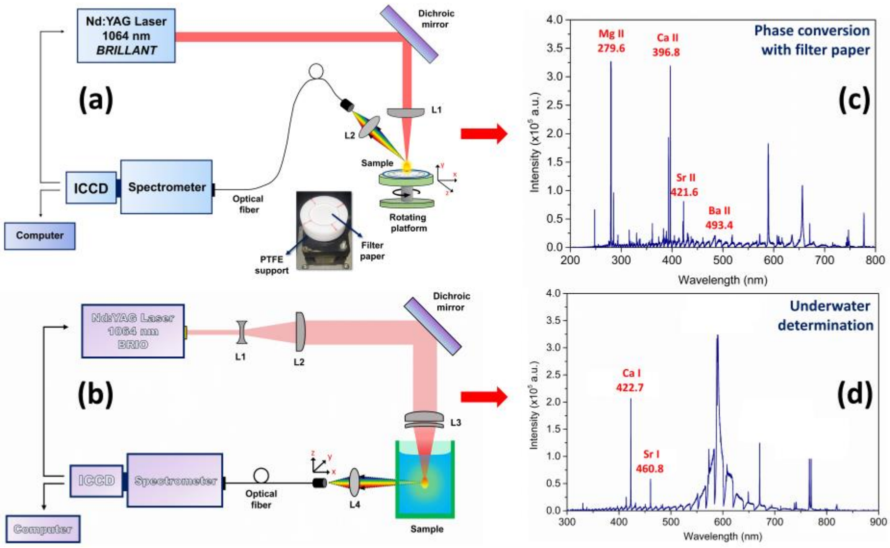

Fig. 1. (a) LIBS system for measurements with filter paper, (b) LIBS system for underwater measurements, (c) LIBS spectrum with phase conversion method and (d) LIBS spectrum with underwater measurement method.

ACKNOWLEDGEMENTS

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Laser induced breakdown spectroscopy of underwater manganese targets in presence of electrolysis

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When a pulsed nanosecond laser hits a solid target immersed in water immediate plasma formation occurs. Later on the plasma expansion gets confined due to the surrounding liquid and leads to transient quenching followed by fluid mechanical effects such as formation of high speed shockwaves and cavitation bubbles. Performing under water Laser Induced Breakdown Spectroscopy (LIBS) has been a challenge due to severe confinement effect imposed due liquid medium [1,2]. In this work, efforts were put on to enhance the LIBS signal emission intensity for a submerged Manganese target in presence of electrolysis. For this, manganese target in distilled-deionized water was irradiated by a pulsed Nd:YAG laser (Wavelength 532 nm, Repetition Rate 10 Hz, Pulse duration 6ns, and Energy 25 mJ) in presence of an electric field applied via two parallel plates Copper electrode connected to 0-30 V DC power supply. Fig 1 shows the recorded LIBS spectra performed at 0 V and 30 V wherein the predominant peak shows enhancement in LIBS signal. This has inference onto material processing as antiferromagnetic manganese oxide is also formed during laser irradiation at Manganese Water interface.

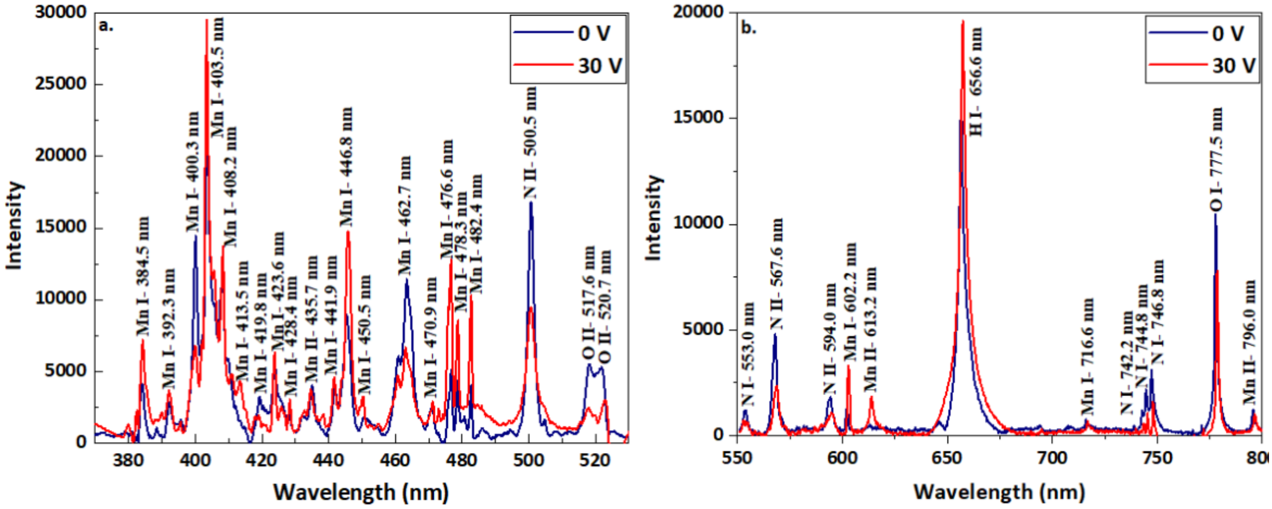

Fig. 1. LIBS spectra of manganese target in water at applied voltage of 0 V (blue line) and 30 V (red line) from (a) 370-530 nm, and (b) 550-800 nm wavelength

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Diagnosis of melanoma using blood based on laser-induced breakdown spectroscopy with machine learning methods

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There are two challenges in the diagnosis of melanoma. The first is to identify melanoma from healthy control, and the second is to confirm the melanoma stage [1]. Herein, a diagnostic approach of melanoma using blood was proposed based on laser-induced breakdown spectroscopy (LIBS) with machine learning methods. The blood samples were collected from 12 mice with injected melanoma during 0-4 weeks. For each stage, differences in the principal components of all mice's spectra were analyzed by principal component analysis (PCA) and T-distributed stochastic neighbor embedding (t-SNE). The results indicated that no spectra of anyone mouse was considerably different from those of other mice. The training and test sets were divided according to each mouse in a ratio of 3:1. For identification and staging of melanoma, considerably different divisions of training and test sets (DTTs) were excluded by the Wilcoxon test [2]. From the rest DTTs, 1 DTT was randomly selected to analyze the identification effect specifically, and 10 DTTs were randomly selected to verify the identification effect. In melanoma identification, combining with moving average smoothing method (MA), BP neural network based on Adaboost (BPNN-Adaboost) performed best among BPNN、K-Nearest Neighbor (kNN), support vector machines (SVM) and their ensemble learning based on Adaboost, with an accuracy of 91.14% for the random DTT and the accuracies of 87.38%~95.08% for the 10 random DTTs. In staging identification of early and late sick mice, the accuracies of BPNN-Adaboost model were 88.36%~96.80%. Moreover, the mean element importance was evaluated by random forest using above 10 DTTs. Elements Fe and Ca were important for melanoma identification, and elements Fe was important for stage identification. These results demonstrated that LIBS detection of blood samples with the machine learning methods could accurately diagnose and staging melanoma.

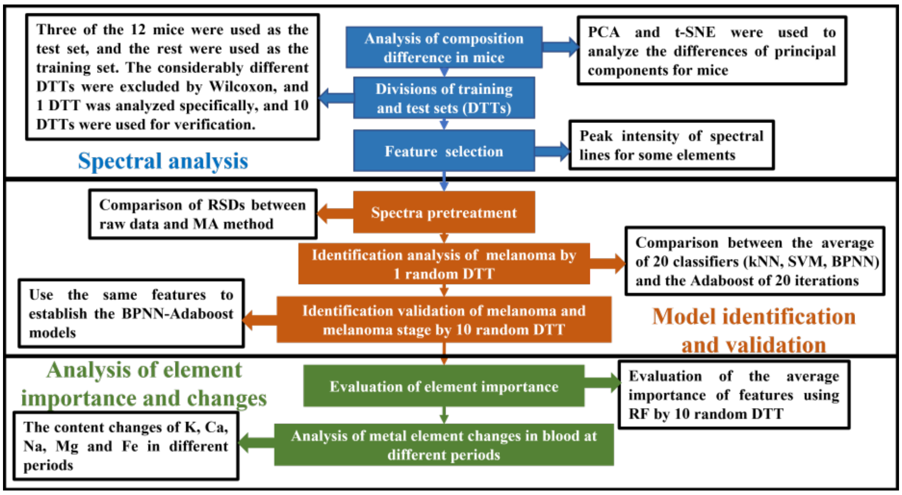

Fig. 1. Data analysis process.

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Effect of pulse properties of a Q-switched fiber laser source on the laser induced breakdown plasma

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Unarguably, one of the engines of LIBS development is the technological innovation of the laser sources, since every year more stable instruments with better beam parameters, quicker pulse repetition rate and higher pulse energy become available. One of the laser types which went through significant development over the last decade are the fiber lasers. Modern fiber lasers able to operate in Q-switched mode, and the pulse energy is in the mJ range[1]. They employ a long, fused silica optical fiber doped with rare earth metals as an active medium, and the pumping of this active medium is achieved by a semiconductor laser at one the end of the fiber. This construction is very robust and is able to operate continuously with a high very high pulse repetition rates (up to the MHz range), and it also allows the change of the temporal pulse profile (waveform) [2].

Generally speaking, the time profile of pulses released by the fiber laser can be divided into two parts: an initial, high intensity peak, and a tail with a gradually decreasing intensity. We investigated how the duration and shape of the pulse affects the ablation rate and the LIBS signal, when the total pulse energy was kept constant. We found that the elongation of the pulse lowers the intensity of the LIBS signal, but it can improve the ablation rate significantly.

The signal enhancing capabilities of consecutive laser pulses with short interpulse delays are well known in the literature [3,4]. Most MP-LIBS experimental setups are limited by the number of laser sources or the number of pulses the laser source can generate, but this is not the case for fiber lasers, where the number of applied pulses can be "indefinite". Although the lifespan of the plasma is short (1-2 µs) due to the relatively low pulse energies, the follow-up pulses cannot directly interact with the plasma generated by earlier pulses, but we observed that a signal enhancing effect can still be realized. This we attribute to the surface-heating properties of microplasma, which causes the surface not to cool back to room temperature by the time the next pulse arrives. It was also established that the spectral background does not elevate, if the emission of plasmas generated by multiple laser pulses are integrated together. We also studied the influence of the above experimental parameters on the plasma properties (e.g. lifetime, temperature).

ACKNOWLEDGEMENTS

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Combined Plasma Stationary Model and Stochastic Optimisation for Calibration-Free analysis of Cosmic and Ocean Samples

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Laser-induced breakdown spectroscopy (LIBS) is a versatile technique capable of analysing a wide range of unique specimens, from samples analysed on ocean floor and Mars, from molten metal to radioactive waste. However, in many cases, appropriate certified reference materials may not be available for calibration. Under the assumption of optically thin plasma subject to local thermodynamic equilibrium (LTE), Boltzmann plot analysis, also referred to as calibration-free (CF) LIBS analysis [1], can be used. However, fulfilling all the necessary requirements can be challenging, with extreme conditions such as open space or deep sea further complicating the calibration process.

Assuming a uniform plasma under local thermodynamic equilibrium, it is possible to synthesise a spectrum for a given elemental composition, temperature, electron density, and other conditions [2]. Multiparametric optimization can be used to fit the model to the experimental data, with the relative elemental concentrations and plasma conditions serving as variables. A gradient-free optimisation method has been chosen for this task.

The model was tested on metallic and non-metallic multicomponent samples, with various shapes of the loss function considered to account for analytical lines of different intensities and highlight different detail of the spectra. The stability of the solution was verified through repeated runs with randomly-chosen initial parameters.

It has been shown that the homogeneous plasma model is sufficient to predict several elements with lines in narrow spectral regions, while a multi-zone model with different temperatures and electron densities provides the best results for the full spectra, although the accuracy is lower. Our algorithm was employed to fit several Curiosity ChemCam and Mars 2020 Perseverance SuperCam spectra, yielding the composition of the studied object.

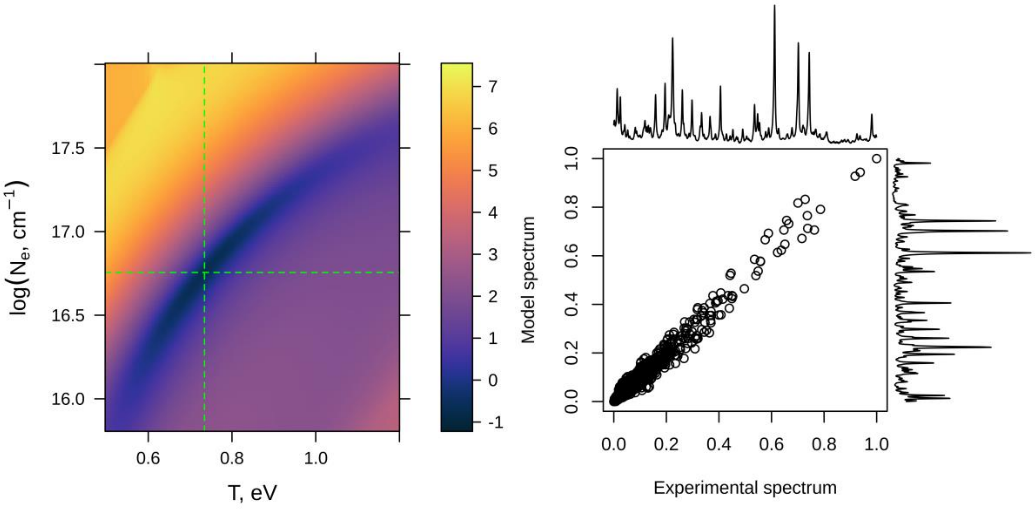

Fig. 1. Left: logarithm of the loss as a function of plasma temperature and electron density only, with green dashed lines showing the optimum. Right: experimental spectrum of a C9 steel sample compared against the best fit model spectrum.

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Calibrating a handheld LIBS SciAps Z300 to analyze spodumene and petalite for Li-exploration in the Barroso-Alvão aplite-pegmatite field, Northern Portugal

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The Barroso-Alvão aplite-pegmatite field is a very promising Li-deposit with thousands of aplite-pegmatites that can contain high-concentration of Li-minerals: spodumene and petalite. However, they are not easy to distinguish from the Li-barren and even the spodumene-rich from the petalite-rich aplite-pegmatites. Thus, a set of calibrations for a handheld LIBS SciAps Z300 has been developed to identify and analyze these two minerals [1], becoming a great tool in helping to identify the Li-bearing aplite-pegmatites and their type of Li-mineralization. Since spodumene has more Li than petalite and currently petalite is not being mined to produce Li-metal, the handheld LIBS can be used to aid the first stages of Li-exploration by directly analyzing the minerals in the outcrops, or even in drilling cores. Nineteen spodumene crystals and fifteen petalite crystals have been collected from 22 aplite-pegmatites and divided into three parts (four when the crystal was larger than 2 x 1 cm) to produce these calibrations. The first part went to a certified laboratory and was analyzed by ICP-MS; the second one was made into pellets to be analyzed by the handheld LIBS; the third part was kept in crystal to compare it to the pellets analysis; and finally, when the size of crystal allowed, a fourth part was used to produced thin-sections aiming to control the crystal purity and possible paragenesis.

Calibrations lines for Li, Al, Si, Be, Na, P, K, Mn, Fe, Ga, As, Rb, Sr, Nb and Sn were created by plotting the ICP-MS concentrations against the intensity ratios of spodumene and petalite.

Fig. 1. ***Handheld LIBS SciAps Z300 used to produce the set of calibrations to analyze spodumene and petalite from the Barroso-Alvão field.***

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Improving LIBS quantification accuracy through multi-pulse laser energy study

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Abstract:

In the past decade, Laser-Induced Breakdown Spectroscopy (LIBS) has gained popularity as a chemical analysis technique, but its ability to accurately quantify chemical properties still poses a challenge. This study examines the potential to improve LIBS performance by varying plasma conditions and ablated volume using sampling at distinct pulse energies to increase observation data. A quantification pipeline is then implemented using Partial Least Squares Regression, with a two-stage train and leave-one-out cross-validation approach. The methodology is tested on two datasets aimed at quantifying lithium concentration, one with synthetic samples and another with real-world drill samples from a mining context. The results demonstrate that using multiple pulse energies significantly enhances the accuracy of LIBS quantification, as shown by the reduced mean absolute error and matrix effect. These findings pave the way for more robust calibration procedures for LIBS, potentially leading to reliable in-situ analysis of geological samples and several industrial applications.

Keywords: LIBS, laser energy, multivariate analysis

Testing a screening methodology to identify Critical Raw Materials with Laser-Induced Breakdown Spectroscopy

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Meeting the growing demand for Critical Raw Materials (CRM) is one of the greatest challenges for the next decades in Europe and worldwide. In this context, research and development are required regarding resource availability, multi-scale CRM identification and characterisation, and environmental impact of mining and processing CRM. Flexible, rapid and reliable measurement techniques are needed to enhance our capacity of CRM exploration, exploitation, recycling and environmental impact monitoring.

We tested a fast and semi-automated CRM screening methodology using Laser-Induced Breakdown Spectroscopy (LIBS) and machine learning. Samples from Belgian zinc-lead (Zn-Pb) deposits were chosen for this test since this type of mineralisation is known to potentially host elements such as germanium (Ge) and gallium (Ga), increasingly demanded for the development of green energy technologies and therefore classified with high criticality in the EU [1]. Of equal importance is the fact that many elements in these deposits can turn into contaminants for the environment as a result of their mining and beneficiation, including Zn and Pb and others such as cadmium (Cd), arsenic (As) and thallium (Tl). LIBS therefore stands out as an ideal technique since it can provide a quasi-complete geochemical characterisation of these materials.

A total of 408 hand samples from the RBINS collection were selected for screening to represent a variety of rock and mineral types from four different Zn-Pb districts in Belgium. Samples were not prepared or cleaned in order to test the sensitivity of LIBS acquisition for minor elements (CRM and associated contaminants). The screening consisted of 30 randomised single-shot LIBS spots per sample, using a Python-based software to automatise spot data acquisition with time between measurements set up between 5 and 10 seconds depending on the sample to allow for manual navigation time between points and optimal placement for refocusing. Machine learning models were developed to handle the large volumes of spectral data generated with this approach, consisting of unsupervised methodologies for mineral identification, and a more supervised and targeted approach for elements identification and classification based on reference atomic spectra database [2].

Preliminary results show that this screening approach of randomised LIBS spots and machine learning data processing and analyses can successfully identify many of the minor elements of interest such as Ge, Cd and As, even with no sample preparation. LIBS screening can be used as a rapid, flexible and reliable first step measurement to direct further research in these occurrences. Although being developed with a focus on Belgian deposits, this methodology is being developed further to optimise minor element identification pipelines to ensure its applicability to different geological deposits and environmental needs.

ACKNOWLEDGEMENTS

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Study of matrix effect in aerosol LIBS measurements: ambient gases and multi-element aerosol

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Laser-Induced Breakdown Spectroscopy (LIBS) has been widely studied as an analytical tool for elemental qualitative and quantitative concentration measurements in different applications [1, 2]. However, concerning LIBS analysis in aerosol, matrix effects due to the carrier gas employed and the concomitant mass present in the probe volume must be considered to correctly interpret LIBS signals.

In this work, LIBS measurements were carried out by adding different percentages of Ar and He in air atmosphere inside the LIBS measurement chamber. In particular, an enhancement of the signal-to-noise (S/N) ratio of the 324.7 nm Cu I emission line is obtained with Ar and He in air instead of air as carrier gas. In these conditions, plasma showed a longer lifetime, resulting in improved S/N measurements in the 50-75 µs delay range.

Moreover, the addition of other elements (matrix elements- Na, Mg, and Cr) in the probe volume was investigated. To this purpose, the effect on Cu emission line was analysed by varying their relative concentration of matrix elements with respect to copper concentration. The results show an increase in Cu emission line intensity by increasing the relative concentration, as shown in Fig. 1.

Finally, the combined effect of the carrier gas and the concomitant mass addition of the matrix elements were studied, varying the delay time from 20 µs to 60 µs. The results show a general signal enhancement for the highest amount of matrix element mass concentration and a longer plasma lifetime in an Ar and He rich environment.

The results are discussed to provide insight into the physical processes occurring in the laser-induced plasma in the presence of ambient gases and matrix elements, thereby affecting the LIBS signal.

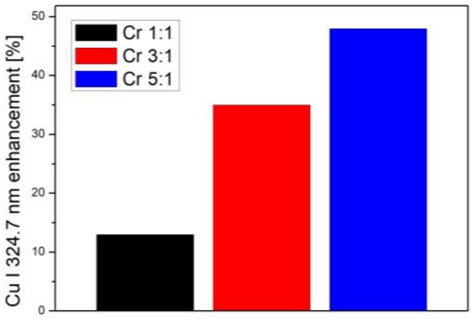

Fig. 1. Cu I 324.7 nm emission line enhancement respect to pure Cu S/N due to 1:1, 3:1 and 5:1 Cr to Cu ratio

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Automatic recognition of minerals: contribution of the LIBS portable tool

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The growing demand for raw materials is pushing mining companies to consider less accessible deposits and more complex mineralized structures. Thus, increasing the need of rapid and accurate geochemical data. Using portable spectroscopic tools, geologists have now the ability to generate reliable elemental, quantitative, and mineralogical information directly on the field with minimal sample preparation to support time and cost-effective decision-making during exploration or drilling campaigns. In this context, the use of portable laser-induced breakdown spectroscopy techniques (pLIBS) to develop innovative geochemical approaches for mineral prospection seems more promising than ever [1]. A single spectrum acquired within seconds using a handheld LIBS device can contain up to 23,000 values providing qualitative information on the elemental composition of a sample as well as the ability to assess the concentrations of these elements by building quantitative models [2]. Yet, applying machine learning methods to the massive amount of spectral data acquired on rock samples can open new perspectives such as performing automatic mineralogical recognition from elemental analyses [3]. To do so, unsupervised learning methods K-means clustering (K-means) and self-organizing maps (SOM) as well as supervised machine learning methods, artificial neural network (ANN), and K-nearest neighbors (K-NN) were applied on handheld LIBS data. The purpose of this study was to be able to assign the spectral signal obtained at each analytical spot to a specific mineral phase based on the distinct spectral signature of separate minerals. Reference spectra of pure mineral samples were collected as reference data for supervised machine learning techniques, KNN, and ANN. Both whole spectra and targeted spectral regions were tested as input data to assess the best performance while optimizing computational time. Known mineral samples were used to test and validate classification and clustering results. Rock samples from the Beauvoir granite, a highly differentiated peraluminous granite characterized by extreme lithium concentration (> 6000 ppm) and significant Nb, Ta, Sn, Be, Cs, and Rb contents were investigated to determine minerals proportion, in particular lepidolite, the main Li-bearing mineral.

ACKNOWLEDGEMENTS

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Compositional analysis of ZnMgO ternary oxides using the calibration-free laser-induced breakdown spectroscopy (LIBS)

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We report qualitative and quantitative analysis of ZnMgO ternary compound using laser-induced breakdown spectroscopy (LIBS). Four samples of ZnMgO were prepared with varying concentrations of ZnO and MgO (82%, 18%), (56%, 44%), (69%, 31) and (59%, 41%) respectively. The laser-induced plasma was produced using the fundamental (1064 nm) harmonic of a Q-switched Nd: YAG laser by varying the laser irradiance from 9 to 20 GW/cm^2. The emission spectra were acquired at the optimized laser irradiance of 15 GW/cm^2 using the broadband high-resolution spectrometer LIBS+ 2500 (Ocean optics Inc., USA). The qualitative analysis of the emission spectra reveals that it mainly consists of neutral and singly ionized lines of zinc, magnesium, oxygen, and a few trace elements as an impurity. The calibration-free LIBS technique was employed for the compositional analysis of ZnMgO samples, and the results were compared with the known concentration, which are in close agreement with each other [1,2].

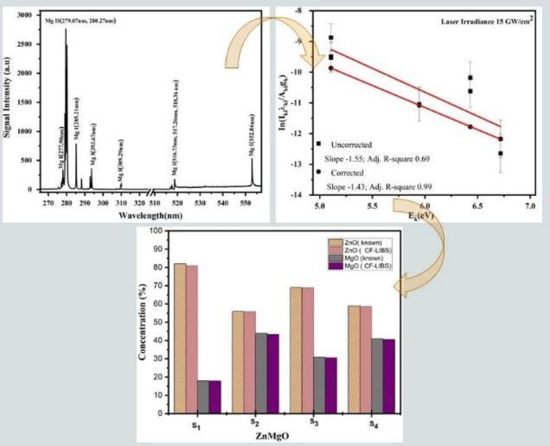

Fig. 1. **Emission spectra of ZnMgO, Boltzmann plots, and analytical results of sample constituents**

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Knowing the Unknown: Identifying Post-consumer Plastics with LIBS and Deep Neural Networks

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Plastic waste requires fast and accurate sorting methods to lessen the devastating effects on the environment. Laser induced breakdown spectroscopy (LIBS) combined with machine learning (ML) is capable of identifying and classifying different types of plastics rapidly [1-3]. However, the sample size corresponding to each plastic considered in previous works was limited. Most of the previously reported studies employed the same datasets for both training and testing their ML models; this is not the case in real-time, where we must deal with post-consumer plastics of uncertain types.

In this study, we considered six classes of regularly used plastics (PET: Polyethylene terephthalate, HDPE: High-density polyethylene, PVC: Polyvinyl chloride, LDPE: Low-density polyethylene, PP: Polypropylene, and PS: Polystyrene) and from each class, five different used plastics were collected (a total of 30 samples). An inexpensive, small, and portable Czerny Turner CCD spectrometer was used with a picosecond Nd: YVO_4 laser to conduct the LIBS experiment. A total of 200 spectra from each sample were recorded. The identification process made use of two potent deep learning techniques, namely artificial neural networks (ANN) and convolutional neural networks (CNN). LIBS spectra of four samples per category were utilized for training the networks, while the fifth was used for testing and was kept hidden from the trained model to simulate the real-time situation better. Similar methodologies were employed for all the samples iteratively. Using Grid Search Cross Validation (GSCV), we repeatedly tuned the hyperparameters that govern the loss function of ANN and CNN. The findings show that ANN and CNN can be effectively used to identify previously unrecognized pieces of post-consumer plastic.

ACKNOWLEDGEMENTS

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Characterization of laser produced plasmas re-excited with high voltage discharges on heated soil samples

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The interaction of a high voltage discharge that re-excites a laser-produced plasma on soil samples at room temperature and heated to 400°C is studied with spatial and temporal resolution. The goal is to analyze the physical processes occurring in the plasma that give rise to the increase in the signal obtained by Laser Induced Breakdown Spectroscopy (LIBS) [1].

The ablation plasma was produced by concentrating the fundamental emission of a nanosecond Nd: YAG laser with a fluence of 250 J/cm^2 on loamy soil targets. The high voltage discharge was produced using a coaxial cable charged up to 12 kV, serving as a capacitor, discharged by means of two electrodes placed 6 mm apart. The discharge produced was of the oscillatory type with an approximate duration of 7 µs, delivering a total of 220 mJ of energy. The delay between the laser and the high voltage pulse was kept fixed at 1.5 µs after the laser onset using a gated high-voltage switch. The target was placed on top of a metal plate, which acted as a lid for a ceramic urn with a halogen lamp, which allow to heat the sample. The plasma was then imaged by means of a plano-convex lens at the entrance slit of a Czerny-Turner spectrograph coupled to an intensified CCD camera (ICCD). From the spectra, the temperature and electron density of the plasma as a function of time was obtained for different radial and axial positions. This study was carried out for the different experimental configurations used: LIBS, LIBS re-excited by the high voltage discharge, with both experiments performed at room temperature and 400°C. Additionally, high-speed photographs were acquired with the ICCD under the different experimental conditions investigated.

Preliminary results demonstrate that the electron density and temperature of the plasma do not change significantly with either radial or axial position but they do increase when the high voltage discharge is applied. Additionally, the plasma volume increases as the sample is heated mainly due to the decrease in air density around the sample.

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Predictive model for cadmium concentration in cocoa beans using laser-induced breakdown spectroscopy.

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Cocoa (Theobroma cacao L.) and its derivatives can be considered commodities with health benefits due to their high content of polyphenols and antioxidants; nevertheless, it has been identified as an important source of cadmium (Cd), which is a transition metal without biological function and of recognized toxicity in humans, affecting the kidneys and calcium absorption in bones. In this research, a predictive model is proposed to determine Cd concentration in cocoa beans of Colombian origin, based on LIBS, FAAS (Flame Atomic Absorption Spectroscopy, as a reference technique) combined with PLSR-1 (partial least squares regression). It took advantage of the agility to generate LIBS spectra, which together with the Cd concentrations determined by FAAS, and the chemometric procedures, allowed the construction of the model. The multivariate predictive model was developed using 46 cocoa bean samples, with Cd concentrations in the 0 to 1 mg kg-1 range. An increase in the LIBS signal was evidenced in the Cd emission lines when the sample was subjected to a solid-liquid-solid transformation (SLST). Monte Carlo cross-validation was used, with 60% of samples for calibration and the remaining for testing. A range error ratio (RER) of 7.92 was obtained, which allows it to be classified as a screening model. The standard error of cross-validation (SECV) and standard error of calibration (SEC) are 0.12 mg kg-1 and 0.05 mg kg-1, respectively. The proposed procedure is framed within the alternatives for the chemical analysis of cocoa.

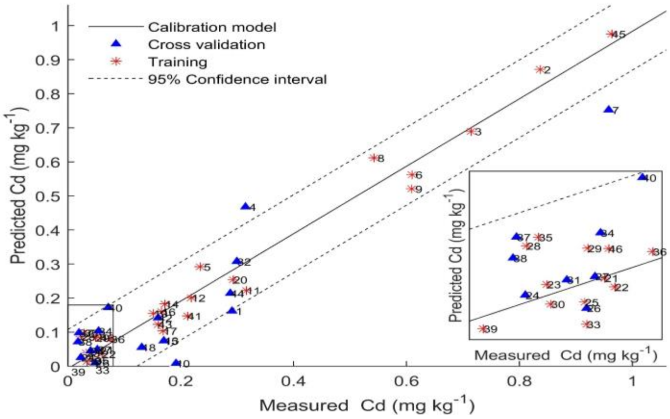

Fig. 1. Correlation of measured values versus values predicted by the PLSR-1 model. Dashed lines: 95% confidence band. Samples with measured concentrations close to 0.1 mg kg^{-1} are presented in the box.

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Production Water Analysis by Combining Electro Spray on Paper (EPS) and Laser-Induced Breakdown Spectroscopy (LIBS) techniques.

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Production waters contain high concentrations of salts and other compounds, so it is important to have a technique capable of analysing liquid samples at high concentrations without any or minimal sample preparation. The electrostatic atomization on paper known as Electro Spray on paper (EPS) of brines and its application in the production of microdroplets and that are excited through the coupling of EPS with the technique Laser-Induced Plasma Spectroscopy (LIBS) and thus obtain the quantitative analysis of these solutions. The technique (EPS) allows to eliminate the difficulties associated with the interaction of the laser pulse with the liquid sample [1] and the LIBS technique provides unique advantages such as the ability to make quick measurements, in situ, to make a quantitative analysis of production waters at different concentrations [2]. By coupling these two techniques, LIBS- EPS, the quantitative analysis of production waters was carried out for the elements: Na, K, Mg and Ca. Quantitative analysis was performed by constructing calibration curves of solutions prepared from different salts.

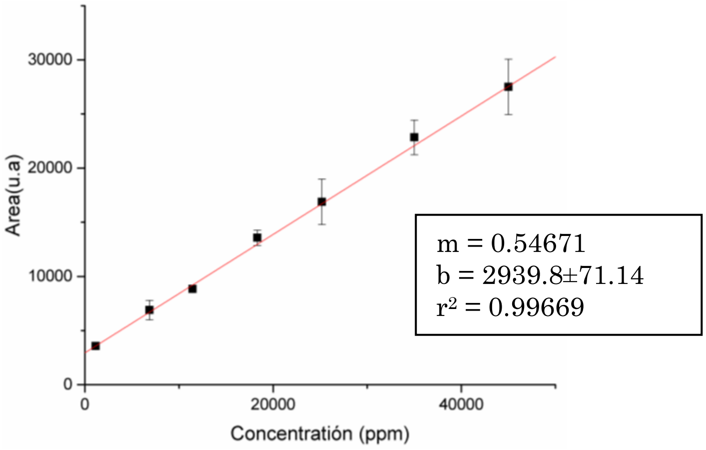

Fig. 1. Na calibration curve (Error bars: standard deviation).

Table 1. Determination of Na+ concentration of different samples

Sample	Theoretical (ppm)	Experimental (ppm)	%Error
Production water	6377	6408,05	0,49
24-hour urine	920-5060	4024,19	-------
Blood serum	3229,2	3158,45	2,19
Solution prepared in the laboratory	27480	28102,23	2,26

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Multi-Elemental Analysis of the Solid-Electrolyte Interphase in Lithium-Ion Batteries using LIBS: Insights into F, Li, H, C, O, and P Distributions

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Lithium-ion batteries (LIBs) are the key energy storage device of the 21st century due to their high energy density. Therefore, they are frequently used in electrical devices like smartphones and electric vehicles. However, little is known about the composition of the solid-electrolyte interphase (SEI layer), which readily forms on the negative electrode upon charge and discharge of the battery. Lithium hexafluorophosphate is used as conducting salt in the LIB electrolyte that tends to decompose under formation of toxic compounds like organo(fluoro)phosphates. While an investigation of these compounds in the interphases is of major importance for the assessment of potential safety hazards, the detection of F remains a challenge due to its high ionisation potential, hampering detection using conventional methods, like LA-ICP-MS.

In this work, laser-induced breakdown spectroscopy (LIBS) was used to detect F, Li, H, C, O, and P in the SEI layer of LIBs. The batteries were prepared using graphite anodes, metal-oxide cathodes and fluorine-containing electrolyte. The cells were then charged and discharged to 3.6V. Using a 193 nm laser, the samples were analysed using two different simultaneous detection configurations based on a multi-channel complimentary metal-oxide semiconductor (CMOS) detector and an intensified charge coupled device (ICCD) detector.

It was determined that F detection with ICCD is advantageous compared to CMOS detection as an unambiguous allocation of decomposition products on the anode surface is possible. (Fig. 1.) It was confirmed, that the SEI layer has an organic surface in contact with the electrolyte and an inorganic layer below it. Finally, inorganic SEI components like LiF were determined as part of the decomposition of $LiPF_6$ and fluorinated organic compounds were identified in the SEI arising from the addition of additives to the electrolyte.

In conclusion, ICCD detection enhances the resolution of low-concentration analytes, enabling comparison with other elemental distributions within the same sample. Using LIBS, analytes in the SEI layer were identified and the influence of different electrolyte constituents on its elemental composition was analysed.

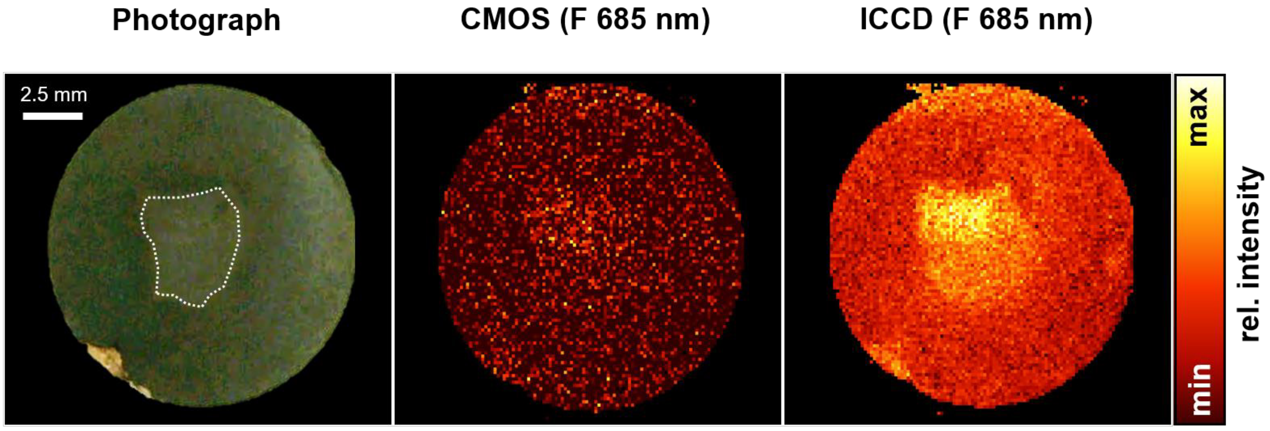

Figure 1. Photograph and LIBS images of F 685 nm accumulation in the SEI of a battery cycled with LP57 electrolyte detected with a CMOS and ICCD detector. White border in photograph shows decomposition product accumulation in the SEI. Laser spot size: 150 µm.

LIBS imaging of selenium ores

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Selenium detection by LIBS has been described in only a few publications so far. For example, one of these works studied solar cells [1], and another one characterized plasma formed in Ar/H_2 mixtures used to generate selenium hydride [2]. However, to our knowledge, the application of LIBS for the detection of selenium in geological materials was not yet done.

Based on earlier publications [1,2], spectral emission lines Se I 196.09 nm, Se I 203.98 nm, and Se I 206.3 nm are suitable for selenium detection. However, matrix-related interferences must be taken into account before the choice of appropriate lines. Selenium frequently occurs together with copper in mineral phases due to the chalcophile nature of both elements. Thus, interferences of selenium lines with those of copper are expected (especially with emission lines Cu II 203.67 nm and Cu II 204.37 nm).

We studied selenium-copper minerals represented by berzelianite (Cu_2Se) and umangite (Cu_3Se_2) from localities in the Bohemian Massif, Czech Republic, where they are locally associated with uranium mineralization. [3]. Our work demonstrates the distinguishing of spectral lines of Se and Cu. The detection capability of Se spectral lines was verified by Se and Cu standards. In this case, no interference from copper was observed. These results are essential for research on selenium-rich minerals characterization and imaging of selenium and copper distribution.

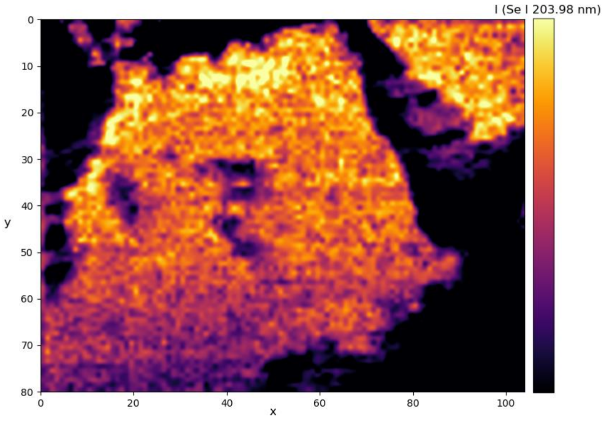

Image of selenium distribution in berzelianite

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LIBS in Precision Agriculture: Approaching on-site soil analysis

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Spatial variations in soil properties on agricultural land, in particular different soil chemical parameters, are relevant for the soil fertility and thus for crop yields. The usually homogenous fertilization of fields can lead to local over or under fertilisation. This can be avoided by using precision agriculture. It is based on the measurement of spatial variations within a field, e.g. by means of chemical sensors, which avoids time-consuming and costly soil sampling and laboratory analysis. However, only a few sensor technologies are currently used, such as geoelectric, potentiometric pH, gamma-ray and spectral-optical sensors. The method presented in this work is laser-induced breakdown spectroscopy (LIBS). It provides direct and spatially well resolved data on nutrient content without any sample preparation. It is therefore a suitable tool for the direct on-site analysis required in precision agriculture.

Previous work on this topic included the characterization of different calibration methods based on machine learning techniques for the determination of soil parameters [1, 2]. These parameters are the total amount of metal nutrients (K, Ca, Mg, Mn, Zn, Cu and Si) and non-metal nutrients (N, P, S) as well as so-called secondary parameters such as soil pH, soil texture and humus content. The measurements were carried out using a laboratory LIBS system and samples that were dried, sieved, homogenized and pressed into pellets. These studies do not reflect real field conditions with large variations in moisture, soil density, soil porosity, surface roughness and the presence of larger stones and plant roots. To address these issues, several experiments will be carried out including variation of the pressure during pellet preparation (as well as using loose soil), different moisture contents and particle size distributions.

Another topic of the presented work is the development of a field spectrometer for proximal soil sensing, which is part of a sensor platform of our project partner ATB (Potsdam, Germany). The continuously collected soil is deposited on a conveyor belt, above which the LIBS sensor and other chemical sensors such as XRF, Raman, NIR, MIR sensors are mounted. The sensor platform allows continuous measurement of different soil parameters. In the future, these measurements will be used to create maps of the various soil parameters, which can then be used to make fertiliser recommendations to farmers. In parallel, selected points in the field were measured using a portable LIBS spectrometer (SciAps). Soil samples are taken from these points and analysed by the handheld spectrometer and our laboratory bench top spectrometer. The results of this comparison are presented and discussed.

ACKNOWLEDGEMENTS

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Characterization by laser-induced breakdown spectroscopy of new functionally graded materials obtained by additive manufacturing

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Traditional composite materials have developed into functionally graded materials (FGMs), which are characterized by the variation in composition and structure gradually over volume, resulting in corresponding changes in the properties of the material. Though there are several methods available for manufacturing FGMs, additive based metal deposition technologies, in particular, systems working under the Directed Energy Deposition (DED) basis, have proven to be more flexible. The laser-based DED process operates by flowing powder under the focal point of a laser where it melts and solidifies on a substrate. 3D components are then built vertically on a layer-per-layer basis, where horizontal layers are made by successively overlapped laser scans. When two or more feeders containing different powders are used simultaneously, a mixed composition results according to each of the feeder settings. As these can be continuously changed along the process, the manufactured piece will display a varying composition as defined by the user, resulting in a FGM. Both, the powder feeder settings and the laser process parameters (energy, speed…) must be accurately controlled in order to perform the graded deposition with the required precision. Furthermore, the composition of the resulted manufactured pieces must be characterized as feedback for the optimization procedure of the manufacturing parameters. In this work, FGMs manufactured from steel and nickel alloys by means of laser-DED in the horizontal and vertical directions have been characterized by laser-induced breakdown spectroscopy (LIBS). First, coatings with a fixed composition but different proportions were analysed, which served as a reference to select the optimal experimental parameters and to build calibration curves for the analysis of the FGMs. Subsequently, the characterization of the FGMs was carried out by generating lateral profiles and 2D compositional maps, verifying that the variation in composition obtained from the LIBS analysis coincides with the specifications of the addition of material in the manufacturing process. The results obtained in this work demonstrate the capability of LIBS technique for the control and optimization of the FGMs laser-DED process.

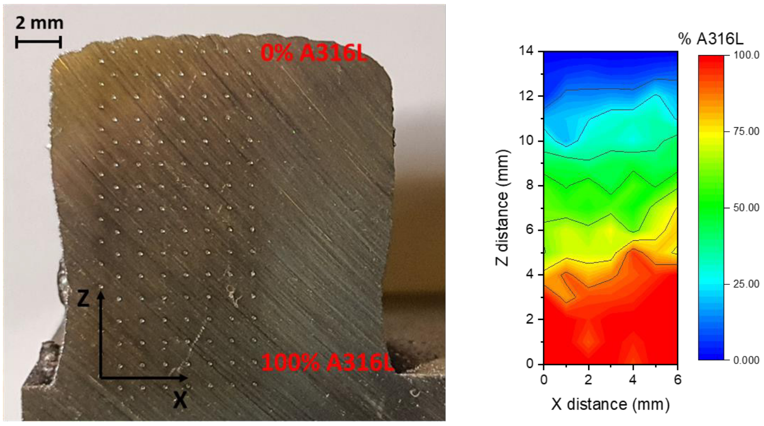

Fig. 1. Section of a vertical FGM where the craters after LIBS analysis are visible (left). LIBS compositional map of %A316L in the analyzed area (right).

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LIBS Analysis of Volatile Elements in Molten Metal

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Laser-induced breakdown spectroscopy is uniquely suited to analyze the vapor-phase contribution of emission signals from volatile elements in molten metal [1]. In the metals industry, such elements may be crucial as alloying elements or detrimental as trace contaminants in the final product. The volatility of elements is directly related to their stability in the melt and their potential for dross formation. Although the vapor pressure of a pure chemical component at a given temperature is a fixed quantity, the behaviour of the same element in solution can be very different and dependent on external factors, most notably the presence of other elements in the melt. Industrially, it is important to understand and to be able to utilize such effects to optimize product quality and minimize waste.

In the present work, we have specifically studied the vapor pressure of magnesium in aluminum alloys using DTE's liquid metal analyzer. Magnesium is one of the most important alloying elements in the aluminum industry, typically present in quantities between 0.05 wt% and 5 wt%, depending on the type of alloy. The stability of Mg in the melt can be strongly affected by the presence of small amounts of other group-II elements, including Be, Sr, and Ca (see Fig. 1). We have systematically mapped the influence of such elements on the vapor-phase contribution of Mg in the laser-induced plasma. We will discuss the nature of Mg emission and self-absorption in the presence of Mg vapor above the melt surface, as well as the reasons for the observed reduction in the vapor phase contribution when other elements are present in the melt.

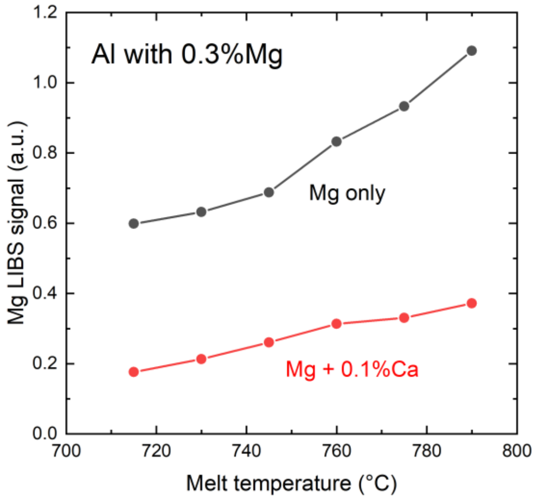

Fig. 1. Effect of Ca on the vapor phase contribution to the LIBS signal of Mg.

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Machine Learning Prediction of Stark Broadening Parameters for Accurate Plasma Modeling

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Stark broadening parameters are crucial for analysis and modeling spectra from various emission sources. For instance, the lack of known Stark parameters for atomic lines in white dwarf spectra hinders accurate analysis and interpretation. Despite decades of experimental and theoretical studies to retrieve Stark parameters and regular additions to existing databases, only a small percentage of known transitions are covered. Obtaining new values remains an important and often challenging task. Experimental studies face limitations such as plasma source inhomogeneity, spectral interferences, insufficient spectral resolution, and non-equilibrium particle interactions. Broadening of some emission lines like lines of doubly charged atomic ions cannot be observed in laboratory plasma due to low Stark broadening values. Quantum chemical calculations are limited by high computational costs and strong electronic state interactions or relativistic effects for heavy atoms. However, rapid advancements in machine learning (ML) methods have resulted in their high efficiency and accuracy in many scientific areas including spectroscopy. Artificial neural networks (ANNs) have been successfully implemented for tasks ranging from hyperspectral image analysis to predicting reaction rates or substance properties based on its structure. These considerations led us to the application of ML for predicting Stark parameters.

We created a table format to represent electronic level configurations, terms and energies for each atomic or ionic transition. Our database contains approximately 1000 atomic and ionic transitions with experimental Stark parameter values. The availability of parameters measured at different temperatures allows us to add a temperature parameter to the database and predict temperature-dependent Stark broadening parameters using ML methods.

We trained and tested several classical machine learning models (KNN, Random Forest, Gradient Boosting) and ANNs (TabNet and custom MLP) for predicting Stark broadening and shift parameters and tested the results on independent subsets. Boosting algorithms demonstrated the highest accuracy after implementation of data scaling and augmentation procedures. ANNs were not yet competitive with classical ML models but their accuracy strongly depends on the size of the training dataset. Adding new experimental values to the database in future could improve their accuracy. We also tested model generalization by evaluating them on an independent subset of transitions for three chemical elements not seen in the training set.

We added predicted Stark parameters for a large number of transitions to a thermodynamic model simulating low-temperature plasma emission [1]. Comparing experimental and simulated spectra with predicted Stark parameters shows that having parameters for many transitions benefits spectra interpretation and plasma diagnostics.

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Process analysis in industrial lithium enrichment by LIBS

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The path to a CO2-neutral energy supply and mobility based on renewable energies can only be successful with a variety of energy storage systems. One of the most flexible storage options is the battery, which is currently based almost exclusively on lithium batteries. Before large-scale recycling of batteries becomes possible from 2030 onwards, lithium supply has to be realised through mining. To this end, new regions are being developed around the world and production volumes are being increased significantly.[1]

The preferred way to increase production volumes is to optimise the individual steps in the lithium extraction process. In addition to positive economic effects such as an increase in lithium yield, process monitoring can also lead to an improved environmental balance through a significant reduction in the use of materials and energy. Starting with the hard rock and brine, the composition of the material must be determined before and after each process step. Complex analysis conditions during the production process, such as changing aggregate states and high temperature differences, have made monitoring difficult until now. At-line or off-line monitoring using inductively coupled plasma optical emission spectrometry (ICP-OES) or atomic absorption spectroscopy (AAS) requires complex sample preparation,[2] but in-line techniques such as X-ray fluorescence (XRF) spectroscopy do not work for light elements like lithium.[3]

LIBS is a promising method for inline monitoring which allows non-contact multi-element analysis in real time. The selection of process steps for process analysis is based on the highest economic and environmental impact. In this study the influence of different measurement requirements (state of aggregation, water content, concentrations of lithium and impurities, etc.) was investigated. For the quantification different multivariate regression models (e.g. PLS: Partial-Least-Squares, LASSO: Least Absolute Shrinkage and Selection Operator, SVM: Support Vector Machine) were tested.

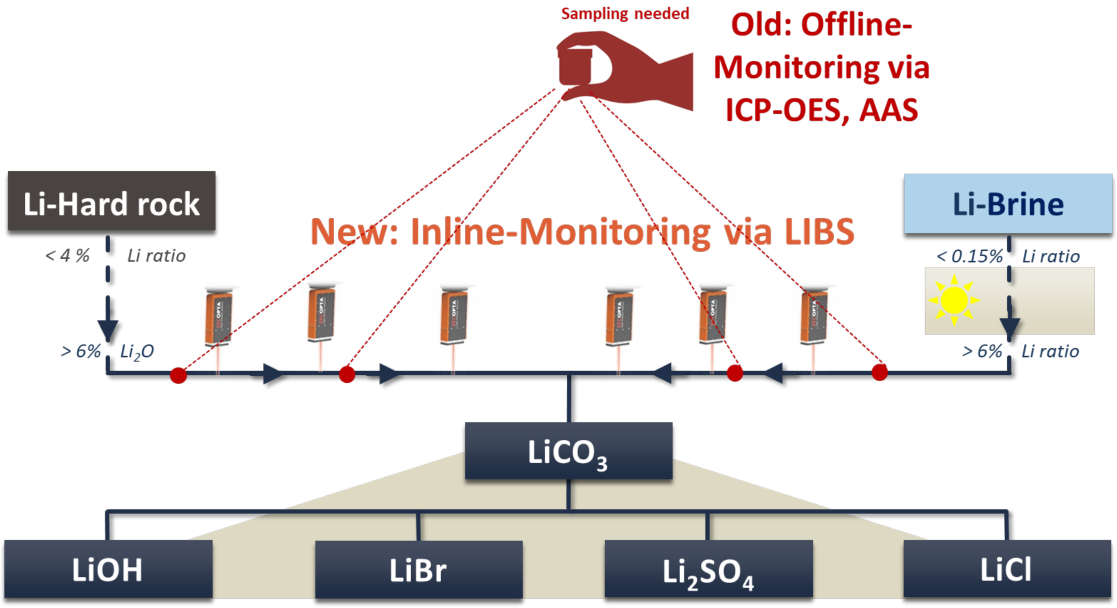

Fig. 1. Flow chart of Lithium extraction from brines and hard rocks

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Material aspects in laser-induced breakdown spectroscopy analysis of algae on filters

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Determination of heavy metals in algae is an important environmental issue. The typical employed instrumentation is Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [1]. However, the algae must be filtered from a parent solution and the filter is consequently decomposed and analysed. On the other hand, Laser-induced Breakdown Spectroscopy (LIBS) can directly analyse dried and/or pelletized algae [2] or just ablate an algae sediment on the filter [3]. Quantitative analysis of the algae on the filter is, beside others, complicated by different intensities of spectra depending on the deposit and the hardness of the filter underlay. The whole filter area is fixed to a microscopic glass with a double adhesive tape. The fixation must be done very precisely. The emission signal will decrease and the filter is perforated if it does not touch the glass properly. Also the concentration of the contaminants in the solution influences the total plasma emission. The character of the system filter-tape-glass is investigated in dependence on the sticking layers and filtered solution. It is shown how the total spectral emission, plasma parameters and lines intensities change (e.g. ionic-to-atomic line ratio decrease) in dependence on the hardness of the sticking. The observed intensities changes are supported with shadowgraphic studies of shockwaves and crater depths at 1064 nm LIBS. The shockwave is slightly decreased on a softer or more impregnated filter system. An appropriate combination of the total emissivity, lines ratios and shadowgraphy can then be used for internal standardization. This is very important because the surface concentrations of analytes are tens of ng per square cm. Quality and consistent filter preparation and corrections for the aforementioned effects can improve the trueness of the quantification.

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ANN-based features conversion of dimensionally reduced LIBS data for calibration on synthetic spectra

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One of the main difficulties of calibration in LIBS measurements is the requirement of preparation calibrated samples of sufficient clarity and accuracy. A possible solution of this problem is application of the ML (machine learning) based calibration operating on synthetic data. Admittedly, the synthetic spectra generators which use limited physical models, as for example the LIBS tool provided by NIST, produce spectra significantly different from those being measured during experiments. Thus, the models of conversion between experimental and synthetic spectra are essential if training on synthetic data is expected to be feasible.

In our previous work[1] we successfully investigated the possibility of training ML systems with synthetic data prepared with the use of an especially designed tool: SimulatedLIBS [2]. Since the models have shown good performance for spectra prepared in this way, it is important to expand their operation range to experimental data.

The investigation presented in this contribution is a step for obtaining this goal. The simulated spectra correspond to a range of brass alloys with arbitrary concentrations of their chemical constituents. ML models for regression and classification (predicting chemical concentration or the classes based on the spectra) are trained with dimensionally reduced synthetic spectral data (DRSSD), whereas different sets of data simulate experimental spectra (i.e. is noisy and transformed by acquisition characteristic functions) (SES). Then, other models are trained which use dimensionally reduced SES as the input and DRSSD of corresponding chemical contents as targets.

To verify the performance of the proposed conversion models, a number of SES spectra will be processed with their use and put as inputs on ML systems for chemical contents regression and classification trained by DRSSD. Thus, the validation will take into account the performance of two models: one for data conversion and second for characterisation of the chemical contents.

PCA is applied as the dimensionality reduction method and for training the chemical composition predicting models mostly ANNs are employed, however linear and logistic regression are also tested for regression and classification respectively. For the conversion models, ANNs and CNNs are under investigation.

Positive verification of the system’s performance strongly facilitates the calibration of LIBS method by opening possibilities of doing this with synthetic data.

Fig. 1. *General scheme of the ML-based calibration on synthetic data*.

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kHz micro-LIBS imaging: a new way to see the future of LIBS

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Standard LIBS imaging systems provide adequate measuring times at frequencies < 100 Hz for most applications. In the case of measuring large areas of several cm² equivalent to several millions of spectra with a high spatial resolution in the range of 10 µm, standard 100 Hz LIBS-based imaging systems have a measurement time of 3 hours per cm² and a faster system could become advantageous [1,2]. In contrast to traditional approaches, the use of a kHz laser for LIBS-based imaging instrument allows to produce elemental images with high resolution over large areas in a reduced time of around 17 min per cm² with a 10 µm measurement step.

In this work, we present a new kHz micro-LIBS imaging instrument based on the use of a compact passive Q-switch laser from Cobolt AB and a high throughput detection system (kymera 328i coupled to a sCMOS camera from Andor technology). The concept of this original instrumentation will be detailed as well as the analysis workflow to reconstruct compositional images from the recorded LIBS spectra. We will introduce figures-of-merit presented together with the chemical and mineralogical characterization of mine ore samples. As a result, an area of 20 cm^2, inspected with a resolution of 15 µm, proves the system's capability to carry out a large-area high-quality compositional image (with an image definition close to 4K; i.e. ~ 8.3 millions of pixels, producing around 80 GB of data). Such type of images can be obtained in less than three hours (c.f. figure 1), opening the way to numerous applications in various domains. A performance comparison between a more conventional 100 Hz instrumentation will finally be proposed, as well as some perspectives, concerning in particular the processing of such huge dataset.

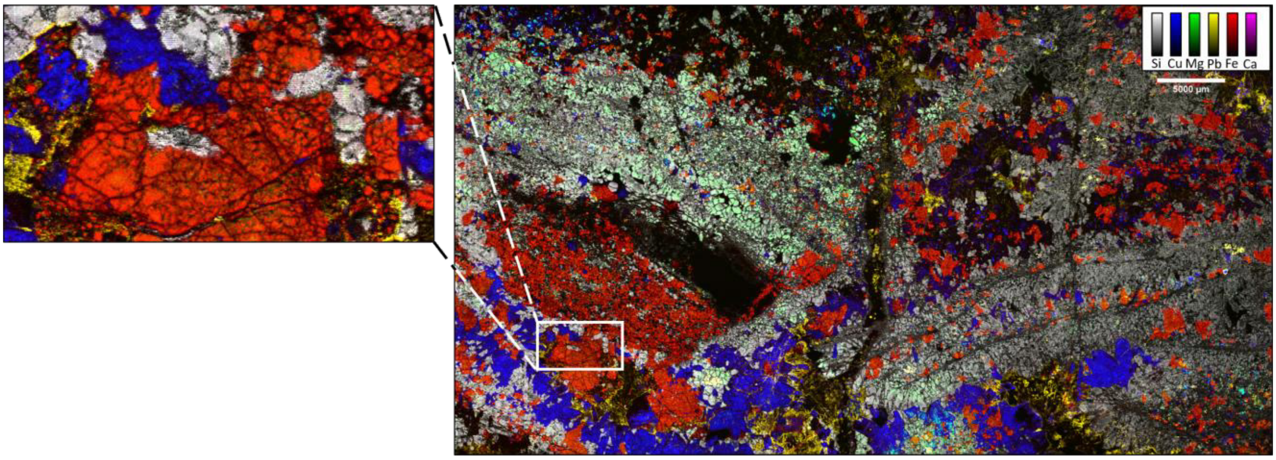

Fig. 1. Elemental map of Si, Cu, Mg, Pb, Fe and Ca on a mine core sample. 4000x2200 with 15 µm measurement step representing 19.8 cm², analyzed in around 2h30min.

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Characterization of molybdenite and other hosted species in drill-cores by laser-induced breakdown spectroscopy (LIBS).

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Molybdenum (Mo) has a strategic importance for the Chilean economy, being one of the main producers in the world with an annual participation of 17% [1]. The determination of Mo concentration in drill core is essential to know the economic potential of a deposit. In addition, Mo veins are structurally related to other valuable metals such as rhenium (Re) or tungsten (W) usually ignored in the valorization and metallurgical recovery. Conventional assays used for geochemical characterization consist of visual analysis by an expert geologist and other spectroscopic methods, e.g., ICP-OES, which are time-consuming and generate polluting residues. Laser-Induced Breakdown Spectroscopy (LIBS) emerges as a viable option in the study of drill cores, ideal for elemental analysis, requires minimal sample treatment and can provide information on the spatial location of the mineral of interest [2]. This work proposes the use of LIBS and chemometrics to determine molybdenite in cores and identify the presence of metals linked to Mo lattices, to provide additional information for metallurgical processes. Sections of drill-core samples were analyzed with a LIBS setup consisting of a 1064 nm Nd-YAG laser with an energy of 300 mJ/pulse and a duration of 6 ns (Nano LG300-10, Litron Lasers, Warwickshire, UK). Detection was performed under ambient conditions with a 6-channel CCD spectrometer (Aurora, Applied Spectra, USA), with a spectral range from 185 to 1049 nm and an average resolution of 0.12 nm. The delay time was set at 0.55 µs and the integration time at 1.05 ms. The achieved results provide signals of Mo and Re, as well as other elements mainly found in the matrix, such a silicon (Si) or aluminum (Al). The signals obtained made it possible to generate an elemental distribution map related to the concentrations of the mineral species present.

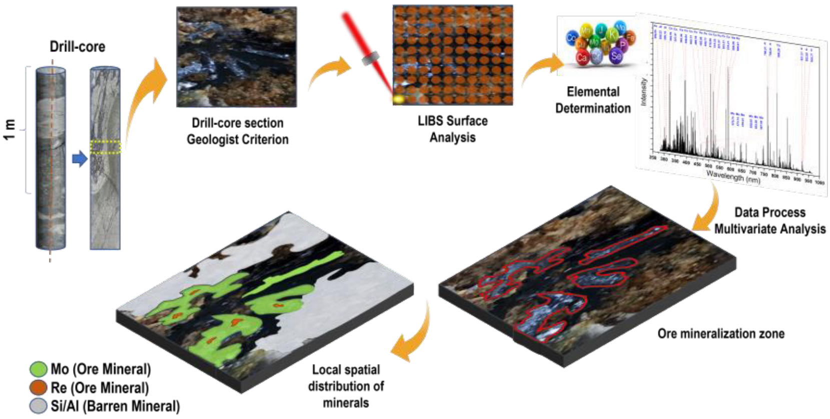

Fig. 1. Molybdenite distribution maps achieved by LIBS and chemometrics

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Synthesis of Gold Nanoparticles by Ring-Oven Technique for NELIBS Applications

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Despite its versatility, the direct determination of metal ions by LIBS in liquid samples is challenging due to the formation of splash, in addition to the poor limit of detection, usually around mg L^{-1}. The use of paper as a support for these samples is one of the strategies used to overcome these inconveniences, in addition to a pre-concentration step. The ring-oven technique employs a device to heat a disk of filter paper, on which sample is added drop by drop at its center, being transported to the edge of the paper while the liquid is evaporated.[1] As a consequence, the analyte is concentrated in the form of a ring, which can be analyzed by LIBS.[2] Improved ablation in LIBS can be achieved with the use of metallic nanoparticles, known as Nanoparticle Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS). The present work aims to improve LIBS sensitivity by the production of gold nanoparticles (AuNP) on the surface of a filter paper (Whatman 40) by means of a ring-oven device, with subsequent concentration of analyte (Cu (II) ions was chosen to proof of concept). The AuNP ring (Figure 1a) was formed by sequentially dropping 100 µL of $HAuCl_4$ (3.5 x 10^{-5} mol L^{-1}), HCl (0.01 mol L^{-1}) and sodium citrate (7.8 x 10^{-2} mol L^{-1}) solutions. Subsequently, 100 µL of Cu(II) standard solutions were dropped onto the paper, followed by 100 µL of a 0.01 mol L^{-1} HCl solution used to ensure the transference of all copper ions to the ring. The drop rate was 21.3 µL min^{-1}. As a means of evaluating the signal enhancement, Cu(II) ion rings were also prepared using the same solution. The filter paper disk was placed on a rotating platform, which allowed to fire 120 laser pulses (Q-switched Nd:YAG laser, Brilliant Quantel B, 1064 nm, 20 Hz and 5-ns pulse) to fulfill the ring circumference (Figure 1b). Measurements were taken 3 cm above the laser focal point so the size of the crater formed was sufficiently large to overlay the ring; therefore, pulse energy as high as 250 mJ was used. The emitted radiation was collected with a 5-mm diameter lens, focused on the tip of 105-µm diameter optical fiber, which guided the radiation to an echelle polychromator (Andor Technology) and an ICCD detector (iStar DH 734, Andor Technology). The irradiance at the focal point was 8.67 x 10^{12} W cm^{-2}. Comparing the emission intensities of Cu I (324.76 nm) obtained in the calibration curves (Figure 1c), there was a sensitivity increase of 2.6x with the use of AuNP ring compared to the measurements performed with the Cu(II) ions ring alone. These results demonstrate the feasibility of preparing AuNP rings directly on the filter paper, which is a powerful tool to increase LIBS signal.

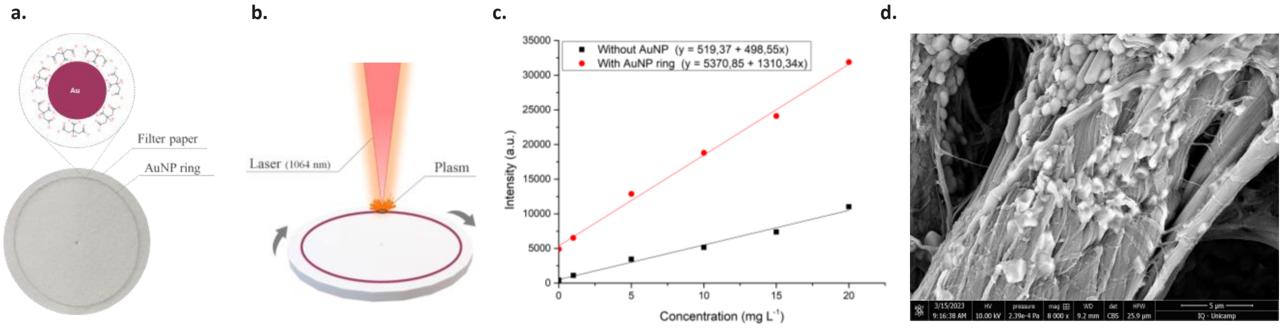

Fig. 1. a) Filter paper disc with AuNP ring; b) Scheme of ablation on a filter paper placed on a rotating platform; c) Calibration curves for Cu(II) ions. d) MEV of AuNPs on filter paper.

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Design of compact low-cost Standoff Laser Induced Breakdown Spectroscopy Instrument

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The real time identification of samples in environment where the human intervene is hazardous have urged the need for a rapid but also an accurate investigation technique. The feasibility of Laser-Induced Breakdown Spectroscopy (LIBS) have been explored based on the application of interest, such as process control[1], planetary exploration[2], and explosives detection[3], environmental monitoring etc. LIBS in standoff mode has been explored a lot however, most of the work is limited to laboratory. There are very few instances of realtime Standoff-LIBS (STLIBS) instruments, however these are expensive.

We report the development of low-cost STLIBS instrument for the identification of samples up to 6.5 m. A picosecond Nd: YVO_4 laser was focused onto the samples at a standoff distance using a combination of concave and convex lenses. A low-cost custom made telescope was used for the collection of light. The focusing light from telescope is guided into a low-cost, compact and portable Czerny Turner CCD spectrometer using a 600µm fiber.

A total of 100 spectra with 100ms integration time were acquired on plastics. The $1/R^2$ relation of max signal as a function of distance was evident from the results. The spectral data at 2m was used to create a model using Artificial Neural Networks (ANN) and the data from other distances is tested on the model. The prediction rates are very promising and further motivates us to implement ANN model for any distance.

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µLIBS imaging of archaeological material from Gallo-Roman Lugdunum

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The Ancient Theatre (late I c. BC) and Odeon (early II c. AD) on the hill of the Fourvière in Lyon, France, are two of the most prominent monuments from the Gallo-Roman settlement Lugdunum. Built during the time when Ludgunum was the capital of the Gallia Lugdunensis province and possibly the most important city in the West of the Roman Empire, it features a remarkable collection of carefully selected construction materials from various Mediterranean queries (Carrare, Chemtou, Kyros, Téos, Baveno, etc.). Different studies have been conducted to determine the exact origin of marbles and other rock materials present on the site. Nevertheless, in many cases their exact provenance remains ambiguous, hindering knowledge about ancient craftsmanship and trade routes.

We report a study of marbles and other rocks from the Ancient Theatre and Odeon of Lugdunum, applying for the first time Laser-Induced Breakdown Spectroscopy (LIBS) to determine their elemental composition. We use the micro-LIBS (µLIBS) technique to investigate in detail the elemental distributions across the heterogeneous surface of the samples. A spatial resolution of approximately 15 µm allows us to simultaneously reveal fine morphological and geochemical features of the samples that may provide important clues regarding their provenance.

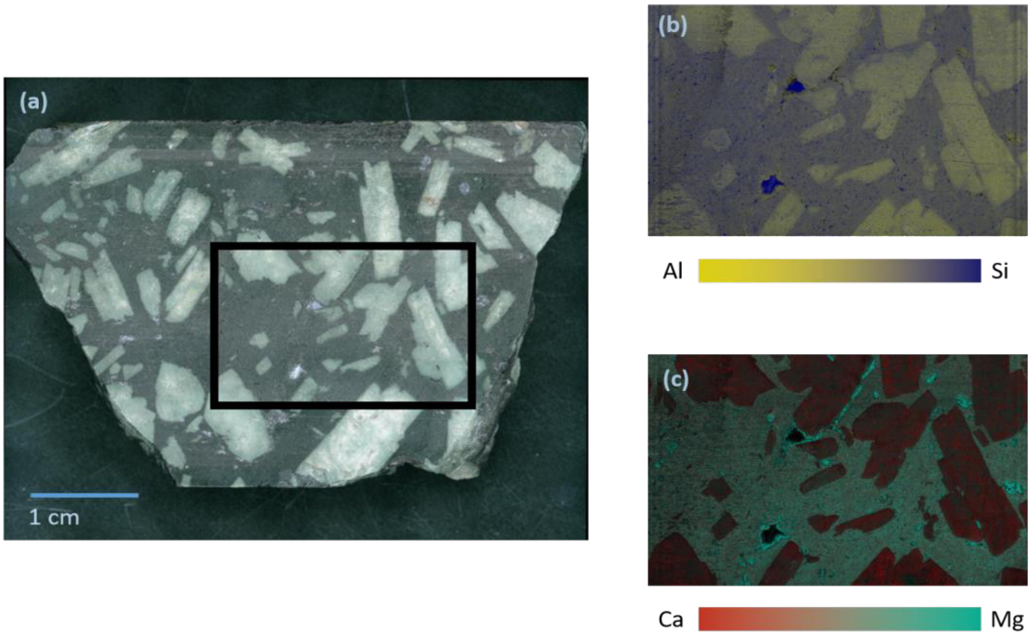

Fig. 1. Green porphyry from Greece. Optical image (a); µLIBS images of aluminium and silicon (b), and calcium and magnesium distributions (c).

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Determination of the self-absorption coefficients of a Zn-based alloy using laser induced breakdown spectroscopy (LIBS)

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The LIBS and especially the CF-LIBS quantification method are heavily influenced by the self-absorption effect, which has been investigated in this study to analyze a zinc-based alloy. The sample was ablated using a Nd:YAG laser operating at its fundamental radiation and an energy of 50 mJ. The plasma emission was collected for different delay times (from 0.8 to 12 µs) via an optical fiber connected to an Echelle spectrometer (Aryelle 200-LTB) coupled with an ICCD camera. The resulting spectra were recorded and analyzed with a suitable software.

We used in our work El-Sherbini method [1] for quantifying the effect of self-absorption on atomic and ionic lines of the Zn-based alloy (Zn, Al, Cu), this technique is applicable to lines that have known Stark broadening parameters, and it relies on knowledge of the plasma's electron number density N_e. The value of N_e was determined using Gigosos' formula [2], which involves measuring the Stark broadening of the H_α line profile.

In order to determine a time window in which is less affected by the self-absorption effect, we examined the evolution of N_e and the self-absorption coefficients as function of delay times.

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LIBS and light-scattering imaging of automotive brake-wear particle emissions

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Brake emissions (and other non-exhaust emissions) are a major source of traffic-related emission [1]. Tighter regulations in the coming years (EU7) that for the first time limit non-exhaust emissions increase the pressure on OEMs and suppliers understand the processes that cause emissions so that they can be reduced. Brake emissions are usually measured through a sampling method connected to particle metrology systems to determine the size distribution and concentration or filters to weight the mass or perform elemental analysis in the lab [2]. As the sampling position is 2-3 meters away from the brake, spatio-temporal information on the origin and transport of the particles is lost. Optical metrology allows a in-situ, non-intrusive measurements near the brake, promising a deeper understanding on the underlying particle creation, shedding, mixing and transport mechanisms.

In this study, a combination of particle light-scattering visualization, laser-induced breakdown spectroscopy (LIBS), and plasma visualization is developed for in-situ brake emissions analysis. The LIBS plasma is created by laser pulses at 1064 nm and the light sheet for particle visualization is at 532 nm. Two different brake pads are investigated in a dynamometer with the brake disk rotating at constant velocity while pressure is applied to the brake. A first qualitative analysis of the LIBS signal intensities show clear differences in relative mass concentration between different sampling points, which is consistent with the light-scattering images of the particles. A quantitative analysis of the LIBS signal yields the elemental composition. Furthermore, together with the imaging of the plasma the influence of the fluctuation of plasma position on the recorded signal can be determined.

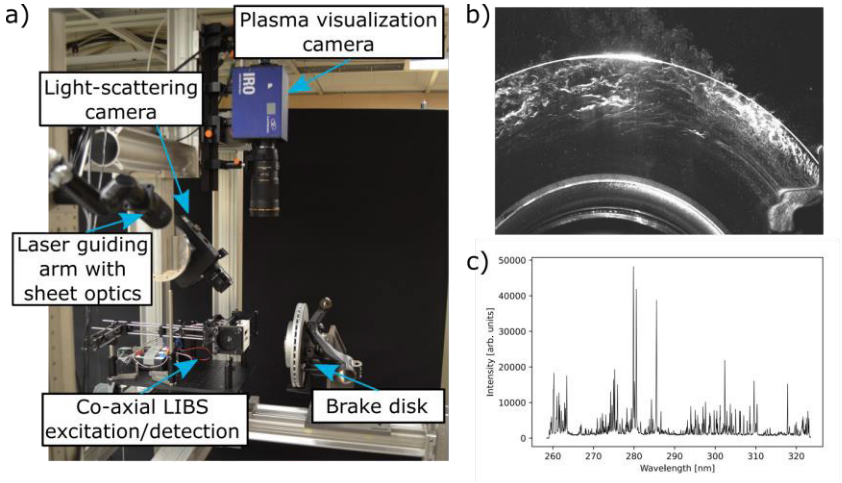

Fig. 1. a) Optical arrangement for LIBS on brake emissions, including particle light scattering visualization and plasma imaging. b) Image from particle light scattering visualization. c) Spectrum of bulk sample of used ECE brake pad.

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Determination of chlorine migration in polymers using LIBS

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High-performance polymers like polyimides, play an important role in the miniaturization and weight reduction of microelectronic devices. Due to their high thermal stability, high chemical resistance and high mechanical toughness, they function as an insulating film, passivation layer or mechanical stress buffer in a variety of different applications. To improve the durability and reliability of electronic devices, the uptake and migration of corrosive species especially chlorine is of utmost importance.

In order to simulate different exposure scenarios, commercially available polyimide films were exposed to various aqueous solutions containing potassium chloride. [1] LIBS is then used to obtain lateral mapping and depth profiling of the tested area (Ø = 30 mm) to sustain insight into the migration behaviour. Quantification was realized using in-house prepared polyimide standards doped with an organic chlorine compound. Depending on the corrosive test parameters, different migration profiles were obtained.

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Implementation of atomic and molecular laser-induced fluorescence for spatially resolved plasma diagnostics

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Laser-induced fluorescence (LIF) is a versatile tool with numerous applications in the fields of spectroscopy and plasma diagnostics. One of its primary uses is in the study of molecular rovibronic states, where LIF can provide valuable information on the structure and dynamics of these states. Additionally, LIF can be employed to observe fluorescence decay, which is useful for studying collision processes or measuring the natural lifetime of a given energy level. Another important application of this method is the study of species spatial distribution in laser-induced plasma based on their selective excitation by a tunable laser for better understanding of the processes and equilibrium in plasma. However, implementing spatially-resolved measurements requires the development of fluorescence schemes containing information about the electronic states and the combination of wavelengths for excitation and observation of fluorescence. Constructing fluorescence schemes can be challenging as the necessary data may not always be available in literature. Therefore, the primary purposes of this study are to design fluorescence schemes for Ca and Fe atoms as well as for their corresponding monoxides (CaO and FeO), and to apply these schemes to investigate species distribution within laser-induced plasma.

To perform the experiment, we used pulsed Q-switched Nd:YAG (532 nm) and tunable Ti:Sapphire (1st and 2nd harmonics) lasers. We used pellets made from ultrapure iron oxide (II, III) (Fe_3O_4) and calcium carbonate ($CaCO_3$). The second harmonic of the Nd:YAG was focused on the target surface to produce laser plasma. A Ti:Sapphire laser beam was directed parallel to the surface of the sample to excite the fluorescence of the studied particles. A system of linear stages provides the positioning of the probing beam in the plasma with an accuracy of 0.2 - 0.4 mm. The experiments were carried out in a vacuum chamber at pressures of 100 and 10 Torr and interpulse delays of 10 and 15 μs, respectively.

For atomic calcium, we proposed and implemented a scheme of nonresonant fluorescence based on transitions between the 4s4p ($^3P°$)–$4p^2$ (^3P) states [1]. The wavelength of Ti:Saphire laser was set at 428.301 nm, allowing us to observe fluorescence at 430.523 nm. The scheme for CaO molecular fluorescence involves transitions between $B^1\Pi$ and $X^1\Sigma^+$ states [2]. In the fluorescence spectra, we observed CaO molecular bands at 408.43 (0, 1 band) and 421 nm. We assigned the transition at 421 nm to the (0, 3) vibrational transition based on calculations of vibrational level energies using molecular constants since there is no assignment in literature. It should also be noted that by slightly changing the wavelength of the exciting laser, we observed selective excitation of rotational states. Fe atomic fluorescence scheme employs excitation at 396.926 nm and fluorescence at 406.359 and 413.206 nm between $3d^7(^4F)4s$ (a^3F) and $3d^7(^4F)4p$ ($y^3F°$) electronic states. The close proximity of the excitation wavelengths for CaO and Fe enabled the simultaneous observation of fluorescence from both species in a meteorite sample. In the case of FeO, we developed an excitation-emission scheme using near-infrared bands (823 and 835.5 nm), but their assignment to electronic states remains impossible. Using these LIF schemes in our experiments, we were able to investigate spatial distribution trends in the plasma core for all four particles fluorescence intensity. Our experimental approach provided us an opportunity to investigate molecule formation pathways in laser-induced plasma, including dissociation of ablated material, recombination into diatomic molecules, or reactions with atmospheric oxygen.

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Investigation of Fuel Retention on Plasma-Facing Components using Resonant Laser-Induced Breakdown Spectroscopy

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Fuel retention and impunity deposition analysis is very important for the long operation of fusion devices. Laser-Induced Breakdown Spectroscopy (LIBS) has gained prominence for its flexibility and capability to conduct on-site quantification and depth profiling for such applications. The depth profiling technique helps to study the depth of the fuel retention in the first wall and reveals interfaces between various materials within a layered sample at differing depths [1]. The study involves utilizing laser pulses to vaporize sample materials and subsequently detecting the resultant plasma. The precision of depth analysis hinges on factors such as depth resolution and ablation rate. However, the conventional ns-LIBS setup has higher ablation rate, and heat affected zone. The non-uniform distribution of laser energy in the radial direction can hinder depth profile accuracy [1]. Addressing these challenges, Resonance-Laser Induced Breakdown Spectroscopy (RLIBS) is introduced to enhance depth resolution and lower the ablation rate.

An integrated system of Resonant Laser Ablation (RLA) with Optical Emission Spectroscopy (OES) employs a single tunable laser for material vaporization. To investigate depth profiles of W-based samples pertinent to fusion and plasma-facing components (PFCs) in fusion reactors, Calibration-Free Laser Induced Breakdown Spectroscopy (CF-LIBS) is incorporated [2]. The vaporization process employs a tunable nanosecond OPO (EKSPLA NT342C) laser, with wavelengths aligned to W excitation levels at 291.1 nm (resonance conditions) and 253 nm (non-resonance conditions). OES signals are captured from 150 consecutive laser shots, utilizing a UV-NIR Echelle spectrometer (ME5000, 200-975) with an iCCD camera. Optimal plasma conditions are achieved through gate delay and collecting window adjustment.

RLIBS features a streamlined experimental setup, utilizing a single laser beam for both ablation and simultaneous plasma excitation unlike other excitation schemes such as RELIBS and LIBS-LIF making the experimental setup significantly modest for online application. Despite yielding a slower ablation rate, resonant conditions offer superior depth resolution compared to non-resonant conditions. Recorded spectra undergo analysis as normalisation using a sensitivity curve, with peak assignments referencing different atomic databases. The study involves a comparison of signal enhancement between resonant and non-resonant conditions, along with ablation rate determination through a 3D laser scanning confocal microscope equipped with a red laser.

This investigation underscores the potential of RLIBS for advancing depth profiling in fusion device materials, contributing insights into fuel retention mechanisms and refining techniques for plasma-material interactions.

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Composition and depth analysis of zirconium diboride using vacuum UV LIBS

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Zirconium diboride (ZrB_2) is a compound which exhibits extreme physical and chemical properties like high melting point around 3000^{o}C, hardness more than 30 GPa and elastic modulus at around 440 -460 GPa whose usage can extend from walls of high temperature facilities for thermal protection to structures of space vehicles [1]. These properties are significantly affected by the concentration of Boron in the compound [2]. Laser Induced Breakdown Spectroscopy (LIBS) is a well-developed technique for onsite analysis of stoichiometry of the compound. In LIBS the plasma is formed on the surface which enables to measure solid, liquid and gaseous samples with little to no preparation. But conventional LIBS carried out in UV-near infrared (NIR) is not successful in efficiently detecting lighter elements like Boron (B) [2] whose atomic emission lines are in the vacuum ultraviolet (VUV) region. Hence the experiment has to be conducted in a vacuum environment or within inert gas environment to detect the atomic lines of Boron. To study the thermal tolerance of ZrB_2 compound the series of pulses from a laser is shot to ablate the material. The ablation crater profile at each shot is analyzed to understand the amount of material lost in terms of volume [3]. The depth profile elemental analysis is done by CF approach from spectra recorded by echelle (Michelle ME5000, Andor Technology) and VUV spectrometer (McPherson) using the NIST [4] and Kurucz atomic spectral line database [5]. The elemental composition results from LIBS are compared to the X-ray energy-dispersive and wavelength-dispersive spectroscopic analyses. Other compounds with other stoichiometry of the same elements like ZrB, Zr_3B_4 and ZrB_{12} can be tested to compare against thermal tolerance of ZrB_2.

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Application of Spatial Heterodyne Spectrometer for LIBS and Raman Spectroscopy

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Laser-Induced Breakdown Spectroscopy (LIBS) is a versatile optical emission technique for elemental analysis that finds plethora of applications [1], and Raman is a laser spectroscopic technique to determine intricate bonding in molecular structure. The spectrometers commonly used in LIBS and Raman applications are dispersive spectrometers that have etendue/throughput limitations that limit their sensitivity. To overcome these limitations, the Spatial Heterodyne Spectrometer (SHS) was developed, an interferometry-based spectrometer designed for higher throughput, higher resolution, and no moving parts [2]. The SHS, in its simplest arrangement, is similar to the Michelson interferometer, in which the mirrors are replaced by diffraction gratings set in the Littrow configuration[2].

SHS experiments were carried out at BAM, Berlin. The laser used was a DPSS 532 nm CW laser. A dichroic mirror and several filters, such as a bandpass filter and a 3.0 neutral density filter, were used to adjust the desired bandwidth in the visible spectral range. To form the interferogram recorded by the Retiga-R1 camera, a 1-inch beam splitter and 300 lines/mm gratings were used. A hybrid experimental setup was constructed to record LIBS and Raman spectra with identical SHS Littrow configurations. The LIBS experiment used additional focusing lenses, optical fibers, and motorized translation stages, while the Raman experiment used a 5x microscopic objective.

To verify the SHS spectra, the incoming radiation was additionally analyzed using an Ocean Optics spectrometer (resolving power R ~ 2000). In the case of a brass sample, the SHS spectra were compared with the spectrum obtained on an LTB Echelle spectrometer (R ≈ 9000). The resolving power of the developed SHS spectrometer was about 8900 at a Littrow wavelength of 561 nm and covered the wavelength range of 51 nm. Among the studied samples were brass, silicon wafer, sulfur, white marble, and others. For a brass sample, the resolving power of the SHS was comparable to that of the Echelle spectrometer, i.e., R ≈ 9000 (Fig. 1). Increasing the camera exposure time increased background noise for the silicon wafer but was minimal for the sulfur sample. For white marble, similar Raman spectra were obtained with and without a microscopic objective with an increase in laser power of only 10%. Detailed information about the apparatus, the studied samples, and the results will be detailed in the presentation at the conference.

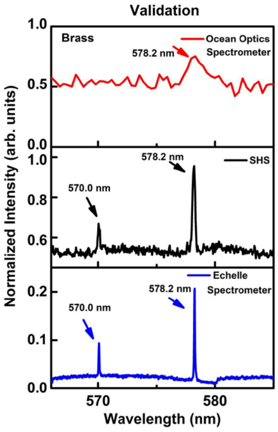

Fig. 1. Cu I LIBS emission lines from Brass sample from handheld Ocean optics spectrometer, SHS, and echelle spectrometer.

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Detection and estimation of a Microplastic particle size by laser-based spectroscopy techniques

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Microplastic pollution is a growing concern in the modern world due to its ubiquitous nature and potential harm to the environment and human health. These tiny plastic particles, measuring less than 5 millimeters in size, are generated from a variety of sources, including plastic packaging, cosmetics, and industrial waste. They accumulate in oceans, freshwater bodies, and soil, posing a serious threat to marine life, wildlife, and human health. Detection of the microplastic particles in various environments rapidly and reliably can improve the chances of preventing the microplastic pollution. To present a potential of using laser-based spectroscopy techniques for this application, we have chosen Laser-Induced Breakdown Spectroscopy and Raman spectroscopy.

It was already proven in several papers, that detection of microplastic particles by LIBS and Raman spectroscopy is possible [1,2]. In this work we focused on polyethylene particles as PE is the most common polymer type in the world [3] and the danger of PE particles entering fragile ecosystems is high. This work shows, that the PE microplastic particles are detectable by both selected techniques. In addition, we show, that the changes in size of the particle can be correlated to signal changes in both techniques and thus a size calibration can be formed. This calibration was made for particles sizing from 250 µm down to 1 µm.

The work shows successful PE particle identification by both LIBS and Raman spectroscopy as well as a particle size estimation by changes in spectral response. Both spectroscopy methods were able to discriminate the polymer signal from other accompanying signals. As the particle size gets below the spot size of the LIBS technique a combination of spectral responses occur. The combination of background (epoxy) and microplastic particle signals can be deconvoluted to be processed separately.

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Laser-induced breakdown spectroscopy readout of magnetic microbeads-based immunoassay

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Laser-induced breakdown spectroscopy (LIBS) has already been proven as a promising readout method for nanoparticle (NP) based immunoassay in standard 96-well microtiter plates (MTPs) [1]. Nevertheless, another alternative solid phase for biomolecule immobilization could explore the LIBS potential. Magnetic microbeads (MBs) are composed of an iron-based core and an outer layer of polymers or organic ligands. They are the only magnetic component within the system, which brings numerous advantages, such as preconcentration and efficient separation of the target molecule through external magnetic field application. As they are not bound to any surface, they can be used for real-time monitoring and lab-on-chip analysis [2]. Due to the multi-elemental detection capability of LIBS, the characteristic elemental signature of a label (NP) and the MB can be detected simultaneously, thus the presence of the MBs and the immunoassay complex (analyte, antibodies, label) are confirmed in one analysis. In this work, we investigate the various type of MBs and optimal photon-upconversion nanoparticles (UCNPs) concentration, as well as the multiplexing possibility in LIBS analysis. The simultaneous detection of Y II spectral line and iron spectral lines confirms the presence of labels (UCNPs) and MBs in one analysis. The elemental mapping also shows the distribution of MBs within the designated area.

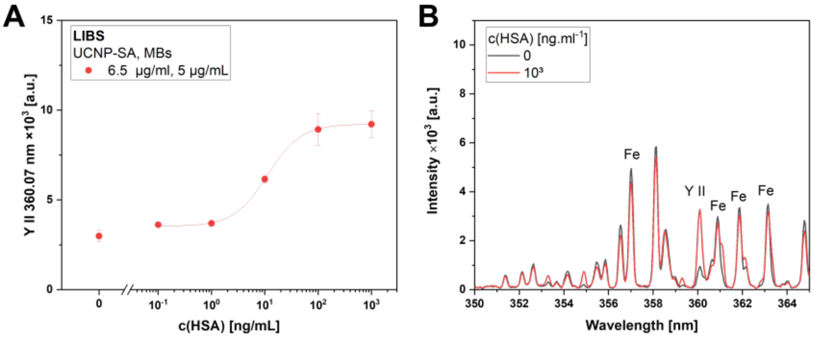

Fig. 1. Indirect detection of HSA labeled with yttrium-based UCNPs (6.5 µg/mL) on MBs (5 µg/well) by LIBS.

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Utilizing Laser-Induced Breakdown Spectroscopy for Heavy Metal Bioimaging in *Cannabis sativa* L.

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The accumulation of heavy metals in soil is a big concern in agriculture nowadays because of the effects of heavy metals on food safety, crop growth and health of soil organisms. Plants grown in heavy metal-contaminated soil can exhibit altered metabolism, growth reduction, lower biomass production and metal accumulation [1].

Cadmium (Cd) is a widely distributed non-essential trace element. Cd concentrations in soil and groundwater can be elevated by both geogenic and anthropogenic sources. Sources of Cd include mining, atmospheric deposition of combustion emissions and Cd-containing fertilizers. Elevated Cd doses are carcinogenic to humans. Concentrations of cadmium in soil range from 0.01 to 1 mg/kg with the worldwide mean of 0.36 mg/kg [2].

Determination of exact distribution of heavy metals in plants is paramount for an assessment of toxicity and possible health risks. Laser-Induced Breakdown Spectroscopy (LIBS), based on the principle of laser ablation, could be a very promising tool in ecotoxicology. This method is capable of the detection of broad range of elements. Additionally, it gives us information about spatial distribution of studied elements in the sample which enables a retrospective study of pollutant migration within the plant. It is possible to map the whole plants or only chosen parts of plant samples [3].

In this study, industrial hemp *Cannabis sativa* L. was grown in cadmium contaminated water and soil. Toxicity of cadmium was assessed on the basis of macroscopic toxicological endpoints. LIBS was used to demonstrate the spatial distribution of cadmium in plants. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) was used to determine exact concentrations of Cd in all plant parts (root, stem, leaves). Cadmium was mostly accumulated in roots of the plants and showed high bioaccumulation properties.

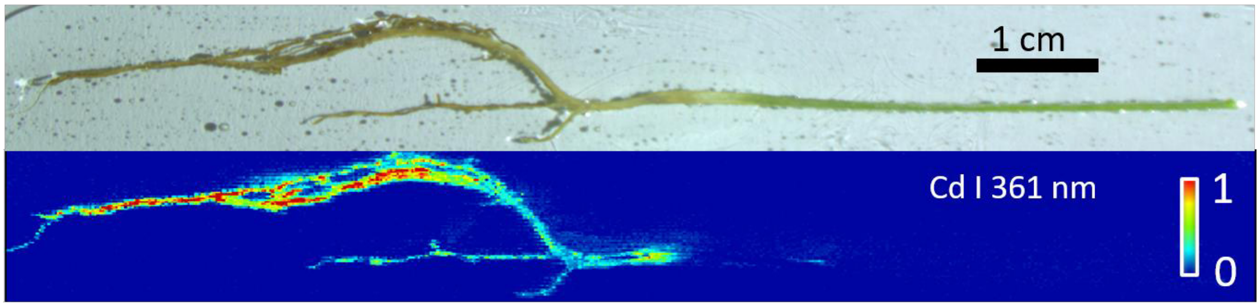

Fig. 1. LIBS 2D elemental map of Cd in the 1-week-old plant *Cannabis sativa* L. Concentration of Cd in the soil was 10 mg/kg.

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Advanced correlative imaging of malignant melanomas using LIBS, LA-ICP-MS and immunohistochemistry

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New methods are constantly being sought to assist histologists in diagnosing and analysing tumors. Now, standard excision, the surgical removal of cancerous tissue, including a safety margin of healthy skin, followed by microscopic examination of the specimen, is most used for diagnosis. The problem is the correct estimation of the safety margin during tumor removal. Often incorrect tumor removal of insufficient safety margin leads to the need to repeat the surgery, which can be dangerous, especially for the elderly [1]. Despite that histological examination is the leading diagnostic tool for skin cancer, there is an effort to discover a novel method suitable for preliminary screening.

Since cancerous tissue changed the shape of the cells and their chemical composition, bioimaging techniques such as LIBS and LA-ICP-MS can be used to image the elemental composition of the tissue, which shows differences in composition of biotic (e.g., C, P, Ca, Mg) and trace (e.g., Zn, Cu) elements between healthy and cancerous tissue [2].

Analysis was performed using LIBS and LA-ICP-MS, and spatial distributions of selected elements were constructed. Immunohistochemical studies were chosen to complete the biological information and further confirm the tumor area. The antibody used was Melan A, which labels melanocytes and is used to diagnose malignant melanoma. The aim of this study is to show the potential of correlation of data obtained from all already mentioned methods. The next aim is to demonstrate on many malignant melanoma samples that the magnesium, which we can measure in a short time with and with a sufficient spatial resolution by LIBS, could serve as a biomarker for diagnosing skin cancer in the future.

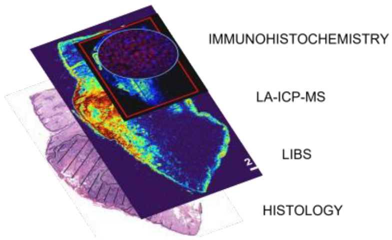

Fig. 1. Correlative imaging of tumors using different techniques.

ACKNOWLEDGEMENTS

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Brno Ph.D. Talent Scholarship Holder – Funded by the Brno City Municipality.

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Chemical Analysis of Spent Coffee Ground filled Polypropylene (SCG/PP) by Laser Induced Breakdown Spectroscopy (LIBS)

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Spectroscopic techniques are necessary for in situ plastic-type identification and characterization [1]. Laser Induced Breakdown Spectroscopy (LIBS) is a fast technique for multi-elemental analysis method. Fourier Transform Infrared Spectroscopy (FTIR) is suggested for molecular identification often as a spectroscopic technique. The study aimed to evaluate the performance of both techniques, LIBS and FTIR methods on spent coffee ground filled polypropylene (SCG/PP) as a green composite. Green composites were prepared with polypropylene matrix and spent coffee ground (SCG) powder collected from cafeteria waste. After the sample plates were molded, analysis on SCG/PP was carried out with LIBS and FTIR. For LIBS measurements, diode pumped Nd: YAG with 100 mJ energy, 4.4 ns pulse length, 10 Hz repetition frequency and a Czerny Turner type spectrometer with 0.1 nm resolution were used. The photons emitted from the plasma were collimated by a parabolic mirror with a focal length of 4 inches and transferred to the slit of the spectrometer with optical fiber. Elements and molecule structures in SCG/PP green composite were identified from the LIBS spectrum. FTIR was used for the identification of functional groups in the SCG/PP green composite. The casework results demonstrated that both LIBS and FTIR show great potential for the chemical characterization of green composites. Fig.1. illustrates the ST LIBS system setup for SCG/PP green composite analysis.

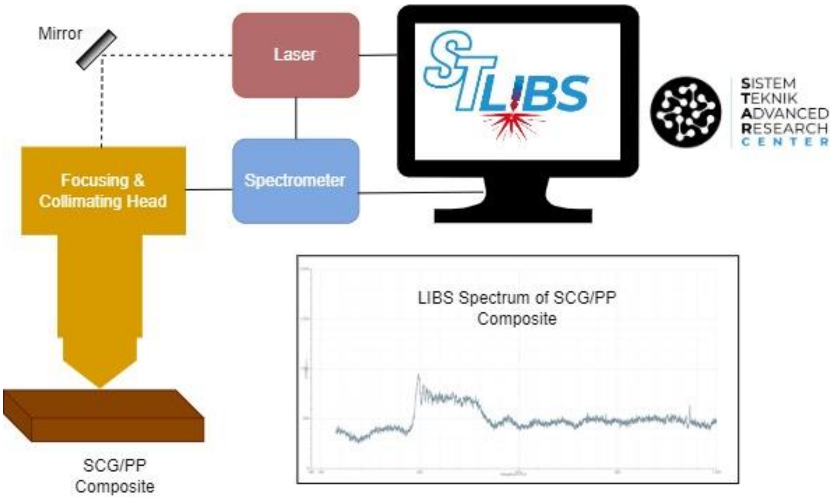

Fig.1. ST LIBS system setup for SCG/PP green composite analysis

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This study was carried out within the scope of the master's thesis.

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Python library for the retrieval of valuable information from LIBS spectra

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Having lacked a universal tool for the retrieval of element-specific information from the LIBS spectra, we developed a Python-based library. Being fully integrable in the classical data processing pipelines and centered around the idea of elemental fingerprints (Fig. 1), the library provides a user-friendly interface for the exploration, processing, and interpretation of the LIBS spectra. We hope that this tool might assist the students and computer science/machine-learning experts entering the field and further enhance the productivity of experienced LIBS practitioners.

The poster outlines the main library features, possible application scenarios, and ideas for its further tuning. Keeping up with the spirit of an open-source project, the attendees are encouraged to stop by, exchange, and share their experiences with the processing of LIBS data, as this interaction is expected to stimulate the future library developments.

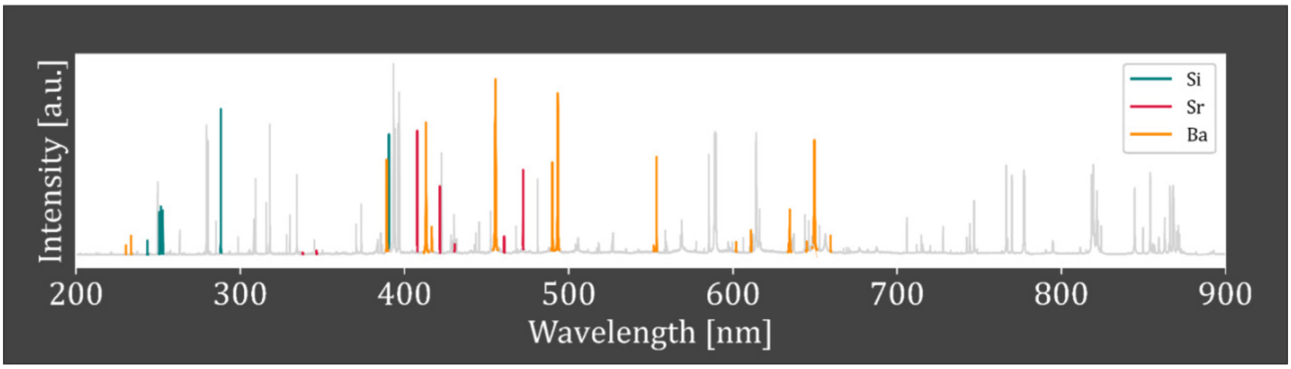

Fig 1. Elemental fingerprints of Si, Sr, and Ba in the NIST 1411 sample

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Precise determination of organic and inorganic carbons in a Martian soil simulant under the Martian CO_2 atmosphere

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Carbon, as an important element for Mars explorations, directly impacts the search for extraterrestrial life and the investigation of the habitability. The uses of orbiters, landers and rovers have allowed the identification of various chemical forms of carbon on Mars [1,2]. Carbon emission lines have also been detected using laser-induced breakdown spectroscopy (LIBS) available in Mars rovers (Fig. 1a; the example of in-situ spectrum obtained by the Zhurong rover [3]). Nevertheless, quantitative determination of carbon using LIBS is yet precluded, due to the CO_2 atmosphere contributing to carbon emission lines as evidenced by numerous studies. In addition, determining an element constituent of a material, under an ambient gas containing the same element, represents an intrinsic challenge of LIBS that currently limits its applications.

In our laboratory therefore, LIBS experiments were conducted under the simulated Martian atmosphere, with samples resulted from a mixture between synthetic Martian soils and carbonates or organic materials. Univariate regressions using the C I 247.9 nm line exhibit unsatisfactory performances for inorganic carbons (Fig. 1b), although it shows a better performance for samples containing organic carbons. The difference may attribute to a lower plasma temperature due to a reduced laser absorption by organic materials, leading to a weaker excitation of the CO_2 atmosphere. Faced to such impasse, multivariate models based on back-propagation neural networks (BPNN) were firstly developed for sets of samples containing organic and inorganic carbons, respectively, and then for the ensemble of the two sample sets (Fig. 1c). Besides an impressive improvement of the correlation of the both training and test data to the model, the root mean square errors of prediction (RMSEPs) of 0.133 wt%, 0.036 wt%, and 0.062 wt% respectively for the three cases of inorganic C, organic C and the mixture of the both, are much improved compared to the reported studies in the similar contest of the Mars exploration application with LIBS [4].

The mechanism of improvement with a machine learning model is further investigated, by analysing the features selected for model training and their connection weights between the input layer and the hidden layer within a 3-layer neural network. The observations reveal that the implications of the two types of features with positive and negative correlations with the carbon concentrations in the samples. More specifically for inorganic carbon, the negatively correlated features from the Mars soil predominate, while for organic carbon, the feature contributions from the both the soil matrix and the carbon-bearing compounds with positive correlation are quite balanced. Finally for the joint set of inorganic and organic carbon samples, a majority of features are contributed by positively correlated lines from the carbon-bearing compounds, including carbon-related C I and CN lines. The implications of these observations in the performance of the machine learning models will be discussed in detail in our presentation.

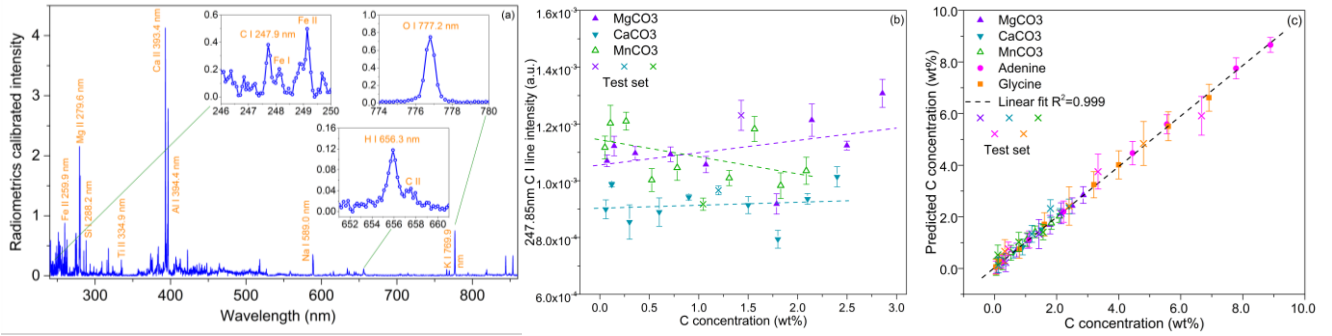

Fig. 1. (a) An in-situ spectrum of a scientific target on Mars; (b) laboratory univariate models for inorganic carbons using the 247.8 C I line; (c) machine learning multivariate model for the ensemble of both inorganic and organic samples.

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Multidimensional Regularization: Quick Fix for Abel Inversion of Noisy Data

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The inverse Abel transform allows extraction of radially-resolved values of an axially symmetric function by analyzing its projections along observation axis. In the context of laser induced plasma, the Abel inversion can be used to obtain spatial profiles of temperature and electronic density, thereby facilitating a range of different applications such as measuring Stark broadening parameters. Despite the inherent advantages of Abel inversion, its practical application is complicated by a number of intricacies, namely, symmetry distortion, self-absorption, temporal evolution of plasma, and experimental noise. The latter, in particular, can drastically alter the reconstructed profile from a noiseless counterpart and, moreover, excessive data points can result in noise amplification. While reduced sampling [1] helps to improve the precision, it also reduces the trueness of reconstructed profile.

The present work demonstrates that regularization can effectively handle noisy data, providing an efficient means of achieving both high precision and trueness in a single step. Instead of reducing the number of points we have applied the algorithm of Abel inversion with regularization. The method of regularization described in the literature [2] involves applying a penalty to a solution of inverse transform along the radial coordinate. It was augmented with penalty for non-smoothness along the height coordinate. The new method was applied to analysis of data obtained from ablation of calcium carbonate in a vacuum chamber at 10 torr. Through this, we were able to obtain spatial distributions of relative atomic and ionic concentrations, temperature and electronic density. Temperature was measured using Saha-Boltzmann plot and electron density was determined from the Stark broadening of spectral lines.

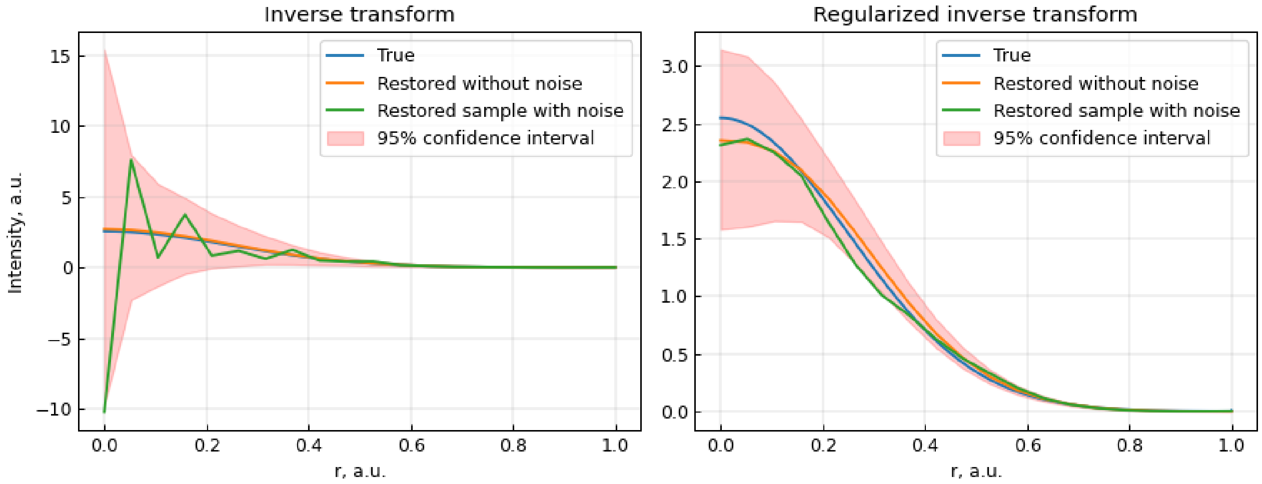

Fig. 1. The difference between onion-peeling algorithm (left) and the same algorithm with regularization (right) applied to a Gaussian profile with noise.

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ANALYSIS OF OSCILLATORY ION SIGNAL VIA LANGMUIR PROBE OF LASER ABLATED RUBY PLASMA

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The studies on laser matter interaction have been growing significantly due to its utility in pulsed laser deposition, material processing, micromachining etc. Interaction of Laser with solid material produces an expanding transient plasma plume termed as Laser induced plasma (LIP). The LIP exhibits oscillatory behavior. The LIP is studied using various optical and electrical probes e.g.; Langmuir Probe, Faraday Cup, Optical emission spectroscopy etc. to gain understanding of the underlying physics. In the present paper, Langmuir Probe [1], one of the simplest methods, is employed to study LIP plume expansion of Ruby target as a function of distance w.r.t target and probe bias voltages. The LIP of ruby is generated via focusing a high powered Q switched Nd:YAG laser onto a ruby pellet. The detailed experimental set up is given elsewhere [2]. Ion signal observed at different distances for a biasing voltage of -50 V is shown in Figure 1. The I-V characteristic of LIP is shown in figure 2. The oscillatory behavior has been observed between 0 to 6 μs. In literature, such oscillatory behavior has been reported in presence of ambient gas as well as under vacuum [3]. The oscillation frequency and decay time is observed by fitting the oscillatory part of ion density to sinusoidal exponentially decaying function as shown in Figure 3. The detailed results will be presented during the conference.

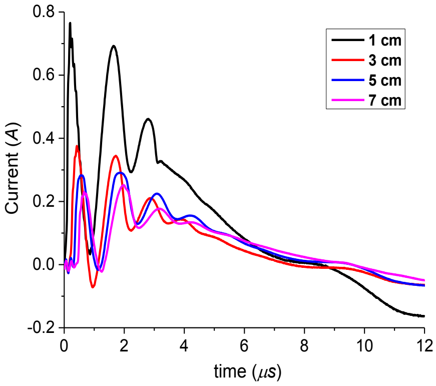

Fig.1. Ion Current at different distance from the target

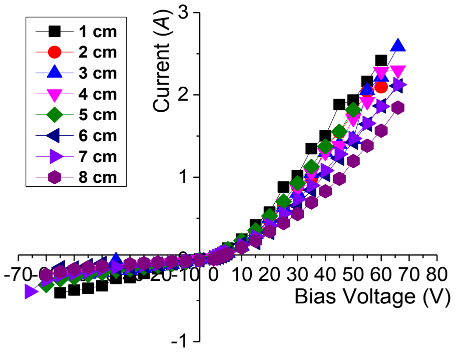

Fig.2. IV Characteristic with distance

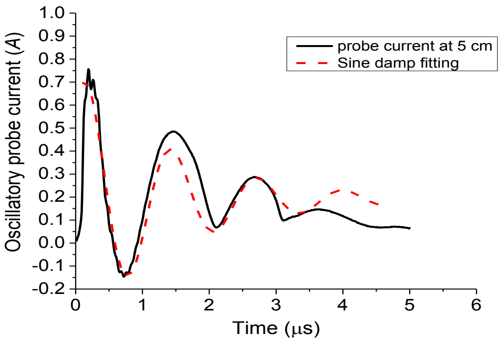

Fig.3. Sine damp fitting of oscillatory probe current at a distance of 5 cm from the target

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Analysis and application of laser-induced plasma polarization effects

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Laser Induced Breakdown Spectroscopy (LIBS), as an emerging spectroscopic technique, has been widely utilized in industry due to many advantages such as simultaneous detection of multiple elements and absence of complex sample pre-treatment [1-3]. Traditional LIBS only collects the intensity spectrum of plasma radiation, however, light waves as a transverse wave, it is also extremely important to analyze the polarization effect of the radiated light. In this work, a polarization spectroscopy detection system, as presented in Fig.1, was developed to analyze the polarization effect of plasma emission. Firstly, the plasma radiation passes through three non-polarizing beamsplitters (NPBS) with a 50:50 beam splitting ratio which divides the radiated light into four equal parts. Subsequently, the radiation passes through four polarization detection systems, respectively, which specifically include optical path 1 for the acquisition of the circularly polarized component of the plasma radiation, optical path 2 for the acquisition of 45° linearly polarized light, optical path 3 for the acquisition of 0° linearly polarized light, and optical path 4 for the acquisition of 90° linearly polarized light. In the experiment, the polarization effects of three characteristic spectral lines of copper alloy at 510.86 nm, 515.57 nm and 522.89 nm were analyzed at 30 mJ energy of 1064 nm pulsed laser. The degrees of polarization (DOP) were calculated using Stokes vectors as 0.1283, 0.2752 and 0.2473, respectively. Currently, we are also exploring the polarization effects of plasma radiation from materials with more complex substrates and the application of polarization spectroscopy in the biomedical field. Hence, the above experimental systems and analytical methods are of great significance in the investigation of the polarization effect of laser-induced plasma.

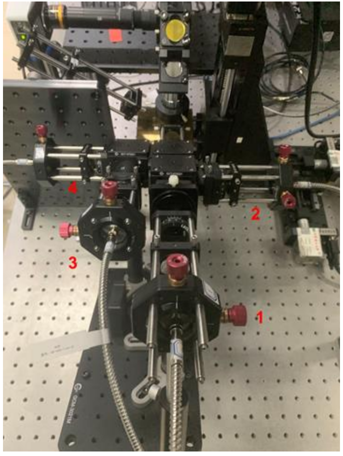

Fig. 1. The figure shows the installation of the polarization spectrum acquisition system.

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Food safety-related qualitative discrimination analysis of herbs by LIBS and Raman spectroscopy

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Spectroscopic methods are increasingly used in the food industry for qualitative and quantitative analysis of raw materials and products. The food industry needs such a method for these tests that requires minimal sample preparation, is fast, simple and cost-effective. Both LIBS and Raman spectroscopies have great potential in this application. They offer rapid and non-destructive analysis, making them ideal for the use in the food industry [1]. Both techniques can provide the chemical composition, allowing discrimination and identification of different types of foodstuff and can also be used to identify contaminants, such as heavy metals, pesticides, and other harmful chemicals. These techniques can also be employed to determine the origin of foodstuff , which can be important when identifying counterfeit products. LIBS spectra are rich in spectral lines and hence in analytical information, therefore can successfully be used for sample identification or classification; on the other hand, Raman spectroscopy is particularly useful for the analysis of organic compounds. The use of machine learning methods can significantly facilitate the evaluation of both qualitative and quantitative instrumental analytical measurements [2,3].

Our research project involved herbs (e.g. parsley, basil, cilantro, mint, rosemary) and focused on the goal of the the classification of these samples by using their LIBS and/or Raman spectra. We investigated the influence of experimental parameters on the accuracy and repeatability of the classification by both spectroscopies. Fresh and dry plants were both studied. We tested the discrimination performance of multivariate chemometric methods such as principal component analysis (PCA), linear discriminant analysis (LDA), and random forest (RF), also employing optimization involving normalization and variable selection approaches. We compared the performance of LIBS and Raman standalone spectra, as well as their fused datasets (after balancing). The constructed models were also tested in the assessment of authenticity of commercial, dried herbs (more than 15 samples). Our results indicate that the combination of LIBS and Raman data can be effectively used in food safety applications.

ACKNOWLEDGEMENTS

The financial support from the National Research, Development and Innovation Office of Hungary (NKFIH, within project TKP2021-NVA-19), as well as from the Mexican National Council of Science & Technology (via project CONACYT 809802) are kindly acknowledged.

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Progress Report on LIBS and Multi-Spectral Imaging for use in Wind Turbine Blade Inspection.

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A preliminary investigation is being conducted to evaluate the effectiveness of combining Stand-off Multi-Spectral Imaging (SMSI) and Laser-Induced Breakdown Spectroscopy (LIBS) [1] for damage inspection and contamination classification on wind turbine blades. SMSI images were analyzed using image processing algorithms to identify damage and/or contamination on the blade surface. The results of the SMSI analysis were compared to those obtained using LIBS, combined with a chemometric analysis of the spectral signature of the plasma emission, to determine the elemental composition of the blade surface. The SMSI analysis provided high-resolution images that allowed for accurate identification and localization of the damage and/or foreign surface material, while LIBS provided detailed information about the elemental composition of the contaminants. The combination of LIBS and multi-spectral imaging has been used previously for nitrogen detection in soil [2], whereas multi-spectral imaging and chemometrics have been successfully combined for toxin detection in milk powders [3].

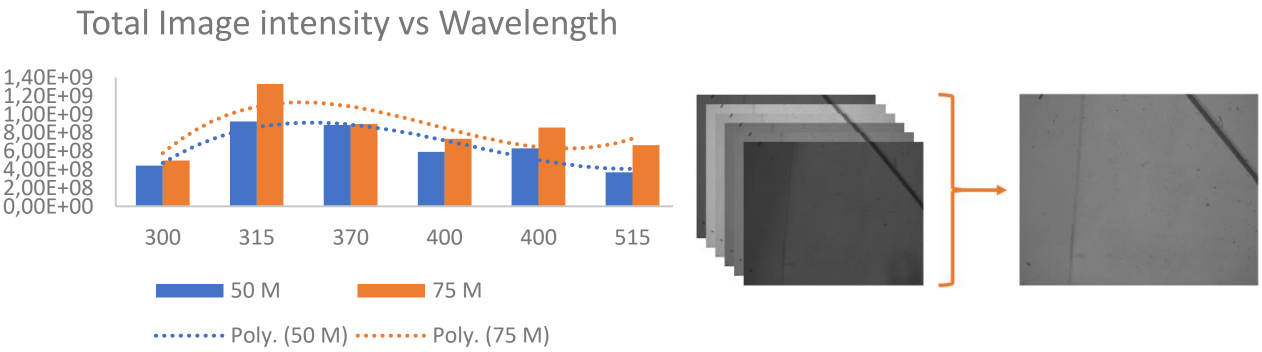

Fig. 1. (LHS) Total image intensity vs wavelength plot of each image taken using six different spectral filters. This was performed at 50 and 75 meters from the wind turbine's surface. (RHS) The six spectrally filtered images for each distance were combined to make a multi-spectral image.

ACKNOWLEDGEMENTS

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Investigating critical metals Ge and Ga in complex sulphide mineral assemblages using LIBS mapping

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LIBS mapping is a powerful tool for visualizing chemical heterogeneity of geological materials [1, 2 and references therein]. Fast data acquisition, minimal sample preparation, multi-elemental detection and high dynamic range are key advantages of LIBS compared to other techniques. In this contribution we show that LIBS maps can provide geologists and engineers with a wealth of information including identification, characterization and quantitation of the different mineral phases, and detection of trace-elements together with their distribution within their host minerals [e.g., 3].

Several ore samples from Kipushi mine, DRC, were selected from the university collection. These ores are known for their mineral complexity and economic value as they contain critical metals such as Ge and Ga.

Analyzing colocalisation of major elements in the extracted LIBS maps allowed the reconstruction of the mineralogy. Detected minerals include chalcopyrite [$CuFeS_2$], bornite [Cu_5FeS_4], chalcocite [Cu_2S], sphalerite [ZnS], galena [PbS], tennantite-(Zn) [$Cu_6(Cu_4Zn_2)As_4S_{12}S$], germanite [$Cu_{13}Fe_2Ge_2S_{16}$], renierite [$(Cu^{1+},Zn)_{11}Fe_4(Ge^{4+},As^{5+})_2S_{16}$], tungstenite [$WS_2$], betekhtinite [$Pb_2(Cu,Fe)_{22-24}S_{15}$] and a series of non-sulphide gangue minerals. SEM-EDS analyses are planned to check this LIBS-derived mineralogy. Relative abundance and grain size of the different minerals can be easily evaluated by image analysis of the LIBS maps. These minerals are preferential hosts for trace-elements Ga and Ag, with Ga being preferentially enriched in chalcopyrite and, to a lesser extent, in renierite, and Ag occurring within bornite and tennantite, with some migration in fractures affecting other sulphides.

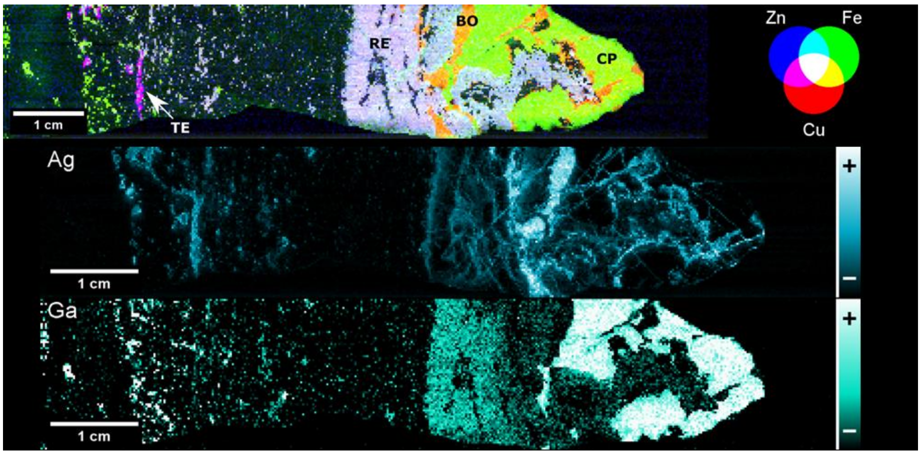

Fig. 1. LIBS maps of a sulphide ore from Kipushi Mine, Democratic Republic of Congo. Upper : RGB composite map for Zn, Fe and Cu. Middle : silver map. Lower : gallium map. BO : bornite, CP : chalcopyrite, RE : renierite, TE : tennantite-(Zn)

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Molten salt setup analysis

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The CEA is developing safer and more modular next-generation reactors. Among the diversity of new reactors considered, there is a family that would use molten salts as coolant (MSR). This solution offers many advantages but requires solving some problems related to the corrosion of metals by salts.

The corrosion study can be quite long and would be considerably accelerated if an in-situ measurement of the chemical composition of the salts was available. Because LIBS technic is an all optical sensor, it would make it possible to achieve this. However, the constraints related to temperature, inertness of the salts, narrowness of access make accessibility non-trivial. The work will present the optical study that has been done as well as the stability study of the signal obtained with the selected setup on a simulating liquid medium.

Novel Non-metallic Substrate Surfaces for Laser-Induced Breakdown Spectroscopic Analysis of Liquids

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To solve the problem of inhomogeneous distribution of liquid samples on the substrate surface for laser-induced breakdown spectroscopic [1] analysis of liquids, a sample loading target patterned with periodical geometric structures [2] was designed and fabricated. For this purpose, two different geometrical shapes, triangular prisms, and cylinders of two different feature sizes, 5 micrometers, and 20 micrometers, were photo-lithographically patterned on 5” diameter Si-wafer substrates, and dry etched to 10 micrometers height. Final products were obtained after 1-micron thick silicon nitride films [3] coated over patterned substrates and diced into one-inch size squares each containing 36 patterned sample loading areas.

The analytical capability of the fabricated products was tested for toxic, heavy metal analysis in aqueous environments and quantified in comparison with non-textured surfaces. Improvements in LIBS signal strength were obtained. Among the three different geometric designs, the ones with 20-micrometer diameter cylinders exhibit a more effective task in increasing LIBS signal intensities of the Pb element compared to that of a 5-micron cylinder and 5-micron triangular prism designs. Results can be associated with an increased path length and enhanced absorption of the laser beam on the micro-structured substrate surface via multiple reflections.

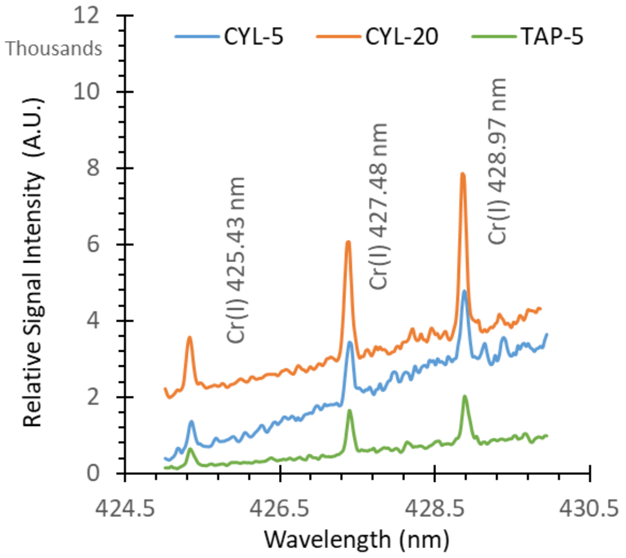

Fig. 1. LIBS signal intensity for chromium lines on three different structured surfaces

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Laser-Induced Breakdown Spectroscopy studies of metalloproteins at reduced pressures

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Heavy metals and particularly cadmium are concerning because they may cause severe health complications and fatalities in humans, even at low concentrations [1]. Certain proteins containing thiol groups have the ability to bind with Cd^{2+} present in the body fluids, e.g., blood. Besides, low molecular weight proteins like metallothionein and high molecular weight proteins like albumin, transferrin, and α2-macroglobulin can also bind with Cd in the blood [2].

Laser ablation at reduced pressures [3] creates plasma with higher electron density and temperature compared to ones observed at atmospheric pressure conditions. In addition, in the absence of interfering gases around the expanding plasma, the number of collisions decreases, and hence the background levels lead to enhanced plasma emission signals. In order to maximize Cd emission lines experimental and instrumental LIBS parameters were optimized. The variation in the LIBS emission signal of Cd at 226.5 nm and 228.8 nm with respect to ambient pressure is shown in Fig. 1. The maximum enhancement was observed at 100 torrs ambient pressure.

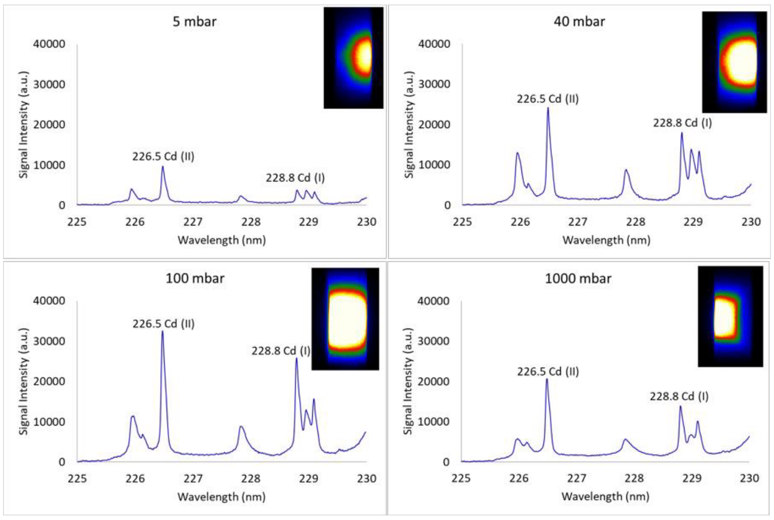

Fig. 1. The variation in the LIBS emission signal of Cd at 226.5 nm and 228.8 nm with respect to ambient pressure.

In this study, a laser-induced breakdown spectroscopic method for the determination of Cd in metal-binding proteins was developed. For this purpose, Bovine Serum Albumin (BSA) and Human Serum Albumin (HSA) standard protein samples were incubated in Cd standard solution for several hours at room temperature. The sample solutions underwent filtration through cut-off filters via centrifugation. The unreacted cadmium in a liquid filtrate and fraction containing cadmium-bound protein was collected and analyzed individually, via dried-droplet LIBS methodology [4] on silicon wafer substrates. Experimental results will be discussed.

ACKNOWLEDGEMENTS

The authors thank NMSC personnel of İYTE for their help in the preparation of metalloproteins.

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Analysis and discrimination of single meteorite particles in an optical trap (OCOT-LIBS)

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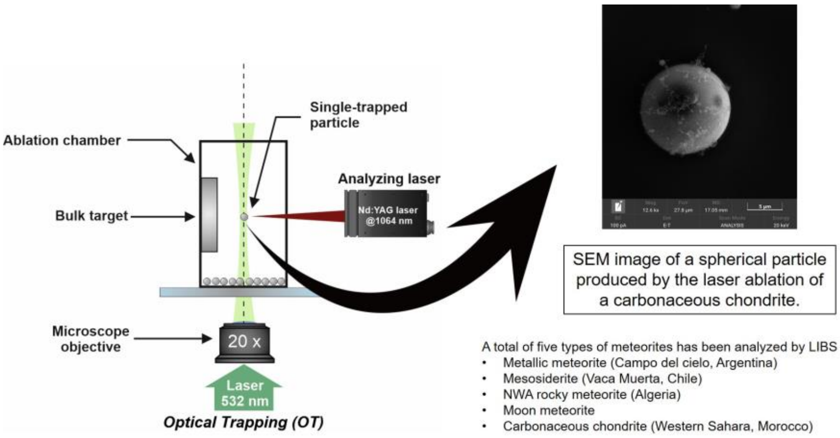
The search to discover the composition of extraterrestrial matter and determine whether it differs from what we know on Earth has been a desire that has motivated researchers for years. Thousands of micro-meteorites are falling to Earth every day. Most of these meteorites have a rocky composition, but others are mainly composed of iron and nickel [1]. However, because they are small particles, up to 100 microns in size, their search, collection and identification is very tedious. In this work, the authors introduce a specific methodology for evaluating the full elemental composition of single micro-meteorites fabricated by laser ablation of bulk targets. A total of five types of meteorites has been analyzed by LIBS: metallic meteorite (Campo del cielo, Argentina), mesosiderite (Vaca Muerta, Chile), NWA rocky meteorite (Algeria), moon meteorite, and a carbonaceous chondrite (Western Sahara, Morocco). For this purpose, bulk meteorite samples were directly ablated within an ablation cell, originating dry aerosols consisting of multielemental particles (Figure 1). The in situ generated particles were first optically trapped in air and, then, analyzed by laser-induced breakdown spectroscopy (LIBS) [2-4]. The morphology and size dispersity of the generated particles was evaluated by scanning electron microscopy. Thus, spherical particles, ranging 1-10 microns, generated by the direct ejection of melted drops during laser ablation were individually analyzed. Differences among LIBS spectra were appreciable and a classification based on the elemental composition was performed.



SEM image of a spherical particle produced by the laser ablation of a carbonaceous chondrite.

A total of five types of meteorites has been analyzed by LIBS
- Metallic meteorite (Campo del cielo, Argentina)
- Mesosiderite (Vaca Muerta, Chile)
- NWA rocky meteorite (Algeria)
- Moon meteorite
- Carbonaceous chondrite (Western Sahara, Morocco)

Fig. 1. Schematic representation of the experimental procedure.

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Sensitive and accurate determination of nitrogen in simulated Martian soil and environment with LIBS spectrum fusion and regression based on neural network

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Nitrogen is a key element necessary for the emergence and development of life. It is one of the elements targeted by the landed missions on Mars in accordance with their scientific goals of investigation of habitability and search for traces of life. A gas chromatography mass spectrometer (GCMS) instrument on board the Mars Science Laboratory Curiosity rover has revealed the existence of oxidized nitrogen-bearing compounds on Martian surface with an equivalent nitrogen concentration up to 0.01 wt% [1]. Although the detection with laser-induced breakdown spectroscopy (LIBS) also on board the Curiosity rover is desirable, the current performance of LIBS for nitrogen analysis does not show the capacity in terms of limit of detection (LOD) and accuracy. Research on a suitable method should therefore be first engaged in laboratory in order to guide further improvements of LIBS instrument on board Mars rover, as well as the data treatment method. Beyond the sensitivity issue, matrix effect also affects LIBS determination of nitrogen, especially due to its various chemical speciation in geological materials. Method research should answer thus double requirements of improving the sensitivity and reinforcing the robustness of the models.

In our laboratory therefore, LIBS experiments were conducted under a simulated Martian atmosphere, with samples resulted from a mixture between Martian soil simulant ((JMSS-12) [2] and nitrogen-bearing compounds. An experimental configuration of double detections with a narrow bandwidth Czerny-Tuner (CT) spectrometer and a broad bandwidth Echelle spectrometer, was implemented in this work, in such way that the first ensured a sensitive detection of emission lines from nitrogen and the second complemented with those from major elements in the sample. The fusion of the simultaneously acquired spectra took into account the emission characteristics of the both two types of elements, necessary for an effective and robust multivariate regression based on a neural network. In addition, for a better treatment of different chemical speciation of nitrogen in samples, generalized spectrum was used for training of regression models, after an unsupervised clustering having assigned a type label to each training spectrum. The trained model was tested by independent test samples, resulting in a limit of detection (LOD) of 0.18 wt%, and a root mean square error of prediction (RMSEP) of 0.041 wt% as shown in Fig. 1 (b), representing a step forward to nitrogen detection using LIBS on Mars [3].

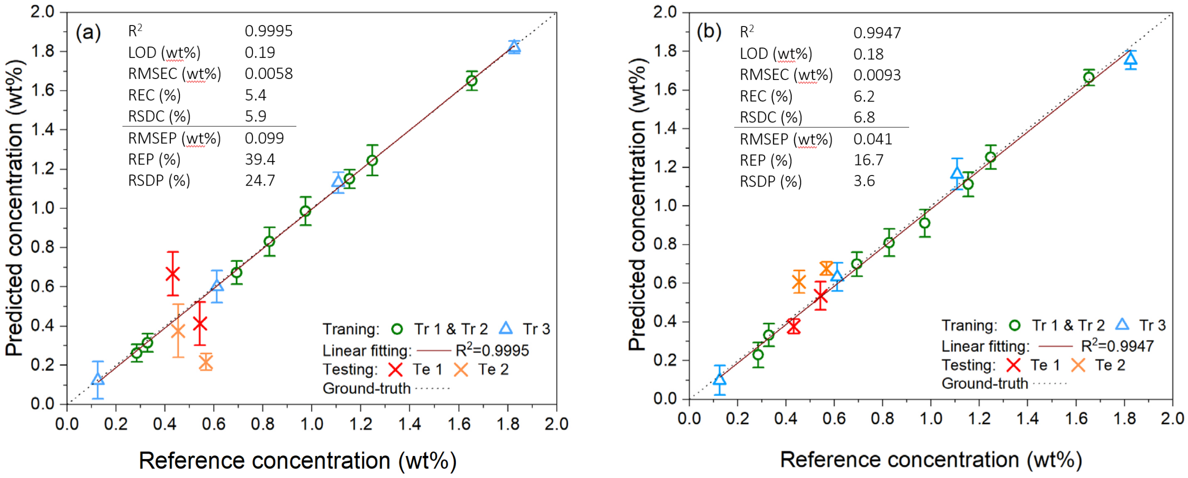

Fig. 1. Multivariate models based on BPNN, trained with the selected features of the fused pretreated spectra of the training samples (a), and with the generalized spectra by including the sample type label in the selected features (b).

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Development of μ-LIBS system for the mapping of inclusion-rich drill cores

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The economic potential of mineral deposits in Chile is determined by the concentrations of Cu, Mo, Fe, S, Au, and Ag through drill core analysis [1]. Petrographical and mineralogical studies require analytical methods capable of providing the distribution of major and minor elements in geological samples. Typically, the initial mineral identification is carried out by a petrography-specialized geologist, by visual inspection of the rocks and drill cores, determining the mineralogical composition and structure using polarized light microscopy [2]. For quantifying these elements, sophisticated methods such as Electron Probe Micro Analyzer (EPMA), X-Ray Photoelectron Spectrometry (XPS), and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) are employed [3]. However, these methods have certain limitations in zones or when samples require a conductive surface. The main goal of this work is to develop a platform for microanalysis using Laser-Induced Breakdown Spectrometry (μ-LIBS) with a particular focus on inclusion-rich cores for the chemical composition of minor elements, mainly Au and Ag.

The μ-LIBS setup depicted in Figure 1 consists of a Q-switched Nd:YAG laser (Quantel, Big Sky Laser, Bozeman, USA) being used at its fundamental wavelength (λ=1064 nm) and energy of 13 mJ per pulse. The laser was converted into vertical beam by reflector mirror and focused onto the sample with a microscope objective 10x magnification lens. The spatial resolution of the ablation crater is generally within 70-100 μm and around 30 μm depth. Surface roughness has shown a significant influence on the experimental results. The plasma emission was collected by a lens and dichroic mirror of high reflectivity from 230 nm to 300 nm, then focused by a focus lens and guided into an optical fiber spectrometer (multichannel, Avantes). The developed system allowed generating elemental distribution maps of the samples.

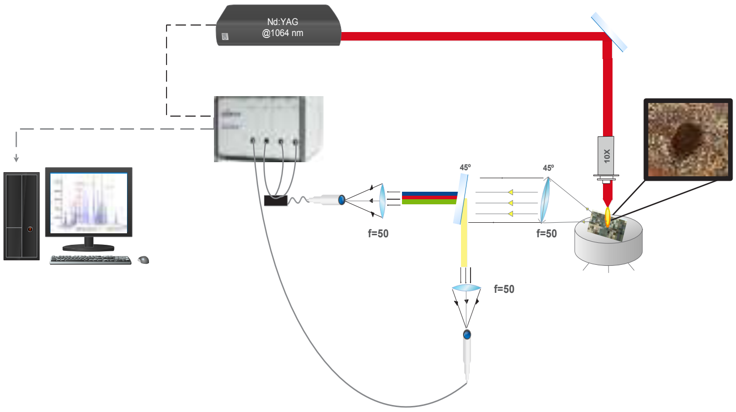

Fig. 1. μ-LIBS setup for monitoring Au and Ag on drill core

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Interpretable Mineral Identification using Laser-induced breakdown spectroscopy

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Laser-induced breakdown spectroscopy (LIBS) is a powerful technique that allows the study of the chemical composition of a sample, performing localized analysis and elemental mapping[1, 2]. In a geological context, this capability can be utilized to determine the mineralogical constitution of rock samples through the analysis of their major elements, having a high potential to be applied in geological science or mining industries.

In this work, we present an algorithm to perform mineral identification in sample areas with similar mineralogic composition, using unsupervised clustering algorithms of the spectral information obtained by the LIBS mapping. Through this pipeline it is possible to identify the different minerals on the sample in a fast, automatic, and precise way. In addiction, this methodology is capable to perform automatic cluster labeling by the input of the features expected to be present in each mineral (elemental lines). The results obtained showed to be in accordance with the expected mineral regions, highlighting the advantage of using this tool to optimize this process.

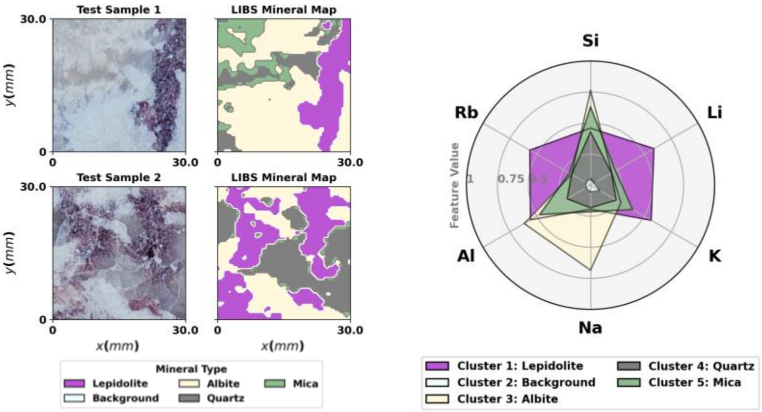

Fig. 1. A. Test samples mineral identification results. B. Cluster labelling and feature mean value coordinates obtained for the centroid for each element of interest.

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Elemental Mapping of 3D structures using Laser-induced breakdown spectroscopy

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Laser-induced breakdown spectroscopy technique is frequently used to study the sample composition and obtain the spatial distribution of the chemical elements along its surface, resulting in 2D elemental maps. Recently, solutions to integrate these 2D maps into 3D models have been explored[1], allowing context-based and interactive analysis which extends the interpretation capability of these tools. Yet, such approaches are still two-dimensional. Truthful 3D elemental mapping requires depth mapping which can be done with multiple shots in the same spot, yet with limited ranges up to few millimetres.

In this work, we explore a new methodology performing LIBS mapping in a set of cuts along the transversal plane of the sample and utilizing ParaView software to reconstruct the internal structures based on the distribution of the different major elements. Our preliminary results demonstrate the capability of such processing and analysing pipeline to provide informative reconstructions of the 3D internal distribution of elements, which may provide an additional tool for context-based interpretations in subjects such as quality and process control or geological sciences.

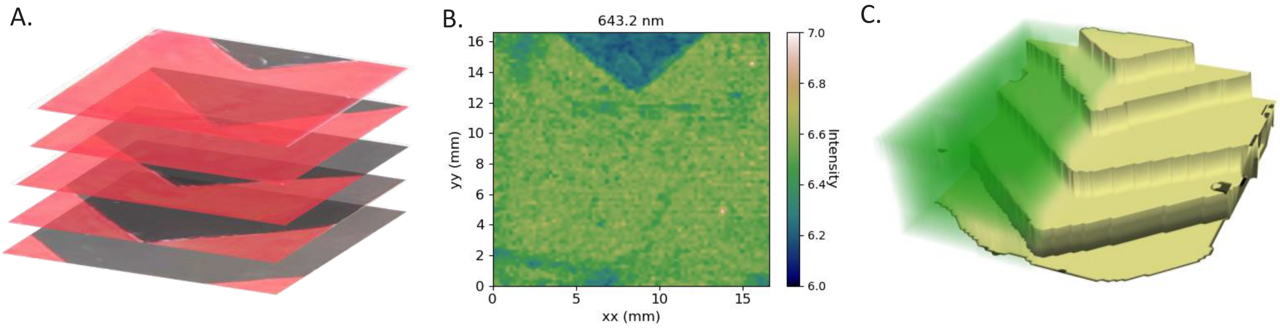

Fig. 1. A. Set of painted coverslips to simulate a simple structure. B. LIBS map of the first coverslip. C. Reconstruction of the sample structure from LIBS mapping results using ParaView.

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Opportunities in collaborative LIBS and Hyperspectral imaging: from sensor fusion to knowledge distillation

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Collaborative multimodal sensing leverages the information gathered from different sensing modalities to find synergies or cooperation strategies that enhance the capabilities of standalone techniques. On the context of spectral imaging, more specifically, mineral identification, two techniques are predominantly used, laser-induced breakdown spectroscopy (LIBS) [1] which allows us to study the elemental composition of a sample surface by analysing the resultant spectrum of atomic emission and hyperspectral imaging (HSI) [2] that gathers the reflected electromagnetic radiation of a sample surface, related to its optical properties.

Whitin this context, this work explores possible synergies that may arise from combining both these techniques, known to provide complementary information. For that we explore two different approaches, (I) effectively increase our features space using mid-level fusion to combine LIBS and HSI taking advantage of their complementary information, and (II) a knowledge distillation approach, where the Laser Induced Breakdown spectroscopy is used as a supervisor for hyperspectral imaging, aiming to increase the performance, as well as, the interpretability of the model allowing us to better take advantage of HSI's information rich spectra, that when combined with its fast acquisition speeds could pave ways for new systems with higher throughputs to be developed.

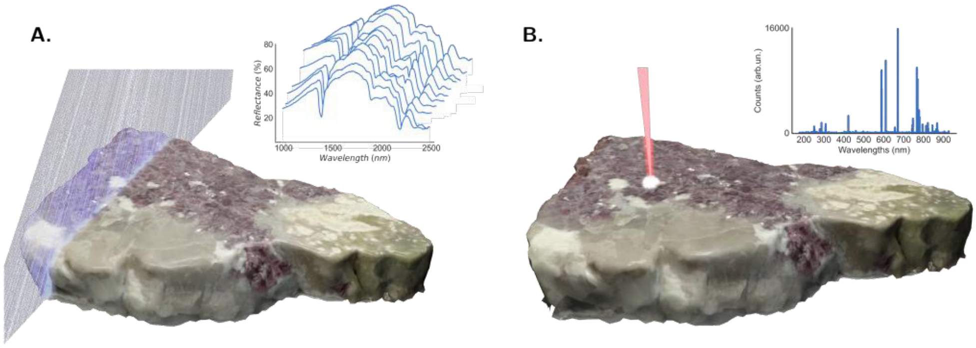

Fig. 1. Illustration of the scanning principles behind each technique. A. HSI, the dataset generated with each scan is a collection of spectra corresponding to the scanned line. B. LIBS, the data generated at each scan corresponds to the spectrum at the targeted point.

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Interactive three-dimensional chemical element maps with Spectral Imaging and photogrammetry

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Laser-induced breakdown spectroscopy (LIBS) is a powerful technique for elemental analysis of materials. Combined with a whiskbroom scanning technique, imaging is enabled, and it is able captures the spectral information of a scene at each pixel, resulting in a three-dimensional data cube that contains both spatial and spectral dimensions [1]. However, conventional spectral imaging systems only provide two-dimensional spatial information on the sample surface posing challenges for data visualization and analysis, which limits the understanding of the spatial distribution and correlation of elements in complex samples.

Within this context, this work explores the combination of spectral imaging techniques and photogrammetry to deploy a versatile solution for the creation of three-dimensional spectral imaging models. First, by making use of a numerical algorithm that is able to match features in the spectral image with those of the three-dimensional model, we show how to match the mesh from distinct sensor modalities. Then, we describe a possible visualization workflow, making use of dedicated photogrammetry [2] and visualization software to easily deploy interactive models. Overall, the results demonstrate the versatility of our approach and pave for the development of novel spectral imaging diagnostic strategies that are able to deliver better qualitative analysis and insight in the three-dimensional space.

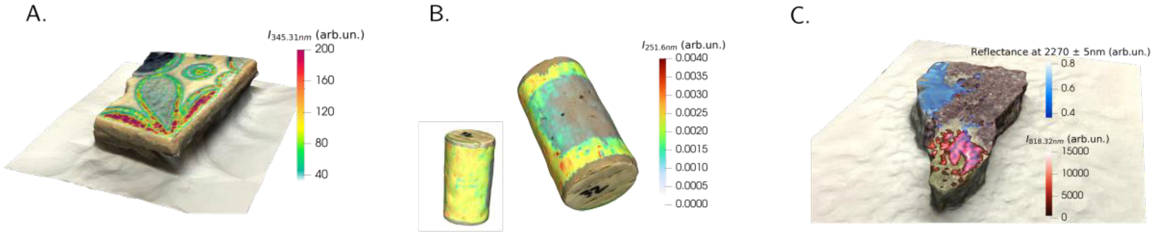

Fig. 1. Illustrative results of the potential of the approach for the generation of interactive visualization models, applied to (A.) Heritage applications (Distribution of Cobalt on the surface of a Portuguese Tile, using the Cobalt line at 345.3nm), (B.) distinct geometries (distribution of silicon on a cork, using the Silicon line at 251.6nm), and (C.) multimodal sensing (LIBS and hyperspectral data of a lepidolite-albite rock).

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Industrial LIBS system for quality assessment of functional coatings in cork stoppers

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The cork stopper industry has a constant presence in daily life by providing means to seal containers such as the commonly known wine bottles. To ensure a good performance in terms of sealing capability and to facilitate correct insertion/removal of the cork stopper from the bottleneck, manufacturers apply a surface treatment, which is usually paraffin and silicon based.

Unfortunately, the resulting coatings can have unwanted features such as wrong amounts of surface treatment product or uneven depositions, which can lead to deviations in quality. The difficulty of correcting these irregularities comes from the lack of proper tools to evaluate the cork stoppers in a timely manner. Current methodologies are slow, destructive, lack representativity of the batch and most of the time are done through indirect methods.

Laser-induced breakdown spectroscopy (LIBS), as a micro destructive technique, allows for the possibility of a depth analysis without destroying the samples at a larger scale[1]. It can also perform elemental analysis in real-time reducing the time between production and batch evaluation.

In this work, an industrial LIBS system prototype was built to allow online analysis of the cylindrical-shaped cork stoppers. Parameters such as pulse energy and spectral region were optimized to operate at the laser highest repetition rates, minimize costs and avoid loss of vital information. Using multiple shots per spot, depth profiles were obtained from different treatment processes and used to determine their effect in the thickness and its distribution. The mean of the number of shots needed to reach the end of the silicone layer and the standard deviation were shown to be able to represent coating thickness and uniformity for each cork stopper, respectively. These results show that LIBS is a promising method to evaluate the thickness and uniformity of future depositions.

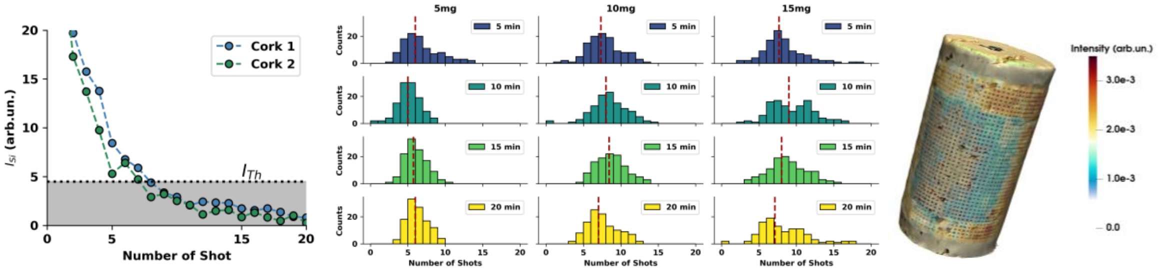

Fig. 1. (Left) Intensity of the silicon line dropping with the increasing depth, (Center) distribution of the number of shots required to reach the threshold and (Right) silicon intensity map of a cork stopper that had a section shielded from treatment overlayed on a 3D projection of the cork stopper.

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Novel Solutions for Finding Relevant Maps in LIBS Imaging datasets

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Laser-induced breakdown spectroscopy has recently become an important tool for the study of the spatial distribution of chemical elements at a sample surface, a technique called LIBS imaging. The standard pipeline adopted for spectral LIBS imaging datasets often revolves around identifying elements suspected to exist within a sample and generating maps based on their characteristic emission lines. Despite this being the most common approach, maps containing relevant information are often discarded due to the lack of tools to identify relevant structures within the captured data, which can rapidly scale for a complex sample featuring hundreds to thousands of atomic, ionic, and molecular emission lines. Considering that, this work presents an algorithm based on the Fast Fourier Transform (FFT), capable of autonomously identifying emission lines or spectral regions containing meaningful spatial structures that can be further associated with relevant features for imaging analysis.

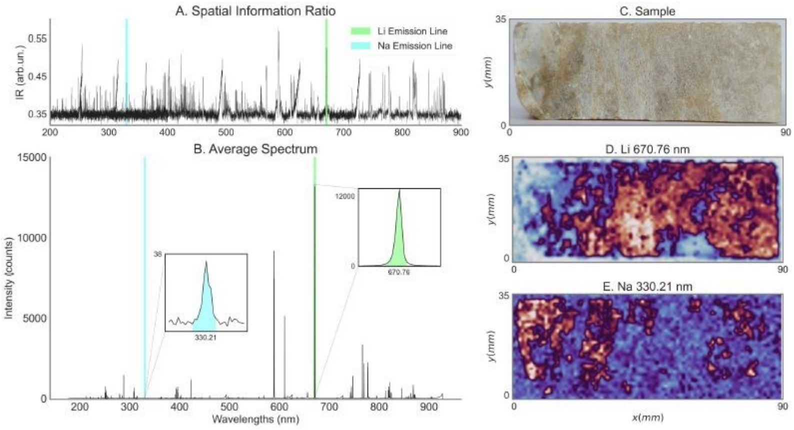

Figure 1. A. Graph of the FFT Score as a function of the wavelengths. B. Average Spectrum with two of the most prominent peaks shown C. Image of the sample being analysed. D. and E. Lithium and Sodium maps generated by the selected emission line in figure A, respectively

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Cellulose Nanocrystal-ZnO hybrid systems: Design, Characterization and ZnO quantification with LIBS technology

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Hybrid materials based on cellulose nanocrystals and metal oxides have been established as an outstanding class of materials. They can be obtained by different synthetic approaches – hydro/solvothermal synthesis; sol-gel; precipitation, among others – and their multifunctional character was already proved in a wide range of applications, which include, but are not limited as anticancer, anti-diabetic, antimicrobial; photocatalysts and as wound-healing agents.[1,2] Nanocellulose is an ecofriendly and an economically feasible natural material extracted from native cellulose, well known due to its remarkable physical and biological properties, and metal-oxides particularly zinc oxide exhibit a wide range of functional properties. [1,3] As a result, nanocellulose materials complement zinc oxide nanoparticles, impairing their functional properties in the hybrid system.

Herein, we report the design, structural characterization (FT-IR; PXRD and morphological analysis), and the ZnO quantification with the LIBS technology of two hybrid materials (**HM1** and **HM2**) – **Figure 1**, where commercial cellulose nanocrystals (**CNC**) and zinc salts were used as starting building blocks in a hydrothermal approach. The hydroxyl groups on the surface of the cellulose nanocrystals exhibited here a bi-functional role, acting as a template and as a capping agent for the synthesis of the ZnO particles and ultimately for the hybrid preparation.

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