BOOK OF ABSTRACTS

10th Euro-Mediterranean Symposium
on Laser-Induced Breakdown Spectroscopy

EMSLIBS
2019

8 – 13th September 2019 | Brno, Czech Republic

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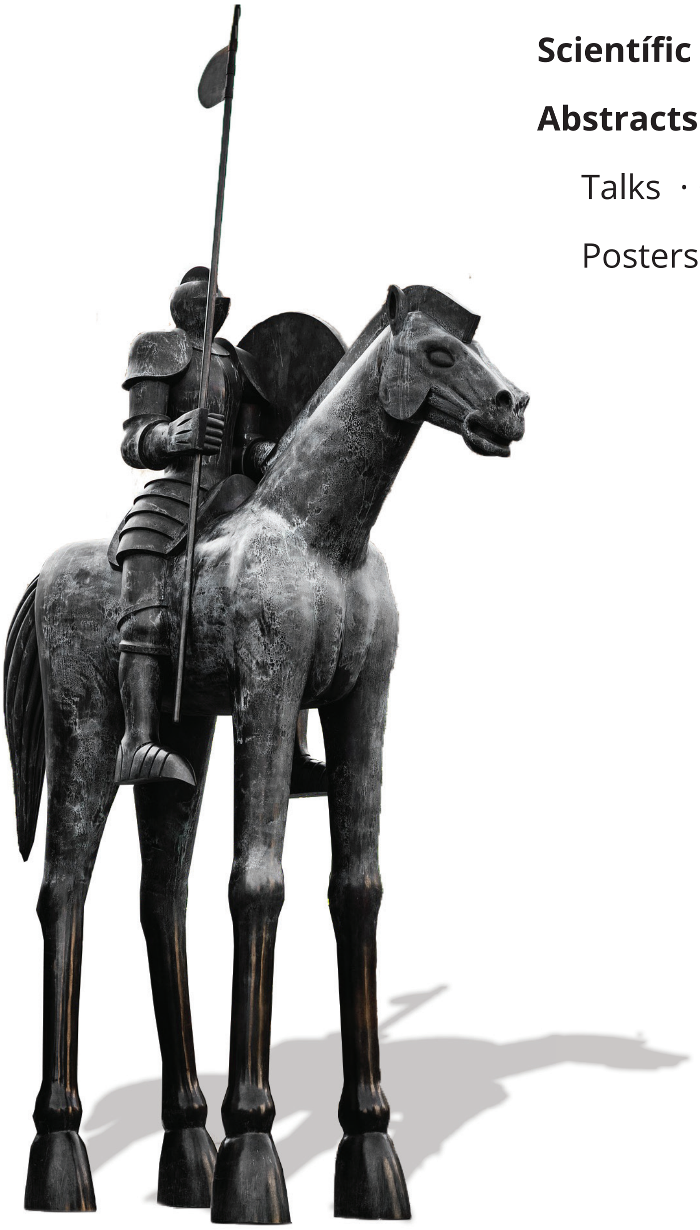

Welcome words

Dear colleagues,

welcome and thank you for joining us at the 10th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy!

We are excited to get the possibility to organize the jubilee, 10th EMSLIBS here in Brno, in the heart of the South Moravian region of the Czech Republic. With more than 200 registered attendees, we believe that this symposium will be not only the biggest but also the most remarkable event dedicated solely to LIBS this year.

First, let us express our gratitude to everyone who contributed to the organization of EMSLIBS 2019. The list is long and we would not like to forget anyone. The organizers of the previous symposiums have continuously provided valuable collaboration and friendly advice. The international scientific committee members, the sessions chairs and all the authors of workshops, talks and posters have significantly contributed to the scientific soundness of the whole symposium. We are delighted that throughout EMSLIBS 2019, every morning we can honor our award-winning colleagues and listen to their heritage or keynote presentation.

Especially, we would like to cordially acknowledge the support of numerous partners and sponsors of the symposium. Special thanks goes to the members of the local organizing committee, particularly to Pavel Pořízka and his team that made not only the symposium but all the connected activities possible. We should also express our thanks to Jakub Vrábel and Erik Képeš who have the biggest credits for organizing the LIBS CONTEST.

Finally, yet importantly, we express our gratitude to all invited and regular presenters and all attendees of EMSLIBS 2019. Your contribution and presence changes EMSLIBS from a regular symposium to THE LIBS EVENT OF 2019. We hope that this symposium fulfills all your expectations and that you will depart not only with a significant amount of new, practical information but also with great memories.

Sincerely,

Prof. Jozef Kaiser
EMSLIBS 2019
conference chair

Prof. Vincenzo Palleschi
EMSLIBS 2019
conference chair

Prof. Viktor Kanický
Head of Ioannes Marcus Marci
Spectrocopic society

Organizers

To organize the EMSLIBS symposium, we have established a team from LIBS groups based at the Brno University of Technology, Masaryk University and the Central European Institute of Technology. Our leaders are Prof. Jozef Kaiser and Prof. Viktor Kanicky, both of them possess considerable expertise in the laser-based spectroscopy and are also members of international committees. This symposium is also co-organized by the Ioannes Marcus Marci Spectroscopic Society, the spectroscopic society of the Czech Republic.

Local organizing committee

Jozef Kaiser – Conference Chair
Viktor Kanický – Conference co-Chair
Pavel Pořízka – Event coordinator
Karel Novotný – Poster session coordinator
Kateřina Kočendová – Participant coordinator
Andrea Chyťová – Catering & Social Event coordinator
Zuzana Chládová – Marketing and graphical interface
Jan Novotný – Design and operation of the website
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Petra Bláhová – Symposium trips coordinator
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Tomáš Zikmund – Feel-bad manager
Jakub Vrábel – EMSLIBS contest coordinator

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Scientific session

We have been striving to deliver a balanced program of the symposium, with rich scientific and social events. The scientific program is divided into three main sessions: oral, poster, and workshops. In general, the sessions are related to current topics and applications that are of paramount interest to the LIBS community (from plasma fundamentals, through bio-applications and chemometrics, to industry and applications with great expectations in the future).

Oral session

Going swiftly around Sunday workshops, we get to the main scientific session. We have selected 55 oral presentations that will be extended with 8 vendor presentations. All presentations are going to take place in the presentation room (see the map of EMSLIBS venue). All speakers are requested to deliver their presentations in powerpoint or pdf format beforehand, no later than during the last break (coffee, lunch) before their dedicated session. Please, deliver your presentations to the presentation room.

Poster session

We are happy about the number of submitted posters, which is 130 in total. However, their number led us to the decision to make two separate poster sessions instead of a permanent one. Both poster sessions will take place in the Aula.

Posters in the first session may be displayed from Monday after lunch until Tuesday evening. From Wednesday morning until Thursday afternoon, the second poster session will take place. Be aware of your particular poster session, the distribution is given below.

Both poster sessions will be spiced up with social events on Monday and Wednesday evening, starting at 18:00.

Student awards

We appreciate the participation of young researchers and we support their further research endeavours. We have selected 12 students' talks and included them in the main session. Moreover, we have highlighted 63 students' posters. Please, note that it is mandatory to present your talk/poster in person in order to win the prize. We will present the best students and award their research during the gala dinner on Thursday.

The best students' contributions will be selected by a scientific committee which was established for this purpose:

Karel Novotný – Czech Republic
Saara Kaski – Finland
Madhavi Martin – USA
Johannes Pedarnig – Austria
Pavel Veis – Slovakia

Scientific program

EMSLIBS 2019 will take place at the Faculty of Social studies of Masaryk University in Brno. Permission to Scientific session is only with your badge. To receive your badge you have to visit our registration booth first. Registration booth will be open:

Sunday 8th, 12:00 – 21:00
Monday 9th, 7:30 – 18:00
Tuesday 10th, 8:00 – 18:00
Wednesday 11th, 8:00 – 18:00
Thursday 12th, 8:00 – 16:30

In general, all accepted abstracts are marked as follows:

- H **Heritage speaker**
- K **Keynote speaker**
- I **Invited speaker**
- S **Student**
- V **Vendor**

SUN 8TH SEPTEMBER

12:00	**Registration open**		
	Workshops (chair: Porizka)		
14:00 – 15:30	W1	**Bousquet & Motto-Ros**	From qualitative to quantitative LIBS using univariate analysis
15:30 – 16:00	**Coffee break**		
	Workshops (chair: Porizka)		
16:00 – 17:30	W2	**El Haddad**	Multivariate data analysis
17:30 – 18:00		**Vrábel**	EMSLIBS Contest
18:00	**Icebreaker**		

MON 9TH SEPTEMBER

	08:30 – 08:45	**Opening**		
		Heritage (chair: Kaiser)		
H	08:45 – 09:30	H1	**Niemax**	The arduous way of LIBS becoming an established technique
		Fundamentals I (chair: Kaiser)		
I	09:30 – 09:50	FU21	**Gornushkin**	Equilibrium chemistry in laser induced plasmas and plasma chemical reactors
I	09:50 – 10:10	FU2	**Vadillo**	Femtosecond laser ablation: as fun as it gets
S	10:10 – 10:30	FU3	**Roldan**	Quantitative analysis of Indium in sphalerites by CF-LIBS using pre-classification by PCA
	10:30 – 11:15	**Coffee break**		
		Fundamentals II (chair: Gornushkin)		
I	11:15 – 11:35	FU4	**Labutin**	Application of spectra modeling for Laser-Induced Breakdown Spectroscopy
	11:35 – 11:55	FU5	**Skočić**	Model function for Optical Time of Flight signal in Laser Induced Plasma
	11:55 – 12:15	FU6	**Yu**	Physical and Statistical Studies of the Influence of Minor Elements on Plasma Temperature and Emission Intensity in LIBS Measurements
I	12:15 – 12:35	FU7	**Veis**	Fundamentals of simultaneous Vacuum UV - UV LIBS for quantification
	12:35 – 14:10	**Lunch**		
		Mapping (chair: De Giacomo)		
I	14:10 – 14:30	MA1	**Motto-Ros**	LIBS-based Imaging: critical focus on current status and future directions
S	14:30 – 14:50	MA2	**Dietz**	LIBS Microscopy for Elemental Imaging of Heterogeneous Samples
S	14:50 – 15:10	MA3	**Müller**	Detection of REE-rich areas in Storkwitz drill cores using LIBS and a combination of normalization, clustering and spatial raster analysis
S	15:10 – 15:30	MA4	**Leprince**	In situ, quantitative, elemental imaging of lung tissues
	15:30 – 16:15	**Coffee break**		
		Biology (chair: Motto-Ros)		
I	16:15 – 16:35	BI1	**Rehse**	Bacterial Limit of Detection Reduction Utilizing A Novel Sample Preparation Protocol
I	16:35 – 16:55	BI2	**Martin**	Switchgrass and Woody Biomass Elemental characterization using Laser-induced Breakdown Spectroscopy
I	16:55 – 17:15	BI3	**Melikechi**	Classifying diseased and healthy biomedical samples one laser pulse at a time
I	17:15 – 17:35	BI4	**Boyaci**	LIBS Applications for Food Safety and Quality
	18:00	**Poster session I. / beer tasting**		

TUE 10TH SEPTEMBER

		Key note (chair: Niemax)		
K	08:45 – 09:30	K1	**Omenetto**	Critical considerations on the use of several experimental methodologies to evaluate self-absorption effects in atomic emission spectroscopy
		Quantification I (chair: Niemax)		
I	09:30 – 09:50	QA1	**Palleschi**	Self-absorption is your friend: exploiting self-absorption for improving the accuracy of Laser-Induced Breakdown Spectroscopy analysis
I	09:50 – 10:10	QA2	**Deguchi**	Improvement of LIBS Quantitative Capability for Remote Elemental Detection Using Collinear Long and Short DP Laser
S	10:10 – 10:30	QA3	**Touchet**	Direct isotopic analysis of solids by laser-induced breakdown self-reversal isotopic spectrometry (LIBRIS)
	10:30 – 11:15	**Coffee break**		
		Quantification II. (chair: Palleschi)		
I	11:15 – 11:35	QA4	**Bousquet**	Advanced data processing to improve the analytical performance of LIBS
I	11:35 – 11:55	QA5	**Wang**	Origin of Measurement Uncertainty and its Reduction methods
	11:55 – 12:15	QA6	**Pelascini**	Calibration-free laser-induced breakdown spectroscopy for industry
S	12:15 – 12:35	QA7	**Rollin**	A standard methodology for characterization of matrix effects in laser-induced breakdown spectroscopy
	12:35 – 14:10	**Lunch**		
		Chemometrics (chair: Bousquet)		
	14:10 – 14:30	CH1	**El Haddad**	Mineral Quantification by Laser-Induced Breakdown Spectroscopy for In-Field Rock Characterization
	14:30 – 14:50	CH2	**Jorge**	Self-Learning Artificial Intelligence Methodology for the Accurate Quantification and Classification of Laser Induced Plasma Breakdown Spectroscopy applied to Geological Lithium Surveys in Portugal
	14:50 – 15:10	CH3	**Sun**	Machine Learning for Classification and Regression of LIBS Spectra from ChemCam Calibration Targets
	15:10 – 15:30	CH4	**Duponchel**	Embedded k-Means Clustering for a deep exploration of megapixel LIBS imaging data sets
	15:30 – 16:15	**Coffee break**		
		Mining (chair: Kaski)		
I	16:15 – 16:35	MI1	**Sabsabi**	A look at LIBS instrumentations as an emerging tool for mining applications
	16:35 – 16:55	MI2	**Cousin**	New quantification of Barium for MSL/ChemCam Mars data, and implications for geological interpretations
	16:55 – 17:15	MI3	**Forni**	Fluorine detection on Mars: experiments and geological interpretation
S	17:15 – 17:35	MI4	**Schmitt**	Quantification of Lithium in pegmatites using handheld Laser Induced Breakdown Spectroscopy : a new approach for mining exploration
	19:00	**Mendel museum / wine tasting**		

WED 11TH SEPTEMBER

		Key note (chair: Noll)		
K	08:45 – 09:30	K2	**Hahn**	LA-LIBS: High repetition rate ablation in combination with aerosol LIBS for quantitative analysis of solid samples
		Hyphenated systems (chair: Noll)		
I	09:30 – 09:50	HY1	**Kaski**	LIBS, Raman and LIF in analysis of rocks containing rare earth elements
S	09:50 – 10:10	HY2	**Marmatakis**	Coupling LIBS to SSI-MS. Interference of plasma formation with mass analysis
I	10:10 – 10:30	HY3	**Zheng**	Development of in-situ spectroscopy and its ocean applications
	10:30 – 10:50	HY4	**Fantoni**	Complementary characterization of ancient Roman frescoes by PIXE and LIBS techniques
	10:50 – 11:35	**Coffee break**		
		Molecular (chair: Martin)		
	11:35 – 11:55	MO1	**Gaft**	Molecular LIBS and Plasma Induced Luminescence of BaF2:Tm3+
S	11:55 – 12:15	MO2	**Yang**	Double-pulse laser synchronization aimed at simultaneous detection of intensified atomic and molecular signals for space exploration
	12:15 – 12:35	MO3	**Bordel**	Evaluation of the spatial and temporal distribution of atomic and molecular species at different LIBS plasma conditions
I	12:35 – 12:55	MO4	**Samek**	Analysis of biological samples combining data from LIBS, Raman spectroscopy and LA-ICP-MS
	12:55 – 14:30	**Lunch**		
		Vendor (chair: Novotný)		
V	14:30 – 14:45	V1	Pfeifer	LTB Lasertechnik Berlin GmbH
V	14:45 – 15:00	V2	Mandel	AtomTrace a. s.
V	15:00 – 15:15	V3	Machaqueiro	SciAps
V	15:15 – 15:30	V4	Colin	Quantel Laser/Lumibird
V	15:30 – 15:45	V5	Dubouski	SOL Instruments
V	15:45 – 16:00	V6	Hubert	Femtonika s.r.o.
V	16:00 – 16:15	V7	Leosson	DT-Equipment & Innovation Center Iceland
V	16:15 – 16:30	V8	Gorju	Imagine Optic
	16:30 – 16:45	**Symposium photo**	←	**MEETING POINT – REGISTRATION BOOTH**
	18:00	**Poster session II.**		
		19:00	EMSLIBS committee meeting	

THU 12TH SEPTEMBER

		Key note (chair: Pedarnig)		
K	08:45 – 09:30	K3	**Laserna**	Chemistry in the laser-induced plasma. An astrobiology perspective for Mars exploration.
		Nanoparticles (chair: Pedarnig)		
I	09:30 – 09:50	NP1	**De Giacomo**	NELIBS vs LIBS: dealing with outstanding advantages and real limits
	09:50 – 10:10	NP2	**Novotný**	LIBS assessment of spatial photon-upconversion nanoparticle distribution in model plants (R. sativus and L. minor)
S	10:10 – 10:30	NP3	**Salajková**	Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS) as a technique for elemental analysis of microdrops at sub ppm level
	10:30 – 11:15	**Coffee break**		
		Industry (chair: Galbács)		
I	11:15 – 11:35	IN1	**Noll**	Challenges and perspectives of inverse production for sustainable material recycling – what LIBS can contribute
I	11:35 – 11:55	IN2	**Pedarnig**	Quantification of the vulcanizing system of rubber in industrial tire rubber production by laser-induced breakdown spectroscopy
S	11:55 – 12:15	IN3	**Smetaczek**	Investigating the Li+/H+ exchange in garnet-type solid electrolytes using LIBS
	12:15 – 12:35	IN4	**Wilsch**	Mobile LIBS-System for evaluation of concrete structures on-site
	12:35 – 12:55	IN5	**Lednev**	Laser induced breakdown spectroscopy for in-situ multielemental analysis during metal additive manufacturing
	12:55 – 14:30	**Lunch**		
		Future LIBS (chair: Veis)		
I	14:30 – 14:50	FT1	**Galbacs**	Exploring the potential of LIBS for the in-field analysis of nuclear samples
I	14:50 – 15:10	FT2	**Grisolia**	LIBS developments for fusion applications
S	15:10 – 15:30	FT3	**Purohit**	Polydispersity and fractionation in laser ablation studied by LIBS in an optical trap
	15:30 – 15:50	FT4	**Alwahabi**	Enhancement Limitations of Microwave-assisted LIBS: Application to Sulphur Detection
	15:50 – 16:10	FT5	**Fricke-Begem.**	LIBS for robotic alloy sorting
	16:10 – 16:30	**Last coffee**		
	16:30	**Free time**		
		17:00 Registration closing		
	19:00	**Gala dinner**		

Abstracts

Talks

The arduous way of LIBS becoming an established technique

Kay Niemax [1]

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A brief history of LIBS, a talk based on personal experience starting in 1985.

Equilibrium chemistry in laser induced plasmas and plasma chemical reactors

Igor B Gornushkin [1], Sergei V Shabanov [2], Matthieu Baudelet [3], Tobias Völker [1], Gerd Wilsch [1], Roman A Kornev [4], Petr G Sennikov [4]

1. *BAM Federal Institute for Materials Research and Testing, Germany*
2. *University of Florida, Dept of Mathematics, USA*
3. *University of Central Florida, Dept of Chemistry, USA*
4. *Institute of Chemistry of High-Purity Substances of RAS, Russia*

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A goal of this work is to apply the model, which was initially developed for laser induced plasmas [1], to plasmas used in chemical reactors, in particular, the inductively-coupled-RF discharge plasma [2]. The model predicts equilibrium chemical compositions of reaction mixtures as functions of plasma temperature and stoichiometry of reactants. The mixtures investigated are $BCl_3/H_2/Ar$ and $BF_3/H_2/Ar$ where Ar serves as the plasma-forming gas and H_2 as a binding agent which binds the active species Cl and F and Cl- and F-containing intermediates to produce gaseous B and its condensate. An additional goal is to obtain information about intermediate reaction products for different ratios of BCl_3/H_2 and BF_3/H_2 and at different temperatures and different Ar flow rates. Also, chemical reactions in laser induced plasmas (LIPs) created on calcium hydrate and calcium carbonate targets in argon are modeled and compared to experiment.

References

[1] Shabanov SV, Gornushkin IB (2018) Appl Phys A 124:716

[2] Sennikov PG, Kornev RA, Shishkin AI (2017) Plasma Chem Plasma P 37:997–1008

Femtosecond laser ablation: as fun as it gets

José M Vadillo [1], Irene M Carrasco [1], Sadia Manzoor [1], Javier J Laserna [1]

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Target irradiation with a femtosecond laser adds to all the excitement of working with nanosecond excitation, the amusement of the ultra-short regime: plasmas are tinier, the emission is lower, the power densities are huge and the laser-matter interaction is so peculiar that new phenomena can be observed. The talk will provide an overview of different experiments performed on solid samples under femtosecond irradiation (800-nm, 35-fs) above the plasma formation threshold. Once the plasma is formed, the ions or photons emitted are used to determine the composition of the samples, performing fundamental studies on fragmentation and some other of interest. A comparison with similar performed on the nanosecond regime will be commented as well. An important aspect of our research is related to the timeline of the laser-matter interaction and how the target evolves up to the phase-explosion and plasma formation. Thus, pump-probe phase-change microscopy has been included within the arsenal of time-resolved techniques available. With our current set-up, time resolution in the order of 100 fs is attainable up to 3 ns after laser arrival, allowing the recording of images covering different aspects of laser-matter interaction as the formation of the free-electrons plasma and the formation of Newton rings that evolve at supersonic speeds. Taking advantage of the pump-probe set-up, fast spectroscopy has been done, being able to capture events with picosecond resolution. With such resolution, the dilemma of the time-scale where CN formation occurs in molecules containing or not C-N bonds has been faced.

Quantitative analysis of Indium in sphalerites by CF-LIBS using pre-classification by PCA

Alicia Marin Roldan† [1], Samuel Moncayo† [2], Sadia Manzoor [2], Pavel Baco [3], Jorge Omar Cáceres [2], **Pavel Veis** [1]

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2. *Department of Analytical Chemistry, Faculty of Chemistry, Complutense Avenue S/N, 28040 Madrid, Spain*
3. *State Geological Institute of Dionýz Štúr, Regional Centre, Jesenského 8, 040 01 Košice, Slovak Republic*

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An emerging interest in the exploration and exploitation of indium (In) has aroused due to its increasing demand in many technological applications. Sphalerite is the most important ore of Zn, also containing In in concentration ranging from few to hundreds of ppm [1,2]. However, In is hardly identified using conventional methods and new techniques are highly demanded. Laser induced breakdown spectroscopy (LIBS) has demonstrated outstanding performance over conventional techniques for analyzing geological material [3]. The presence of thousands of Fe emission lines and its low concentration within the geological matrix hinders its detection and makes the In quantification a real technological challenge. The aim of the present work is the quantification of In in sphalerite by combining a pre-classification based on principal component analysis (PCA) to the detection of In spectra within the geological matrix and the subsequent Calibration Free quantification of only those spectra containing In. A Q-switched Nd:YAG laser operating at the fourth harmonic (CFR, Quantel, ≤80 mJ/pulse) was used for generating plasma. Optical plasma emission was simultaneously detected by a broadband Echelle spectrometer (ME 5000 + iCCD iStar, Andor Technology) and a high resolution THR 1500 spectrometer (Jobin-Yvon) within In emission wavelength range. Measurements were obtained under Patm collecting 200 spectra per sample. Indium and other major and minor elements (i.e. Zn, S, Fe, Mn, Cu, Ca, Cd) were observed. We successfully applied LIBS to the analysis of sphalerites classifying the mineral phases by PCA. In the In-containing samples, the quantitative analysis by CF-LIBS has been successfully carried out. This methodology allows the correct classification and the successful quantification of In in sphalerite samples. The results demonstrate the potential of this methodology to help in the characterization of In-containing minerals for mining purposes.

References

[1] Wierzbicka-Wieczorek, M; Lottermoser, BG; Kiefer, S; Sindern, S; Gronen, L; Hensler, AS, Indium distribution in metalliferous mine wastes of the Iberian Pyrite Belt, Spain-Portugal, Environmental Earth Sciences, 78 8, 253 (2019).

[2] Bauer, ME; Seifert, T; Burisch, M; Krause, J; Richter, N; Gutzmer, J, Indium-bearing sulfides from the Hammerlein skarn deposit, Erzgebirge, Germany: evidence for late-stage diffusion of indium into sphalerite, Mineralium Deposita, 54 2, 175-192 (2019).

[3] Fabre, C; Devismes, D; Moncayo, S; Pelascini, F; Trichard, F; Lecomte, A; Bousquet, B; Cauzid, J; Motto-Ros, V., Elemental imaging by laser-induced breakdown spectroscopy for the geological characterization of minerals, Journal of Analytical Atomic Spectrometry, 33 8, 1345-1353 (2018).

Acknowledgement

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† Authors (AMR and SM) have equal contributions.

Application of spectra modeling for Laser-Induced Breakdown Spectroscopy

Timur A. Labutin [1], Sergey M. Zaytsev [1], Andrey M. Popov [1]

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Laser-induced plasma is a short-lived emission source, and its geometry, temperature and electron density are rapidly changed. Although this provides an opportunity to select an appropriate condition for particular application, an interpretation of spectra of laser-induced plasma is still rather complicated task. Thus, anyone needs the tool for explanation of the experimental spectra and deducing the plasma parameters. We suggested an algorithm for relatively simple emission spectra modeling and line identification that can be useful for LIBS applications as well as in other fields of analytical atomic spectrometry. We found that the accuracy of the experimental data fitting by the model can be achieved even with a regular grid of parameters (temperature, electron density, plasma mass). A few discrepancies are primarily related to inhomogeneity of the laser-induced plasma and to the absence of data on Stark broadening parameters. The developed algorithms are useful for choice of the best analytical line under certain plasma and spectrometer parameters in terms of: (i) spectral interferences, (ii) transmittance and (iii) intensity, for estimation of detection limits of trace elements in a known sample matrix, for detection of erroneous entries in databases, including transition probabilities and Stark parameters. Due to the rough estimation of plasma parameters the modeling provides fruitful information to plan LIBS studies (either plasma diagnostics or analytical studies) prior to experimental measurement. Besides planning of LIBS studies, the developed tool can be useful for critical evaluation of experimental data. In particular, we have clearly demonstrated that the C I 247.856 nm line cannot provide any analytical information for carbon determination in steels. The modeling made possible re-calibration of a spectrum by its shape only. Evaluation of possible spectral interferences from weak lines of major constituents and strong lines of minor and trace elements was very helpful for sensitive determination of light rare earth elements in geosamples, for which the lack of certified reference materials is still a serious problem, with limit of detections below their Earth's crustal abundances. Future development of the tool is the consideration of plasma inhomogeneity to improve plasma diagnostics by model spectra and the implementation of an optimization algorithm for multi-parametric fitting.

Acknowledgement

The reported study was funded by RFBR according to the research project № 18-33-20244 mol_a_ved.

Model function for Optical Time of Flight signal in Laser Induced Plasma

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Optical Time of Flight measurement in Laser Induced Plasma is analyzed. We considered how the shape of OTOF signal depends on the geometric details of the expanding plasma plume. Under the assumption that expansion of the plasma plume is isotropic we derived an expression that takes into account geometry of plume, size of the vertical opening of the entrance slit and aperture of the lens system. We have demonstrated importance of the geometric details considering two OTOF signals recorded for different vertical openings of the entrance slit while the rest of parameters were exactly the same. Relying on derived expression the temperature and the center of mass velocity had consistent values no matter if they are inferred from OTOF signal for large or small vertical slit opening. For the same OTOF signals Shifted Maxwell-Boltzmann function, common in TOF experiment, failed to correctly reproduce center of mass velocity.

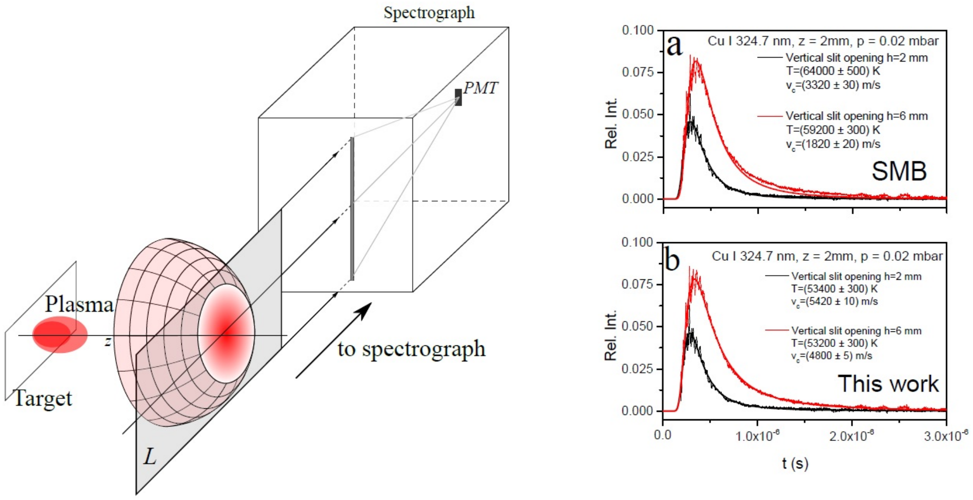

Fig. 1.: Left: Plasma front at the position of entrance slit. Right: Comparison of the results.

Acknowledgement

This work is part of the "Determination of atomic parameters on the basis of spectral line profiles"
(ON 171008) project supported by the Ministry of Education and Science of the Republic of Serbia.

Physical and Statistical Studies of the Influence of Minor Elements on Plasma Temperature and Emission Intensity in LIBS Measurements

Yuqing Zhang, [1], Chen Sun, [1], Liang Gao, [1], Zengqi Yue, [1], Sahar Shabbir, [1], Weijie Xu, [1], Mengting Wu, [1], Wenxu Xu, [2], Yishuai Niu, [2], **and Jin Yu** [1]

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Precision of LIBS analysis of a minor or trace element can be influenced by the presence in the material, of other minor or trace elements. Concentration variations of those elements can lead to a kind of matrix effect, whether such variations correspond to the average concentrations in a sample or the inhomogeneity in element distribution on the sample surface. In this work, we observed fluctuations in the temperature and the emission intensity of the plasmas induced on different steel samples and for a given sample, at different positions on the sample surface. We first compared the emission intensity fluctuations to those of the plasma temperature. We further developed a machine learning-based algorithm to correlate LIBS spectra to the positions on the sample surface where the spectra were induced by laser ablations. 20 certified reference steel samples were used for this study. They were chosen with concentration gradients of minor elements usually contained in a steel, in such way that the concentration of iron as the matrix element varies from 69.27% to 99.74%. For every sample, 112 replicate spectra (assuming statistically equivalent) were recorded with 1064 nm and 80 mJ laser pulses, each of them was integrated over 200 subsequent laser pulses uniformly distributed in 10 linearly arranged ablation craters. The 112 lines of 10 ablation craters were gathered in two matrices of 56 lines (28 x 2) and impressed on the two half parts of the circular surface (dia. ~ 40 mm) of a cylindrical sample (Fig. 1d). The measured plasma temperatures are shown in Fig. 1a. We can see that the temperatures for different samples do not exhibit a stable value, the matrix effect due to the minor element concentrations is therefore obvious. Although, the general tendency is an increase of the temperature with the iron concentration, it is however difficult to extract a simple relation between these two factors, indicating a multivariate dependence of the temperature. We remark also in the same figure that for a given sample, a quite large dispersion of the temperature, indicating statistical fluctuations in the LIBS spectra, which can also be contributed by the fact that the ablation craters are spread over a certain area on the sample surface (Fig. 1d). The corresponding fluctuations in plasma emission intensity is shown in Fig. 1b with the ratio of two iron ionic lines (Fe II 232.7 nm and F II 235.7 nm lines), normalized with the corresponding iron concentrations. For different samples, the barycenters of the data distributions spread in a direction defined by a straight line of y=ax.

Comparing to the temperature fluctuation shown in Fig. 1a, although some correlations can be found for a part of the samples, one cannot deduce a general relation between the plasma temperature fluctuation and that of the line intensities. For a given sample, large dispersion along the straight line can be observed, due to experimental fluctuations. Inhomogeneous distributions of minor elements and physical properties (roughness, density…) on the sample surface would also contribute, since different spectra were induced at various positions on the sample. We further used an unsupervised clustering algorithm, t-distributed stochastic neighbor embedding (t-SNE) algorithm [1] to see whether individual spectra would cluster according to the positions on the sample surface where they were generated by ablation. The obtained results are shown in Fig. 1c. We can first see that globally the individual spectra are clustered into the 20 different samples (Fig. 1c). A zoom-in on a given sample (n°14 for example) shows that the data points are gathered into 2 sub-clusters (Fig. 1d). A check on the labels of the spectra reveals the correspondence of the 2 sub-clusters to the 2 parts of the sample surface where the measurement craters are respectively performed, demonstrating the statistical nonequivalence of the replicate measurements.

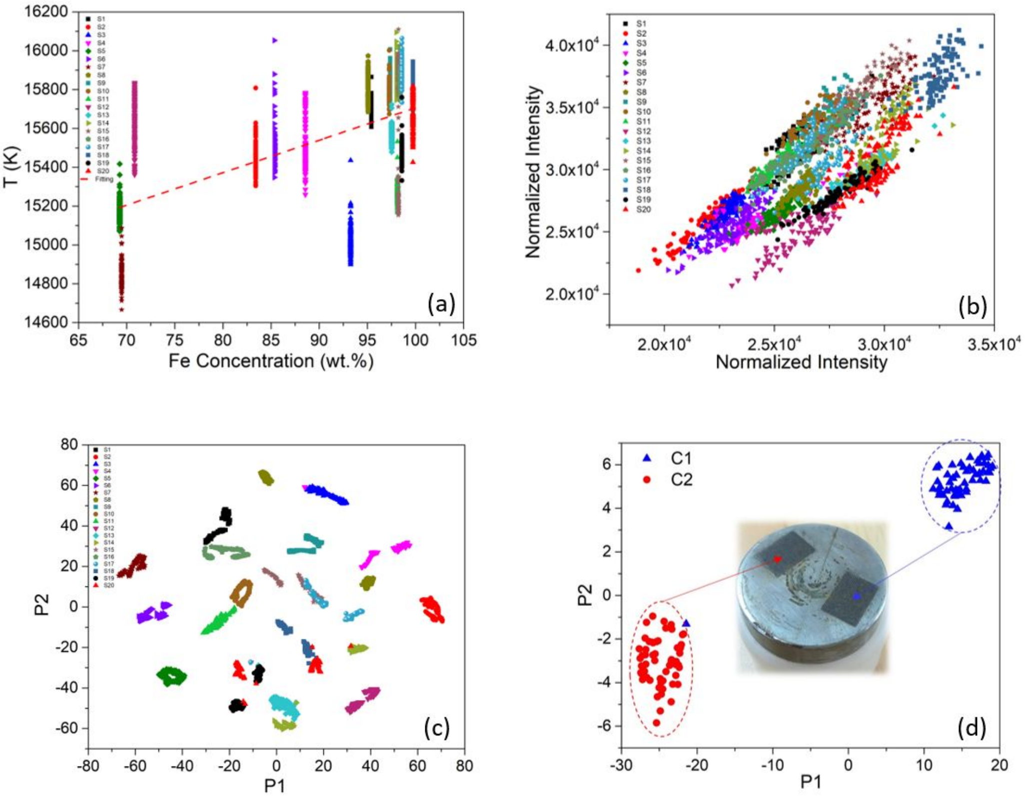

Fig. 1.: (a) Plasma temperatures displayed as a function of iron concentration; (b) Intensity ratios between 2 Fe II lines normalized by iron concentration; (c) Clustering according to 20 samples; (d) Clustering of the spectra from a sample.

References

[1] Laurens van der Maaten, Geoffrey Hinton, Journal of Machine Learning Research 2008, 9, 2579-2605.

Acknowledgement

This study was supported by the National Natural Science Foundation of China (Grant Nos. 11574209, 11805126, and 11601327) and the Science and Technology Commission of Shanghai Municipality (Grant No. 15142201000).

Fundamentals of simultaneous Vacuum UV - UV LIBS for quantification

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Laser Induced Breakdown Spectroscopy (LIBS) is well-established method for the elemental analyses of the composition of materials based on atomic emission of spark created by a laser beam focused on the surface. LIBS spectra recorded simultaneously in vacuum UV (VUV) range (McPherson 234/302, 115-300 nm, MgF2 lens, DH734 iCCD Andor) as a complementary spectra for classical UV-NIR spectral range (broadband echelle type spectrometer ME5000, DH734 iCCD, Andor, 230-950 nm),has already proved to be helpful in certain cases; e.g. light elements analysis (e.g. B, C, P, S, etc.) [1], because UV-NIR spectra do not contains neutral ionized lines of these light elements. Sulphur could be efficiently detected in VUV range by LIBS spectroscopy [2]. VUV spectra could help to construct more precise Saha-Boltzmann plots, using also double ionized spectral lines (e.g. Si, Ge, Zn, Sn, W etc.), to improve the determination of electron temperature [M. Pribula, P. Veis et al, Physica Scripta 2016] for more precise CF LIBS in certain cases. Simultaneous VUV and UV-NIR LIBS measurements were realized under oxygen free atmosphere (typically He and Ar) in order to prevent the light absorption of wavelengths<200 nm. A fundamental point for the correct use of the VUV spectral range is the calibration of spectral response of the whole spectral system (by N2 LBH molecular band emission spectra) and evaluation of cross-correlation coefficient (by comparing Si LIBS spectra in the common spectral range 230-300 nm). Examples of applications of simultaneous VUV and UV-NIR LIBS for quantification in thermonuclear fusion (W, LiSn for divertor walls), in geology (Sphalerites, Pyrite, Galena, volcanic Sulphur, volcanic Ash), nano-layers (ITO, MoS2/Si, MoOx)[M. Bodik, P. Veis, P. Siffalovic et al, Phys. Chem. Chem. Phys., 2019, DOI: 10.1039/C9CP01951K] or bones [3]will be presented.

References

[1] VEIS, P., MARÍN ROLDÁN, A., KRIŠTOF, J. , Plasma Sources Science and Technology 27 (2018) 095001

[2] JAŠÍK, J., HEITZ, J., PEDARNIG, J.D., VEIS, P., Spectrochimica Acta Part B 64 (2009) 1128.

[3] MARÍN ROLDÁN, A., MANZOOR, Sh. , KRIŠTOF, J., VEIS. P., Spectrochimica Acta Part B 156 (2019) 13.

Acknowledgement

This work has been supported by SRDA (No. APVV-15-0641 and APVV-16-0612) and Scientific Grant Agency of the Slovak Republic (VEGA No. 1/0903/17).The authors (Sh. Manzoor , D. Anglos, V.K. Unnikrishnan) also thank SAIA for the National Scholarship Program of Slovak Republic.

LIBS-based Imaging: critical focus on current status and future directions

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During recent years, important developments have been achieved in the application of laser induced breakdown spectroscopy (LIBS) for elemental imaging. This approach can be distinguished by its ease in use, tabletop instrumentation, multi-elemental capability, detection of light elements, as well as operation at ambient conditions. This is furthermore the only all-optical technique providing space-resolved elemental information with ppm-scale sensitivity and µm-range resolution [1]. Compared to most of the other elemental imaging methods, LIBS has the advantage of a fast operating speed allowing to provide large-scale microscopic images in reasonable time periods. These advantages, in particular the all-optical design and the fast operation speed, make this approach very attractive to be used in research laboratories for routine investigations in various domains including biology, industry, geology and medicine. In this presentation, we will first describe the main key points for conducting micro-LIBS imaging experiments. A general and critical overview of this approach will be then addressed with the aim of highlighting some of its remaining challenges. A discussion about the current performances (resolution, operating speed, and sensitivity) and possible perspectives will be finally proposed.

References

[1] Jolivet L., Leprince M., Moncayo S., Sorbier, Lienemann C.-P., Motto-Ros V., Spectrochim. Acta - Part B 151 (2019) 41-53.

LIBS Microscopy for Elemental Imaging of Heterogeneous Samples

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Laser-Induced Breakdown Spectroscopy (LIBS) with pulsed laser excitation is an established method for analyzing the elemental composition of unknown samples based on their characteristic emission spectra. However, heterogeneous samples like concrete require high spatial resolution for a proper classification of the matrix phases [1-3]. An automated LIBS imaging system is used to provide high spatially and spectrally resolved images of the elemental distribution with an lateral resolution corresponding to the laser spot size. The system is able to analyze both the atomic and molecular emission with several spectrometers over a broad spectral range simultaneously. Critical corrosion effects like chloride induced pitting corrosion in concrete can substantially reduce the lifetime of infrastructure buildings. Since chlorides only diffuse into the cement phase of the concrete the diffusion profile of chlorides is of great interest. The "LIBS-microscope" is able to visualize the elemental spatial distribution of chlorine in concrete by evaluating both the atomic and molecular emission. Measurements with the LIBS microscope are compared to the results of the standard wet-chemical potentiometric titration which, however, provides a reduced spatial resolution of typically 10 mm. Another drawback of the chemical analysis is the need of a correction factor to estimate the aggregate fraction because the matrix phases cannot be separated before performing the analysis. In practical applications this concrete-dependent factor is not known exactly. LIBS analysis, however, does not need any correction factor.

References

[1] C. Gottlieb, S. Millar, S. Grothe, G. Wilsch, "2D evaluation of spectral LIBS data derived from heterogeneous materials using cluster algorithm", Spectrochim. Acta Part B, 134: 58-68 (2017), DOI 10.1016/j.sab.2017.06.005.

[2] T. Dietz, P. Kohns, G. Ankerhold, "Quantitative determination of chlorides by molecular LIBS", Spectrochim. Acta Part B, 152: 59-67 (2018), DOI 10.1016/j.sab.2018.12.009.

[3] C. Beresko, P. Kohns, G. Ankerhold, "Surface Element-Mapping of Three-Dimensional Structures by LIBS", Spectrochim. Acta Part B, 99: 20-27 (2014), DOI 10.1016/j.sab.2014.06.004.

Acknowledgement

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Detection of REE-rich areas in Storkwitz drill cores using LIBS and a combination of normalization, clustering and spatial raster analysis

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Fast and innovative space-resolved methods are a key to future exploration of ore deposits. LIBS may provide a quick overview of elements of interest, their concentrations and distribution. However, rock heterogeneity and matrix effects interfere with an interpretation of samples with unknown concentrations, making LIBS analysis a challenging task. In a BMWi promoted project, we used a stationary LIBS system (Nd:YAG Q-switched 20Hz 1064nm laser and a high-resolution 285-964nm Echelle spectrometer) to analyse segments of a drill core from Storkwitz (Germany) for the occurrence and distribution of Rare Earth Elements (REE). The Storkwitz complex is a heterogeneous mixture of carbonatite related fragments, host rock fragments of granitoids and paleozoic sediments. These clasts are embedded in a carbonatitic matrix containing various minerals that can be separated into fluor and non-fluor bearing phases. Storkwitz is known for REE enrichments that are bound to the former. Major rock forming elements as well as light REEs and their indicators were evaluated using LIBS. Here, REEs mostly occur in the matrix and the rims of rock fragments, which makes their separation necessary to determine areas of element enrichment. We performed a Principal Component Analysis before partitioning matrix and clasts with different clustering algorithms. Afterwards, spatial raster analysis was used to classify areas with possible REE enrichment. The samples had to be split into different parts that were measured over multiple days. To compensate for the intensity differences linked to fluctuations of the instrument over the course of the entire measurement, selected standards were used for normalization. Validation measurements demonstrate that LIBS is an effective technology for the discovery of light REE in a highly heterogeneous material with respect to their spatial position and their geological surrounding. Current research focusses on possibilities for REE quantification with LIBS.

In situ, quantitative, elemental imaging of lung tissues

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The presence, absence or dysregulation of endogenous and exogenous chemical elements or agents, particularly metals and minerals, has a great interest in various medical specialties. The environmental and occupational exposures to dust, metal agents or nanoparticles are responsible of several diseases such as sarcoidosis, lung fibrosis and chronic beryllium disease. However, it is generally difficult to diagnose and to correlate the symptomatology with the nature of the agent(s) and the potential occupational/environmental exposure. This is mainly due to the lack of available technologies able to detect these agents in a routine way compatible with conventional histo-pathology analysis. Indeed, conventional methods are not successful to identify the causative metal agent in several pathological situations. The LIBS imaging is a good candidate to overcome the limitations of the current technologies. In particular, we demonstrate that all-optical design of LIBS combined with the state of the art performances (sensitivity, spatial resolution, and acquisition speed) is suitable for histological analysis and our previous results have boosted LIBS technology from pre-clinical stage to several medical applications. In this work, we developed a LIBS instrumental set-up combining a control of the ablation process in human paraffin-embedded tissues, enhanced performances in terms of spatial resolution. These improvements combined with an appropriate methodology allow to promote LIBS technic as a quantitative method. The mass of in situ metal (nano)particles, reflecting the global respiratory exposure of animals is demonstrated. Based on this analytical validation we achieved to count metal particles in human lung tissues with medical interest. We also optimized instrumental settings solutions for the elemental analysis of thin slices of fresh frozen tissues. These results validate the first steps towards the use of LIBS imaging in medical pathology laboratories.

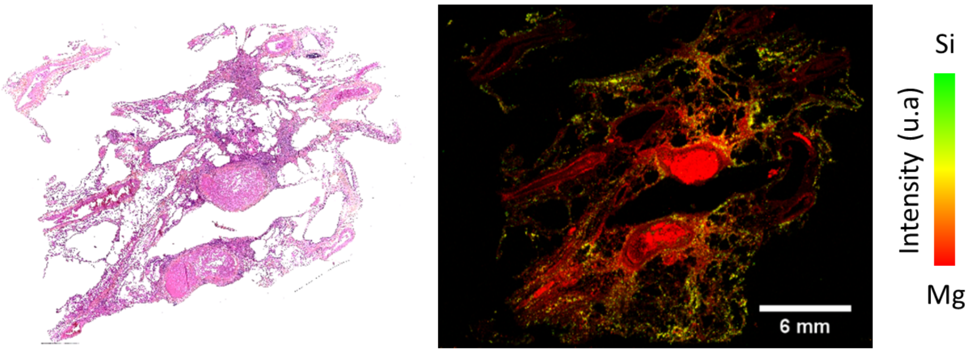

Fig. 1.: Images of human lung tissue with conventional histological staining (HES, left) and complementary LIBS elemental image (right) representing Magnesium (red) and Silicon (green).

References

[1] B. Busser, S. Moncayo, J.-L. Coll, L. Sancey, et V. Motto-Ros, « Elemental imaging using laser-induced breakdown spectroscopy: A new and promising approach for biological and medical applications », Coord. Chem. Rev., vol. 358, p. 70–79, 2018.

[2] S. Moncayo et al., « Multi-elemental imaging of paraffin-embedded human samples by laser-induced breakdown spectroscopy », Spectrochim. Acta Part B At. Spectrosc., vol. 133, p. 40–44, 2017.

[3] B. Busser et al., « Characterization of foreign materials in paraffin-embedded pathological specimens using in situ multi-elemental imaging with laser spectroscopy », Mod. Pathol., nov. 2017.

Bacterial Limit of Detection Reduction Utilizing A Novel Sample Preparation Protocol

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We have been investigating the use of laser-induced breakdown spectroscopy (LIBS) for the rapid identification of bacteria in clinical specimens. The ability to rapidly identify harmful pathogens in such specimens is crucial for initiating appropriate treatment of infectious diseases that can kill within hours of the onset of symptoms. Current laboratory techniques can take as long as 24-72 hours for a positive identification, but the use of LIBS as a real-time diagnostic could reduce that time to minutes. The current protocol involves concentrating the bacterial cells in a liquid suspension with a volume up to 2 mL into a small circular deposition area 1 mm in diameter upon a nitrocellulose filter medium (with pore size of 0.45 microns) by centrifuging the suspension through a custom-fabricated cone device and centrifuge tube insert. By reducing the cell concentration in various suspensions, the limit of detection was calculated. A calibration curve constructed from forty spectra obtained from each of nine different concentrations returned a LIBS bacterial limit of detection of 10,865 +/- 3,712 CFU per laser ablation event for bacteria deposited on filters using the metal cone. This represents a factor of 50 reduction in the limit of detection compared to our previously reported value. Laser ablation of the filter medium and other elemental contaminants yielded a non-zero background signal when a control experiment was performed in the absence of bacterial cells. The sources of this non-bacterial signal were investigated and preparation steps which might reduce or eliminate this undesired background signal will be discussed. The use of the insert device to separate bacterial cells from larger undesirable contaminants in the liquid will be described. Testing was performed on several representative species of bacteria to investigate the ability of chemometric models to differentiate the cells and the effect of the reduced cell count on the bacterial limit of identification will be presented. The reduction of the limit of detection to clinically relevant levels using a simple and quick preparation protocol suggests that this technique is appropriate for use in clinical testing environments by non-LIBS technicians.

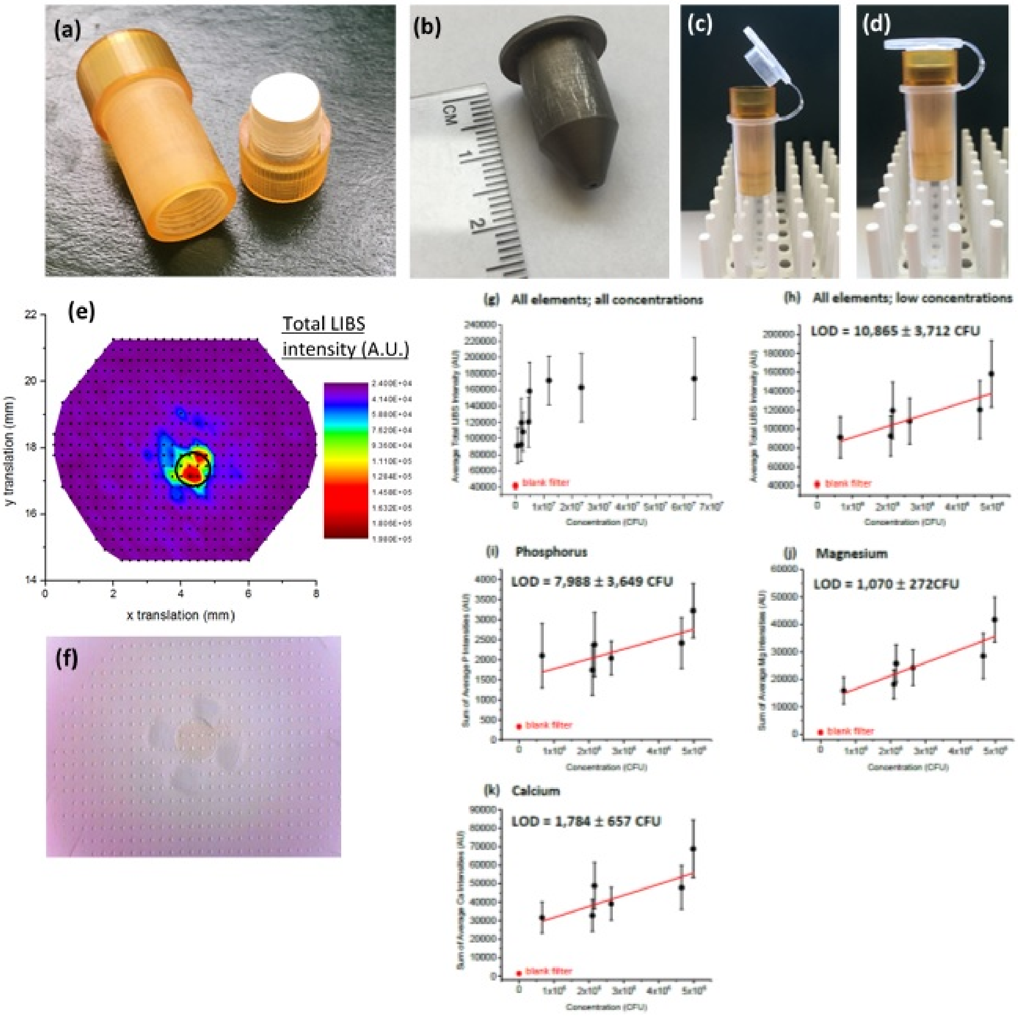

Fig. 1.: (a-d) Pictures of the disassembled centrifuge insert, filter paper, and metal concentrating cone. (e-f) Color map of LIBS intensity and photograph of the filter paper post-ablation. (g-k) Bacterial LOD plots utilizing various elements in the LIBS spectra

References

[1] REHSE, S.J. A Review of the Use of Laser-Induced Breakdown Spectroscopy for Bacterial Classification, Quantification, and Identification, Spectrochim. Acta B 154 (2019) 50-69. https://doi.org/10.1016/j.sab.2019.02.005

[2] PAULICK, A.E., MALENFANT, D.J., REHSE, S.J. Concentration of Bacterial Specimens During Centrifugation Prior to Laser-Induced Breakdown Spectroscopy Analysis, Spectrochim. Acta B 157 (2019) 68-75. https://doi.org/10.1016/j.sab.2019.05.012

[3] MALENFANT, D.J., PAULICK, A.E., REHSE, S.J. A Simple and Efficient Centrifugation Filtration Method for Bacterial Concentration and Isolation Prior to Testing Liquid Specimens with Laser-Induced Breakdown Spectroscopy, Spectrochim. Acta B 158 (2019) 105629. https://doi.org/10.1016/j.sab.2019.05.018

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Switchgrass and Woody Biomass Elemental characterization using Laser-induced Breakdown Spectroscopy

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The elemental characterization of 74 samples of switchgrass and poplar hardwood samples using laser-induced breakdown spectroscopy (LIBS) was undertaken. The elements of interest that were detected were, silicon, potassium, calcium, magnesium, phosphorus, and sulfur. These elements are important components of the ash content of switchgrass and some hardwood biomass. Hierarchical models using principal component analysis (PCA) and partial least square analysis (PLS) was used to determine the presence of the specific elements mentioned above. A 532 nm laser with 45 mJ of laser power was used to excite the samples of switchgrass plant material and the emission of all the elements present in the plant samples was recorded in single spectra with a wide wavelength range of 200-800 nm. The results were compared to the laboratory standard technique, e.g., ICP-OES system, to determine the true values for major micronutrients such as, Si, K, Ca, Mg, P, and S.

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Classifying diseased and healthy biomedical samples one laser pulse at a time

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Early diagnosis of diseases is crucial to increase the survival rate and quality of life of patients. This is particularly correct for the case of cancers. Developing non-invasive screening methods would represent a key step towards point-of-care large scale screening and prevention of asymptomatic tumors such as Epithelian Ovarian Cancer (EOC) and others. However, despite numerous advances that provide important tools to fight cancer, this disease still poses great challenges to diagnosis and treatment and remains one of the leading causes of death worldwide. In recent years, we have explored the possibility of using of Laser-Induced Breakdown Spectroscopy (LIBS) and machine learning algorithms to discriminate biomedical samples obtained, through minimally invasive techniques, from diseased and healthy sources (humans and mice). This approach yields encouraging results in terms of classification accuracies and potentially early diagnosis. We will present our most recent results obtained and will report on the effects of various substrates used for the LIBS measurements on the classification accuracy. We conclude that LIBS is likely to play an important role in the future development of point-of-care preventive techniques for the rapid, early and accurate diagnosis of diseases such as cancers and others.

References

[1] Rosalba Gaudiuso, Ebo Ewusi-Annan, Noureddine Melikechi, Xinzi Sun, Benyuan Liu, Luis Felipe Campesato, and Taha Merghoub, “Diagnosis of melanoma in biomedical fluids using laser induced breakdown spectroscopy and machine learning”, submitted to Spectrochimica Acta Part B Atomic Spectroscopy, March, 2018. https://doi.org/10.1016/j.sab.2018.05.010

[2] N. Melikechi, Y. Markushin, D. Connolly, J. Lasue, E. Ewusi-Annan, S. Makrogiannis “Age specific classification of discrimination of blood plasma samples of healthy and ovarian cancer prone mice using laser-induced breakdown spectroscopy”, Spectrochimica Acta Part B Atomic Spectroscopy, 123, 33-41 (2016). https://doi.org/10.1016/j.sab.2016.07.008

LIBS Applications for Food Safety and Quality

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The preferential choice of food items depends on the individuals' life styles, diet, health, religious belief, current trends. Therefore, accurate labeling is crucial to help consumers make conscious choices. Food is the main source of different elements, which are essential, trace and fundamental for human diet and health. Elemental composition of food is a very important indicator to understand food quality, nutritional value, authenticity and origin of food. Besides, it is fundamental to assess the presence of nutrients in the food products from the nutritional point of view. Therefore, determination of elements and their amounts is crucial for food safety and quality. Food fraud is worldwide problem due to economic gain and demand of analytical tools is increasing day by day to investigate the foods. In order to fulfill the increasing demand on multi-elemental information for product monitoring, rapid and sensitive analytical techniques which are capable of detecting major and trace elements with good precision and accuracy are required. Recently developed spectrometric methods provide rapid, practical, on-line analysis in foods. From these methods, laser induced breakdown spectroscopy (LIBS) has ability to determine multi-elemental composition with high potential for rapid food analysis. In our research group, it was shown that LIBS has a great potential for analysis of different food groups such as identification of meat and milk species, determination of whey adulterated milk powder, determination of ash and protein contents of cereals. In addition to the promising results of LIBS on food applications, future respects of these methods and ongoing studies for portable systems were evaluated and discussed in the study.

Critical considerations on the use of several experimental methodologies to evaluate self-absorption effects in Atomic Emission Spetroscopy

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Self-absorption is an integral part of the emission signal in analytical atomic spectroscopy. It is therefore not surprising that its theoretical characterization, experimental assessment and possible correction methodologies have received in the past, and are still receiving, continuous attention in the literature dealing with plasma spectroscopy in general, and laser-induced plasmas in particular. This talk will highlight some methodologies and/or approaches that have gained little or no popularity in the field – for example, measuring the lifetime of the emitting level, using the self-absorbed radiation as excitation source for atomic fluorescence measurements, and taking a closer look at the spectral profile of the noise in the emission signal. Moreover, some experimental approaches published in the recent literature, such as, for example, the idea of depleting the lower level of the transition involved in the emission measurement, will be critically addressed. Finally, examples in which self-absorption can be advantageous rather than detrimental in analytical plasma spectroscopy will be discussed.

Self-absorption is your friend: exploting self-absorption for improving the accuracy of Laser-Induced Breakdown Spectroscopy analysis

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Self-absorption is traditionally considered as one of the main physical effects in laser-induced plasmas affecting the accuracy of LIBS quantitative analysis. Many strategies have been devised in the past to correct self-absorption effects, in most of the analytical applications of LIBS the use of self-absorbed lines for analytical purposes is avoided. On the contrary, several researchers have recently proposed the exploitation of self-absorption effect to improve the analytical performances of LIBS. The approach of Cristoforetti and Tognoni [1] makes use of the elemental Columnar Density, while Aragón and Aguilera [2] presented a method based on the so-called C-sigma plot. In this communication, we introduce a synthesis of the two approaches, called Extended C-sigma method, which extends the range of validity and greatly simplify the calculation of the plasma parameters and elemental concentration with respect to the former methods.

References

[1] G. Cristoforetti, E. Tognoni, Spectrochim. Acta - Part B At. Spectrosc. 79–80 (2013) 63–71

[2] C. Aragón, J.A. Aguilera, J. Quant. Spectrosc. Radiat. Transf. 149 (2014) 90–102.

[3] G. Cristoforetti et al., Spectrochim. Acta - Part B At. Spectrosc. 65 (2010) 86–95.

Improvement of LIBS Quantitative Capability for Remote Elemental Detection Using Collinear Long and Short DP Laser

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In this study, a collinear Long and Short-Double Pulse-Laser Induced Breakdown Spectroscopy (LS-DP-LIBS) method was proposed to improve the detection ability and the measurement accuracy by the control of the plasma cooling process using the long pulse-width laser radiation. 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. It was demonstrated that the detection capability of LIBS was improved using this method and it was also applicable to samples at a distance. The system has a potential of practical LIBS applications including steel-making processes, boilers and so on.

Direct isotopic analysis of solids by laser-induced breakdown self-reversal isotopic spectrometry (LIBRIS)

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Isotopic analysis by LIBS at atmospheric pressure is possible in some cases, yet it is generally limited by the small isotopic shift compared to the spectral lines broadening, induced by the Stark effect due to a high plasma electron density. Laser Ablation Molecular Isotopic Analysis (LAMIS) was proposed to overcome this limitation [1-2]. Instead of measuring atomic lines, this technique uses the molecular emission, whose isotopic shift can be much higher than the atomic one. Its feasibility has been demonstrated on several elements (H, B, C, N, O, Cl, Sr, Zr, U). However, for lithium, an important element of interest in the nuclear field, the dissociation energy of molecules likely to form in the plasma is too low to get an exploitable LAMIS signal. Therefore, we propose a new method called LIBRIS (Laser-Induced Breakdown self-Reversal Isotopic Spectrometry) to perform direct isotopic analysis of solids at atmospheric pressure. This technique is based on the self-reversal of intense emission lines. Such lines are composed of an emission and an absorption peak. The emission peak stems from the heart of the plasma and has a greater spectral width than the absorption one because of a bigger electron density than in the periphery of the plasma plume. Isotopic analysis is possible thanks to the precise determination of the wavelength [3] of the self-absorption peak, which shifts with the isotopic abundance. We will introduce the LIBRIS technique for direct isotopic analysis of solid lithium compounds at ambient pressure. We particularly studied the influence of the laser ablation wavelength, of the detection time delay and gate width, and of the ambient atmosphere on analytical performances. In the best experimental conditions, we obtained a relative accuracy on isotopic abundance of 6Li lower than 10%. Matrix effects will be discussed in relation with the Stark shift observed on the absorption peak, leading to a potential bias of the wavelength measurement.

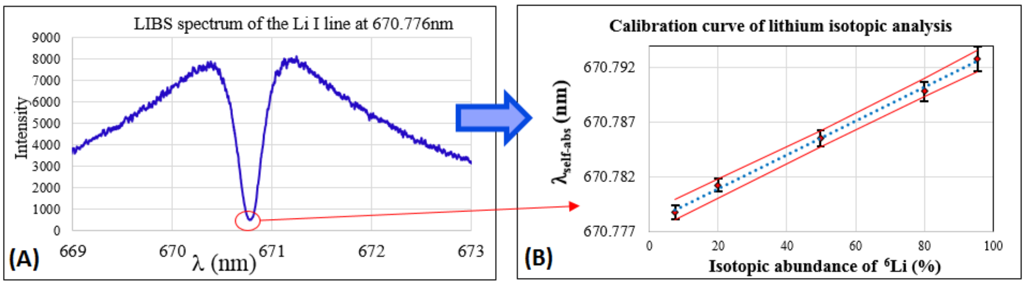

Fig. 1.: (A) LIBS spectrum of lithium resonant line at 670.776nm with natural isotopic abundance (7.5% 6Li); (B) Calibration curve of lithium isotopic analysis (R^2=0.998).

References

[1] H. Niki, T. Yasuda, I. Kitazima, Measurement technique of boron isotopic ratio by Laser-Induced Breakdown Spectroscopy. Fujui University, 1998. DOI 10.3327/jnst.35.34.

[2] A. A. Bol'shakov, X. Mao, J. J. Gonzalez, R. E. Russo, Laser Ablation molecular isotopic Spectrometry (LAMIS): current state of the art. Berkeley University, 2016. DOI 10.1039/C5JA00310E.

[3] A. Rastegari, M. Lenzner, C. Feng, L. Arissian, J. C. Diels, K. Peterson, Eploiying shock wave and self-absorption for high resolution laser induced breakdown spectroscopy . New Mexico University, 2017.

Advanced data processing to improve the analytical performance of LIBS

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LIBS allows to achieve sorting as well as multi-elemental quantitative analyses. However, it has been demonstrated by V. Motto-Ros et al. in 2018, in the context of quantification, that the analytical performance is strongly influenced by different steps of data processing, including the line selection, the way of extracting the relevant signal after baseline removal, and the selection of the best univariate calibration model, being linear or quadratic. We will describe in a first part how a series of key-steps of data processing allows to correct potential drifts of the LIBS instrument, to filter out irrelevant data, and thus to improve the sampling of the LIBS measurement. Then, we will present multivariate approaches for sorting and quantitative analysis, as well as figures of merit allowing to objectively determine the models providing the best analytical performance.

Origin of Measurement Uncertainty and its Reduction methods

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Laser-induced breakdown Spectroscopy (LIBS) has been regarded as the “future superstar” of chemical analysis and shown great potential in different fields.. However, severely hindered by its quantification performance due to relatively low repeatability and accuracy, LIBS was not able to realize wide commercialization. The aim of this work is to understand more about the oringination of measurment uncertainty of LIBS and find ways to reduce the uncertaities. It was found that for LIBS measurment, the most uncertainty was contributed by the variation of total number density, which was from a process that the interaction between surrounding gas and plasma make the upper part of plasma crashed with the lower part, making the plasma morphology greatly changed and resutling a flucatuated collected LIBS signal. Plasma modulations were therefore proposaled by spatial confinement, beam shaping, surrounding gases etc. to generate a more stable and repeatible plasma morphology.

References

[1] Investigation of intrinsic origins of the signal uncertainty for laser-induced breakdown spectroscopy
Yangting Fu, Zongyu Hou, Tianqi Li, Zheng Li, Zhe Wang, Spectrochimica Acta Part B: Atomic Spectroscopy, 2019, 155, p67-78

[2] Zongyu Hou, Zhe Wang*, Jianmin Liu, Weidou Ni, and Zheng Li, "Combination of cylindrical confinement and spark discharge for signal improvement using laser induced breakdown spectroscopy", optics express, 2014, 22(11), 12909–12914

[3] Zongyu Hou, Zhe Wang*, Jianmin Liu, Weidou Ni, and Zheng Li, "Signal improvement using cylindrical confinement for laser induced breakdown spectroscopy", optics express,2013, 21(13), 15974-15979

Calibration-free laser-induced breakdown spectroscopy for industry

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Under investigation since two decades, calibration-free laser-induced breakdown spectroscopy (CF-LIBS) was mostly ignored in industrial applications. This is mainly due to the poor analytical performance reported in literature and the still remaining unclarities of model validity in the vast area of experimental conditions. CF-LIBS analyses have much higher exigencies in the choice of experimental conditions than calibrated LIBS measurements. Indeed, the need of sufficiently large signal-to-noise ratio is mostly in opposition to the requirement of model validity. The high electron density needed to ensure local thermodynamic equilibrium is associated to continuum emission that reduces unavoidably the signal-to-noise ratio for elements with low mass fractions. Recent investigations have shown that accurate modeling of the plasma emission spectrum is possible if the experimental conditions were properly chosen [1]. This opens new perspectives for calibration-free laser-induced breakdown spectroscopy. As an example, analyses of multielemental thin films have been demonstrated with analytical performances higher than those of traditional techniques [2]. In this presentation, we propose to give a critical point of view on possible industrial applications that arise from these news perspectives of CF-LIBS.

References

[1] Hermann J., Grojo D., Axente E., Gerhard C., Burger M., Craciun V., Phys. Rev. E 96, 053210 1-6 (2017)

[2] Hermann J., Axente E., Pelascini F., Craciun V., Anal. Chem. 91, 2544 (2019)

A standard methodology for characterization of matrix effects in laser-induced breakdown spectroscopy

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In order to study matrix effects in LIBS among metal matrices, an approach based on ablation and plasma characterization is being developed. For that purpose, Boltzmann plots and Stark broadening measurements based on emission lines of iron, a common impurity over the different samples, have been used. Yet, from one matrix to the other, different sets of lines are used, which often yield significantly different results on the electron temperature and density. Furthermore, even using a common set of lines, we found that the lack of control of the samples composition is detrimental to a precise characterization of the plasma: measurement biases are introduced by the varying iron concentration or the interferences of lines of the matrix or other impurities. To alleviate this problem, the objective of this work is to precisely characterize matrix effects observed in pure metals using a standardized method of plasma characterization. This method consists in depositing and drying a droplet of an iron solution at the sample surface. In this way, a tracer is added to the solid sample, analogously to the standard addition method used in quantitative analysis of liquids. Plasma characterization is achieved by ablating the thin iron deposit in the same time as the bulk material and by analysing the iron lines. It has been verified that 1) the iron deposit enables to introduce the desired lines in the spectrum, 2) the deposit does not modify the ablation nor the resulting plasma, which enables to still observe and quantify the matrix effects. This method has been successfully applied to a dozen pure metal matrices and has enabled to observe matrix effects in the plasma that are strong enough to induce significant consequences on quantitative analysis. Due to its possible use in all kinds of samples and its limited biases, the proposed method may be of interest for applications such as CF-LIBS or calibration transfers.

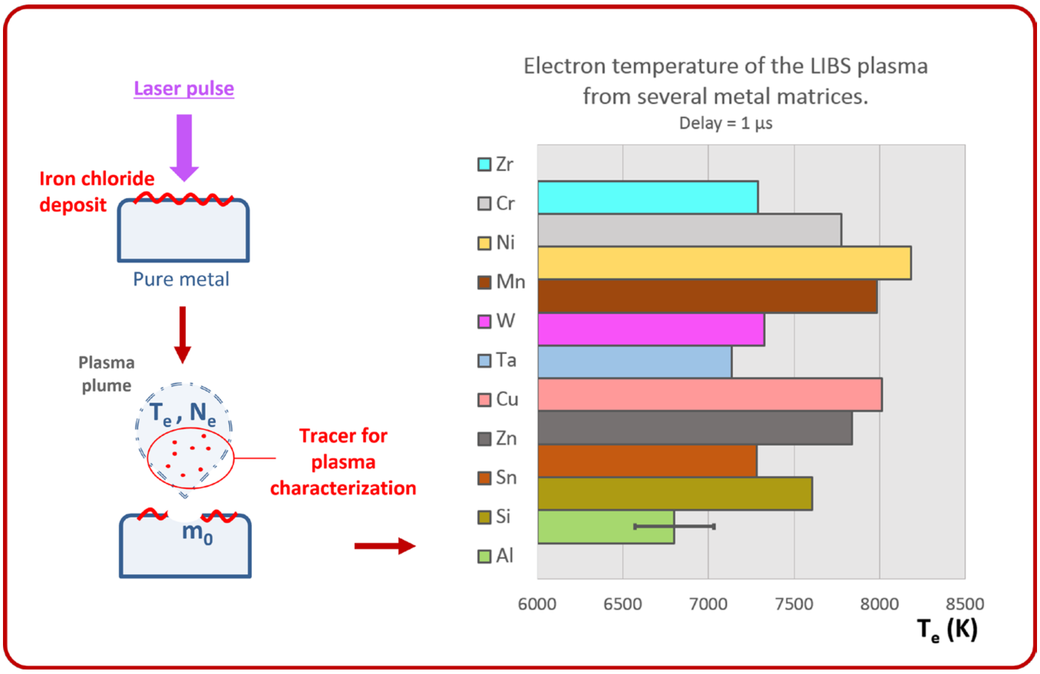

Fig. 1.: Plasma characterization using an iron chloride deposit.

Mineral Quantification by Laser-Induced Breakdown Spectroscopy for In-Field Rock Characterization

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Mining industry is looking for ways to improve their process through real time characterization of their ore as an alternative to current laboratory-based techniques, which are labor intense and time consuming. For instance, quantitative mineral analysis (QMA) performed using energy-dispersive x-ray spectrometry and scanning electron microscopes (EDS-SEM) provide reliable information on the mineral abundance and texture of prepared rocks. This information helps in the optimization of the mining and milling processes, and to define the value of a deposit. Real-time analysis of coarse rock streams would greatly enhance the decision-making processes driving the mining operation efficiency; however, electron-microscope-based instruments suffer from their offline character and are not adapted for in-field measurements due to their need for labor-intensive sample preparations and strict measurement conditions, which are prohibitive or unrealistic for large scale, rock streams measurements. Laser-induced breakdown spectroscopy (LIBS) has the characteristics to be a good candidate for in-field measurements, which could be scalable to perform automated mineralogy measurement in coarse rock streams. The use of a multivariate curve resolution – alternating least square method to the LIBS data allowed the identification, quantification and imaging of minerals on rock tiles [1], even in the presence of mixed mineral phases within the laser spot area. Mineral abundance and imaging are obtained with success for the mineral phases, e.g. bornite, chalcopyrite, chlorite, K-feldspar, albite, fluorite and calcite. We will present the recent results of quantitative imaging on tiles, and the quantitative mineral point-counting on several tiles and rocks. Our results showed a high opportunity of LIBS to be deployable in the mine not only for elemental analysis but also for mineral online prediction to improve the efficiency of the mining process in terms of time and cost.

References

[1] El Haddad J, de Lima Filho ES, Vanier F, Harhira A, Padioleau C, Sabsabi M, Wilkie G, Blouin A (2019) Multiphase mineral identification and quantification by laser-induced breakdown spectroscopy. Minerals Engineering 134:281-290.

Self-Learning Artificial Intelligence Methodology for the Accurate Quantification and Classification of Laser Induced Plasma Breakdown Spectroscopy applied to Geological Lithium Surveys in Portugal

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Laser induced plasma breakdown spectroscopy (LIBS) spectral information is highly structured and complex. Its complexity is introduced by the dynamics of induced plasma breakdown resulting in super-positions and multi-scaled interference. Developing new methodologies that are able to interpret the structure/geometry of the spectral information spaces is paramount to attain systematically accurate quantification and classification. Herein, a new self-learning artificial intelligence methodology is presented which is able to breakdown the spectral signals geometry information into high-dimensional spaces. The local features of these spaces are accurately correlated to the chemical composition by performing feature space transformations, searching directions of co-variance. It further allows to self-learn by establishing knowledge maps of both quantification and classification, using these to evaluate a priori the predictability of new estimates. Benchmarks on quantification and classification of Lithium ore samples will be presented.

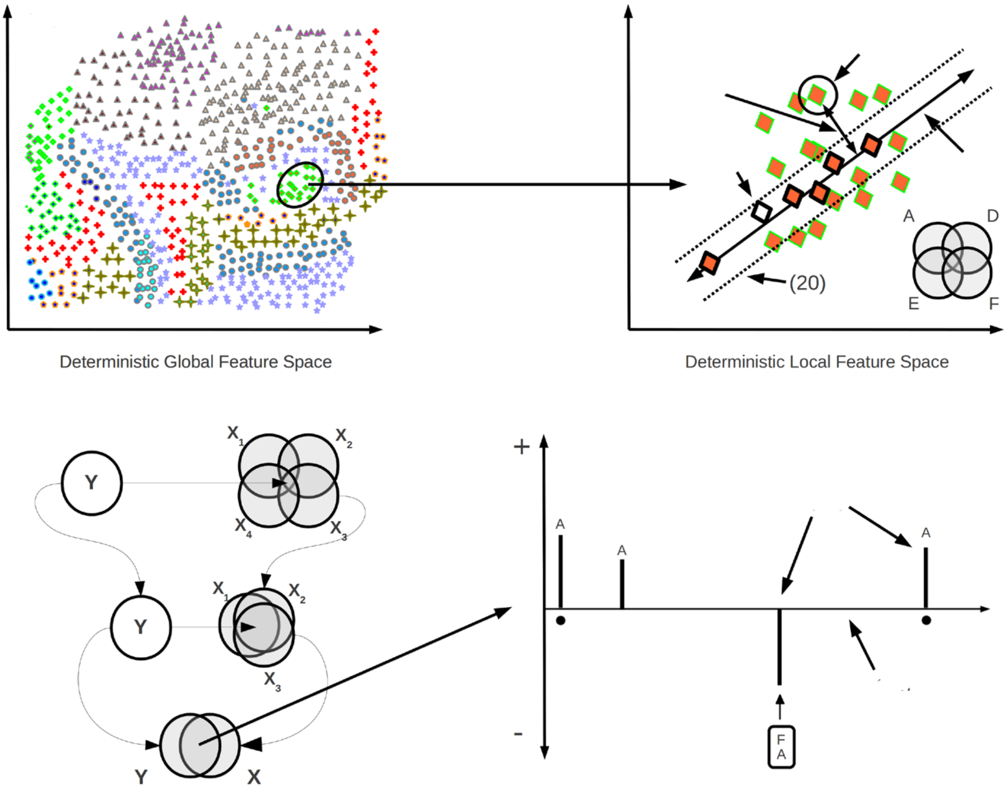

Fig. 1.: Predictability determination by covariance eigen-vector.

Acknowledgement

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Machine Learning for Classification and Regression of LIBS Spectra from ChemCam Calibration Targets

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Laser-induced breakdown spectroscopy (LIBS) provides the major technology of the ChemCam instrument onboard the Curiosity rover in activity on Mars since August 2012. Responding to the major objective of the mission to study the environment for the life and its evolution on Mars, LIBS records emission spectra from rocks, soils on the Mars surface, even under it. Carriers of information about the elemental composition of the materials and physical and chemical states of their presence, the LIBS spectra sent back to Earth need to be minutely treated and analyzed in order to extract as much as possible useful information in relation to the scientific objectives of the mission. The exactitude and reliability of such extractions guarantee the quality and quantity of the scientific results produced by the mission. For this purpose, the CheCam team has prepared 408 references samples, called ChemCam Calibration Targets (CCCT) for laboratory tests. The compositions of the CCCT samples represent the varieties of minerals and rocks that we can find on Mars including SiO2, TiO2, Al2O3, FeOT, MgO, CaO, Na2O, K2O. The LIBS spectra of the ensemble of CCCT samples have been obtained by the ChemCam team in a simulated Mars environment with the similar experimental conditions as onboard Curiosity rover on Mars. These spectra have been treated and analyzed by the ChemCam team to build prediction models for qualitative and quantitative analysis with LIBS spectra sent back by the ChemCam instrument. Even if the used chemometric classification and regression methods have provided good results, they leave however rooms for improvements. In our team in Shanghai Jiao Tong University we have started to work on new generations of LIBS data treatment methods base on machine learning algorithms since the end of 2016. Recently developed collaborations with the French ChemCam team in Toulouse have facilitated the application of our data treatment techniques (initially developed for samples of application interests on Earth, soil, steels, geological samples…) [2,3] to the CCCT LIBS spectra. We present here our first results with a collection of 80 samples randomly selected from the CCCT samples. Basically, two methods have been developed based on machine learning for classification and regression as a first step for the treatment of the all the CCCT spectra. For classification, an unsupervised model has been developed based on the Random 2D projection algorithm, which is a nonlinear algorithm. The model training was totally unsupervised, allowing clustering of the spectra according to their inherent data characteristics. The obtained results are shown in Fig. 1a, here colors represent different rock types. We can see the gathering of a significant part of the spectra according to their rock types. Even though such classification is still uncompleted with the model in its current state, a comparison with the results from a PCA model (Fig. 1b) already shows a significant improvement. For regression, a multivariate model has been developed [2,3] based on a back-propagation neural network (BPNN). The obtained results are shown for SiO2 (Fig. 1c) and FeOT (Fig. 1d). Determination coefficients of R^2=0.97 for SiO2 and R^2=0.93 for FeOT have been obtained, which represents a significant improvement with respect to the published results by the ChemCam team using a PLS SM regression model with R^2=0.94 for SiO2 and R^2=0.89 for FeOT. The improvement is especially observed for FeOT demonstrating the capacity of our model to take into account spectral interference due to the presence of a large number of Fe lines. We are testing our models with more CCCT spectra with improved calculation capacity. Our future efforts may contribute to better regression models based with reinforced robustness and higher prediction accuracy. The understanding to the physical mechanisms underlining the data characteristics of LIBS spectra is also one of our main objectives.

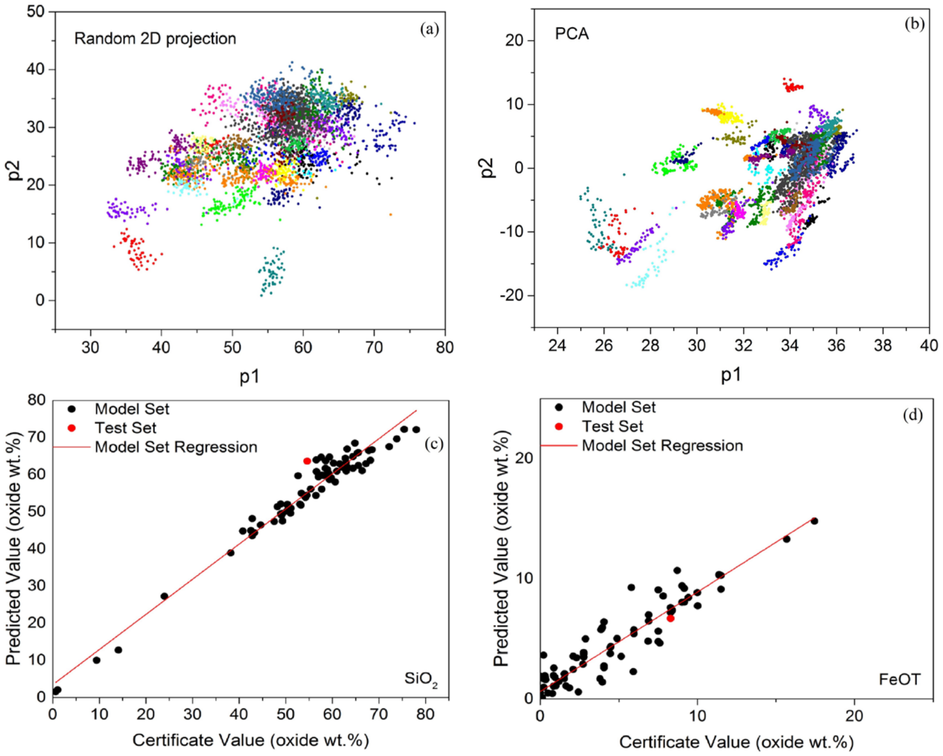

Fig. 1.: Fig.1 (a) & (b) Classification resulted from PCA and the Random 2D projection algorithm; (c) & (d) Calibration curves for SiO2 and FeOT resulted from the developed multivariate regression.

References

[1] Clegg, S.M., Wiens, R., Anderson, R., Forni, O., et al. “Recalibration of the Mars Science Laboratory ChemCam instrument with an expanded geochemical database”. Spectrochimica Acta Part B, 2017, 129, 64–85.

[2] Sun, C., Tian, Y., Gao, L., Niu, Y., Zhang, T., Li, H., Zhang, Y., Yue, Z., Delepine-Gilon, N. and Yu, J., “Machine Learning Allows Calibration Models to Predict Trace Element Concentration in Soil with Generalized LIBS Spectra”. submitted to Sci. Rep. (Feb. 2019).

[3] Patents under review: Chen Sun and Jin Yu, CN201810829668.5 and CN201910398915.5.

Acknowledgement

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Embedded k-Means Clustering for a deep exploration of megapixel LIBS imaging data sets

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Laser-Induced Breakdown Spectroscopy (LIBS) has achieved promising performance as an elemental imaging technology, and considerable progress has been achieved in the development of LIBS over the last several years, which has led to great interest in the use of LIBS in various fields of applications. As a consequence, we are today generating always bigger data sets with millions of pixels which led to new challenges in data analysis. Indeed, we have to develop new strategies in order to find natural groupings of pixels (spectra) considering the complexity of the emission spectra and the high dynamic range of measurement observed from major compounds and minor ones. In this work, we will introduce first, the well-known k-Means clustering (KM) which is one of the most popular unsupervised classification methods. It aims to separate a set of n unlabeled pixels of d dimensions into k clusters. Each cluster is represented by its barycenter, named centroid. KM algorithm starts by choosing randomly k initial pixels as centroids. Then, it runs iteratively following these steps: (i). Based on a chosen distance metric, each pixel is assigned to the cluster whose centroid is the nearest. (ii). The centroids are updated according to the new partition computed in step (i). Steps (i) and (ii) are repeated until pixel assignment is stabilized. This presentation will be also an opportunity to introduce the PBM index in order to estimate the optimal number of clusters. In a last step, a second round of clustering will be applied on each cluster in order will provide even more details about them. A complex mineral sample will be used as a case study to illustrate the potential of the proposed approach.

A look at LIBS instrumentations as an emerging tool for mining applications

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The Laser-Induced Breakdown Spectroscopy (LIBS) technique is a form of atomic emission spectroscopy of a plasma plume induced by laser on the material to be analyzed. LIBS has advanced over the last 50 years to become a successful emerging technology for numerous chemical analysis applications. Breakthroughs in understanding the science of the ablation process and development of improved laser and detector components have led to reliable analytical measurement performance. LIBS has found its way across a variety of applications and disciplines in geology, planetary science, defense, food, environment, industry, mining, biology, etc. The miniaturization of LIBS equipment has opened new opportunities to perform real time measurements and responds to emerging needs under conditions in which conventional techniques cannot be applied, in particular for the detection of precious metals. Exploration of precious metals is very challenging because the cut-off grade continues to decrease with time, as the value of the metals increases. This emphasizes the need for new and fast techniques for increasing productivity and efficiency in the field. The mining industry today is in desperate need of new technologies to face the challenges of increasing labor and material costs, and lower grades due to dilution. Recently, NRC has developed a breakthrough technology based on LIBS within collaboration with major Canadian gold mining companies. The NRC field portable prototype has allowed for the first time to detect gold below ppm level in mineral ore samples and also to provide information on mineralogy of the ore. Such real-time fast analysis of gold helps geologists and engineers make on-the-spot decisions, upgrading the ore by preventing sending gangue to the mill and proficiently manage their mining projects. In this presentation, we will present an overview of LIBS instrumentations with focus on their use in mining applications. We will discuss the LIBS instrumentations in terms of robustness, analytical performance and comparison to conventional techniques.

New quantification of Barium for MSL/ChemCam Mars data, and implications for geological interpretations.

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The detection and concentration of minor and trace elements in geological settings is of great help to understand the different geological processes they have been through. This is of particular importance when the geological context of the rocks is unknown, or not well constrained. This is the case with planetary missions, such as on Mars with the Mars Science Laboratory (MSL)/Curiosity rover. The ChemCam instrument, onboard the rover, uses the Laser-Induced Breakdown Spectroscopy (LIBS) technique in order to assess the chemistry of the analyzed targets [1,2]. ChemCam can detect several minor and trace elements: H, Li, C, N, F, P, S, Cl, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Ba, and Pb, but only a few of them are well quantified for now: F, Mn, Ba, Zn, Li, Rb, Sr. This study focuses on a revisited Ba quantification. Minor elements quantification with ChemCam is performed using univariate techniques [3], where the Ba line is located at 455.53 nm. This ionized Ba line is the most intense in the range 240-900nm, from the NIST database. Nevertheless, it is strongly overlapped by Si and Ti lines, which makes the peak fitting harder and tends to bias the result when the target is enriched in SiO2 [3]. However, Ba substitutes easily with K and therefore is found in K-feldspars. It is found as well in Ca-rich minerals (plagioclase, pyroxenes and amphiboles) but also in apatite and calcite, as it substitutes with Ca too. Ba is also found in high amount in clays and in Fe and Mn oxides, on to which it is adsorbed. Its quantification is therefore of great importance, as Curiosity has sampled several kinds of Fe and Mn oxides during its traverse, and is now exploring the clay-bearing unit. Recently, we have found another ionized Ba line that shows almost no overlap with other element lines, located at 614.3 nm. This line is promising, even if the LOD is higher than previously (180 ppm). It's used to predict the Ba content of the ChemCam's > 20000 observations on Mars.

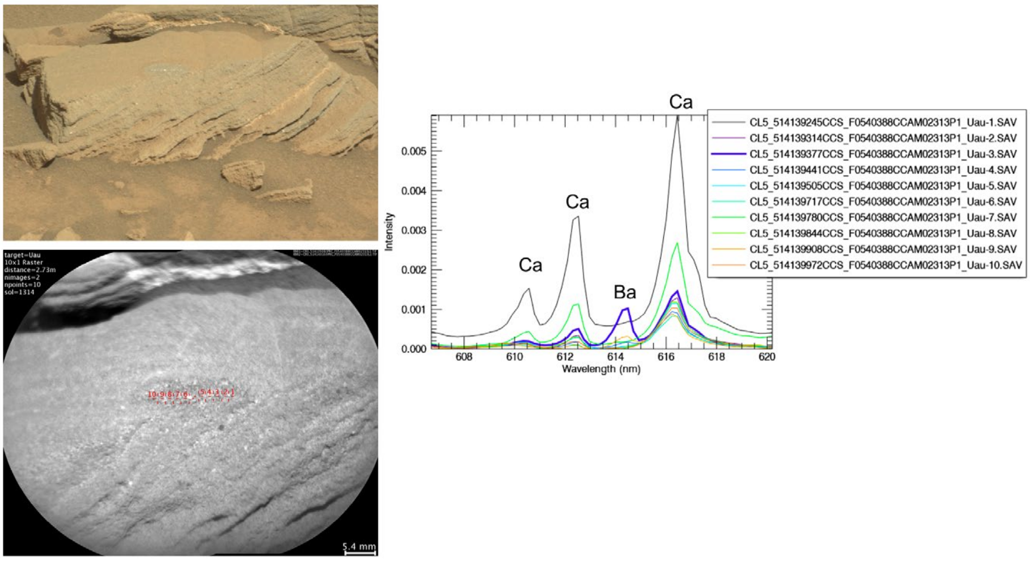

Fig. 1.: Images and ChemCam spectra of Uau target sampled on sol 1313. Point 3 is one of the highest Ba content (3000ppm), associated with a potassium feldspar composition. Top Left: MastCam image (1314MR0062670020700536E01_DXXX.IMG), bottom left: ChemCam mosaic(C

References

[1] Wiens R., Maurice S., et al. (2012) Space Sci. Rev. 170 (1-4), 167–227 .

[2] Maurice S. , Wiens R.C. , et al. (2012) Space Sci. Rev. 170 (1-4), 95–166 .

[3] Payré V., Fabre C., et al (2017) J. Geophys. Res. Planets, 122, doi:10.1002/2016JE005201.

Acknowledgement

The development and operation of the ChemCam instrument was supported in France by funds from the French space agency, Centre National d'Etudes Spatiales (CNES). Support was also received from INSU/CNRS. Support for the development and operation in the U.S. was provided by NASA to the Mars Exploration Program and specifically to the MSL team. Imaging and chemical data presented here are available in the NASA Planetary Data System http:// pds-geosciences.wustl.edu/missions/msl.

Fluorine detection on Mars: experiments and geological interpretation.

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Laser-induced breakdown spectroscopy (LIBS) obtains emission spectra of materials ablated from the samples in electronically excited states. Additionally, when the plasma cools down, elements can recombine and molecular emission lines are observed. Recent experiments [1] have shown that, when occurring, these molecular emissions can be much brighter than the associated atomic lines especially when halogens and REE are concerned. These molecular emissions have been observed in several ChemCam [2] spectra and allowed the first ever detection of fluorine on the surface of Mars [3]. Experiments under martian conditions with various mixing ratios of F and Cl in apatites were performed to better constrain their composition. These experiments allowed us to derive a calibration curve for the F content and confirmed a detection limit for fluorine of 0.2 wt.% and put an upper limit of Cl detection of 0.3 wt.%. Over the seven years of observations, ChemCam detected over 1000 points containing fluorine. This represents 0.5 % of all the observations. Two types of relationships between the fluorine and the others elements can be identified: the first one relates fluorine with calcium. In this case the F-bearing phases are either apatite or fluorite. Often it is not clear to disentangle between the two phases unless phosphorus is detected, which is not easy given the detection limit of about 3.0 wt.% phosphorus with ChemCam. The second type relates fluorine with silicon and aluminium. In this case, the F-bearing phase could correspond to phyllosilicates, possibly micas (biotite, muscovite), which are known to contain fluorine. Fluorine has been detected in very different geological settings along the stratigraphic column of Gale Crater (fig..1). We will show some examples of the occurrences of these two types of mineralogy and present some hypotheses for their formation in terms alteration conditions.

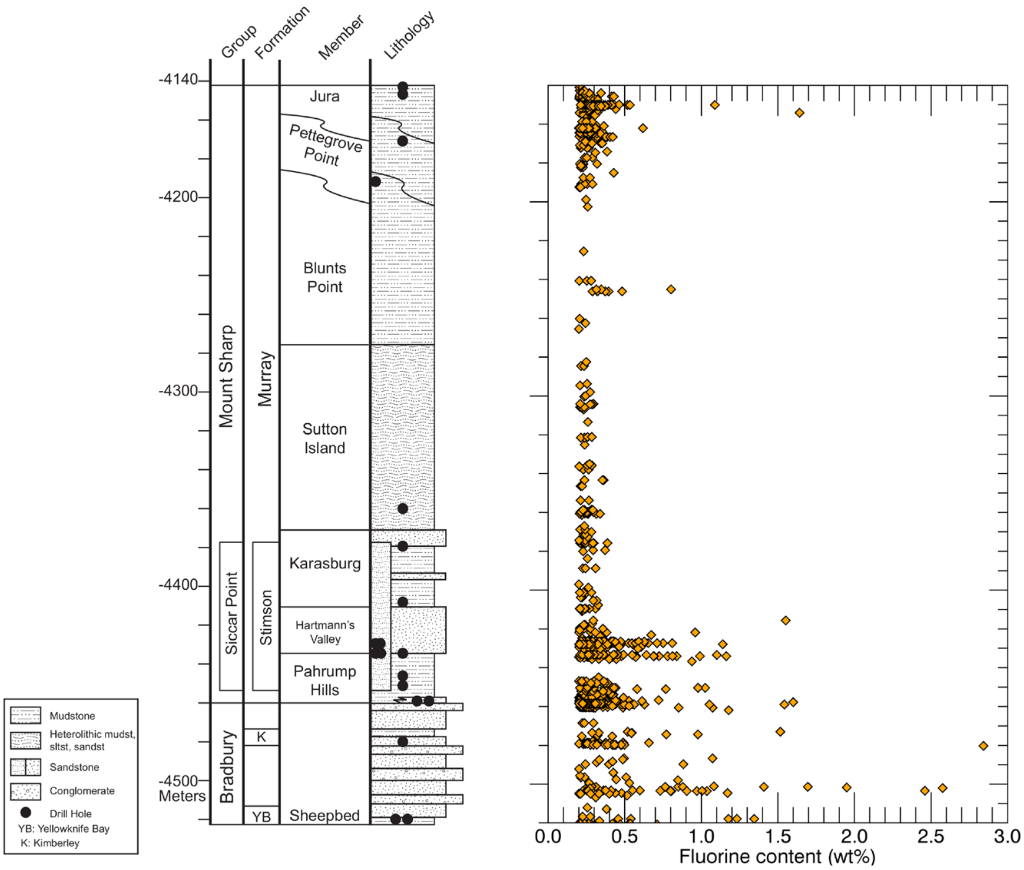

Fig. 1.: Stratigraphic distribution of the fluorine detections. Only detections less than 3 wt% F are displayed.

References

[1] Gaft, M., L. Nagli, N. Eliezer, Y. Groisman, and O. Forni (2014), Elemental analysis of halogens using molecular emission by Laser-Induced Breakdown Spectroscopy in air, Spectrochim. Acta, Part B, 98, 39–47.

[2] Maurice S., et al. (2016), ChemCam activities and discoveries during the nominal mission of the Mars Science Laboratory in Gale crater, Mars, Journal of Analytical Atomic Spectrometry, 31, 863-889.

[3] Forni, O., Gaft, M., Toplis, M.J., Clegg, S.M., Maurice, S., Wiens, R.C. , Meslin, P.-Y. et al. (2015). First detection of fluorine on Mars: implications for Gale Crater's geochemistry. Geophys. Res. Lett. 42 (4), 1020–1028 .

Acknowledgement

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Quantification of Lithium in pegmatites using handheld Laser Induced Breakdown Spectroscopy : a new approach for mining exploration

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Rechargeable lithium-ion batteries have become indispensable for consumer electronics and for powering electric cars. European Li-deposits are mainly associated with pegmatites, but beyond the geological unknowns, Li-exploration also suffers from technical difficulties. As light element, Li is hard to measure using classical techniques. If recent developments provide direct recognition of Li and Li-bearing minerals, such as LIBS (Laser-Induced Breakdown Spectroscopy) handheld spectrometers, with detection down to dozens of ppm level, its direct quantification must be undertaken regarding precise analytical protocol as it's done for any other analytical instrument in laboratory. Thus, any potential matrix or chemical effects relating to the mineral phases, self-absorption of emission lines, spectral interference with other elements… should be considered during the data analysis. In order to obtain consistent Li quantification from thousands of ppm to several wt %, we have selected a large range of well characterized Li-rich minerals such as spodumene (LiAlSi2O6), lepidolite (K(Li,Al)3(Si,Al)4O10(F,OH)2) and petalite (LiAlSi4O10). To investigate matrix effects, synthetic glasses have been realised, using the crushed selected minerals after fusing in an oven at 1400°C, and powder pellets were obtained from the same crushed minerals. Their chemical homogeneities have been cross-checked using micro-XRF and micro-LIBS mappings on millimetric or centimetric minerals, with a 10-micrometer space resolution. Different calibration curves have been established using these different samples. The relative standard deviation of the calibration depends on the selected Li-emission lines, the normalization (or not) of the signal, the number of laser spots per samples, etc… These calibration curves can be implemented in the handheld LIBS to give us an idea of the Li content directly on the field, which can be very useful for lithium exploration in a near future.

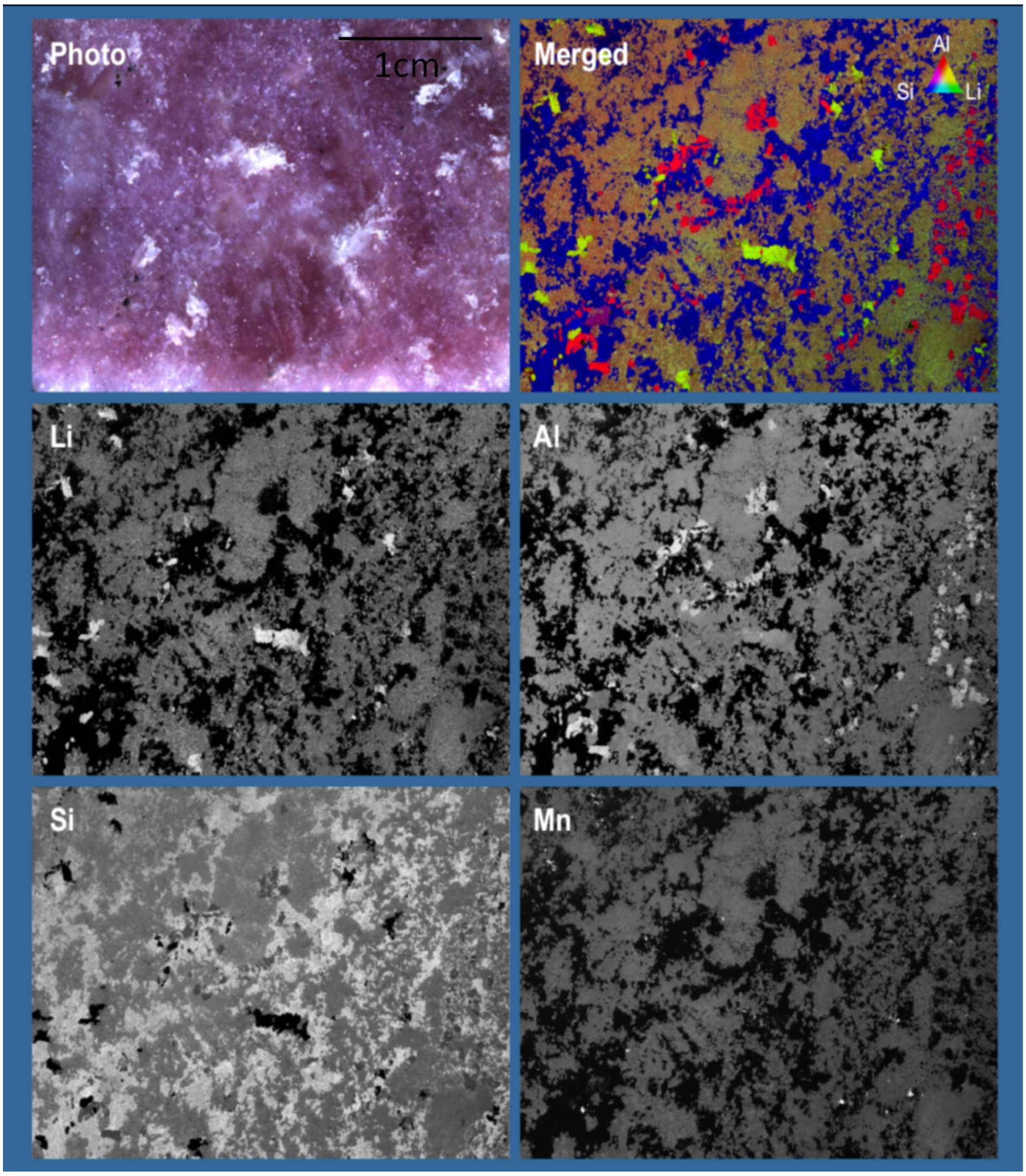

Fig. 1.: Micro-LIBS cartography on pegmatitic rocks containing lepidolites and montebrasites (Gonçalo, Portugal). Realised with 2400 x 1600 spectrum, with a spot diameter of 12µm.

References

[1] FABRE, C., DEVISMES, D., MONCAYO, S., PELASCINI, F., TRICHARD, F., LECOMTE, A., BOUSQUET, B., CAUZID, J. a MOTTO-ROS, V. Elemental imaging by laser-induced breakdown spectroscopy for the geological characterization of minerals. JAAS, 2018. DOI: 10.1039/c8ja00048d

LA-LIBS: High repetition rate ablation in combination with aerosol LIBS for quantitative analysis of solid samples

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LIBS has gained in popularity as an analytical scheme for rapid materials analysis, although the complex plasma-analyte interactions are directly related to the ultimate analyte response and quality of the results. Careful analysis of laser-induced plasmas and the resulting emission processes can play a vital role in understanding the many complex issues associated with the plasma-analyte interface, thereby providing an essential step forward in quantitative analysis. Based on new understanding of the important issues of analyte vaporization and transport, laser-ablation laser-induced breakdown spectroscopy (LA-LIBS) was proposed as a novel analytical scheme with goals of improved analyte response, as well as minimization of sample matrix effects and use of non-matrix matched standards, by separating the ablation sampling event and the analytical laser-induced plasma event. One drawback of the LA-LIBS approach is lower sensitivity due to the relatively small mass of analyte sampled following plume transport. To overcome reduced sensitivity, the laser ablation step was explored using a kHz laser, increasing by orders of magnitude the analyte sampling rate for subsequent transport and LIBS aerosol analysis. This methodology was explored for a series of metallic standard samples to allow quantitative assessment of the scheme as implemented. Overall, the value of LA-LIBS as an accurate and versatile analytical tool is demonstrated for direct analysis of solid materials.

LIBS, Raman and LIF in analysis of rocks containing rare earth elements

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Rare earth elements (REEs), which are in the periodic table scandium, yttrium and the lanthanoids, are critical raw materials. REEs are needed for example, in permanent magnets used in windmill technology needed for in construction of carbon-neutral society to answer environmental challenges. As the demand of REEs will exceed the current supply in the near future, there is a need to find new sources and boost the beneficiation of the existing ones. REEs can be found from about 200 different minerals as carbonate, phosphate, silicate, halide and oxide compounds. In general, REE-rich minerals occur in nature in carbonatite and alkaline type rocks and e.g. carbonatite rocks commonly contain ~3500 ppm REEs. For optimal beneficiation of the rock, the knowledge of the location of mineral grains, their shape and size and the possible chemical variations of REEs within the minerals should be obtained as quickly and early as possible. Our answer is the development of laser spectroscopy techniques; laser-induced breakdown spectroscopy (LIBS), Raman spectroscopy and laser-induced fluorescence (LIF) for the analysis of REE-bearing rocks. The spectral data set obtained from these complementary spectroscopy measurements has been used to construct maps of the REE-bearing rock surface, giving insight in the rock composition.

Coupling LIBS to SSI-MS. Interference of plasma formation with mass analysis

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The combination of laser induced breakdown spectroscopy with sonic-spray ionization (SSI) mass spectrometry (MS) is a promising tool for fast and straightforward analysis providing both the elemental composition and the molar mass of metal-organic compounds and metal containing biomolecules. [1] The analysis relies on the use of pneumatic nebulizer to generate an aerosol spray form the analyte solution in water/acetonitrile. The aerosol is fed into the inlet of the mass spectrometer at a constant flow, 15-20 μL/min, and mass spectra are collected. In parallel, it is interrogated, at a repetition rate of 5-10 Hz, by pulses from a nanosecond laser (Nd:YAG, λ = 1064 nm) that give rise to the formation of strongly emitting plasma, off of which time-resolved LIBS spectra are recorded. In the present study we have examined how and what extent formation of plasma, taking place at the region between the nebulizer edge and the mass spectrometer inlet, might influence the recorded mass spectrum. For example, diatomic molecules, such as OH, generated in the plasma plume can lead to gas phase cluster formation. The effect is related to sample matrix and is evident in presence of free metal ions, while it is minimized in the case of covalently bonded molecules or co-ordination compounds. We explored possible reaction pathways of the OH radicals with analytes having aromatic rings. It is shown that the ablation process has some, but clearly not significant interference, with the molecular MS measurements, and can further be reduced with proper synchronization settings that enable collection of mass spectra out of phase with respect to the plasma events.

References

[1] MARMATAKIS K., PERGANTIS S. A., ANGLOS D., Elemental and molecular analysis of metal containing biomolecules using laser induced breakdown spectroscopy and sonic spray ionization mass spectrometry: A step towards full integration and simultaneous analysis, Spectrochim Acta B 126, 103-109 (2016)

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Development of in-situ spectroscopy and its ocean applications

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The advanced application of Raman/LIBS techniques to the deep sea has been made possible by the availability of remotely operated vehicles (ROVs) with the payload, power, communication, and manipulation ability to deploy and control such an in-situ spectral system at full ocean depths. With the aid of ROVs, we have applied in-situ Raman spectroscopy to the geochemistry of hydrothermal vent and cold seep fluids [1]. In 2015, a compact 4000 m rated LIBS system was developed and deployed for depth profile investigations of sea water around the hydrothermal field at the Manus area [2]. In this talk, I'll give an overview of deep-sea Raman/LIBS systems we developed, so far, with a detailed introduction of an ultra-compact deep-sea LIBS system and its performance. To improve the capability of LIBS in its sea applications, many efforts have been made in laboratory in recent years. For a better understanding of underwater-LIBS, different plasma diagnostic methods were tried with time- and space-resolved spectroscopy, fast imaging as well as spectral-resolved imaging techniques. Both single-pulse and double-pulse LIBS in bulk water were investigated with special attentions on the laser focusing conditions and the impacts of the most common oceanic parameters (pressure, temperature and salinity) on LIBS signals. The relevant typical results will be given, in this talk, and the opportunity and challenge for LIBS being an in-situ technique in sea applications will also be discussed briefly.

Fig. 1.: A deep-sea LIBS system deployed on the ROV of “Faxian” (left) for the sea trial in 2015, and a concept diagram (right) showing the hybrid spectral system and its possible applications to hydrothermal vent.

References

[1] X. Zhang, Z.F. Du, R.E. Zheng, Z.D. Luan, F.J. Qi, K. Cheng, B. Wang, W.Q. Ye, X.R. Liu, C. Lian, C.A. Chen, J.J. Guo, Y. Li, J. Yan, Development of a new deep-sea hybrid Raman insertion probe and its application to the geochemistry of hydrothermal vent and cold seep fluids, Deep Sea Research Part I: Oceanographic Research Papers, 2017, 123: 1-12.

[2] J.J. Guo, Y. Lu, K. Cheng, J.J. Song, W.Q. Ye, N. Li, R.E. Zheng, Development of a compact underwater laser-induced breakdown spectroscopy (LIBS) system and preliminary results in sea trials, Applied Optics, 2017, 56(29): 8196-8200.

Acknowledgement

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Complementary characterization of ancient Roman frescoes by PIXE and LIBS techniques

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Within a regional project for technology transfer an archaeological site in Rome, named Villa della Piscina (area Centocelle), has been selected. This mansion was in use for about 7 centuries, since the republican period to the late empire. The examined fragments of frescoes, formerly excavated from the ruins, had been attributed to rooms inside thermal baths, built in the second half on the first century A.D. Extensive spectroscopic studies have been carried out inside the project in order to assign the complete color palette and other materials employed (plaster, mortar etc.). Most of the surface pigments have been characterized by Raman spectroscopy and by FT-IR measurements [1]. In order to complete the study, LIBS and PIXE [2] were utilized to determine atomic composition and to reveal also trace elements, which may contain information on the provenance of the materials and support their dating. From PIXE, the average element concentrations inside the penetration layer (in order of 10 μm) were determined. However, this technique individuated up to 13 elements (heavier than Na) in the examined materials while LIBS, identified up to 23 elements including the light ones and the traces. LIBS offered the unique possibility to investigate subsurface layers with depth resolution of about 1 μm, making possible to distinguish composition of surface contamination, painting and preparation layer (rich in Pb). The stratigraphic LIBS analysis showed that also some pigments contain Pb (present in white lead) while certain colors had been whitened by adding kaolinite. In the last case, a very good correlation between intensities of Ti and Al lines is evident in the LIBS spectra during depth profiling of the pigment's layer. As PIXE supplied quantitative data for all observed elements, an attempt to exploit these data for calibration of LIBS stratigraphy will be presented. Complementarity between the two techniques will be illustrated for the considered application.

References

[1] M. Sbroscia et al. Raman and FT-IR spectroscopy for the reconstruction of the decorative motives of Villa della Piscina, presented at TECHNART 2019, Bruges, in press.

[2] V. Lazic, et al. Applications of LIBS for CH: A comparison with XRF and PIXE techniques, Spectrochim. Acta B 149, 1–14, 2018.

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Molecular LIBS and Plasma Induced Luminescence of BaF2:Tm3+

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BaF2 activated by trivalent thulium is an interesting matrix for Laser-Induced Plasma (LIP) as a potential source for the emission of halogen and alkaline earth element molecules and Plasma Induced Luminescence (PIL) of Rare Earth Elements (REE) with long decay times in luminescent matrix1-3. After a long delay time of 10-70 □s, the relatively short-lived narrow atomic and ionic plasma emission lines disappear, and band emission dominates the spectrum. The origin of those bands is twofold: ultraviolet, green, extreme red and infrared series of BaF molecules and luminescence of Tm3+ in BaF2 matrix. The comparison with laser-induced luminescence reveals that spectrum of PIL corresponds to short UV photoexcitation, while the longer UV wavelength generates different luminescence spectrum (Fig.).

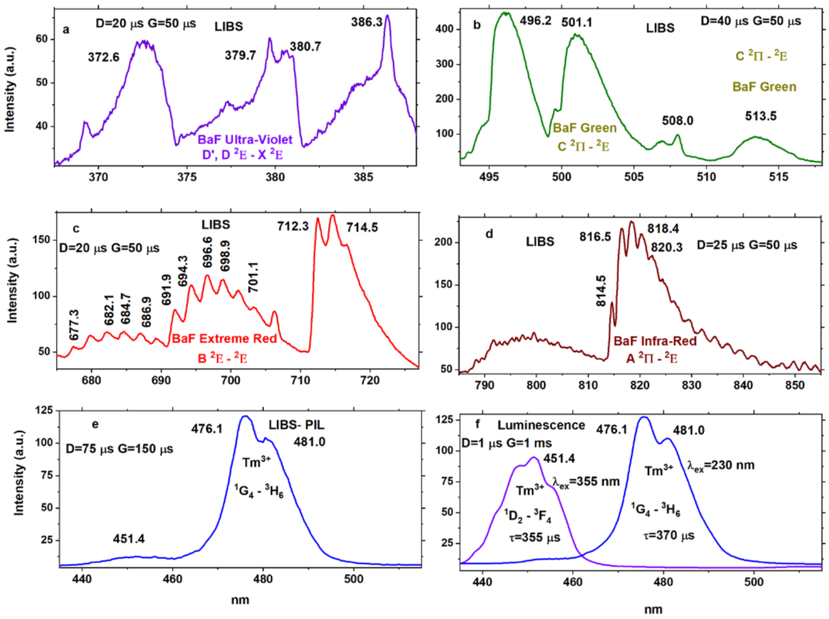

Fig. 1.: Figure. Breakdown spectra with molecular BaF emission (a-d), plasma-induced luminescence of Tm3+ (d) and photoluminescence under different excitations (e) of BaF2-Tm3+

References

[1] GAFT M. et al. Luminescence excited by laser-induced plasma. Optical Materials 34(2011)368

[2] GAFT M. et al. Elemental analysis of halogens molecules. Spect. Acta 95(2014)39

[3] GAFT M. et al. Imaging REE in minerals by molecules and PIL. Spect. Acta 151(2019)12

Double-pulse laser synchronization aimed at simultaneous detection of intensified atomic and molecular signals for space exploration

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A double pulse laser system that combines Raman spectroscopy and laser induced breakdown spectroscopy (LIBS) using one laser and one ICCD is demonstrated. The study attempts to improve the atomic signals of LIBS while simultaneously extracting the desired molecular signals from Raman. In low pressure conditions such as the lunar atmosphere, the detection of plasma emission is difficult due to the low electron density and short persistence time causing a rapid plasma expansion. Moreover, in the integration of the spectroscopic system aimed at space exploration, the system size and weight should be minimized. Simultaneous molecular and atomic detection that gave highly resolved spectra of both LIBS and Raman at pressure below 0.07 torr is achieved. First, a low-energy laser pulse was used to produce a small plasma and to detect the molecular signals through the inelastic scattering effect. Then, the laser pulse at a higher energy is used to produce a larger plasma plume for detecting the atomic signals. Amongst eight rock samples tested, plasma stacking by generating two sequential plasmas produced from the double-pulse laser on Calcite for example enhanced the signal intensities of calcium and oxygen lines by twofold, compared to a conventional LIBS. Noting the importance of discriminating the type of minerals during space exploration, the signal enhanced plasma emissions from the present setup may lead to highlighting the features of weak spectra and detecting otherwise blind signals from the conventional LIBS setup.

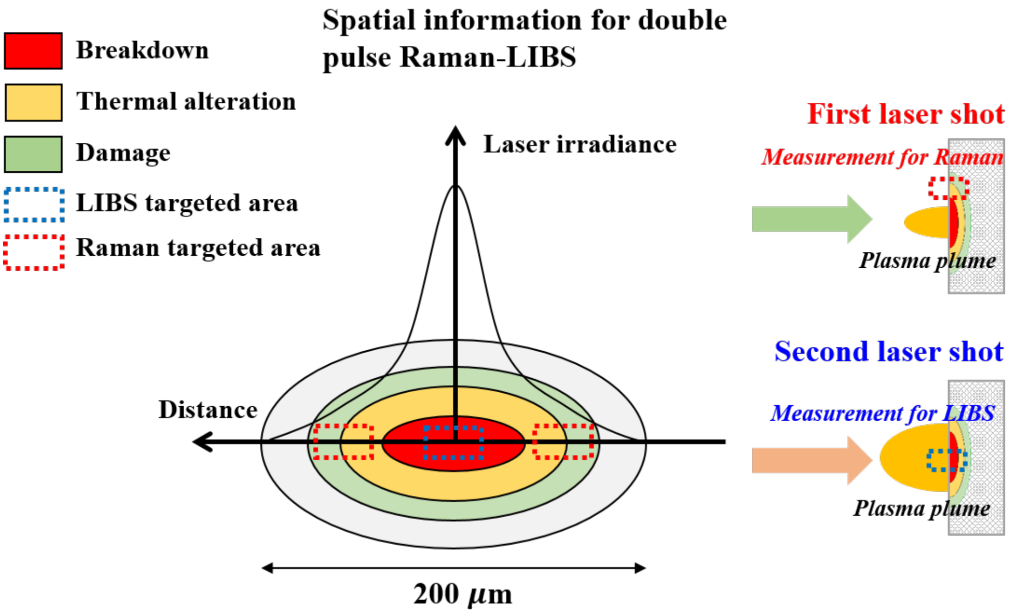

Fig. 1.: Schematic of the proposed double pulse Raman-LIBS arrangement

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Evaluation of the spatial and temporal distribution of atomic and molecular species at different LIBS plasma conditions.

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It is well known that sensitivity to detect halogens by atomic spectroscopy techniques, and in particular by LIBS, is poor. To overcome this limitation some alternative strategies have been investigated, such as carrying out the LIBS analysis in a He atmosphere [1], or the detection of the emission produced by metal-halogen molecules formed in the LIBS plasma [2]. In this last option, delay times used to acquire molecular emission are long to assure the atomic emission is low and recombination processes have taken place. Moreover, this method could be no restricted to the analysis of samples containing both, halogen and metal. For example, it was shown that CaF molecules could be formed by nebulizing a Ca-containing solution while a F-containing sample is being ablated [3]. In this work the spatial distribution and temporal evolution of CaF emission is investigated to find out the dynamic of the molecular emission in comparison with the atomic one, and the possible spatial discrimination between atomic and molecular signals. In addition, this study also investigate changes produced in the plasma by the nebulization of a Ca-containing solution during sample ablation. [1] C. Derrick Quarles, Jr., J. J. Gonzalez, L. J. East, J.H. Yoo, M. Morey and R.E. Russo. J. Anal. At. Spectrom. 29 (2014) 1238-1242 [2] M. Gaft, L. Nagli, N. Eliezer, Y. Groisman and O. Forni. Spectrochim. Acta B 98 (2014) 39–47 [3] C. Alvarez-Llamas, J. Pisonero, and N. Bordel, J. Anal. At. Spectrom., 32, (2017) 162–166.

References

[1] [1] C. Derrick Quarles, Jr., J. J. Gonzalez, L. J. East, J.H. Yoo, M. Morey and R.E. Russo. J. Anal. At. Spectrom. 29 (2014) 1238-1242

[2] [2] M. Gaft, L. Nagli, N. Eliezer, Y. Groisman and O. Forni. Spectrochim. Acta B 98 (2014) 39–4

[3] [3] C. Alvarez-Llamas, J. Pisonero, and N. Bordel, J. Anal. At. Spectrom., 32, (2017) 162–166.

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Analysis of biological samples combining data from LIBS, Raman spectroscopy and LA-ICP-MS

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We report on the application of selected analytical laser-based techniques to the analysis of biological samples such as bacteria, algae an yeast. The main thrust of this investigation was to use the technique of laser-induced breakdown spectroscopy (LIBS) which offers simple, fast and real time spectrochemical analysis, with little need for sample preparation. However, at some instances LIBS experiences considerable restrictions for specific elements in analytes. Such elements typically do not have spectral lines which are free from interference emission from other, more abundant, matrix elements, or their spectral lines are in regions not accessible to a particular spectrometer system. This may lead to some errors or measurements restrictions when performing sample analysis. To partially overcome this problem, it has been proposed to combine the primary technique of LIBS with another techniques, namely Raman spectroscopy nad LA-ICP-MS. Here, Raman spectroscopy provides precious information about the overall chemical composition of the sample of interest and LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) enables sensitive elemental analysis to be performed directly on selected samples. In this work, this combination is subject to our investigations to highlight some of its merits. Specifically, we attempted to merged data from LIBS and Raman which helps to enhance discrimination and classification accuracy of selected microorganisms.

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Chemistry in the laser-induced plasma. An astrobiology perspective for Mars exploration

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Since the first uses of LIBS, it is known that the laser induced plasma, as many other atom reservoirs, is a dynamic system that evolves rapidly to stable species after the end of the laser pulse. LIBS of metallic targets, which is the best established body of knowledge in this area of research, reveals the existence of a limited number of reactions between the excited and ionized atoms and atmospheric oxygen. The oxides formed may be used for characterizing the original sample, as for instance using the recently demonstrated application of LIBS for isotopic analysis at atmospheric pressure. The case of LIBS of organic compounds is much more complex. Recent investigations reveal that reactions in the plasma between fragments formed by dissociation of the original compound and by reactions of these fragments with the gas surrounding the plasma are extensive. While these reactions tend to complicate the spectroscopy and its interpretation, the products formed and the way they interact can be exploited for assigning the identity of the original compound. In this talk, a discussion of the several factors affecting the plasma chemistry of a number of molecular compounds will be presented. Factors influencing the formation of emitting species and some applications in the chemical analysis of organic samples with a view on astrobiological research will be discussed.

NELIBS vs LIBS: dealing with outstanding advantages and real limits.

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Nanoparticle Enhanced Laser-Induced Breakdown (NELIBS) has been proposed for the first time as a methodology for improving the sensitivity of LIBS, several papers on NELIBS applications has been published and the number of laboratories that are working on this approach is continuously growing. To the growing interest in NELIBS applications, is not corresponding an adequate effort to understand the basic mechanisms allowing the enhancement in Laser ablation based techniques, when nanostructures are used for the sample preparation. This talk is aimed to clarify the outstanding advantages but also the implicit limits of NELIBS, in order to outline when NELIBS is recommended and when its advantages do not worth the use of NELIBS with respect to conventional LIBS. For this task, fundamental aspects of laser-NP interaction as well as classical drawbacks of LIBS will be discussed.

References

[1] Dell'Aglio, M., Alrifai, R., De Giacomo, A., Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS), a first review (2018) Spectrochimica Acta - Part B Atomic Spectroscopy, 148, pp. 105-112.

[2] Koral, C., Dell'Aglio, M., Gaudiuso, R., Alrifai, R., Torelli, M., De Giacomo, A., Nanoparticle-Enhanced Laser Induced Breakdown Spectroscopy for the noninvasive analysis of transparent samples and gemstones (2018) Talanta, 182, pp. 253-258.

[3] De Giacomo, A., Dell'Aglio, M., Gaudiuso, R., Koral, C., Valenza, G., Perspective on the use of nanoparticles to improve LIBS analytical performance: Nanoparticle enhanced laser induced breakdown spectroscopy (NELIBS) (2016) Journal of Analytical Atomic Spectrometry, 31 (8), pp. 1566-1573.

LIBS assessment of spatial photon-upconversion nanoparticle distribution in model plants (R. sativus and L. minor)

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Lanthanide-doped photon-upconversion nanoparticles (UCNPs) are a new type of luminescent nanomaterials, the most commonly composed of NaYF4 nanocrystals doped with Er3+ and Yb3+. UCNPs have become widely used as luminescent labels because of their unique optical properties, which could lead to the replacement of traditional organic dyes and quantum dots [1]. However, analogously to other classes of nanomaterials, UCNPs may eventually find their way into the environment. Because environmental organisms may come into contact with discarded UCNP-containing products, it is important to evaluate the possible environmental risks of UCNPs. In the present study, radish (Raphanus sativus L.) and common duckweed (Lemna minor L.) were treated with an aqueous dispersion of carboxylated silica-coated photon-upconversion nanoparticles containing rare-earth elements (Y, Yb, and Er). The total content of rare earths and their bioaccumulation factors were determined in the root, hypocotyl, and leaves of R. sativus after 72 hours, and in L. minor fronds after 168 hours. In R. sativus, translocation factors were determined as the ratio of rare earths content in hypocotyl versus roots and in leaves versus hypocotyl. The lengths of the root and hypocotyl in R. sativus, as well as the frond area in L. minor were monitored as toxicity endpoints. To distinguish rare-earth bioaccumulation patterns, two-dimensional maps of elemental distribution in the whole R. sativus plant and in L. minor fronds were obtained by using laser-induced breakdown spectroscopy with a lateral resolution of 100 μm. Obtained results revealed that the tested nanoparticles became adsorbed on L. minor fronds and R. sativus roots, and got transferred from roots through the hypocotyl into leaves in R. sativus. Our results show that bioaccumulation patterns and spatial distribution of rare earths in nanoparticle-treated plants differ from those of positive control (the mixture of YCl3, YbCl3, and ErCl3).

References

[1] F. Wang, X. Liu, Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals. Chem. Soc. Rev. 38 (2009) 976–989. https://doi.org/10.1039/b809132n

Acknowledgement

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Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS) as a technique for elemental analysis of microdrops at sub ppm level

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Nanoparticle Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS) is a recently used modification of LIBS technique, where the use of nanoparticles decreases Limits Of Detection (LOD) or even in some particular cases enables the detection of minor elements not detectable with conventional LIBS. In the previous studies NELIBS applications have been presented on different kinds of samples such as metals, transparent samples, fresh samples and liquids. As it is well-known, solutions can be successfully analyzed with LIBS either directly in the liquid phase, e.g. by Double Pulse (DP) techniques or by depositing and drying drops of solution on a substrate. While DP-LIBS enables an analysis of solutions down to ppm levels, the method of drying several drops of solution virtually does not have any LOD limitation, as far as there is no restriction in the available amount of solution. On the contrary, if only a few microliters of the solution are available for the analysis, sensitivity can become a major issue in LIBS analyses. In these cases, the use of NPs can strongly improve the LIBS sensitivity. In the present work, the use of NELIBS as a tool for the elemental chemical analysis of microdrops of solutions with analyte concentration at sub-ppm level has been investigated in different liquid environment in order to check the analytical capabilities of NELIBS in aqueous, organic and biological solution. The results reveal some important characteristics of the plasmon-enhanced ablation and of the emission intensity enhancement during NELIBS. In the frame of these observations, new interesting applications such as the quantification of metals in protein systems and the elemental analysis for forensic purposes will be discussed.

Acknowledgement

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Challenges and perspectives of inverse production for sustainable material recycling – what LIBS can contribute

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The advance of automated production has triggered tremendous productivity gains in developed countries worldwide. Well-defined raw materials and primary products are used to produce complex semi-finished products and, ultimately, end products, through the massive use of automated processing and production processes. These often contain a wealth of valuable raw materials to ensure the desired properties and functions. The number of elements of the periodic table, which thus find their way into the final product, tends to increase. This applies in particular to high-tech products such as electronics of computers and mobile phones, but also to automobiles and tools for machining. At the end of the product lifetime, many recyclables occur still as material mixtures. Conventional recycling methods provide only very limited content-related sorting in order to obtain high-quality material fractions. In most cases, a preconditioned mass flow is processed metallurgically in order to recover some of the valuable metals.

But which chances are opened up if these products are disassembled at the end of their use with modern methods of production technology and are sorted based on inline gained chemical information, in order to win high-quality fractions? From these the valuable materials contained can be obtained in a more efficient way than now. What are the challenges of this so-called inverse production? Approaches to this are presented and exemplified by recent developments for the disassembly of electronic boards, with which hitherto inaccessible sorting fractions with high-value enrichment can be obtained.

Laser-induced breakdown spectroscopy and laser processing technology play a key role in the sketched measurement tasks. Recent developments of scanning LIBS systems will be presented which serve to identify valuable materials in electronic components and tool steels.

Quantification of the vulcanizing system of rubber in industrial tire rubber production by laser-induced breakdown spectroscopy

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The properties of rubber critically depend on the concentration of the vulcanizing system. We present an advanced laser-induced breakdown spectroscopy (LIBS) method to analyze the vulcanizing system (Sulfur and Zinc oxide, 0-3 wt%) in rubber under ambient conditions (air) and we demonstrate in-line measurements in the industrial rubber production. The faint sulfur lines in the near-infrared became measureable by plasma excitation in collinear double-pulse geometry and time-gated detection of emission. The weak Zn lines in the ultraviolet were measured due to their superior intensity stability compared to the stronger lines in the deeper UV. S and ZnO were quantified in different rubber materials prepared from the most important polymers in rubber production. The mean error of prediction of concentrations RMSEP was ≤0.07 wt% for S and ≤0.33 wt% for ZnO. Other chemical elements can be analyzed also and the rubber production may be controlled using LIBS as process analytical sensor.

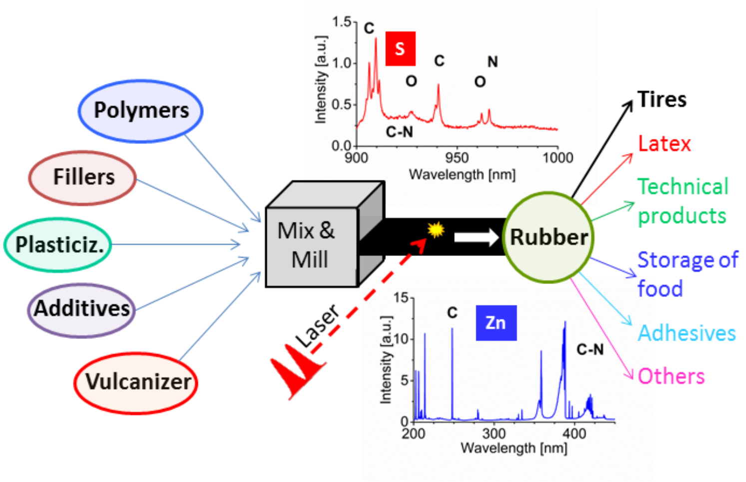

Fig. 1.: LIBS analysis of the vulcanizing system of rubber in industrial tire rubber production.

References

[1] TRAUTNER, S, LACKNER, J, PEDARNIG, JD., et al., Analytical Chemistry 91 (2019) 5200-5206.

Acknowledgement

Financial support by the Austrian Research Promotion Agency FFG is gratefully acknowledged (K-project imPACts 843546). We thank the teams in Technikum and production of KRAIBURG for their assistance.

Investigating the Li+/H+ exchange in garnet-type solid electrolytes using LIBS

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Since current Li-ion batteries suffer from limitations due to the chemical instability of their utilized organic electrolytes, a lot of research is focused on replacing them with more stable inorganic solid ion conductors. Cubic Li7La3Zr2O12 (LLZO) garnets show high Li-ion conductivity as well as good electrochemical stability, making them very promising solid Li-ion conductors to be employed in future Li-ion batteries [1]. However, the application of LLZO could be hampered by its reactivity with water leading to Li+/H+ exchange in the crystal structure of the garnets [2, 3]. To investigate and understand this phenomenon, information about the exact H+ uptake is of uttermost interest. In this work, we present a method for the spatially resolved determination of H in LLZO garnets using LIBS. Reliable signal quantification was obtained by preparing matrix-matched standards, carefully optimizing the measurement parameters (e.g. atmosphere, laser energy, gate delay) and applying appropriate signal normalization as well as background correction. Li+/H+ exchange caused by immersion in different media was investigated by conducting depth-profiling experiments on various LLZO samples, confirming significant H+ uptake during treatment with protic solvents.

References

[1] R. Murugan, V. Thangadurai and W. Weppner, Angew. Chem. Int. Ed., 46 (2007), 7778-7781

[2] Y. Jin and P.J. McGinn, J. Power Sources, 239 (2013), 326-331

[3] G. Larraz, A. Orera and M.L. Sanjuán, J. Mater. Chem. A, 1 (2013), 11419-11428

Mobile LIBS-System for evaluation of concrete structures on-site

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In view of the ageing of vital infrastructure facilities a reliable condition assessment of concrete structures is becoming of increasing interest for asset owners to plan timely and appropriate maintenance and repair interventions. For concrete structures reinforcement corrosion induced by penetrating chloride is the dominant deterioration mechanism affecting the serviceability and eventually structural performance. The determination of the quantitative chloride ingress is required not only to provide valuable information on the present condition of a structure, but the data obtained can also be used for predicting future development and associated risks. At present wet chemical analysis of ground concrete samples by a laboratory is the most common test procedure for determination of the chloride content. As the chloride content is expressed by mass of binder, the analysis should involve determination of both the amount of binder and amount of chloride contained in a concrete sample. The chloride profile obtained is based on depth intervals of 10 mm. LIBS is an economical viable alternative providing chloride contents at depth intervals of 1 mm or less. It provides two dimensional maps of quantitative element distributions and can locate spots of higher concentrations like in a crack. The results are correlated directly to the mass of binder and it can be applied on-site to deliver instantaneous results for the evaluation of the structure. The application of a mobile LIBS system in a parking garage is demonstrated. It uses a diode-pumped low energy laser (3 mJ, 1.5 ns, 100 Hz) and a compact NIR spectrometer. A scanner allows a two-dimensional element mapping. Results show the quantitative chloride analysis on wall and floor surfaces. To determine the 2-D distribution of harmful elements (Cl, C), concrete cores were drilled, split and analyzed directly on-site. Results obtained were compared and verified with laboratory measurements.

Laser induced breakdown spectroscopy for in-situ multielemental analysis during metal additive manufacturing

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Additive manufacturing opens new powerful capabilities for metal parts production directly from three-dimensional digital models as well as superior flexibility for producing internal structures which cannot be fabricated with traditional machinery and unique possibility to grow parts with required design of chemical composition gradient. The development of online sensing and control systems is essential for product quality improvement as well as advancement of additive manufacturing into high-value applications where component failure cannot be tolerated. For the first time, we have demonstrated the feasibility of in-situ quantitative multielemental analysis by LIBS during composite samples production by additive manufacturing. Specifically, we designed a low weight and compact remote LIBS system which was capable to quantitatively analyze both light (carbon) and heavy (tungsten, chromium, nickel) elements during composite coating (tungsten carbide in nickel alloy) synthesis by co-axial laser cladding technique. Coaxial laser cladding is an additive manufacturing technique based on metal powder flow melting by powerful continuous wave laser. Owing to non- uniform distribution of tungsten carbide grains in the upper surface layer the only acceptable choice for LIBS sampling point was in the melt pool at a growing clad. No impact of LIBS sampling on cladding process and clad properties was observed. The feasibility of in situ LIBS quantitative elemental analysis of key components (tungsten and nickel) has been demonstrated during the cladding process. LIBS analysis results were in good agreement with offline measurements by X-ray fluorescence spectroscopy (XRF) and combustion infrared absorption method (CIAM). Finally, LIBS technique was demonstrated to be a good tool for real-time detection of cladding process failures (poor laser beam quality, undesirable variation of components concentrations).

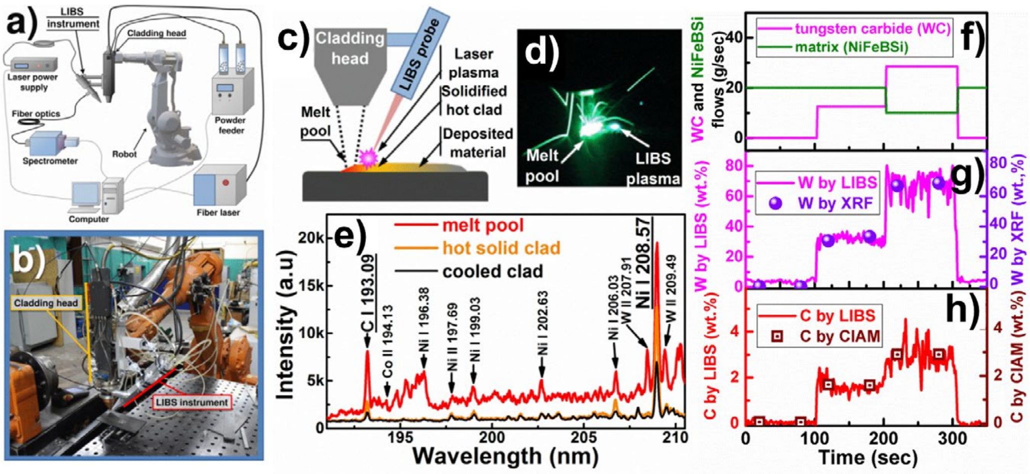

Fig. 1.: Scheme(a) and photo(b) of the coaxial laser cladding setup equipped with the laser induced breakdown spectroscopy (LIBS) system. LIBS sampling spots(c), plasma photo(d) and plasma spectra(e). Gradient coating(f) and in situ LIBS analysis for W(g) a C (h).

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Exploring the potential of LIBS for the in-field analysis of nuclear samples

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The unique potential of LIBS for the analysis of nuclear materials, especially using fiber optic instrumentation, has been recognized by the analytical community relatively early on and it has been used for material analysis at different nuclear facilities (like nuclear power plant, enrichment facility or radioactice waste depository, etc). Most of these applications however, in line with real or then thought limitations associated with LIBS, such as poor accuracy of quantitative analyses or inability to perform isotope-resolved measurements, were monitoring in nature and quantitative measurements were scarce. However, recent progress in technology, methodology and experimental optimizations in the last ca. two decades have greatly advanced the capabilities of LIBS, which now largely alleviate or even eliminate former limitations. This can allow a significant expansion of nuclear LIBS applications. In addition, the technique can be also useful for nuclear security purposes including nuclear forensics. Fast LIBS analysis can identify the origin of a material confiscated by authorities, help the identification of possible smuggling routes and perpetrators, to detect human exposure to certain isotopes or to prevent a potential nuclear terrorist attack. The stand-off/non-contact, virtually non-destructive, trace analytical sensitivity, specific spectral fingerprinting capability, sample preparation-free, short analysis time and other unique features of LIBS promise success also in these applications. This presentation will overview and showcase the current analytical potential of LIBS in nuclear analysis, primarily focusing on in-field applicable approaches and results.

Acknowledgement

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LIBS developments for fusion applications

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During the operation of a thermonuclear reactor which operates with a deuterium/tritium fuel mixture, it is mandatory to measure the tritium concentration and its depth profile in the Plasma Facing Components (PFCs) of the reactor thus reinforcing the measures planned for the estimation of the in situ inventory of tritium which is limited due to safety constraint. Moreover, the composition of the surface of those PFCs in light impurities (oxygen, oxides) which, when they are sprayed can pollute the fusion plasma, have also to be evaluated. Finally, the presence of helium bubbles in plasma-facing materials, helium coming from both the neutron interaction with materials impurities and of the decay of tritium trapped in the CFPs, is a major concern. Indeed, helium bubbles strongly degrade the thermomechanical properties of CFPs designed to evacuate high heat flux densities (~ 10 MW/m2). In order to address all of these open issues, Laser-Induced Breakdown Spectroscopy (LIBS) is the appropriate method. However, LIBS using nanosecond laser pulse has been proved to be irrelevant in determining the T depth profile in metallic samples [1-2]. Thus a specific experimental setup has been elaborated based on the implementation of picosecond laser pulses [3]. In this presentation, we will first recall the main experimental results that our team has obtained in the past 10 years on LIBS for fusion studies. Particularly, the first fusion in situ LIBS experiment will be described [4-5]. Then, our ps-LIBS experimental set up will be described and ps-LIBS results obtained on samples implanted with hydrogen isotopes will be presented. The depth of craters following the ablation has been measured. With pulse energy of ~ 20 mJ, low ablation rates (~ 100 nm/pulse) are obtained confirming that a tritium depth profile measurement is achievable with a depth accuracy of less than 1 µm. The plasma spectroscopic analysis is performed on the [200, 800] nm spectral range for different relevant fusion materials (W, Al as a proxy of beryllium and Si as a benchmark) implanted with mainly D+ ions produced by plasma discharges or ion beams. Temporal studies have been performed to identify the appropriate time window compatible with the plasma in thermochemical equilibrium. Some examples of the results obtained will be shown. We will also present concentration profiles obtained with a double pulse technique, when a second (5 ns) laser pulse is absorbed by the ps-LIBS plasma to increase the signal to noise ratio and enables the measurement of He. Finally, we will conclude describing how the ps-LIBS technique will be introduced in the WEST tokamak device using a remote handling device allowing in situ PFCs characterization. [1] C. Grisolia, A. Semerok, J.M. Weulersse, F. Le Guern, S. Fomichev, F. Brygo, P. Fichet, P.Y. Thro, P. Coad, N. Bekris, M. Stamp, S. Rosanvallon, G. Piazza, Journal of Nuclear Materials 363–365 (2007) 1138–1147 [2] Mercadier, Semerok, Kizub, Leontyev, Hermann, Grisolia, Thro, J. of

Nucl. Mater. 414 (2011) 485–491 [3] Bultel, Morel, Favre, Godard, Benyagoub, Monnet, Semerok, Dinescu, Markelj, Magaud, Grisolia, Fusion Engineering and Design, 2019, https://doi.org/10.1016/j.fusengdes.2019.03.079 [4] A. Semerok, C. Grisolia, Nuclear Instruments and Methods in Physics Research A 720 (2013) 31–35 [5] A. Semerok, D. L'Hermite, J.-M.Weulersse, J.-L. Lacour, G. Cheymol, M. Kempenaars, N. Bekris, C. Grisolia, Spectrochimica Acta Part B 123 (2016) 121–128

Polydispersity and fractionation in laser ablation studied by LIBS in an optical trap

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LIBS characterization of aerosols produced by laser ablation of bulk samples is strongly influenced by variations of physicohemical properties of the elements integrating the matrix. Among the consequences of these changes are differences on the ablated mass quantities, in the morphology of the aerosolized material or, ultimately, the processes occurring within the plasma such as the so-called fractionation effect[1]. This effect results in spectra that do not represent the bulk composition accurately. Single-particle analysis of these samples constitute a new approach to fundamental studies that are still needed for a better understanding of the involved processes. Herein, the OC-OT-LIBS technology[2] has been employed to monitor the particle-to-particle size dispersion and fractionation effects observed in aerosols generated during laser ablation of copper-based alloys. Under this methodology, particles generated inside of the ablation cell were stably trapped on-line in air at atmospheric pressure in an optical trap. Particles were dislodged using both, high and low fluence regimes, and then conveniently manipulated for precise positioning before LIBS analysis. Size dispersion of the aerosol was confirmed by SEM images. Dendrite-structured agglomerates of nano-particles and micron-sized spherical particles were observed in every case along single spherical particles. Concerning LIBS analysis, reduced fractionation was observed when the aerosol was generated at high laser fluence due to the production of smaller particles and featuring a narrower particle size distribution. In general, the particle size distribution ranged from nanometers to ca. 2 micrometers even under high fluence conditions. In this sense, the possibility offered by OC-OT-LIBS to study the single-particle compositional variation in aerosols with detection power in the sub-femtogram regime opens the door to a new way of understanding the fundamental processes that occur during laser ablation.

References

[1] R.E. Russo, X. Mao, H. Liu, J. Gonzalez and S.S. Mao Laser Ablation in Analytical Chemistry-a Review; Talanta 57 (2002) 425–451.

[2] P. Purohit, F.J. Fortes and J.J. Laserna, Spectral Identification in the Attogram Regime through Laser-Induced Emission of Single Optically Trapped Nanoparticles in Air; Angewandte Chemie International Edition 56 (2017) 14178-14182.

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Enhancement Limitations of Microwave-assisted LIBS: Application to Sulphur Detection

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The signal enhancement of laser induced breakdown spectroscopy (LIBS) assisted with microwave radiation is reported for Sulfur at ambient condition. Sulfur was detected at 180.73 nm, using portable spectrometer equipped with a non-gated detector. The effect of microwave power on signal enhancement and plasma parameters have been carefully assessed. The dependence of signal enhancement on upper energy state of the target element was evaluated. The result shows ~2-fold signal enhancement and ~ 1.4 times improvement in limit of detection (LoD) of Sulfur. Using laser energy of 10 mj at 530nm, the Sulfur LoD was 295ppm. It was observed that the upper state energy level of the elements plays an important role for signal enhancement of microwave-assisted LIBS. It was concluded that the microwave radiation can enhance the signal significantly when the upper state energy level of the target element is below 5eV.

LIBS for robotic alloy sorting

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Raw materials play an important role for European industry and their recovery is a key for a sustainable economy. An increasingly broad range of metals is used industrially on a large scale and its supply is partly critical because of high import dependency. Since metals can be remelted without quality reduction, recycling offers a valuable route of raw material supply, not only for pure metals but also for alloys which can be blended directly from scrap of the required composition. However, since the materials cannot be collected in pure alloy fractions, processes are needed which generate well-defined alloy fractions out of an input stream of mixed materials. Due to the high variability of alloys in industrial use, multi-element measurements by LIBS are used for classification of individual scrap pieces in a mixed material flow. When a high number of different alloys can be classified by LIBS, the best use of this technology can be made using a sorting approach which is capable of discharging individual pieces into a large number of fractions in a single pass. For the treatment of input material distributed on a belt conveyor, the patented concept of 3D laser imaging and scanning LIBS has been extended to include image-based automated picking of scrap pieces. A system will be presented which has been developed to demonstrate in an industrial environment the interlinked metal identification by LIBS and robotic sorting of the classified pieces of tool steel and carbide metal. LIBS measurements are carried out remotely over a scanner-guided beam path. The targeted measurement spots are calculated beforehand on the basis of 3D images, taking into account the often highly structured surface geometry. Since tool parts for recycling are often covered by hardening surface coatings, their local removal prior to material analysis is inevitable. Here the removal is limited to the targeted measurement spots and realised without an additional system component by a dedicated laser ablation phase which is integrated in the laser pulse train that also generates the LIBS plasma. A classification algorithm has been worked out which evaluates 14 chemical elements with up to 12 spectral lines each in a multivariate approach to identify individual scrap pieces correctly within a hierarchy of material classes and subclasses. The geometry information is also evaluated to determine handling positions for gripping the individual pieces and allowing a robotic transfer into the alloy fraction defined by the end-users selection.

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Abstracts

Posters

Simulation of the Dynamics of Laser-Induced Plasmas out of Local Thermodynamic Equilibrium

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The reliability of the LIBS technique highly depends on the estimate of the departure from local thermodynamic equilibrium of the laser-induced plasma. When the technique is implemented at low pressure, this departure strongly increases and the question of its impact on the results becomes crucial. The present communication deals with the implementation of collisional-radiative models in numerical codes in order to assess this deviation for an ultrashort (femtosecond, picosecond) or nanosecond laser pulse interacting with a metallic sample at low pressure. A spherical layer model is developed. The plasma is produced by the pulse with a possible laser-plasma interaction according to its characteristic time scale. The plasma expands and relaxes in space. The plasma is described using dedicated collisional–radiative (CR) models [1] whose different versions have been developed according to the metallic target considered (aluminum, tungsten, uranium). These CR models are based on a state-to-state approach involving several hundreds of independent levels [2]. Electrons and heavies kinetic energy is assumed Maxwellian, but at different temperature [3]. Elementary processes are implemented such as excitation and ionization under electron or heavy particle impact. Backward processes driven by the Detailed Balance Principle are also considered. From the radiative point of view, inverse Bremsstrahlung, radiative recombination and spontaneous emission are taken into account. Since the excited states population density is directly obtained, the time-dependent spectra are calculated by integration of the Radiative Transfer Equation. These spectra can then be directly compared to the experimental results.

References

[1] BULTEL, A., MOREL, V., ANNALORO, J., Thermochemical Non-Equilibrium in Thermal Plasmas, Atoms 7 (2019) 5, 1-16

[2] MOREL, V., BULTEL, A., SCHNEIDER, I.F., GRISOLIA, C., State-to-state modeling of ultrashort laser-induced plasmas, Spectrochim. Acta Part B 127 (2017) 7-19

[3] MOREL, V., BULTEL, A., ANNALORO, J., CHAMBRELAN, C., EDOUARD, G., GRISOLIA, C., Dynamics of a femtosecond/picosecond laser-induced aluminum plasma out of thermodynamic equilibrium in a nitrogen background gas, Spectrochim. Acta Part B 103-104 (2015) 112-123

Acknowledgement

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PI_002

Laser-induced plasma with a variable optical path length: a novel approach for absolute measurement of the atomic number densities in the plasma

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The Curve of growth (COG) methodology was firstly applied to laser-induced plasma (LIP) approximately 20 years ago [1,2]. The idea implies registration of emission signal of the self-absorbed line for the set of the samples with a different mass concentration of the investigated element c(El). Then, the fitting of the experimental curve (the line intensity IL vs. c(El)) by theoretical equation using the specific model of LIP is performed. If the plasma temperature T, electron density ne, and optical path length l, and transition probability A and Stark broadening parameter wS/ne of the line are known, we can deduce the coefficient of proportionality between cel and its species number density n(El) in the LIP from the fitting. In the present study, we suggest an alternative approach for the obtaining of the COG. Namely, we produce LIP by focusing the laser beam by a cylindrical lens into the line and observe the plasma in the end on configuration (fig. 1). By varying and controlling the LIP length with the help of the diaphragm we can obtain the emission signal with the different degree of absorption and construct the COG in the coordinates l–IL. Thus, we use only one and the same sample in our measurements. Knowing the T, ne, A and wS/ne, we can fit experimental COG by two parameters (the coefficient of experimental setup and nel) equation for the IL. We have obtained the COGs for Li and Cu on the example of the Mg alloy. We have found n(Li)=1.9e16 and n(Cu)=4.3e13 cm^−3. The experimental ratio n(Li):n(Cu) was in agreement with the atomic ratio in the solid sample: 440±110 vs. 364.

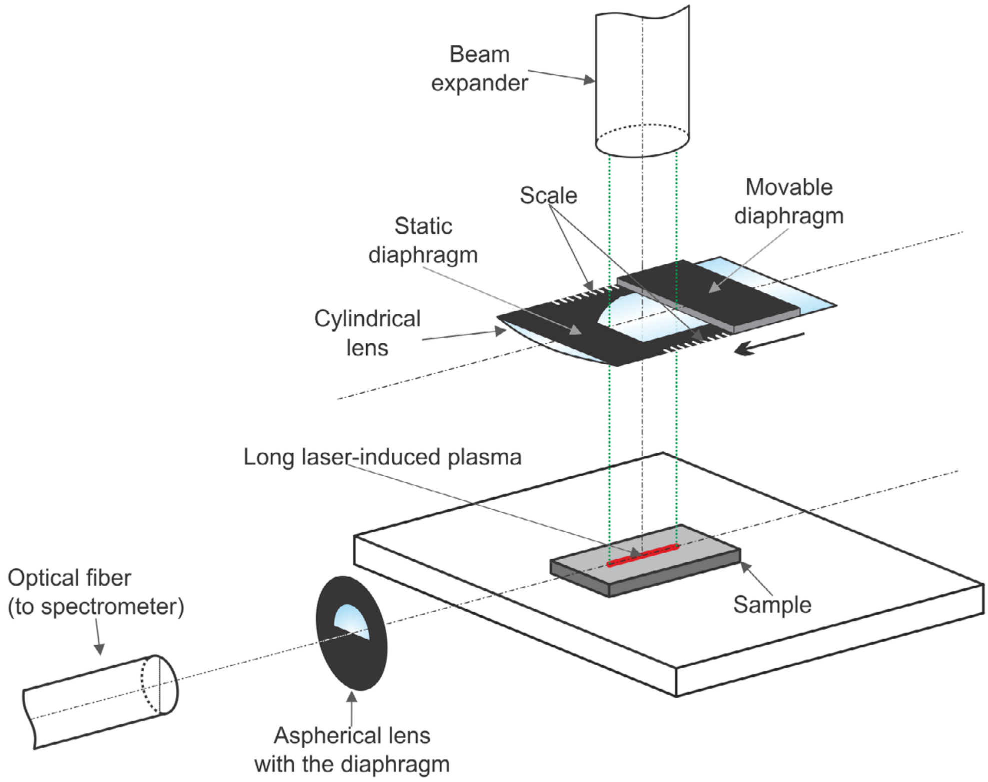

Fig. 1.: A scheme of the experimental setup for producing laser-induced plasma with a variable optical path length.

References

[1] I.B. Gornushkin, J.M. Anzano, L.A. King, B.W. Smith, N. Omenetto, J.D. Winefordner, Curve of growth methodology applied to laser-induced plasma emission spectroscopy, Spectrochim. Acta Part B 54 (1999) 491–503.

[2] C. Aragón, J. Bengoechea, J.A. Aguilera, Influence of the optical depth on spectral line emission from laser-induced plasmas, Spectrochim. Acta Part B 56 (2001) 619–628.

Acknowledgement

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Estimate of the departure from excitation equilibrium of a laser-induced plasma obtained in Argon-Hydrogen mixtures

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Laser-induced plasmas can be used to determine the multi-elemental composition of solid, liquid or gaseous samples. Using a pulsed laser beam focused on the sample, the resulting absorption leads to temperature increase of several 10,000 K, therefore to a neutral phase to plasma transition. During the relaxation phase over which the recombination takes place, a continuum then lines radiation is emitted. Its analysis based on Optical Emission Spectroscopy (OES) may lead to the composition of the plasma, therefore to that of the sample if fundamental assumptions are fulfilled [1]. The most restrictive one is the achievement of the Local Thermodynamic Equilibrium (LTE). Indeed, since only OES is used, the excited states number density is determined. Then, the ground states number density is obtained if LTE is observed and if electron temperature T_e is known, the electron density n_e being enough high. The characterization of LTE is therefore one of the key points of this analysis method, also known as Laser-Induced Breakdown Spectroscopy (LIBS) [2]. In this context, we have focused our attention on Argon-Hydrogen mixtures at atmospheric pressure. Using nanosecond laser sources (532 nm, 6 ns, 40 mJ), laser-induced plasmas have been produced with various Hydrogen mole fractions. The spectra have been recorded and calibrated according to the gate delay over different spectral regions. Large spectral windows have been used (around 60 nm) allowing a sufficiently high number of Argon lines. Using relevant radiation database, the spectra have been calculated assuming LTE by integration of the Radiative Transfer Equation and compared to the experimental ones for each spectral window. The temporal evolution of the electron density and temperature are then derived. The comparison of these evolutions from one spectral window to the other allows to estimate the uncertainty of the (n_e, T_e) determination and therefore to discuss the relevance of the LTE assumption.

References

[1] A.W. Miziolek et al. (2006) Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications, Cambridge University Press.

[2] Igor Savić, Zoran Mijatović, Teodora Gajo, Lazar Gavanski, Stevica Djurović,
The H□ line dip shift measurements in wide range of plasma electron density,
Journal of Quantitative Spectroscopy and Radiative Transfer, Volumes 222–223, 2019,
Pages 215-222, ISSN 0022-4073, https://doi.org/10.1016/j.jqsrt.2018.10.033

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Self-absorption in laser-induced plasmas in simulated Martian atmospheric conditions

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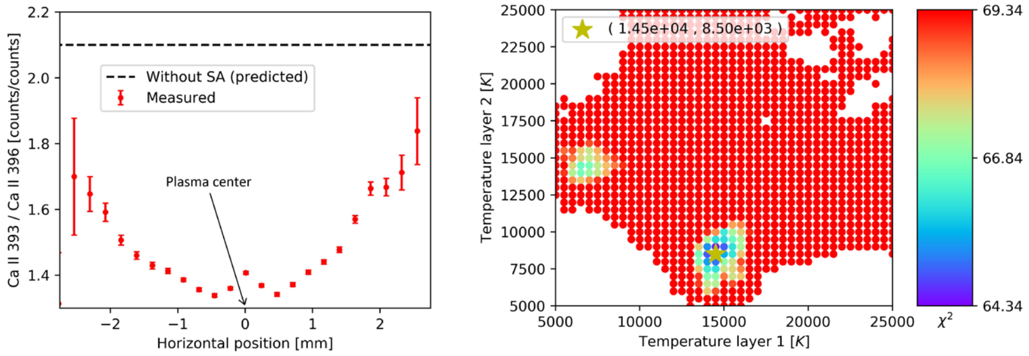
ChemCam on board the Mars rover Curiosity is the first LIBS instrument on Mars. In 2020, two more LIBS instruments will follow [1,2]. Thus, understanding the capabilities and challenges of LIBS in Mars' atmosphere is of high interest. A general challenge of LIBS is self-absorption (SA). The effect of SA depends on the atmospheric conditions. In Earth's atmosphere SA affects the intensities of the emission lines strongly and breaks the linearity of calibration curves which limits their accuracy [3]. While SA is expected to be lower in Martian conditions, no extensive studies on this have been reported. In this study we investigate SA in LIBS spectra acquired in simulated Martian atmospheric conditions. LIBS spectra of salts are obtained with two different setups: A high-resolution LIBS setup with a high spectral range and a plasma imaging setup allowing for spatially resolved measurements of the full plasma at a selected small spectral range. In measurements made with the plasma imaging setup, the effect of SA on the Ca(II) doublet at 393 nm and 396 nm can be observed. Fig. 1A shows the intensity ratio of the two emission lines for line-of-sight measurements through the plasma plume at different distances from the plasma axis. With negligible SA the ratio would be 2.1. We find a strong influence of SA, especially for large effective path lengths through the plasma center. For the calculation of the SA effect in spectra of the high-resolution LIBS setup, the plasma is modelled as a two-layer plasma in local thermal equilibrium. Temperature, electron density, and effective path length of each layer are varied and the resulting simulated spectra are compared to the measurements to find the best fit, see Fig. 1B. From the values of the best fit we find that many strong emission lines are significantly affected by SA, even though the effect is not obvious from the line profiles because of the instrumental broadening.



(A) **(B)**

Fig. 1.: (A): Doublet ratio for different line of sights in a horizontal slice of the plasma. Deviation from the optical thin ratio indicates the amount of SA. (B): Chi-square between measured- and simulated spectrum for different temperatures of the two layers.

References

[1] R. Wiens et al., 2017, Spectroscopy, Vol. 32, Issue 5, pp. 50–55.

[2] X. Ren et al., 2018, EPSC Abstracts, Vol. 12, EPSC2018-759-2.

[3] Y. Tang et al., 2019, Opt. Express, Vol. 27, Issue 4, pp. 4261-4270.

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Determination of Plasma Temperature in Laser-Induced Breakdown Spectroscopy Using Columnar Density Saha-Boltzmann Plot

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To exploit the analytical capabilities of the LIBS technique, the characterization of the LIBS plasma, i.e. the evaluation of plasma parameters, is a crucial step. In this work, laser-induced plasmas were characterized by means of the Columnar Density Saha-Boltzmann (CD-SB) plot method, a modified Saha–Boltzmann plot approach that uses the columnar densities of the species instead of their line intensities. The columnar densities are here calculated by quantifying the self-absorption of resonance lines. It is demonstrated that this is a promising method for the accurate determination of plasma temperature. In fact, the temperatures of the ground and excited states were studied at different delay times after plasma formation and it was observed that they almost have the same value which experimentally validates the proposed approach. The results suggest that at long delay times when thin ionization lines from highly excited levels are barely observable, the CD-SB method is still able to measure the plasma temperature. Furthermore, it was shown that in many cases of interest, the CD-SB approach can be more accurate than conventional Saha-Boltzmann plot since its application is not affected by possible breaches of the LTE approximation and by the uncertainty related to the spectral efficiency of the detection system. These findings provide a new approach for the physical characterization of plasmas and give access to a wealth of information about the state of plasma.

References

[1] Cristoforetti G, Tognoni E. Calculation of elemental columnar density from self-absorbed lines in laser-induced breakdown spectroscopy: A resource for quantitative analysis. Spectrochim Acta - Part B At Spectrosc. 2013; 79–80: 63–71.

[2] El Sherbini AM, El Sherbini TM, Hegazy H, Cristoforetti G, Legnaioli S, Palleschi V, et al. Evaluation of self-absorption coefficients of aluminum emission lines in laser-induced breakdown spectroscopy measurements. Spectrochim Acta - Part B At Spectrosc. 2005; 60(12): 1573–9.

[3] Cristoforetti G, De Giacomo A, Dell'Aglio M, Legnaioli S, Tognoni E, Palleschi V, et al. Local Thermodynamic Equilibrium in Laser-Induced Breakdown Spectroscopy: Beyond the McWhirter criterion. Spectrochim Acta Part B At Spectrosc. 2010; 65(1): 86–95.

Experimental characterization of double pulse laser-induced plasmas on Aluminum and Tungsten targets

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Laser-induced plasmas can be used to determine the multi-elemental composition of solid, liquid or gaseous samples. Using a pulsed laser beam focused on the sample, the resulting absorption leads to temperature increase of several 10,000 K [1], therefore to a neutral phase to plasma transition. During the relaxation phase over which the recombination takes place, a continuum then lines radiation is emitted. Its analysis based on Optical Emission Spectroscopy (OES) may lead to the composition of the plasma, therefore to that of the sample if fundamental assumptions are fulfilled [2]. The most restrictive one is the achievement of the Local Thermodynamic Equilibrium (LTE). Indeed, since only OES is used, the excited states number density is determined. Then, the ground states number density is obtained if LTE is observed and if electron temperature T_e is known, the electron density n_e being enough high. The characterization of LTE is therefore one of the key points of this analysis method, also known as Laser-Induced Breakdown Spectroscopy (LIBS) [3]. Using only one pulse may limit the capacity of LIBS to perform the complete analysis of the target. We think about the particular cases of low elemental mole fraction in the sample or species difficult to excite for instance. Using a second pulse may lead to significant improvements in terms of limit of detection. It consists in irradiating the plasma produced by a first laser pulse by a second one, whose characteristics (wavelength, duration, energy) may be different from the first laser pulse. The delay D_t between the two pulses is a key parameter of the experiment : it directly leads the efficiency of the plasma absorption (by Inverse Bremsstrahlung) of the second pulse. We have performed experiments in such configurations. The first pulse (1064 nm, 30 ps, 14 mJ) is used to produce plasmas on metallic samples (aluminum, tungsten) using a lens of 10 cm in focal length. The second pulse (532 nm, 6 ns, 65 mJ) is focused D_t later with a second lens of 15 cm in focal length on the plasma produced by the ps laser pulse. The beam directions are perpendicular to each other in order to avoid ablating the target with the second pulse. The characterization enables the time evolution of the total radiance, n_e and T_e by a thorough spectroscopic study. The experiments described are set to expose the advantages of a double pulse device.

References

[1] V. Morel, B. Pérès, A. Bultel, A. Hideur, C. Grisolia (2016) Picosecond LIBS diagnostics for tokamak in situ plasma facing materials chemical analysis, Phys. Scr. T167 : 014016. Doi :10.1088/0031-8949/T167/1/014016

[2] V. Morel, A. Bultel, J. Annaloro, C. Chambrelan, G. Edouard, C. Grisolia (2015) Dynamics of a femtosecond/picosecond laser-induced aluminum plasma out of thermodynamic equilibrium in a nitrogen background gas, Spectrochim. Acta Part B 103-104 : 112-123. Doi :10.1016/j.sab.2014.11.014

[3] A.W. Miziolek et al. (2006) Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications, Cambridge University Press.

Acknowledgement

We thank (1) the TRANSAT project funded by the Euratom Research and Training Programme 2014–2018 under grant agreement No754586, (2) the French Federation for Magnetic Fusion Studies (FR-FCM) and the Eurofusion consortium funded by the Euratom Research and Training Programme 2014–2018 and 2019–2020 under grant agreement No 633053 and (3) the French Agence Nationale de la Recherche (ANR), through the programme“Investissement d’Avenir”(ANR-10-LABX-09-01) PICOLIBS project, LabEx EMC3.

Triple pulse LIBS: Laser-induced breakdown spectroscopy signal enhancement by combination of pre-ablation and re-heating laser pulses

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One of the most popular ways to enhance the laser-induced breakdown spectroscopy (LIBS) emission signal is adding an extra laser pulse - so-called double pulse (DP LIBS). There are several possibilities of experimental geometries, but in this, work we focus on orthogonal alignment. Moreover, based on the time order of the laser pulses (with respect to ablation laser pulse) we recognize pre-ablation (the first pulse create air spark slightly above the sample surface) and re-heating (the second pulse re-heat the plasma). The goal of this work is to examine the effect of a combination of both pre-ablation and re-heating. For the purposes of this work, we call such arrangement Triple pulse LIBS (3P LIBS). The interpulse delays for both pre-ablation and re-heating are optimized and afterward, the emission signal intensity of 3P LIBS is compared to all possible experimental arrangements - single pulse, pre-pulse, and re-heating DP LIBS. Moreover, the relationship of signal enhancement and the upper-level energy of selected spectral lines was investigated.

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Development of a fs-LIBS system and study of its analytical performance using simple or double (fs/ns) pulse

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LIBS has undergone a significant growth as an analytical technique over the past decades. Typical experimental set-ups rely on the use of ns-pulsed lasers for the ablation, but fs-laser systems are becoming more relevant in recent years due to their interesting properties such as the increase of spatial resolution [1]. However, the optical emission from the fs-induced plasma is significantly lower. In order to enhance the analytical signal, an orthogonal laser pulse can be used to produce re-excitation processes [2]. This results in an important improvement of the analytical performance while maintaining the benefits of fs-ablation. In this work, we developed a LIBS system allowing two different configurations: single ns-pulse ablation and double fs/ns pulse ablation, in which the fs-laser is used to produce the ablation and the ns-laser orthogonally re-excites the plasma. The experimental set-up was then tested with real samples, comparing the results obtained with both configurations.

References

[1] GUREVICH, E. L.; HERGENRÖDER, R. Femtosecond laser-induced breakdown spectroscopy: physics, applications, and perspectives. Applied spectroscopy, 2007, vol. 61, no 10, p. 233A-242A.

[2] BABUSHOK, V. I., et al. Double pulse laser ablation and plasma: Laser induced breakdown spectroscopy signal enhancement. Spectrochimica Acta Part B: Atomic Spectroscopy, 2006, vol. 61, no 9, p. 999-1014.

Acknowledgement

The authors would like to acknowledge the financial support from the Government of the Principality of Asturias through the project IDI/2018/000186 as well as from the Ministerio de Economía (Spain), through the national project MINECO-17-CTQ2016-77887-C2-1-R.

Laser-induced Breakdown Spectrometry with laser pulses in femtoseconds to picoseconds regime and their influence on ablation quality

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For an efficient laser processing of a material, the selection of laser parameters that couple with the sample holds great importance [1,2]. With respect to pulse width, femtosecond laser ablation in comparison to the nanosecond one, is characterized by a significantly different behavior in the laser-matter interaction resulting in minimum thermal damage and therefore a better spatial resolution. The most significant feature is the lack of laser - plasma interaction, which has been demonstrated in pump-probe phase-change experiments [3]. Such experiments demonstrate that surface alteration occurs in the several hundred picosecond scale, while phase-change starts at around 1 ns after the reaching of the laser pulse. From the spectroscopic point of view, signal emission does not occur before 5 ns. Our communication is focused on the influence of the pulse width, ranging from femtosecond to picosecond, on the laser – matter interaction during laser ablation of solid materials. Modifications in the stretcher-compressor do allow the continuous selection of amplified pulses in the range between 35 fs to 4 ps. The pulses are characterized in the autocorrelation, spectral bandwidth and energy per pulse. A 0.5 m focal-length spectrograph fitted with an intensified CCD or fast single-channel detectors are used to determine the time constants, to establish the fluence threshold, and to record multi-channel spectra from the generated plasmas.

References

[1] Jahan, M. P., Rahman, M. & Wong, Y. S. 11.14 - Micro-Electrical Discharge Machining (Micro-EDM): Processes, Varieties, and Applications. in Comprehensive Materials Processing (eds. Hashmi, S., Batalha, G. F., Van Tyne, C. J. & Yilbas, B.) 333–371 (Elsevier, 2014). doi:10.1016/B978-0-08-096532-1.0

[2] Gunaratne, T., Kangas, M., Singh, S., Gross, A. & Dantus, M. Influence of bandwidth and phase shaping on laser induced breakdown spectroscopy with ultrashort laser pulses. Chem. Phys. Lett. 423, 197–201 (2006).

[3] Carrasco-García, I., Vadillo, J. M. & Javier Laserna, J. Monitoring the dynamics of the surface deformation prior to the onset of plasma emission during femtosecond laser ablation of noble metals by time-resolved reflectivity microscopy. Spectrochim. Acta Part B At. Spectrosc. 131, 1–7 (2017).

Optical modelling of spectroscopic characteristics of a dual-grating tunable spatial heterodyne LIBS spectrometer

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The spatial heterodyne spectrometer (SHS) concept, which is based on an interferometric optical setup, boasts both the Fellgett and Jacquinot advantages. Theoretically it can provide boosted sensitivity and spectral resolution with respect to dispersion spectrometers in a compact, reasonably cheap arrangement without any moving components – this set of characteristics can be attractive to a number of industrial, space and other field applications [1]. The potential of SHS has already been demonstrated in IR and Raman spectroscopies (e.g. [2]), and more recently also in LIBS [3]. The scientific goal of our present project is to apply the SHS concept to the development of an optimized, but practical dual-grating, tunable SH-LIBS setup, which would possess appealing spectroscopic characteristics. During this development, we extensively rely on the computer-based simulation of the optical setup, which is an efficient approach that we found to have been missing from earlier SHS efforts published. It can provide application-specific optimization of the SHS system and predict the performance of the final system. In particular, we use optical simulation to study the effect of various important parameters on the relevant spectroscopic figures of merits of the system. We used the non-sequential ray-tracing mode of the Zemax/Optic Studio software for optical modelling of the SH-LIBS setup (Optical distortions were studied in sequential mode). Characteristics of the setup and interferograms were calculated with at least one million rays. All calculations were carried out for the visible spectral range (400-700 nm), using stepwise extension of monochromatic simulations with 5 nm steps. Wherever applicable, characteristic discrete visible wavelengths from the emission spectrum of Hg discharge lamps (404.7 nm, 435.8 nm, 546.1 nm, 579.0 nm) were used for the calculation of spectroscopy figures of merit and for the validation of simulation.

References

[1] J.M. Harlander, F.L. Roesler, Proc. SPIE 1235, Instrumentation in Astronomy VII, (1 July 1990)

[2] N.R. Gomer, C.M. Gordon, P. Lucey, S.K. Sharma, et al., Appl. Spectrosc. 65 (2011) 849-857.

[3] I.B. Gornushkin, B.W. Smith, U. Panne, N. Omenetto, Appl. Spectrosc. 68 (2014) 1076-1084.

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Design of an optomechanical module for laser-induced plasma imaging

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Laser-Induced Breakdown Spectroscopy (LIBS) is a method of analytical chemistry that provides a qualitative and quantitative analysis of a sample. The ablation process of a sample is fast and dynamic and the change of plasma in time and space is a question of a few microseconds. An examination that provides a good time and space resolution is necessary to understand better the physical processes.

For this reason, the goal of this work is to design a basic optomechanic construction for this type of experiment. Optomechanic modul consist of objective that collects the emited radiation and focus it on the CMOS detector. For each experiment multiple images of the plasma are collected for better accuracy. Firstly basic comparison between the spectroscopic and imaging data is observed. For this experiment size of the plasma is compared with emited radiation colleted with spectometer. Also, the time development of plasma will be observed under different experimental conditions. The goal of this work, in general, is to prove that the morphology of plasma is as it is described in available related literature.

References

[1] MIZIOLEK, A. W., PALLESCHI, V. a SCHECHTER, I. Laser Induced Breakdown Spectroscopy. 1. vydání. Cambridge: Cambridge University Press, 2006. ISBN 978-051-1541-261.

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This research has been financially supported by the Ministry of Education, Youth and Sports of the Czech Republic under the project CEITEC 2020 (LQ1601). This work was also carried out with the support of CEITEC Nano Research Infrastructure (MEYS CR, 2016–2019), CEITEC Nano+ project, ID CZ.02.1.01/0.0/0.0/16_013/0001728.

Tomography of asymmetrical laser-induced plasmas

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Asymmetrical laser-induced plasmas were investigated by a tomography approach based on the inverse Radon transform. Two distinct sources of asymmetricity were investigated: double-pulsed laser-induced plasmas in the orthogonal configuration and single-pulsed laser-induced plasmas under an inclined incidence angle. Both cases were observed at various delay times. The optical thinness of the laser-induced plasmas was achieved by appropriately adjusting the pulse energies. High temporal resolution was achieved by a gated intensified charge-coupled-device camera. The asymmetrical laser-induced plasmas were investigated in terms of their total emissivity, spectrally resolved emissivity, and temperature. The latter was obtained by the Saha–Boltzmann plot method. The images required for the inverse Radon transform technique were obtained with a high angular accuracy and reproducibility provided by mounting the spectrometer on a high-precision nano-positioning rotary stage. The plasmas were induced in the center of rotation of the stage. This arrangement enabled the reconstruction of emissivity which was integrated over the full spectral range (200–800 nm) or over a desired spectral range selected by a bandpass filter (~10 nm). It also allowed for the reconstruction of spectrally-resolved emissivity in each cross-sectional plasma slice by scanning the plasma across a spectrometer slit. The 3D maps of the temperature and electron density were thus obtained for different types of asymmetric plasmas. The work will provide a more detailed description of the two asymmetrical laser-induced plasmas. This might help with the development of LIBS instrumentation using the orthogonal double-pulse geometry, or remote LIBS applications which inherently rely on inclined-angle ablation.

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Improvement in analytical performance of underwater LIBS signal by using the plasma image information

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Laser-induced plasma in water always suffers strong pulse-to-pulse fluctuations due to the multiple breakdown phenomenon, leading to a poor stability of the underwater LIBS signals [1]. Traditional normalization method by using internal standard element is often limited in practical cases due to the lack of proper element as the reference. Using plasma physical parameters to standardize the spectrum has been proven to be an effective way to improve the analytical performance of LIBS [2,3], and the emission distributions of plasma images are closely related to the plasma physical conditions as well as the spectral characteristics. In this work, the correlation between the plasma images and LIBS spectra was studied for underwater LIBS analysis. The spectral lines were standardized by using the corresponding image information and then used for the quantitative analysis. Figure 1 shows the comparison of the calibration curves with different standardization methods. The obtained results showed a good linear relationship between the spectral intensity of different elements and the plasma image intensity (maximum or sum). By extracting the core region of the plasma image, a well regression model between the spectrum and the plasma image can be established by using partial least squares regression (PLSR). With the proposed method, the average relative standard deviations (RSDs) of Li, Mn and Sr were reduced from 9.38%, 9.81% and 11.57% to 5.31%, 3.81% and 2.51%, and the average relative error (ARE) were reduced from 0.1716, 0.0233 and 0.0393 to 0.1128, 0.0206 and 0.0153, respectively.

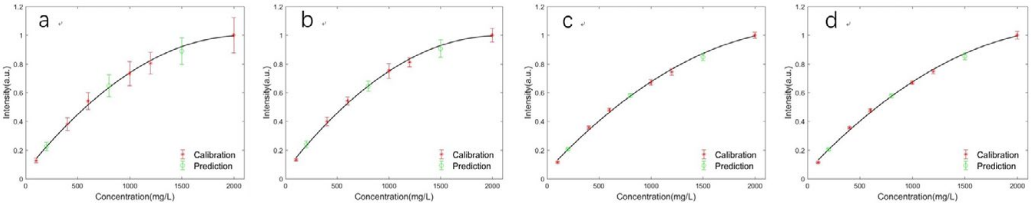

Fig. 1.: Calibration curves of Sr I 460.7 nm line using (a) the original intensity method, (b) the image auxiliary method, (c) the internal standard method, (d) the image auxiliary combined with internal standard method.

References

[1] Ye Tian, Boyang Xue, Jiaojian Song, Yuan Lu, Ronger Zheng. Stabilization of laser-induced plasma in bulk water using large focusing angle. Applied Physics Letters. 2016, 109(6): 061104.

[2] Zhe Wang, Lizhi Li, Logan West, Zheng Li, Weidou Ni. A spectrum standardization approach for laser-induced breakdown spectroscopy measurements. Spectrochim Acta Part B. 2012. 68: 58-64.

[3] Peng Zhang, Lanxiang Sun, Haibin Yu, Peng Zeng, Lifeng Qi, Yong Xin. An image auxiliary method for quantitative analysis of laser-induced breakdown spectroscopy. Analytical Chemistry. 2018, 90(7): 4686-4694.

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LIBS as versatile tool for characterization of LLZO garnets

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The need for high energy density storage has increased the demand for Lithium Ion batteries, especially for applications like electromobility and storage of renewable energy. However current technology suffers from safety concerns, because of the commonly used organic electrolytes. A way to overcome this is replacing them with inorganic solid ion conductors. Cubic Li 7 La 3 Zr 2 O 12 (LLZO) garnets show high conductivity and electrochemical stability, what makes them interesting candidates for solid state Lithium ion batteries. Despite the research effort, the conductivity of LLZO varies significantly and is hard to control. Former studies show [1, 2] that the composition of samples is not homogenous, however, no direct relationship between composition and conductivity could be found [2]. Here we present a LIBS based approach to access the stoichiometry of aluminum stabilized LLZO. The capability of LIBS to measure every element of the periodic table give a significant advantage over previous used approaches, as nonmetals such as oxygen as well as carbon and hydrogen can be measured. The acquisition of the whole spectra allows a non-targeted search for further contaminations. For quantification, matrix matched standards prepared from Al- doped LLZO powders were used. Using imaging, the two-dimensional distribution of the sample stoichiometry was investigated and compared to recent LA-ICP-MS and LA-ICP-OES results. Chemometrical analysis is used to further classify regions on the samples and gain insight into the complex behavior of this class of materials.

References

[1] Wachter-Welzl, A., et al., The origin of conductivity variations in Al-stabilized Li7La3Zr2O12
ceramics. Solid State Ionics, 2018. 319: p. 203-208.

[2] Smetaczek, S., et al., Local Li-ion conductivity changes within Al stabilized Li7La3Zr2O12 and
their relationship to three-dimensional variations of the bulk composition. Journal of Materials
Chemistry A, 2019. 7(12): p. 6818-6831.

PI_015 S

Use of picosecond laser in Laser Induced Breakdown Spectroscopy of tungsten and tungsten based mix layers for diagnostics of relevant fusion wall materials

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Besides the most common use of ns laser for LIBS spectroscopy, ps and fs laser pulses can also be used to excite high-quality laser induced plasma. In the ultra-short pulse duration, LIBS does not cause the overheating of the matrix. Therefore, the ultra-short pulse duration is more suitable and accurate for LIBS detection of the retained fuel in future thermonuclear reactor walls [1]. The use of ps and fs laser improves the homogeneity of laser ablation process and shape of craters. Using the lower energy per pulse (case of ps and fs lasers), the ablation rate would be lowered and thus a better depth resolution can be achieved. The ablation rate of fusion relevant BeW mixed layers at low gas pressure with ns Nd:YAG is of the order of several tens of nanometers per laser shot [2]. In our experiments, the ps laser Pikar-1 (Nd:YAG laser working at □ = 1064 nm, 30 ps duration, operates in the active-passive mode locking and negative feedback) was used for LIBS application. The analyzed sample was placed, under atmospheric pressure, onto the xyz micrometer positioning stage. The emission from the laser plasma plume was measured by the Echelle spectrometer (ME 5000, Andor Technology) equipped with the iCCD camera (iStar, Andor Technology) in the spectral range 200-1000 nm. Afterwards, the spectrum was divided by the sensitivity curve of the spectrometer. For the analysis of W based mix layers we used calibration free (CF) approach. We have calculated the electron temperature by using the Saha-Boltzman plot of W I and II spectral lines and the electron density by the Stark broadening effect of H□-line. We have also simulated the W I-II spectra from NIST LIBS application database and compared them with the experimental spectra [3]. The picosecond laser allows working with lower fluency which leads to a lower ablation which means better spatial resolution. This could help in future analysis of depth profiling of nanolayers in real fusion relevant wall materials.

References

[1] S. Brezinsek and WP PFC contributors, Plasma–wall interaction studies within the EUROfusion consortium: progress on plasma-facing components development and qualifcation, Nucl. Fusion 2017; 57: 116041.

[2] M. Suchoňová, P. Veis, J. Karhunen, P. Paris, M. Pribula, K. Piip, M. Laan, C. Porosnicu, C. Lungu, A. Hakola, Determination of deuterium depth profiles in fusion-relevant wall materials by nanosecond LIBS, Nuclear Materials and Energy 2017; 12: 611-616.

[3] A. Kramida, K. Olsen, and Y. Ralchenko. NIST LIBS Database [Online]. Available: https://physics.nist.gov/PhysRefData/ASD/LIBS/libs-form.html (Date of last access: 24.04.2019)

Acknowledgement

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Spectra modeling to choose an analytical line for determining niobium traces in ferromanganese nodules by LIBS

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Ferromanganese nodules (FMNs) are rich in rare-earth and rare-metal elements and, therefore, they are considered as a promising source for them. The main spectroscopic challenge to analyze FMNs by emission spectroscopic techniques, such as LIBS, is spectral interferences from iron and manganese which have rich emission spectra. As a result, the strongest Nb I line at 405.85 nm is completely merged by Mn I and Fe I lines. Therefore, a task to search for appropriate analytical lines should be solved for analytical application of LIBS to FMNs. In this work, we have demonstrated how spectra modeling by our algorithm described in [1] can provide us an information about possible analytical lines of niobium. As samples we have used the certified reference samples of FMNs produced in Russia (OOPE series, Nb content 20-90 ppm). After spectra building, we selected several spectral ranges to experimentally measure emission spectra of plasma in these ranges for different plasma conditions: "soft" conditions (long delay, cold plasma) and "severe" conditions (short delay, hot and dense plasma). After inspection of 5 spectral ranges where strong Nb lines can be observed we have obtained that only two lines (as predicted by the algorithm) Nb I 509.53 nm and Nb I 410.09 nm are appropriate for analytical usage because of absence of spectral interference. Although the intensity of Nb I 410.09 nm is larger than one of Nb I 509.53 nm, the latter provided smaller detection limit (5 ppm) due to high efficiency of spectrometric system in the range near 500 nm. So, the work has clearly demonstrated the efficiency of spectra modeling to search for analytical lines in complex matrix, such as FMNs.

References

[1] Zaytsev S.M., Popov A.M., Labutin T.A. Stationary model of laser-induced plasma: Critical evaluation and applications, Spectrochimica Acta Part B, 2019, V.158, Article number 105632.

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PI_017

Influence of laser ablation-induced sample surface asperities on LIBS spectrum intensity

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Laser-induced breakdown spectroscopy (LIBS) is known as an elemental analysis technique especially suited for in situ (including remote) and online detection and control . Such applications however present a certain number of constrains which can reduce the performance of the technique due to loss of control of a part of the experimental conditions. Among such conditions, there is the surface state of the samples and especially the surface roughness and asperities. The use of pre-pulses can contribute to reduce the roughness initially present on the material surface, such treatment introduces however other types of surface asperities, by forming ablation craters for example. Study of the influence of ablation crater can also have importance for depth profiling measurements with LIBS, where the signal variation as a function of crater depth should be corrected with the effect of change of laser-surface interaction geometry. The effect of a cavity under the plat surface of a fused silica sample has been experimentally studied, increases in plasma temperature and electron density were observed inside the cavity [1,2]. An enhancement of plasma emission intensity above the sample surface has also been observed when successive laser pulses drew a crater under the sample surface [3]. In this work, we study the effect of crater formation on a sample surface ablated by successive laser pulses on the emission intensity of the induced plasma, we especially correlated the observed intensity variation to the physical properties of the induced plasma. The used target was an aluminum alloy with as minor element, 0.146 wt% of titanium. Ablations were performed on an initially polished sample surface with 1064 nm pulses from a Nd:YAG laser (pulse duration 7 ns and a spot of 130 μm in diameter on the sample). Three incident energies of 7 mJ, 35 mJ and 70 mJ were used in the experiment. The plasma emission was acquired along the lateral direction and at a position 600 μm above the sample surface with an echelle spectrometer coupled to an ICCD camera. As an example of emission intensity change, we shown in Fig. 1 (a) to (b) the intensity variation ratios (compared to the initial intensity on the sample surface) of a neutral line (Al I 309.3 nm line) and an ionic line (Ti II 335.0 nm line). We can see that the emission intensities sensitively depend on the number of laser shots, and for different laser pulse energies, different variation behaviors can be observed. For a small pulse energy of 7 mJ, the emission intensity fast increases with the first laser shots, and undergoes oscillations in a global decreasing evolution, which leads the intensity to become smaller than its initial value at the sample surface after ~ 200 shots. The observed temperature exhibits a similar evolution, which would allow explaining the increase of emission intensity by an increase of the temperature. The evolution of the electron density globally confirms that of the temperature. For higher laser pulse energies of 35 mJ and 70 mJ, the emission intensity first decreases (especially for 35 mJ), than increases before decreasing again. For the both energies, the variation ratio is always higher for Al line (matrix element) than for Ti (a minor element). The difference becomes quite large for 70 mJ. The correlation between the intensity and the temperature is quite good for 35 mJ, but exhibits a clear discrepancy at 70 mJ for the Al line. Again the evolution of the electron density globally confirms those of the intensity and the temperature. Beyond the above first observations, the detailed explanations of the observed emission intensity variation remain quite complicated and would involve several mechanisms related to the laser ablation and the propagation of the ablation plume into the background gas, such as the modification of surface optical property, the shockwave propagation and the laser-supported absorption waves.

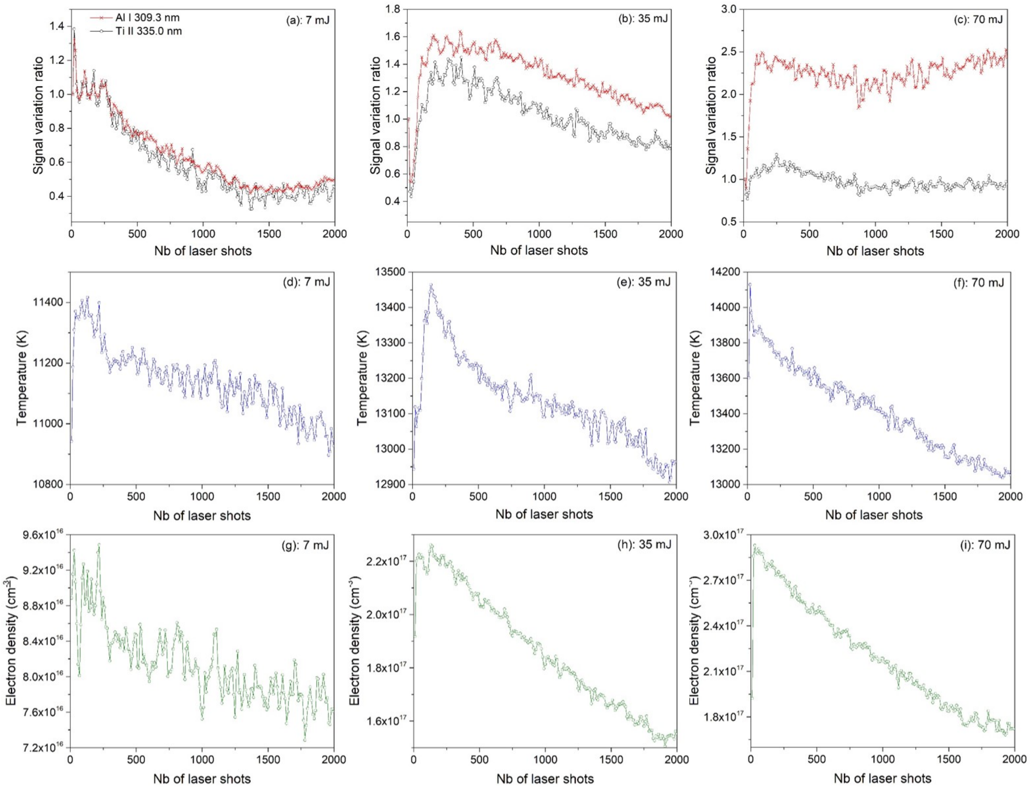

Fig. 1.: Fig. 1 variation as a function of successive ablation laser shots of (a) –(c): emission intensities; (d) – (f): plasma temperature; (h) – (i) electron density for different ablation laser pulse energies of 7 mJ, 35 mJ and 70 mJ.

References

[1] X.Z. Zeng, S.S. Mao, C. Liu, X.L. Mao, R. Greif, R.E. Russo, Laser-induced plasmas in micromachined fused silica cavities, Appl Phys Lett, 83 (2003) 240-242.

[2] X.H. Zeng, S.S. Mao, C.Y. Liu, X.L. Mao, R. Greif, R.E. Russo, Plasma diagnostics during laser ablation in a cavity, Spectrochim Acta B, 58 (2003) 867-877.

[3] [4] K.H. Li, L.B. Guo, X.Y. Li, Z.Q. Hao, J.M. Li, X.Y. Yang, M. Shen, Q.D. Zeng, Y.F. Lu, X.Y. Zeng, Characteristics of spectral lines with crater development during laser-induced breakdown spectroscopy, Appl Optics, 55 (2016) 7422-7427.

Acknowledgement

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Enhancement of laser-induced plasma emission intensity by cylindrical spatial confinement in neon

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The development of methods for increasing the sensitivity of LIBS is an area of research that is relevant for many LIBS applications – elemental surface mapping, depth analysis, etc. Spatial confinement is a very cost-effective method for increase of LIBS sensitivity [1-3]. It consists of geometrical confinement of the expanding laser-induced plasma by insertion of geometrical boundaries which leads to substantial emission intensity enhancement. In this work, we present study the dependence of intensity enhancement by plasma spatial confinement on the ambient pressure of neon in the range 1-760 Torr (varying step) and on the diameter of surrounding cylindrical metal walls with diameters from 2 mm to 8 mm (2 mm step). We compared the laser-induced plasma emission intensity inside and outside of the cylinders in neon gas. The laser-induced plasma is produced by irradiating a certified reference material MBH-212XNA4A (Nickel base, Monel, Ni 62,8%/Cu 29.34%). The results show around 2-fold enhancement at different pressure values and cylinder diameters compared to free expansion without confinement. We evaluated the values of the laser-induced plasma parameters - electron density and electron temperature, as a function of the ambient gas pressure and diameter of the confining cylinders. We used these results to develop a spectroscopic source combining laser-induced plasma and cylindrical hollow cathode glow discharge. This spectroscopic source can enhance the emission intensity by two mechanisms – spatial confinement and additional excitation in the glow discharge. For operation at optimal conditions, a diameter of 6 mm and pressure of 4 Torr, we obtained for this source maximum of 8-fold signal increase and evaluated the contributions of each of the mechanisms. These results are promising for obtaining better sensitivity at low pressure for optical spectroscopy studies, e.g. on-line monitoring of pulsed laser deposition processes.

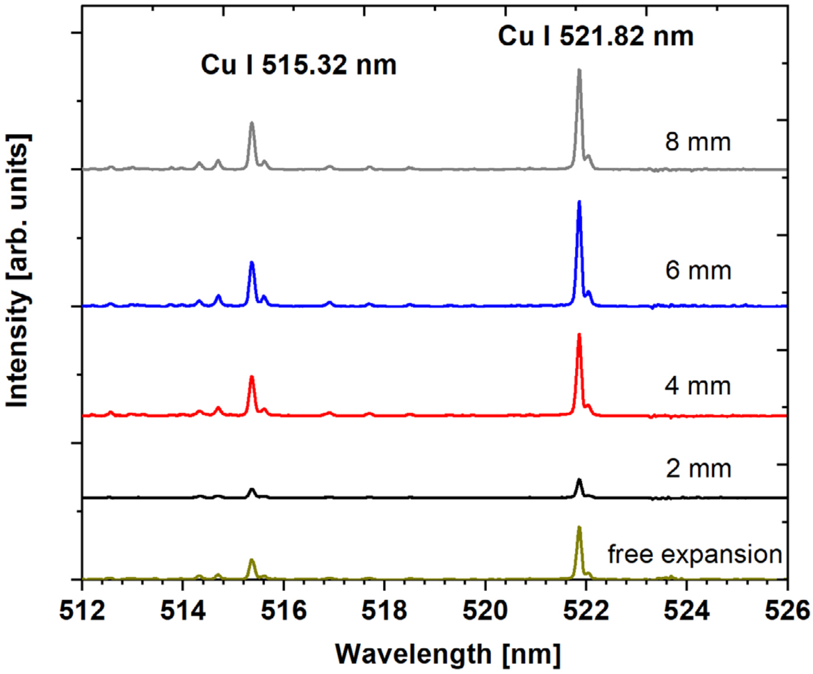

Fig. 1.: Enhancement of the laser-induced plasma emission intensity with cylindrical confinement with different diameters (2-8 mm) compared to free expansion in 10 Torr neon.

References

[1] POPOV, A. M., COLAO, F., FANTONI, R. (2010), Journal of analytical atomic spectrometry, 25(6), 837-848.

[2] CHOI, S. J., CHOI, J. J., YOH, J. J. (2015), Optics Express, 23(5), 6336-6344.

[3] FU, Y., HOU, Z., & WANG, Z. (2016), Optics express, 24(3), 3055-3066.

PI_019

Spark discharge assisted Laser-induced Breakdown Spectroscopy for Signal Enhancement of Cu-Fe alloy

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Laser-induced Breakdown Spectroscopy (LIBS) is a conventional method for the analysis of materials for different applications, such as analysis for industry, biomedical applications, forensic sciences, space exploration, and many others. There has been a significant research effort focused on LIBS, however, it suffers from certain limitations like low sensitivity and higher limits of detection as compared to the conventional analytical techniques. Several methods have been adopted to overcome these limitations, e.g. dual laser pulse excitation, spatial or magnetic confinement of the laser-induced plasma, additional plasma source (glow discharge, microwave or spark discharge, inductively coupled plasma) for increased excitation. In this work, we report the results obtained from spark discharge assisted LIBS. The spark discharge is obtained by discharging a capacitor. We studied the plasma of the spark discharge assisted LIBS and of stand-alone laser-induced plasma by OES. The study is done for a Cu-Fe alloy sample (Cu = 95%, Fe = 5%). Nd:YAG laser (Quantel, λ=1064 nm) was used for the experiment. The laser beam was focused between two tungsten pointed electrodes and it ablated the surface of the sample that resulted in the plasma generation. The separation gap between the electrodes was set at a few mm. The capacitor was discharged to produce the spark discharge in order to reheat the laser ablation plasma. The laser source triggered the DC spark discharge. The spectral signal was recorded by Mechelle spectrometer connected to iCCD (iStar DH743, Andor Technology, temporal resolution = 5 ns). We have demonstrated a significant enhancement of the signal emitted from the plasma for the spark discharge assisted LIBS. We studied the enhancement effect by varying different experimental parameters like the orientation of the electrodes, the capacitance of the capacitors, and registration delay times. An enhancement of the plasma emission was observed to be of the factor of ~100.

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Detection improvement of laser-induced breakdown spectroscopy using the flame generated from alcohol-solution mixtures

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It has been proved that the detection of laser-induced breakdown spectroscopy (LIBS) could be improved by the flame [1,2]. In this work, we applied flame enhanced LIBS for the detection of elements in water, while the flame was generated from the mixture of alcohol and aqueous solution. In the measurements, the flame is functioned as an assistance to enhance the LIBS detection, and also worked as a sampling way for the solution. The obtained results indicate that the detection of manganese, calcium, lithium and magnesium were significantly improved by the proposed method. It is found that the flame actually forms an environment for the laser-induced plasma with high temperature and low electron density. With the method, the quantitative analysis was tried out for the element of manganese, and the internal reference of calcium was used. It is interesting to find that, when mixing with the calcium, the minimum detectable concentration of manganese could be lowered and the intensity was greatly increased. According to the result, it is suggested that the proposed method might be a practical way for liquid detection of LIBS because of the simplicity and the effectiveness.

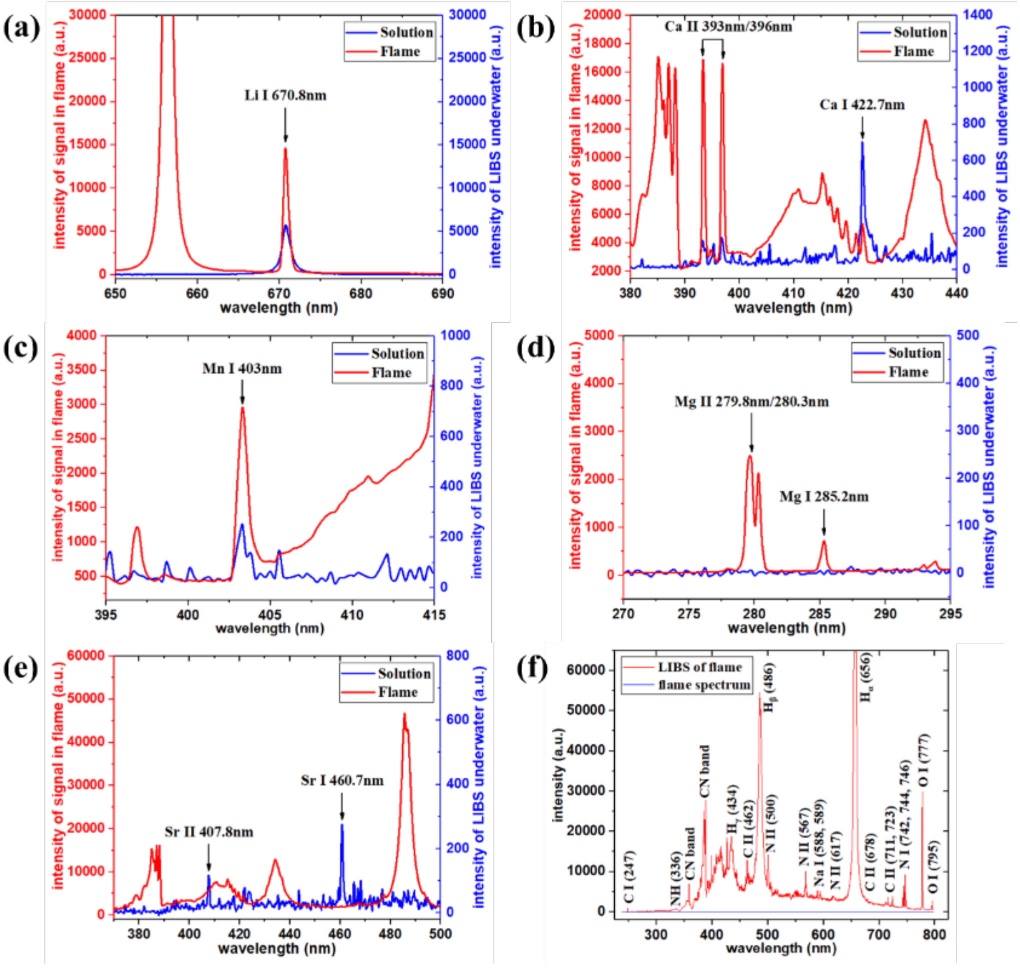

Fig. 1.: Detection comparison between flame-enhanced LIBS, LIBS underwater and the flame: a) Li, b) Ca, c) Mn, d) Mg, e) Sr, f) flame.

References

[1] L. Liu, S. Li, X. N. He, X. Huang, C. F. Zhang, L. S. Fan, M. X. Wang, Y. S. Zhou, K. Chen and L. Jiang, J. F. Silvain and Y. F. Lu, “Flame-enhanced laser-induced breakdown spectroscopy,” Opt. Express 22(7), 7686-7693 (2014).

[2] L. Liu, X. Huang, S. Li, Y. Lu, K. Chen, L. Jiang, J. F. Silvain and Y. F. Lu, “Laser-induced breakdown spectroscopy enhanced by a micro torch,” Opt. Express 23(11), 15047-15056 (2015).

Diode-pumped Nd:YAG/V:YAG composite microchip 1338 nm laser source for LIBS

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Promising laser-light sources for LIBS application are the passively Q-switched diode pumped microchip lasers. [1] Although the generated single pulse energy is relatively low, compared to lasers conventionally used in this application, the diffraction-limited beam of the passively Q-switched microchip laser can be focused to a spot size as small as 1 um in diameter and intensities 1 TW/cm2 could be reached. Up to now in most of the experimental works, neodymium doped crystals like Nd:YAG or Nd:YVO4 as the gain medium emitting at 1064 nm, and Cr:YAG as the saturable absorber were used. [2] We developed a new microchip laser based on combination Nd:YAG/V:YAG, emitting at other neodymium transitions, allowing to generate nanosecond pulses at wavelength 1338 nm. [3] Unlike 1064 nm the radiation at this wavelength is much higher absorbed by water which reduces the dose of radiation reaching retina about hundred-times, making this radiation more "eye-safe". Also the silicone-based detector sensitivity at wavelength 1338 nm is negligible, no special filtering is needed to overcome the CCD dazzling. Both these properties make this radiation source interesting for LIBS. The developed longitudinally diode-pumped Nd:YAG/V:YAG Q-switched microchip laser generated stable and highly reproducible nanosecond pulses with repetition rate 250 Hz at wavelength 1338 nm. The pulse length was 6.2 ns (FWHM) and the mean output power was 33 mW. The single pulse energy and peak power were 0.13 mJ and 21 kW, respectively. Laser was operating in fundamental TEM00 mode. Compact head was developed to integrate the microchip laser system together with the optics for focusing of laser radiation and for collection of laser plasma emission. The laser-induced break-down was successfully reached and corresponding laser-induced plasma spectra were recorded for set of metallic elements and alloys.

References

[1] AMPONSAH-MANAGER, K., OMENETTO, N., SMITH, B. W., GORNUSHKIN, I. B., AND WINEFORDNER, J. D., "Microchip laser ablation of metals: investigation of the ablation process in view of its application to laser-induced breakdown spectroscopy," J. Anal. At. Spectrom. 20, 544-551 (2005).

[2] FREEDMAN, A., IANNARILLI, F. J., AND WORMHOUDT, J. C., "Aluminum alloy analysis using microchip-laser induced breakdown spectroscopy," Spectrochimica Acta Part B: Atomic Spectroscopy 60(7), 1076 - 1082 (2005).

[3] ŠULC, J., JELÍNKOVÁ, H., NEJEZCHLEB, K., AND ŠKODA, V., "Nd:YAG/V:YAG microchip laser operating at 1338 nm," Laser Physics Letters 2(11), 519-524 (2005).

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Pulse Design with a Fiber Laser for Laser-Induced Breakdown Spectroscopy

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Laser-Induced Breakdown Spectroscopy (LIBS) has been getting an increased interest due to its multi element detection and sample preparation free capabilities. Such qualities make LIBS a good promise for in-situ analysis. Currently, portable LIBS systems with small, high repetition rate, laser sources are already present in the market targeting different applications. Such system, however, still present several limitation when dealing with complex samples or underwater operation, due to limited pulse control and low energy range. In this context, more recently, preliminary studies of the use of Fiber Lasers in LIBS applications were presented1–3. These lasers are air cooled and fairly compact allowing for an easier miniaturization, having high quality beams, high average power, good power repeatability and relatively low cost, having a strong potential for LIBS operation, which is still to be fully explored. In this work, a new Fiber Laser with a high degree of control of pulse duration and pulse shape is investigated as a source for LIBS applications. Pulse durations from 10 to 200 ns, repetition rates from single pulse to 250 kHz, and the ability to design tailored multipulse bursts are explored towards the optimization of LIBS operation.

References

[1] Elnasharty, I. Y., Doucet, F. R., Gravel, J. Y., Bouchard, P. and Sabsabi, M., "Double-pulse LIBS combining short and long nanosecond pulses in the microjoule range," J. Anal. At. Spectrom. 29(September), 1660–1666 (2014).

[2] Gravel, J. F. Y., Doucet, F. R., Bouchard, P. and Sabsabi, M., "Evaluation of a compact high power pulsed fiber laser source for laser-induced breakdown spectroscopy," J. Anal. At. Spectrom. 26(7), 1354–1361 (2011).

[3] Veiko, V. P., Lednev, V. N., Pershin, S. M., Samokhvalov, A. A., Yakovlev, E. B., Zhitenev, I. Y. and Kliushin, A. N., "Double nanosecond pulses generation in ytterbium fiber laser," Rev. Sci. Instrum. 87(6) (2016).

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PI_023 S

Ultrasound-Assisted Underwater Laser-induced Breakdown Spectroscopy with High Repetition-Rate µJ-DPSS laser

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The elemental analysis of seawater is often critical to the understanding of marine chemistry, marine geochemistry, and the deep-sea ecosystems. Laser-induced breakdown spectroscopy (LIBS) with the advantage of rapid multi-elements detection, has a great potential for in-situ elemental analysis of seawater. In practice, it is crucial to create a compact, low cost and power saving instrument for the long-term deep-sea observation. A recently appeared diode-pumped solid-state (DPSS) laser seems to be a promising candidate as it is both compact and robust. Additionally, its high repetition rate up to hundreds of kHz can provide a considerable throughput for LIBS analysis. However, the DPSS lasers operate at moderate pulse energies, usually less than one mJ, which cannot sustain stable breakdowns in bulk water. To ensure stable laser-induced plasmas underwater with such a µJ-DPSS laser, we introduced an ultrasound source to assist the breakdown process. The phase interface and mass flow generated by the near-field ultrasound can greatly reduce the breakdown threshold and enhance element-specific emissions. Meanwhile, the high repetition-rate pulses can also improve the breakdown probability and generate unique emission lines originated from the water molecule. We further demonstrate that the high repetition-rate DPSS laser combined with the Echelle spectrometer can provide effective quantitative analysis for metal elements in bulk water.

Acknowledgement

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Laser focusing geometry effects on underwater single- and double-pulse laser-induced breakdown spectroscopy

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Laser-induced breakdown spectroscopy (LIBS) has been proven to be an attractive technique for in-situ elemental analysis in marine applications, with the advantages of multi-elemental and stand-off analysis capabilities. However, compared with that in gases, laser-induced plasma in liquids is far from the ideal case as an emission source for spectroscopic analysis. The plasma generated in water suffers strong confinement and quenching effects, which degrade significantly the quality of LIBS signals and cause strong pulse-to-pulse fluctuations. From a fundamental point of view, laser-induced breakdown process in liquid is quite complicated because of the laser absorption by water, moving breakdown, plasma plume-water interaction, the creation of bubbles, shock wave generation, etc. The mechanisms of laser-induced plasma and LIBS measurement in water are still less well understood compared with those in gas environment. In this work, different plasma diagnostic methods were developed for both single- and double-pulse LIBS in bulk water, including the time- and space-resolved spectroscopy, fast imaging, spectral-resolved imaging, and shadowgraph techniques. Typical composite images of plasma emission together with the surrounding bubble and shock wave were shown in Figure 1. In this presentation, we will show the effects of laser focusing geometry on single- and double-pulse LIBS in bulk water [1-3]. For single-pulse LIBS, we demonstrate that the spherical aberrations lead to an increase in the threshold energy of breakdown, to a formation of an elongated multiple plasma with weak emissions, and to a decrease in the signal intensity as well as LIBS stability. With the aberration minimized focusing, larger focusing angles produce a lower breakdown threshold, a compact plasma with stronger emissions, and a higher signal intensity as well as higher LIBS stability. For double-pulse LIBS, it is shown that by properly post-focusing the second laser pulse beyond the first laser formed bubble, brighter and larger plasmas could be produced due to the higher breakdown efficiency and higher expansion efficiency, which is attributed to a distinct mechanism that the plasma mostly forms at the bubble-water interface and then expands into the gaseous bubble. These results suggest the critical role of laser focusing geometry in producing the ideal plasma source for underwater LIBS. In this presentation, we will also show our latest work on high pressure LIBS and molecular LIBS for bulk water analysis.

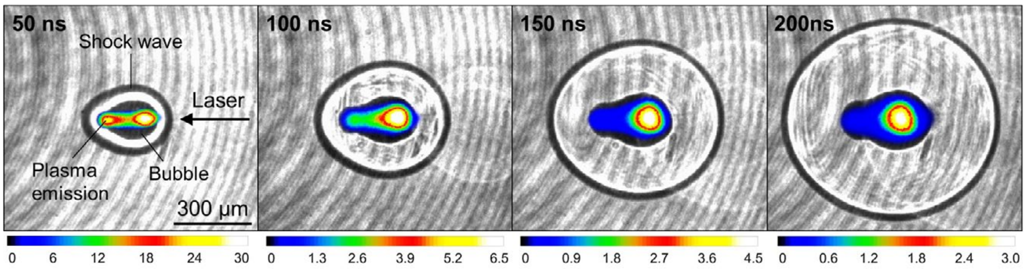

Fig. 1.: Composite images of plasma emission together with the surrounding bubble and shock wave.

References

[1] Y. Tian, L.T. Wang, B.Y. Xue, Q. Chen and Y. Li, “Laser focusing geometry effects on laser-induced plasma and laser-induced breakdown spectroscopy in bulk water”, Journal of Analytical Atomic Spectrometry 34, 118 (2019).

[2] Y. Tian, B.Y. Xue, J.J. Song, Y. Lu and R.E. Zheng, “Stabilization of laser-induced plasma in bulk water using large focusing angle”, Applied Physics Letters 109, 061104 (2016).

[3] B.Y. Xue, Y. Tian, Y. Lu, Y. Li and R.E. Zheng, “Characteristics of the secondary breakdown of DP-LIBS in bulk water with different axial focusing arrangements and laser energies”, Spectrochimica Acta Part B: Atomic Spectroscopy 151, 20 (2019).

Sample temperature influence on laser induced breakdown spectroscopy analysis results

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Additive manufacturing is an actively developing method for producing parts of complex geometry and composition by techniques like coaxial laser cladding. However, to achieve reproducible quality of manufactured metal parts it is necessary to monitor numerous parameters like elemental composition of the deposited material. One of techniques allowing non-destructive online elemental analysis is laser induced breakdown spectroscopy (LIBS). Typically, LIBS is performed at room temperatures, but during laser cladding both the substrate and the deposited material undergo strong heating by a powerful continuous wave (cw) laser. To estimate the effect of high sample temperature on LIBS analysis results a steel sample was heated by a cw laser and then probed by LIBS. Sample temperature, controlled by an optical pyrometer with 50°C accuracy, varied from ambient to melting point. Sample temperature influence on laser plasma spectra and plasma parameters have been systematically studied [1].

References

[1] V.N. Lednev et al. J. Anal. Atom. Spectrom., 2019, 34(3), 607-615.

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The authors gratefully acknowledge the financial support of the Russian Science Foundation (project 16-19-10656).

Spectroscopic study of orange bands of FeO in laser-induced plasma

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Diatomic molecules are observed in emission spectra of meteorites, bolides due to their interaction with Earth's atmosphere [1]. These spectra are usually the sources for calculating of meteor content. However, several molecules (such as FeO) have a complex structure of electronic states that is significantly complicated modeling of spectra at various conditions. The main goal of this work is observation of FeO emission spectra in laser-induced plasma and accurate determination of plasma temperature for these spectra. The evolution of the orange system of FeO bands in the range of 540–650 nm with laser-induced iron ablation is studied. The plasma temperature was calculated by Bolzmann plot for Fe I lines in 510-530 nm. Since late stages of plasma expansion are of our interest we have used a set of 35 Fe I lines, which have relatively low excitation potential. It was demonstrated that the structure of the emission spectra of iron monoxide changes greatly when plasma temperature decreases by a factor of ~2 - from 6400 K at 10 μs to 3100 K at 50 μs. Note that atomic iron lines in the spectra are observed for delays of 10-25 μs. Molecular FeO bands explain well the nature of continuous intense background radiation during laser ablation of steels at late observation times in the range of 530-540 nm. Unfortunately, there is still no detailed assignment of all observed bands, except for bands at 591, 611 nm. Comparison of the obtained spectra with the literature data [2] showed a significant difference between them. It is assumed that the spectra of a laser plasma at temperatures above 2000 K will better describe the burning of meteorites observed in the atmosphere.

References

[1] Borovička J., Berezhnoy A.A. Radiation of molecules in Benešov bolide spectra // Icarus, 278 (2016) P.248-265.

[2] West J.B., Broida H.P. Chemiluminescence and photoluminescence of diatomic iron oxide // J. Chem. Phys., 62 (1975) P.2566-2574

Acknowledgement

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LIBS mapping reaching high performances: from the acquisitions to the treatments

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LIBS mapping has high potential as an analytical tool. Nowadays, the maps are reaching millions of pixels and the subjects of the recent studies (1,2) are complexier. Combining LIBS mapping with other technics shows that it brings new understandings (3). In order to help the user, we codeveloped specifics hardwares and softwares to enhance the LIBS mapping performances. For example, we co-developped the patented solution 'SYSCO' which is an optical system following continuously the position of the plasma in order to adjust the position of the sample. It has been a breakthrough to map irregular surfaces. About the data treatment, as we are often acquiring about a million of spectra, it is impossible to treat manually the whole dataset. Some dedicated softwares have been developed in order to try to keep the quality of the extraction despite the volume of the data. We will also show various tools like an advanced home-made software for mapping which is also including tools to prevent several problems (interference, limits of detections) during the data treatment.

References

[1] FABRE C, DEVISMES D, MONCAYO S, PELASCINI F, TRICHARD F, LECOMTE A, BOUSQUET B, CAUZID J, MOTTO-ROS V. Elemental imaging by laser-induced breakdown spectroscopy for the geological characterization of minerals. Journal of Analytical Atomic Spectrometry. 2018;33(8):1345-53.

[2] CÁCERES JO, PELASCINI F, MOTTO-ROS V, MONCAYO S, TRICHARD F, PANCZER G, MARÍN-ROLDÁN A, CRUZ JA, CORONADO I, MARTÍN-CHIVELET J. Megapixel multi-elemental imaging by Laser-Induced Breakdown Spectroscopy, a technology with considerable potential for paleoclimate studies. Scientific reports. 2017 Jul 11;7(1):5080.

[3] Romppanen, S., Häkkänen, H., Kekkonen, J., Nissinen, J., Nissinen, I., Kostamovaara, J. And Kaski, S.,. Time□gated Raman and laser□induced breakdown spectroscopy in mapping of eudialyte and catapleiite. 2019 Journal of Raman Spectroscopy.

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Femtosecond LIBS imaging with micrometer spatial resolution and femtogram mass detection

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We present femtosecond laser-induced breakdown spectroscopy (fs-LIBS) methods for element imaging with high spatial resolution and subsequent digital reconstruction of chemical images. Fs-lasers produce well defined ablation craters due to limited heat transfer out of the laser-matter interaction volume which is beneficial for high resolution LIBS imaging. Measurements were conducted using a fs-laser that is capable of producing 175 fs pulses at a wavelength of 800 nm which was converted to 400 nm for plasma excitation using a second harmonic generation unit. Samples were placed on a 2D translation stage and each site at the sample surface was measured by one laser pulse. Plasma radiation was detected in backwards direction. LIBS imaging was conducted on different samples: a) commercial Cu grids (150 µm mesh) on polished Mn metal substrate and b) Cu microdot arrays (dot size: e.g. 8 µm x 8 µm, thickness 30 nm) on Si wafer substrates produced by nanoimprint lithography. Our results show accurate digital sample reconstruction for both types of samples. Individual Cu microdots of mass m(Cu) approx. 35 fg and equivalent particle diameter d(Cu) approx. 970 nm were detected by single fs-pulse. Our next measurements will be conducted using a fs laser with 1040 / 520 nm wavelength and 400 fs pulse duration and detecting the plasma emission under oblique angle to verify the results and to attempt fs-LIBS imaging with even higher spatial resolution and lower sampled mass.

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LIBS assessment of spatial cadmium distribution in white mustard

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Quantum dots (QDs) are spherical semiconductor nanocrystals with unique electrical and optical properties. Their use in bioimaging, electronic and optical industry is enabled by their highly stable, size dependant, and consequently tuneable fluorescence.[1,2] The most common Cd containing QDs have a core consisting of CdSe, CdS or CdTe. However, the possibilities of Cd-based QDs applications are limited by the fact that they contain toxic Cd which, depending on the shell of QDs, could be released as highly reactive free Cd^{2+} and could find its way into the environment.[3] Therefore, it is necessary to evaluate the possible risks of Cd containing QDs on various environmental organisms.[2]

The purpose of this study was to determine the difference in toxicity and bioaccumulation of two different types of Cd-based QDs dispersed in aqueous medium in white mustard (Sinapis Alba). Core QDs (CdTe) and core/shell QDs ($CdTe/SiO_2$) were tested and $CdCl_2$ was used as a positive control. After a 72-h exposure, the total content (M_{Cd}) was determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and bioaccumulation factors (BAFs) were established in aboveground and belowground plant parts, the total length of the root was monitored as a toxicologic end-point. Laser-Induced Breakdown Spectroscopy (LIBS) was used to determine the spatial resolution of Cd in model plants. The sample surface area of selected plants was analysed in a raster of spots (map) with a 100□□m step, giving the lateral resolution. Specific areas that showed interesting behaviour of QDs were measured with micro LIBS.

As the obtained results from LIBS measurements have shown, spatial distribution and bioaccumulation patterns of QDs differed from the positive control. The boundary between the root and hypocotyl, where the distribution of QDs varied in between all the Cd sources, was measured by micro LIBS as it was another method of observing the differences in distribution and bioaccumulation of used Cd sources.

References

[1] B. A. Rzigalinski and J. S. Strobl, Toxicol. Appl. Pharmacol., 2009, 238, 280–288.

[2] R. Hardman, Environ. Health Perspect., 2006, 114, 165–172.

[3] P. Modlitbová, P. Pořízka, K. Novotný, J. Drbohlavová, I. Chamradová, Z. Farka, H. Zlámalová-Gargošová, T. Romih and J. Kaiser, Ecotoxicol. Environ. Saf.,

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Characterization of mineralized drilling cores using LIBS-based imaging

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Scanning Laser Induced Breakdown Spectroscopy (LIBS) is an upcoming technology for the characterization of geological sample material in particular fields of application. It has potential for rapid non-destructive and in-situ multi-element geochemical screening, which could in particular be useful for relatively large and unpolished geological samples, such as drilling cores. Geological samples are very complex materials. They consist of numerous different mineral assemblages that usually show a rather heterogeneous distribution. The analysis of materials composed of several different matrixes is very challenging both in quantification and in validation. One of the challenges to be addressed is the choice of reference measurements both for calibration and for validation purposes. The surface (2D) of a geological sample may not represent the bulk (3D) composition of the sample. For coarse-grained geological samples, classification seems very effective for handling matrix effects in LIBS-based images. Classification makes explicit use of the heterogeneous nature of the sample material and the resulting matrix effects. Chemically similar phases will produce similar LIBS spectra with similar matrix effects. Very promising results have been obtained for supervised classification of imaging LIBS data for chromitite ore, as well as for the subsequent quantification of the mineral and metal content. Based on the results, a guideline for supervised classification of LIBS-based imaging data for course-grained geological samples has been developed. Promising results have also been obtained for polymetallic massive sulphide ore. With the appropriate reference measurements and the application of common classification and calibration techniques, it was possible to calibrate the LIBS-based images with respect to the base metals, and provide a semi-quantitative analysis of the base metal distribution in the ore material.

Quantitative micro-imaging of carbon and trace impurities : A breakthrough for refining industry ?

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Nowadays, the purification of petroleum products has become a highly challenging task. Such processes involve heterogeneous catalysts, poisoned by carbon and metallic species over time. Improvement of these processes is therefore a prior objective for refiners to reduce the environmental footprint and to answer the world increasing demand for fuels and chemicals. Carbon and metallic poisons on catalysts imply spatiotemporal gradients in the ppm-range that have never been investigated at the grain scale at such low concentrations. Even so, an accurate knowledge of these elemental distributions is today required to enable a more realistic process modelling. For the first time, we propose a spatially resolved quantification of carbon, nickel, and vanadium up to the ppm-range in porous heterogeneous catalysts. Carbon elemental detection and imaging can be reach only by few techniques (TOF-SIMS, LA-ICP-MS, STXM), which are either not convenient for large samples, not suitable for quantification analysis, or have a too low sensitivity regarding such light elements. We developed a LIBS-based elemental analysis combined with a particular sample preparation method and a specific distance transform based processing. That is the first approach able to show 2D LIBS imaging with a micro-scale resolution, covering a concentration from few ppm to %, as well as quantitative distribution profiles for carbon and metallic trace impurities in catalyst materials at the grain scale (c.f. figure 1). This study highlights the growing interest of LIBS in industry and opens the way of a revolutionized understanding of refining allowing the establishment of accurate models to better predict, control, and improve the purification processes.

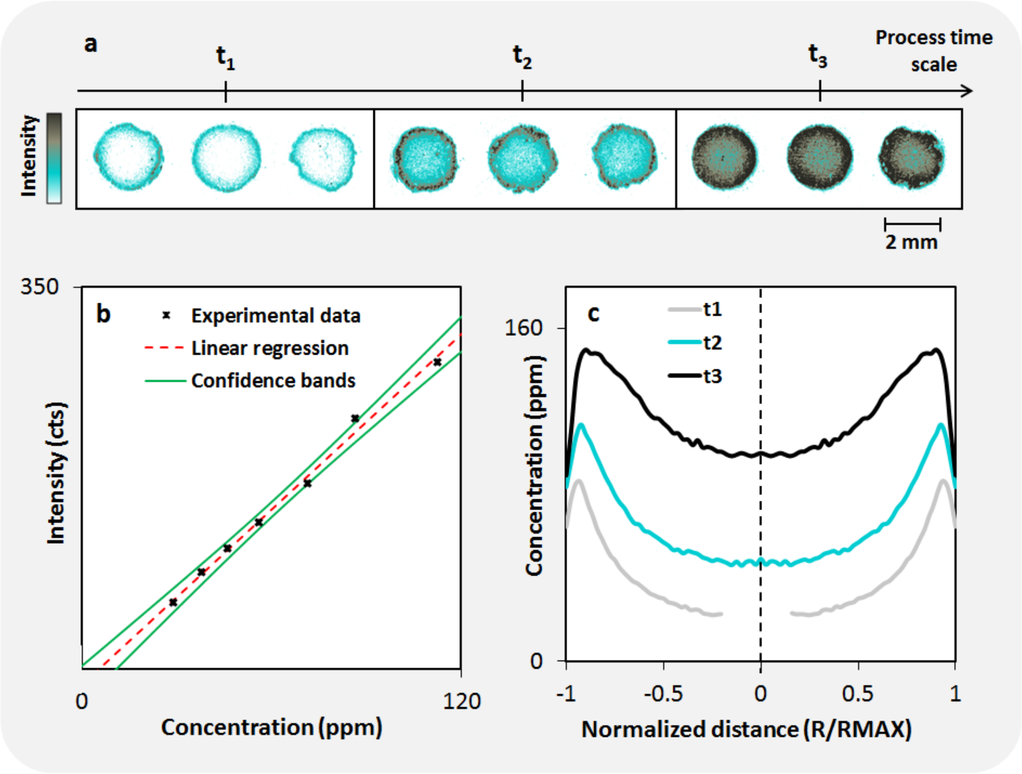

Fig. 1.: Figure 1 : Example of results for vanadium impurities. a) LIBS images of catalysts sections for 3 different process times. b) Calibration curve for quantification. c) Quantitative profiles.

Chemical imaging and analysis of metals by optical emission spectroscopy methods LIBS and LA-SD-OES

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For the element imaging of steel samples, we combined two optical emission spectroscopy techniques, LIBS (Laser Induced Breakdown Spectroscopy) and Spark OES (Spark Optical Emission Spectroscopy) and we investigated differences and advantages of the individual methods to the combination: Laser Ablation-Spark Discharge-Optical Emission Spectroscopy (LA-SD-OES). The combination of both methods uses a voltage of up to 3 kV which is applied to a tungsten electrode connected with a 25 nF high voltage capacitor. A short laser pulse (Nd:YAG, 1064 nm, 7 ns) with pulse energy of 1-90 mJ triggers the excitation of the electric spark. The spark discharge was guided to the laser spot on the sample surface. Hence, a localization of the electric spark and good spatial resolution in element imaging was achieved. A comparison of emission spectra of various materials measured with LIBS and LA-SD-OES displayed differences concerning the line intensities and the appearance of spectral lines exclusively in LA-SD-OES.

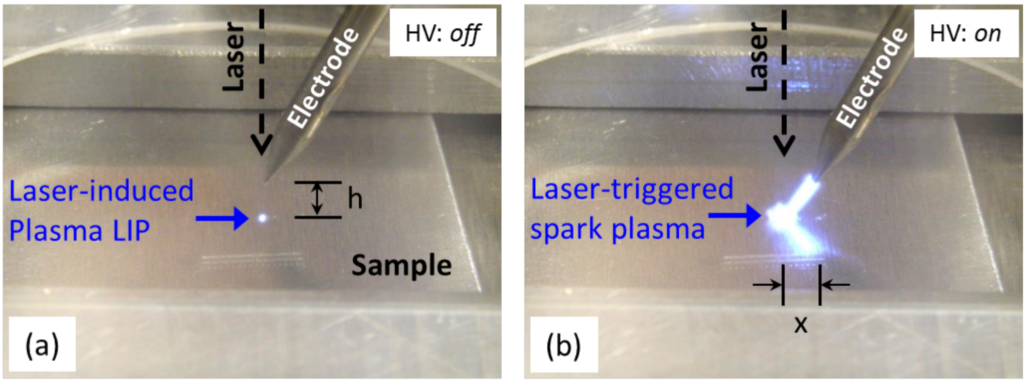

Fig. 1.: Laser-induced plasma (left) and laser-triggered spark discharge plasma (right) on aluminum in air.

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Detection of minerals in Cancer patients' blood serum using LIBS technique

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Abstract Analysis of trace elements in human blood has the potential to reveal retrospective information about an individual's health status and exposure. The most characteristic patterns of a modern human being are deficiency of essential and excess of toxic trace elements. Such a deficiency or excess frequently occurs due to defects in trace element content in some organs or increased requirements of an organism. As trace elements are incorporated into the human body according to the nutritional and health growth process, serum samples of the cancer patients can reflect the body burden during disease probability. Therefore, the most recent basic data on participation of essential trace elements in physiological processes, metabolism, routes and volumes of entering to the body, relation to various diseases, medical applications with a special focus on some minerals. For each element there is an optimum range of concentrations to perform vital functions. At deficiency or excessive accumulation of elements, serious changes can occur in the body, violating activities of enzymes, directly or indirectly dependent on them. The equipment used for the analysis typically involves sophisticated and costly analytical instruments such as the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Atomic Absorption Spectroscopy (AAS). The aim of the present work is to investigate the possibility of using LIBS as a new, non-invasive and promising tool for detection of trace elements in biological tissues such as blood samples which represent a chemically inert and highly mineralized tissue using. So the target was to use LIBS technique in the same analysis for detection of minerals as K, Ca, Mg, Si, Fe, Pb and Zn in cancer patients' serum. Qualitative analysis has been done to detect the presence of trace elements in serum samples where the plasma spectrum showed information about these elements in the sample. This information was in the form of emission lines located at specific wavelengths as well as the intensity and the relative intensities of the lines which are important for analyzing the samples and for detection of heavy metals and minerals. The effects of the experimental parameters on the emission lines were studied and the local thermodynamic equilibrium (LTE) in produced plasma was investigated. The transient plasma condition was verified at specific time region (300–500ns) in the plasma evolution corresponding to its dynamic expanding characteristic. The information obtained from the trace elements' spectra of blood serum in this study substantiates the potential of blood minerals as a biomarker. Keywords: LIBS, blood, Plasma

References

[1] H. R. Griem, Plasma Spectroscopy, McGraw –Hill, Inc. (1964)

[2] W. Lochte - Holtgreven, Plasma diagnostics. North Holland, 135(1968)

[3] W. T. Chan and R. E. Russo, Spectrochim. Acta Part B., 46 (1991), 1471–1486

Implementation of laser spectroscopy in skin tumor analysis

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Skin cancer is the most common type of malignancy in the Caucasian population and its incidence is increasing epidemically. Skin cancer is classified into two groups: non-melanomatous skin cancers, represented by two major forms, Basal Cell Carcinoma and Squamous Cell Carcinoma. The second group figures Malignant Melanoma. The most frequent cutaneous malignancy worldwide isBasal Cell Carcinoma which accounts for 80-85% of all skin cancer, Squamous Cell Carcinoma accounts for 15-20% of non-melanomatous skin cancers. The lowest incidence of the above-named types of skin cancer is Malignant Melanoma which accounts for 4,5% of new cases. On the other hand, it represents the deadliest form of skin malignancy.

Nowadays, the only diagnostic method to perform a histological examination which is typically based on a visual inspection of the tissue sections by light microscopy. The examination itself and determining the type and extent of the skin lesion depends on the pathologist's experience. One of the mean to obtain more information about a particular case is to find out a chemical composition and its distribution in the tumor itself. The presence of increased concentrations of heavy metals was detected in the skin tumors. Laser Spectroscopy techniques (namely Raman spectroscopy and Laser-Induced Breakdown Spectroscopy) may be applied to detect this chemical composition (molecular and elemental) and its distribution.

The objective of the project is the implementation of laser spectroscopy methods to determine the molecular and elemental composition of collected samples of the skin tumors. Provided spectroscopic analysis will extend the information obtained from a standard histological examination. The output will contribute to the emerging field of digital histopathology, providing more accurate information about the tumor itself and its margins, which is one of the main indicators of radicality of the operation.

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Accurate recognition of glioma border tissue based on laser-induced breakdown spectroscopy

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Malignant tumors are a growing problem that threatens the health of human life today. Among them, brain tumor is one of the most serious disease. In 2017, it is estimated that there are more than 23,000 brain and other neurological tumors in the United States with a mortality rate of 70%. Furthermore, the most common type of brain and central neurological system tumors is malignant glioma, with a 4-year survival rate at only 7.1%. One of its main features is to grow in a diffuse manner beyond the location of the primary tumor. Because of this, tumor infiltration boundary is not clear, resulting in difficulty in resecting the total tumor. Nowadays, Magnetic Resonance Imaging (MRI), Ultrasound and Fluorescence angiography have been proposed to identify the glioma infiltrating boundary. However, it is difficult to meet the needs of practical applications in terms of boundary determination accuracy, detection sensitivity, and surgical cost. Meanwhile, the brain shift during the surgery also causes some influences. In this work, we proposed to identify the different regions of the glioma and around tissues by Laser-induced Breakdown Spectroscopy (LIBS) combined with machine learning methods. Several unsupervised learning methods like principal component analysis (PCA) and K-means were used to cluster the spectral data of glioma and besides area. After selecting feature lines with Random Forests (RF), Supervised methods like Support Vector Machines (SVM) and k-Nearest Neighbor (kNN) were used to do the identification. The classification accuracy achieved at 96.0% and 100.0%, respectively. This laid the foundation for the further use of LIBS technology for the determination of glioma infiltration boundaries.

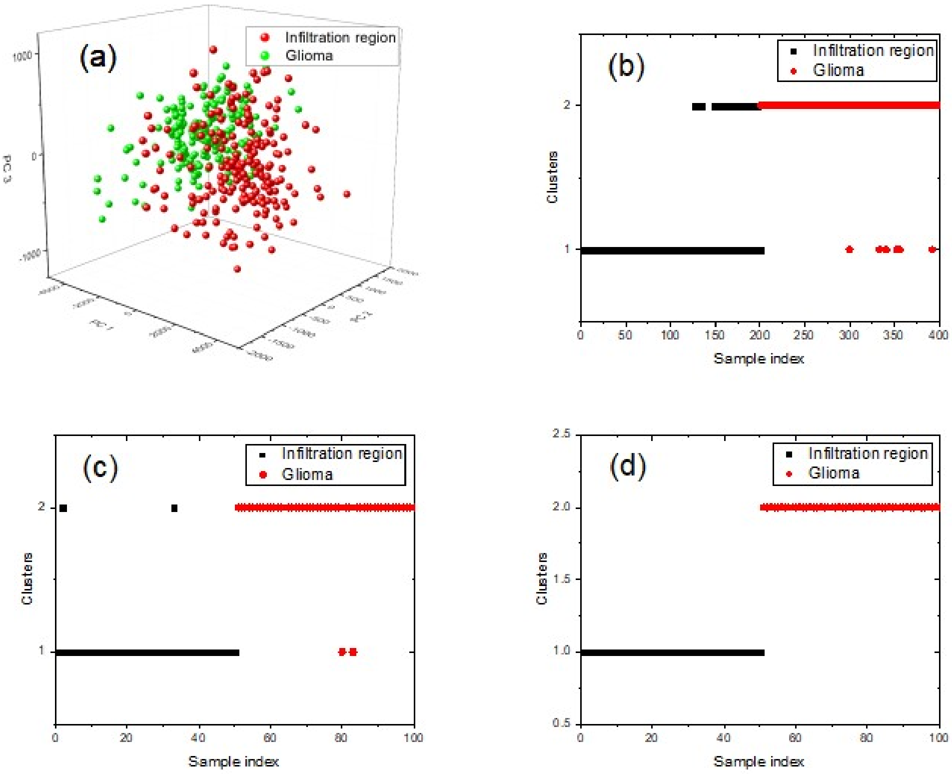

Fig. 1.: The unsupervised clustering and supervised classification results of LIBS spectra from infiltration region and glioma. (a) the clustering results of PCA; (b) the clustering results of K-means; (c) the classification results of SVM; (d) the classification

References

[1] Ostrom Q T, Gittleman H, Liao P, et al. CBTRUS Statistical Report: Primary brain and other central nervous system tumors diagnosed in the United States in 2010–2014 [J]. Neuro-Oncology, 2017, 19(suppl_5): v1-v88.

[2] Pisipati S, Smith KA, Shah K, et al. Intracerebral laser in-terstitial thermal therapy followed by tumor resection to minimize cerebral edema[J]. Neurosurg Focus, 2016, 41(4): e13.

[3] Wang Q, Teng G, Qiao X, et al. Importance evaluation of spectral lines in Laser-induced breakdown spectroscopy for classification of pathogenic bacteria[J]. Biomedical Optics Express, 2018, 9(11): 5837-5850.

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Methodology for the optimization of LIBS analysis of soft tissues

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Biological tissues contain essential trace elements, such as Zn, Cu, Fe, which are known to have an important role in various metabolic processes taking place in the human body. The optimum level of concentration of these elements is needed to maintain the proper function and health of the human body [1]. In this work, we focused on the optimization of laser-induced breakdown spectroscopy (LIBS) methods used for a detection of these elements in soft tissues. Analysis of such samples using LIBS could be used for numerous biological applications in the future, such as the utilization of listed trace metals as the potential biomarkers for cancer tissue diagnostics [2, 3]. Laser-induced breakdown spectroscopy was applied to perform the elemental analysis of soft tissue samples – mouse kidneys. In order to get the optimum signal in the multi-element LIBS measurements of kidneys, the following experimental parameters: side input slit, grating, central wavelength, gate delay, laser energy, and wavelength were adjusted and the signal dependence was studied. The process of optimization of experimental settings and conditions was described. The main goal was to achieve the highest possible signal to noise ratio data. Due to the different sample size, a system of unification and mutual comparison was proposed. All the parameters were tested for zinc and the limits of detection (LOD) were estimated. The analysis accuracy and repeatability were further demonstrated by the determination of the concentration of detected elements. Obtained results suggest the ideal experimental parameters settings in order to obtain the best possible signal to noise ratio to analyze soft tissues using LIBS.

References

[1] C. G. Fraga, Relevance, essentiality and toxicity of trace elements in human health. Mol. Asp. of Med., 2005, 26(4-5), 235–244.

[2] B. Busser, Elemental imaging using laser-induced breakdown spectroscopy: A new and promising approach for biological and medical applications. Coord. Chem. Rev., 2018, 358, 70-79.

[3] R. González de Vega, Quantitative bioimaging of Ca, Fe, Cu and Zn in breast cancer tissues by LA-ICP-MS. Journal of Analyt. Atom. Spec., 2017, 32(3), 671–677.

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This research has been financially supported by the Ministry of Education, Youth and Sports of the Czech Republic under the project CEITEC 2020 (LQ1601). This work was also carried out with the support of CEITEC Nano Research Infrastructure (MEYS CR, 2016–2019), CEITEC Nano+ project, ID CZ.02.1.01/0.0/0.0/16_013/0001728.

Optimizing the Laser Ablation of Soft Tissues

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The issue of laser-matter interaction is of great importance in the material analysis using laser-ablation-based techniques, such as Laser-Induced Breakdown Spectroscopy (LIBS). The distribution of elements in soft tissues is an important source of information, which can facilitate diagnosing. LIBS is shown to be a viable option for qualitative imaging of specific elements in biological tissue material. The laser ablation is driven namely by the proper selection of laser wavelength and irradiance. Optimal soft tissue measurement parameters were determined by the pulse wavelength optimization process. Tested samples were mouse kidneys fixed in paraffin. Gradually, all possible wavelengths of laser pulse were tested: 1064 nm, 532 nm and 266 nm. The energy within the range from 1 mJ to 25 mJ, setting with a step of 5 mJ, was tested for energy laser pulse. The signal dependence of individual elements was monitored with respect to their concentration. Moreover, the resulting wavelength and laser energy values were determined based on the signal-to-noise and signal-to-background ratio calculation. The essence of this research is a fundamental study for future research on the distribution of the selected elements in the tumours. That could lead to the robustness increase in determining the type and extent of malignant lesions based on the deeper knowledge of tissue metabolism.

Acknowledgement

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Nanosecond Laser Induced Breakdown Spectroscopy for Biofouling Analysis and Classification of Fouling Constituents

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Biofouling has been a serious problem affecting marine industry for a long time. Marine biofouling refers to the undesirable growth and adhesion of marine organisms such as barnacles, macro algae and microbial slimes on immersed structures. Biofouling composition is determined by collecting samples from marine structures and vessels and analyzing them in laboratories. Alternatively, an approach of online sensing based on Laser Induced Breakdown Spectroscopy(LIBS), which consists of analysis of the spectral emission from laser induced plasma, can be considered for the elemental composition of biofouling. Since, marine biofilm is an intricate community of bacteria and algae, LIBS spectra can provide an insight into the chemical composition of the biofilm constituents. The analysis of marine biofouling using LIBS has not been attempted previously. In the present work, laboratory scale LIBS technique is used to analyze biofouling samples and its constituent common water-borne algae and bacterial species. LIBS spectra were acquired for Biofilm samples grown on fiber-reinforced plastic (FRP) substrates suspended in the tropical Indian Ocean for a period of 10 days at a depth of 1 m, in the intertidal region at a distance of 480 m from the shore. LIBS database were created under lab controlled conditions for the selected biofilm constituent algae (Nitzchia sigma and Chaetoslorenzianus) and bacterial (Pseudomonas aeruginosa, Bacillus subtilis, E.coli) species. As shown in fig.1, it has been possible to establish the LIBS technique in in-situ conditions for acquiring the spectra and its rapid classification using PCA technique. The database would serve as a means for rapid identification of marine fouling bacteria and algae species. Further studies are planned by introducing an appropriate delay during spectral acquisition in order to avoid adverse influence of continuum.

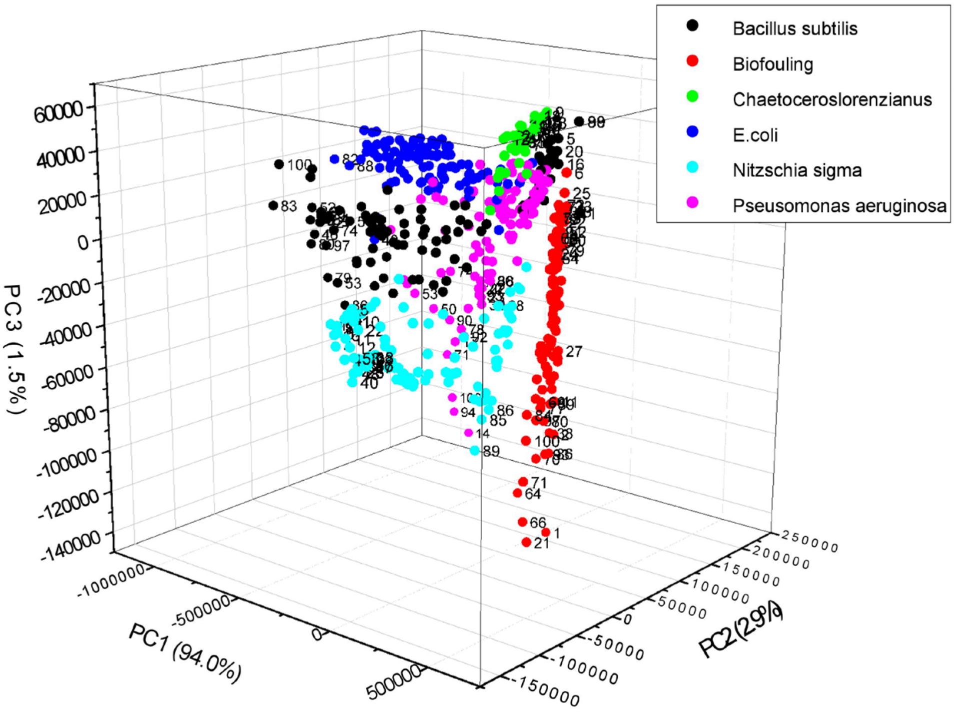

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Fig. 1.: Figure shows Principal Component Analysis (PCA) results classifying the LIBS spectra acquired for biofouling and its constituents qualitatively. Three principal components account for 94.5% of total variation.

References

[1] BENJAMIN A.S. VAN MOOY, LAURA R. HMELO, HELEN F. FREDRICKS, JUSTIN E. OSSOLINSKI, BYRON E. PEDLER, DANIEL J. BOGORFF & PETER J.S. SMITH, “Quantitative exploration of the contribution of settlement, growth, dispersal and grazing to the accumulation of natural marine biofilms on antifouling and fouling-release coatings”, Biofouling, 30 (2), 223–236, 2014.

[2] PAVEL POŘÍZKA, PETRA PROCHAZKOVÁ, DAVID PROCHAZKA, LUCIA SLÁDKOVÁ, JAN NOVOTNÝ ,MICHAL PETRILAK, MICHAL BRADA, OTA SAMEK, ZDENĚK PILÁT, PAVEL ZEMÁNEK,VOJTĚCH ADAM, RENÉ KIZEK, KAREL NOVOTNÝ AND JOZEF KAISER, “Algal biomass analysis by laser-based analytical techniques--a review”, Sensors, 14 (9), 17725–17752, 2014.

[3] R. A. PUTNAM, Q. I. MOHAIDAT, A. DAABOUS, AND S. J. REHSE, “A comparison of multivariate analysis techniques and variable selection strategies in a laser-induced breakdown spectroscopy bacterial classification”, Spectrochimica Acta Part B Atomic Spectroscopy, 87, 161–167, 2013.

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LIBS for real-time monitoring of laser-induced thermal damage in laserosteotomy: from dehydration to full carbonization

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Laserosteotomes will only be clinically applied if they do not carbonize the tissue. This can only be ensured with an irrigation system with correctly tuned water and air flow rate. Well-designed irrigation helps avoiding thermal damage, increases ablation speed, and accelerates healing while too little water leads to bone carbonization, and too much water decreases the ablation efficiency [1]. State-of-the-art for determining the irrigation parameters is to apply water and air flow rates based on pre-performed experiments without monitoring the bone surface in real-time. The lack of real-time monitoring of the laser-induced thermal damage can thus result in carbonization, caused by either a malfunction in the irrigation system or by unexpected changes in the properties of the tissues from patient-to-patient (or even point-to-point due to an inhomogeneous structure). Authors recently demonstrated that LIBS can classify fully carbonized bone from not carbonized one [2]. While such a classification can avoid further carbonization, even localized carbonization on the surface of the bone can still prolong the healing process. There are several stages before full carbonization occurs, such as dehydration and early carbonization. The detection of these early signs makes prospective carbonization prediction possible. This study aims at finding a regression between all steps of laser-induced thermal damage. Therefore, the spectrum of localized plasma generated in the ablation spot, together with the number of shots sent to the bone without irrigation was recorded using an in-house fiber-coupled Echelle spectrometer. Later on, based on the recorded spectra, regression models were trained. The model used were regression tree (single tree and also an ensemble of several trees), support vector machine, and a convolutional neural network. Finally, we calculated the root mean square error of each model and applied the trained models to the data collected afterwards in real-time.

References

[1] H. Abbasi, et al., “Effect of cooling water on ablation in Er:YAG laserosteotome of hard bone”, Proc. SPIE 10453 (2017).

[2] H. Abbasi, et al., “Laser-induced breakdown spectroscopy as a potential tool for autocarbonization detection in laserosteotomy”, J. Biomed. Opt. 23 (2018).

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Lithium from breast milk of medicated mothers affects the thyroid and kidney functions of infants

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Lithium toxicity limits the use of lithium during pregnancy, whereas few studies with very limited sample size have been reported on the impact of lithium on the lactation processes and health of mother-baby pair. Here, we have employed laser induced breakdown spectroscopy to trace lithium in the kidneys of breast feed infants (baby rats) of lithium medicated mothers (rats). The mother was assumed to be a bipolar disorder and was being administered with lithium therapy. With the presence of lithium in the breast milk of lactating mother, the infant's blood demonstrated presence of lithium and elevated urea nitrogen. With further investigation, we found enhanced potassium level as principle component for classification of the subjects other than lithium. The renal enhanced potassium was associated to low Nephrine expression calculated from immunohistochemical stained kidney section of subjects caused by lithium. Previously, we detected lithium traces in the breast milk of mother (rat) administered on lithium. In this article, we employed laser induced breakdown spectroscopy (LIBS) and energy dispersive energy dispersive X-ray fluorescence (XRF) to assess lithium effects in kidney. We applied principle component analysis on LIBS and XRF measured spectra to classify the control and lithium group followed by a supervised linear discriminant analysis (LDA). To measure lithium plasma levels, we employed mass spectroscopy. To assess the primary indicator of likely affected organs suggested by literature, we measured T_4 hormones and blood urea nitrogen (BUN) from the blood of baby rats using enzyme linked immunosorbent assay (ELISA). Further, we also performed immunohistochemical staining on section of infant's kidneys with Nephrin for further investigation.

Characterization of LIBS as the distribution of Lithium and elements throughout the Body

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Lithium-based salts and drugs have been successfully used to treat many mental disorders Including bipolar disorder and Alzheimer's. However, the therapeutic mechanism is not well characterized due to the limitation of detecting lithium in organs and cells. Here, we have employed laser induced breakdown spectroscopy (LIBS) for in situ detection of lithium in biological tissues and organs along with multi-elemental analysis. Besides, we have developed methods to employe LIBS for biological applications. Lithium spectral emission was observed at 670.7 nm in thyroid, salivary gland, mammary gland of subjects (rats) when treated with lithium. We also traced lithium in breast milk of mother rat when administered with lithium. The lithium emission intensity was positively correlated with tissue lithium concentration, which is ~1ppm. LIBS is ideal for characterizing the distribution of lithium and other elements throughout the body.

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The use of laser spectroscopy techniques in studying zooplankton

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It has recently been discovered that some zooplankton organisms (viz. several taxa of sea crustaceans) accumulate trace elements like lithium, arsenic and uranium [1]. Causes and mechanisms underlying this phaenomenon are unclear. It is therefore of interest to find out which changes of chemical composition of tissues accompany the accumulation of the elements. The goal of this study was to establish correlations between analytical signals of Li, As, and U, on the one hand, and analytical signals of other elements and molecules comprising the tissues, on the other hand. To this end, atomic and molecular spectroscopy data were recorded and compared. Atomic spectroscopy was represented by laser-induced breakdown spectroscopy (LIBS) and ICP-MS with laser ablation (LA-ICP-MS). LIBS was chosen based on its rapidity and sensitivity towards light elements (like Li), while LA-ICP-MS was needed to ensure sufficient sensitivity towards As and U. The instrumentation used enabled to obtain emission spectra in a wide wavelength range (186–1049 nm). Molecular composition was studied by Raman scattering spectroscopy (excitation at 780 nm). Bulk composition data, obtained by ICP-AES and ICP-MS after digestion, were also available. Correlations between intensities of atomic emission lines, mass spectrum peaks, and parameters of Raman bands were calculated. We have also made an attempt of sample classification. All this was achieved by well-known chemometric approaches (PLS, PCR, PCA, classification tree, and ordinary LS). The results show that, in general, high level of accumulated trace elements positively correlates with a band-rich Raman spectrum with relatively low fluorescence background. Our collection of samples (ca. 30 pcs.) comprised several crustacean species, and Raman spectral fingerprints of subclass Copepoda were substantially different from those of other taxa. Apart from that, uranium content exhibited weak negative correlations with content of most other elements.

References

[1] LOBUS, N.V. Elemental composition of zooplankton in the Kara Sea and the bays on the eastern side of Novaya Zemlya. Oceanology, 56 (2016), pp. 809–818.

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A comparison of calibration-based and calibration-free analysis of zooplankton by LIBS

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The object of this study is zooplankton, and more specifically, several taxa of crustaceans, some of which show an unusual enrichment of trace elements (mainly Li) in their tissues. A rapid and sensitive method for elemental analysis of zooplankton is required, which would be easy for on-site implementation (i.e., on board during cruises). The LIBS is well suited for this purpose. Due to a lack of certified reference materials, it seems reasonable to use calibration-free (CF) LIBS in this case. We also present a comparison of the CF-LIBS results with those obtained by a conventional (calibration-based) technique. Pelletized samples of zooplankton were ablated by the 4th harmonic of Q-switched Nd:YAG laser (266 nm). Emission spectra were recorded using a Czerny-Turner spectrograph (resolution of 0.05 nm at 589 nm) with a gated ICCD camera within the range of 201–681 nm. Line selection for reliable plasma diagnostics as well as for analytical measurements was guided by modeling which involved solving radiative transfer equations under the assumption of LTE. In general, the obtained element ratios in CF-measurements are consistent with ICP-MS and ICP-AES data. Due to the nature of the samples, analysis involved mainly alkaline and alkaline earth elements (Li, Na, Mg, Si, P, K, Ca, Sr). As for the calibration-based approach, its straightforward use was hampered by differences in colours and reflection coefficients of samples, so that we had to use normalization to obtain valid calibration curves. Differences in sample densities also made contributions to signal uncertainties.

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Double-pulse LIBS spectrometer LEA-S500 for quantitative analysis of the materials of different origin.

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Elemental hair analysis gives an opportunity to detect a disturbance in mineral metabolism, to identify the ratios of vital and toxic microelements in a human body. What is more, it can detect possible reasons for deviations in the neuro-development of children and a source of deterioration of health at an elderly age. [1]. The method's sensitivity helps to accurately detect the elements found in hair. Our methodology is suitable for the routine analysis of 30 micro- and macroelements in human hair. Minimal sample processing is conducted according to the IAEA [2] requirements. Small sample quantity makes it possible to conduct the analysis in different parts of a hair lock. It gives an opportunity to study the evolution of elements concentration that happened within short periods of time, not disturbing the examined person at the same time. Water is essential for the normal functioning of a human organism. The analysis of the solid residue of water on laser elemental analyzer LEA S500 using LIBS methodology is targeted towards getting the most accurate information about the water's elemental composition. Less than 15 mg of solid residue is needed for elemental analysis, hence, the LIBS method can compete with the widespread ICP-OES and ICP-MS methods [4, 5]. The solid residue is pressed into a pill made from polyvinyl alcohol and then used as a base. This way is used for creating calibration samples (e. g. based on calcium carbonate, calcium chloride, magnesium sulfate, etc.). They replicate the contents of a solid residue that contains or does not contain supplements of different microelements.

References

[1] LeClair JA, Quig DW. Mineral status, toxic metal exposure, and children's behavior. J Orthomolecular Med 2001;16:13-32

[2] Preparation of hair for measurement of elements by inductively coupled plasma-mass spectrometry (ICP-MS). Biological Trace Element Research, 1998, v.62, p.167–182

[3] ISO 11885:2007 Water quality. Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)

Acknowledgement

In this work, we report about the applications of the series-produced elemental analyzer LEA S500 for the analysis of different materials of natural and anthropogenic origins. We

have developed the methodology for the analyses of 30 chemical elements in human hair, of a wide range of chemical elements in drinking water.

Critical review on the use of normalization in LIBS

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Laser-induced breakdown spectroscopy (LIBS) allows achieving quantitative multi-elemental analyses. However, the LIBS spectra are very sensitive to the sample chemical and physical properties, as well as to fluctuations of the experimental conditions. The consequence is that significant fluctuations of the LIBS spectra can be observed with a negative influence on the analytical performance of the technique. Finally, many analysts often try to reduce these fluctuations by normalization techniques in order to improve the performance of further quantitative analyses. However, adopting the most relevant normalization approach remains today an open question. A comprehensive state-of-the-art regarding LIBS spectra normalization will be presented, with an emphasize on the most frequently applied techniques. We will present, through selected examples, a critical point-of-view about the different normalization approaches and the necessity to accurately assess them and compare their performance.

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Application of laser induced breakdown spectroscopy for stainless steel alloys quantification

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Laser-induced breakdown spectroscopy (LIBS) is applied to quantitative analysis of 304 and 316 and 4140 steel alloy samples. The plasma is generated by focusing a nanosecond pulsed Nd:YAG laser operating at its fundamental wavelength ; 1064 nm, in ambient air on steel target. Plasma optical emission is collected via an optical fiber of 400 μm diameter and conducted to the 40 μm entrance of an Echelle spetcrometer (ARYELLE 200, LTB) with a spectral resolution of 9000. The spectrometer is coupled to a gated ICCD camera (Andor 334-18F-03). Experimental conditions (i.e. laser energy, delay time, gate width and gain) are optimized for high S/N ratio principally for trace elements. Laser induced plasma are characterized in terms of registered spectra, electron density and electron temperature assuming the LTE and optically thin plasma conditions. The quantification results of samples using the CF-LIBS method were in a good agreement with the micro X ray fluorescence (μXRF) measurements. The correction of self-absorption using internal reference method on CF-LIBS has been discussed. The average relative errors on Cr, Ni, and Fe calculated concentration were less than 5%.

Quantification of binary alloys used in prosthetic implants by laser-induced breakdown spectroscopy

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One of the main problems that cause fixation loosening in prosthesis and implants is the stress shielding due to bone reabsorption with time. This problem can be solved through the development of low Young-modulus alloys like Ti-Nb alloys. In this work, the capability of laser-induced breakdown spectroscopy (LIBS) for the quantification of sintered binary samples with different proportion of Nb and Ti is tested. For that purpose, nine sintered samples where the concentration of niobium varied between 5% and 45% were analyzed and several emission lines from Nb and Ti were compared. In a preliminary step, laser pulse energy and acquisition delay time were optimized taking into account the intensity and the signal-to-background ratio. For the quantification, different procedures were tested (signal intensity, signal-to-background ratio and intensity ratio of Nb and Ti emission lines) and the best results in terms of low data dispersion and good linear fitting were obtained when plotting the ratio of niobium intensity to titanium intensity vs. niobium concentration.

LIBS: A potential tool for accurate quantification of precious elements

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Quantification and certification of the caratage of precious alloys are carried out conventionally by fire assay which is considered to be gold standard and is also very accurate. On the flip side, this method is very cumbersome and also destructive. In recent years, Laser Induced Breakdown Spectroscopy (LIBS) has developed as a versatile elemental analysis tool which attracted enormous attention, owing to its broad range of applications. The advantages of this method are: rapid and sample preparation free analysis with microgram destruction to the sample and possibility of cost effective instrumentation. In view of this, a LIBS based methodology for testing the purity of gold & its alloys with a better accuracy compared to the existing process is carried out. A 532nm optical emission from Nd:YAG (Q-Smart, Qunatel) having pulse duration 6ns is used to achieve breakdown threshold irradiance for gold alloys. The plasma emission from the sample surface is imaged on to the spectrograph slit by using an optical fiber. A high resolution, cross dispersion echelle spectrograph (Mechelle, Andor) system coupled with an ICCD (iStar, Andor) is used for this study. Various experimental parameters such as gate delay, gate width, laser energy etc. have been optimized. Different data analysis methodologies such as calibration free LIBS (CF-LIBS) are attempted to extract meaningful data for accurate quantification. Single shot LIBS measurements, which is of great importance considering the commercial value of the sample, has been successfully tested and the results are encouraging and demonstrating the robustness of LIBS for such applications.

Quantitative Analysis Of Low Atomic Number Elements By Laser Induced Breakdown Spectroscopy Technique

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The Laser Induced Breakdown Spectroscopy (LIBS) technique has several advantages, such as minimal sample preparation, faster results and less damage to the sample compared to other techniques such as X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) [1-3]. In addition to that, it is also a more successful technique for the analysis of light elements. In this work, low atomic number element boron was analysed using a 4.4 ns pulsed Nd:YAG laser and high resolution spectrometer. We performed a quantitative analysis using a line at 249.77 nm of boron atom and developed LIBS application for mining industry. For quantitative analysis Aluminum Oxide powders with different amounts (25%, 50%, 75%) of Boron Anhydride powders were homogenously mixed to form pellets. Fig. 1 shows the LIBS spectrum of Boron and Aluminum Oxide taken from pellets. It is observed that LIBS gives successful results in quantitative analysis of low atomic elements such as Boron, Aluminum and Oxygen.

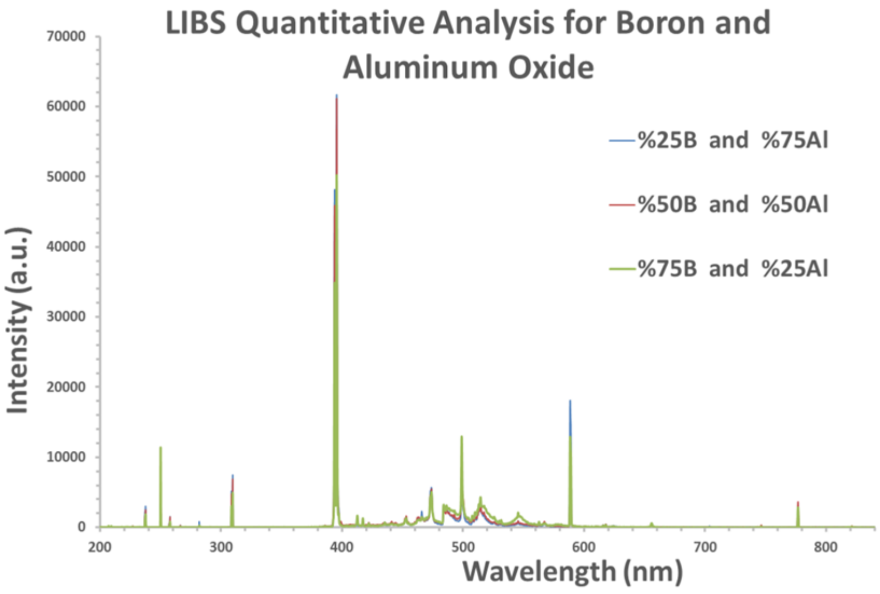

Fig. 1.: Fig1.: LIBS spectrum of Boron and Aluminum Oxide

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Application of CF-LIBS for the detection of trace elements in metallic samples

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According to the LIBS technique, the elemental analysis is carried out by directing a pulsed laser beam on the surface of a layered metal sample. Soon after laser irradiation, the spectroscopic emission is observed and spectra are recorded simultaneously by two detection systems: the first with a wide spectral coverage and moderate resolution, and the second with a higher spectral resolution over a narrow spectral region centered around the emission of a specific trace element (in our case around hydrogen D-alpha line). This set-up offers the possibility to spectrally resolve the line emission from hydrogen and its isotopes, and to make a reliable estimate of the plasma parameters thanks to the numerous atomic and ionic spectral lines collected by the low resolution system. The measurements, conducted at atmospheric pressure, are finalized to combining the data obtained from the two detection systems for the determination of sample composition by application of CF-LIBS technique.

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Experimental design: a helpful tool before LIBS on-site analyses of agricultural soils

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Laser-induced breakdown spectroscopy (LIBS) has been identified as a high potential technique for on-site multi-elemental analysis of agronomic matrices such as soils1. On-site analyses still remain a challenge since external experimental factors such as humidity and heterogeneity can badly impact the acquired signal. Laboratory experimental design represents a potential tool to evaluate this impact before considering in situ analyses. Experimental design results revealed that humidity will be the most significant environmental factor impacting on-site LIBS measurements. It was not possible to record any signal above 30 % humidity, because of the difficulties of creating a plasma on too wet soils. However, spectral normalization seems a efficient tool to overcome the fluctuations of LIBS signal due to humidity.

References

[1] https://doi.org/10.1016/j.trac.2016.08.015

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Evaluation of portable LIBS and portable XRF in the frame of multi-elemental analysis of agricultural soils and plants

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Agronomic research has a growing interest in collecting faster, cheaper and still efficient information about agricultural matrices in order to achieve a better monitoring of soil quality and fertility. Laser-induced breakdown spectroscopy (LIBS) and X-Ray fluorescence spectrometry (XRF) have been identified as high potential techniques for on-site multi-elemental analysis of agronomic matrices such as plants1 and soils2. The study of agricultural soils and plants, more precisely the multi-elemental quantification of several chemical elements of interest, was realized using portable LIBS and portable XRF systems. Both XRF and LIBS quantitative analysis were compared to the concentration values determinate by ICP OES. Good practices related to sample preparation and experimental conditions to achieve relevant LIBS/XRF measurements in laboratory will be discussed. The influence of environmental parameters has been examined in order to assess the robustness of on-site analysis.

References

[1] DOI: 10.1039/C7JA00293A.

[2] https://doi.org/10.1016/j.trac.2016.08.015

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On-site chlorine determination with a mobile LIBS system

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A mobile LIBS system was developed in cooperation with industrial partners for on-site detection of harmful substances in concrete structures. With this system, chlorine detection is possible directly on the structure, such as parking deck or bridges. The mobile system uses a low energy laser with a pulse energy of 3 mJ, a wavelength of 1064 nm, a pulse width of 1.5 ns, a repetition rate of 100 Hz and a NIR-spectrometer in combination with a scanner for two-dimensional mapping. This work presents the quantitative chloride determination of an on-site application of the mobile system. The obtained chloride results on the concrete surface are important as fast indicator for possible damaged areas. During damage assessment or reconstruction work, the civil engineers may use the LIBS data to get a detailed view of the concrete condition. A comparison of the calibration curve and the LOD determined on-site with the mobile system with that of the laboratory system is shown. In some places, drill cores were taken and measured in the laboratory. This makes it possible to determine a chlorine ingress profile. To verify the LIBS results standard analysis using wet chemistry have been done.

Boosting plasmas of low energy lasers with electrical discharge

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Laser-induced plasma spectroscopy (LIBS) is well suited for the detection of chlorine in concrete. However, for the determination of the chlorine spectral line 837.59 nm helium atmosphere is necessary. Chlorides that penetrate the concrete structure, for example from seawater or de-icing salt, can cause corrosion of the steel reinforcement. The critical triggering chloride content is 0.4 wt%. In this presentation, the possibility of electrical spark discharge for using low energy lasers will be investigated. Lasers with different energies, pulse lengths and repetition rates have been compared in order to have a system that is able to detect chlorine even without expensive helium. Calibration lines with and without electrical spark discharge are measured and the limit of detection is determined and compared. With the experimental setup a two-dimensional mapping of different concrete samples will be presented.

Analysis of harmful species in concrete with LIBS and electrical spark discharge

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The Laser-induced Breakdown Spectroscopy (LIBS) is a fast and reliable technique for the detection of harmful species in concrete structures. The ingress of chlorides from sea water or de-icing salt in winter time leads to corrosion of the reinforcement. If chlorine exceeds a specific concentration threshold, the stability of the structure will be reduced which affects the lifetime of building structures. The critical chlorine content based to cement is 0.4 wt.-% based to the cement for reinforced concrete. For the detection of Cl in concrete with LIBS a He purge is necessary. This presentation deals with the enhancement of the laser induced plasma by using electrical spark discharge. The plasma life-time and the atomic line emission have been increased significantly by optimizing the experimental LIBS setup in combination with an electrical discharge. Therefore, the plasma dynamic and the temporal behavior of different spectral lines have been analyzed using a fast iCCD camera. The time-resolved analysis of different elements has been evaluated with respect to their optimal signal-background ratio. In order to compare the setups (with and without electrical spark) different figures of merit (e.g. R^2, limit of detection) using known calibration samples have been evaluated. This work shows the enhancement of elements for the analysis of concrete samples. For the evaluation of a two-dimensional element map a LIBS setup with electric spark discharge have been used. The 2D-map is important to determine and visualize the external ingress of harmful species and to extract an ingress profile. The spark measurements allow to detect Cl without He purge directly in air atmosphere.

Alternative standards for Laser Induced Breakdown Spectroscopy analysis of asphalts

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Recycling of building materials, namely asphalts is an economical and ecological issue. Knowledge of the elemental composition is an important step in the chain of material processing. Determination of minor and trace elements is a frequent task of Inductively Coupled Plasma Optical Emission or Mass Spectroscopy (ICP-OES or MS). Results of this method may be crucial for decisions made on the future re-use of the asphalt mixtures. Ecological and technological aspects should be taken into account. For ICP analysis sample decomposition is required which is a time consuming and complicated procedure. As an alternative Laser Induced Breakdown Spectroscopy (LIBS) can be employed in some cases. It can be applied on solid samples in some selected spots of interest. This is also the case of our study. Determination of sulfur has been especially in our focus. Results of the LIBS analysis in randomly selected spots of the samples were compared with those from ICP-MS. The selection of the spots was governed by the rule that only dark asphalt space among filling stones was ablated. To facilitate the LIBS analysis calibration standards based on cellulose and limestone pressed pellets were used. Because of poor analytical signals of sulfur in OES the LIBS analysis was realized in an enclosed interaction chamber filled with He or at further simplification He was just blown onto the sample surface. The used analytical line was S I 921.29 nm for which no extra optics is necessary. The yielded results show that both the synthetic limestone and the cellulose need some corrections but results of the cellulose calibration were much closer to the reference ICP-MS values. The asphalt is a completely different matrix, however, no asphalt standards are known to us. Both the sets of pellets were prepared by adding a weighed amount of sodium sulfate decahydrate to the limestone or the cellulose powder. The mixtures were homogenized in a mortar by a hand friction process using a pestle and a plastic spoon for several minutes. Especially a very linear calibration dependence for the cellulose standards showed that the homogenization and the measurement were well-made. Finally it can be concluded that the LIBS analysis can be successfully applied on the sulfur determination in asphalts provided that a systematic correction of the intensities is used.

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Quantification of Zn in aqueous solution by laser induced breakdown spectroscopy and liquid-solid matrix conversion

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The subject of this work is the quantification of Zn in aqueous solutions using laser induced breakdown spectroscopy (LIBS) with a focus on possible industrial applications. State of the art measurement methods for Zn quantification in solutions use time extensive chemical processes which do not allow real time measurements in the production process. Although LIBS measurements are rather fast, a measurement directly in the liquid produced poor results regarding sensitivity and repeatability. Furthermore, the splashing of the liquid required extensive cleaning after each single measurement, which made this method unsuitable for practical applications. To bypass these problems, a liquid-solid matrix conversion was applied. Commercially available filtration paper was soaked in the test liquids, then dried and finally measured using LIBS. Submerging the paper in liquid for short time resulted in an inhomogeneous spatial distribution of Zn as revealed by element mapping. However, for longer exposure time this method produced encouraging results, including suitable calibration curves to determine the Zinc concentration in unknown liquids with an R^2 of 0.99 to 0.997.

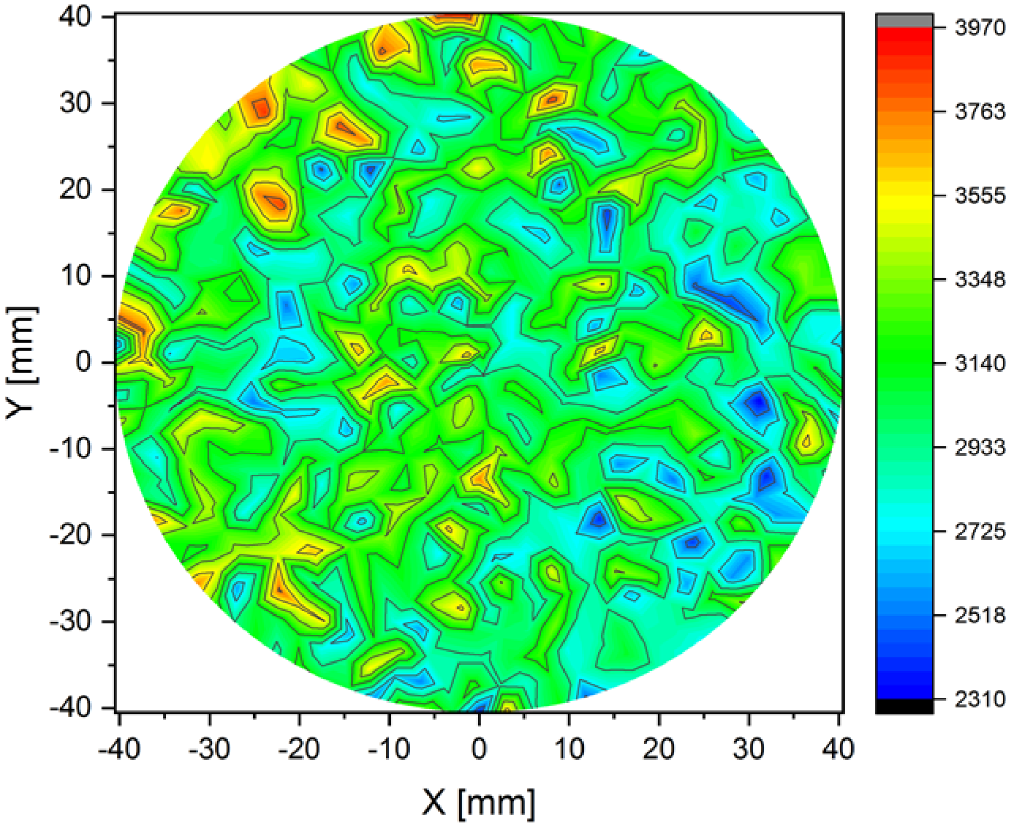

Fig. 1.: LIBS element map of Zn in filtration paper for short-time immersion of the paper in the liquid.

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Elemental Analysis of Aqueous Samples: Challenges and Counter Experimental Strategies for LIBS Measurements

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Laser-Induced Breakdown Spectroscopy (LIBS) is a very appealing technique for spectrochemical analysis. The technique basically is the determination of the elements in materials based on their characteristic atomic emission spectra. LIBS can be applied to analyze liquids since it shows great potential for in situ monitoring of water in the environment, particularly for sewage, chemistry of slurry, mine drainage, impurity in oil, nuclear fuel industry, etc. All the results mentioned in this work have been carried out using a gated detector coupled with echelle spectrograph (i-Star, ME5000-DH734, Andor, Ireland) and a nano second pulsed laser (Q-smart 450, Quantel). We have studied different experimental strategies for elemental analysis of aqueous samples. These include: LIBS studies on (i) the bulk form of the sample solution, (ii) the liquid jet, (iii) on dried sample solution and (iv) Nano-particle Enhanced LIBS (NELIBS). In this work, major challenges for LIBS studies on bulk liquid samples have been analyzed and counter measures have been attempted and reported. In order to check the Limit of Detection (LOD) of the system, LIBS studies have also been carried out on various concentrations of CuSO4 solution and LOD was calculated from constructed calibration curves. The quantification capabilities for most of the aforementioned experimental strategies are found to be at ppm levels. In order to extend the applicability of LIBS, efforts have been made to enhance the signal by depositing Ag nanoparticles on the dried sample solution and then exposed to LIBS. Finally, performanace evaluation of LIBS have been done on realistic samples like milk (both liquid and solid forms) using the developed strategies and the results observed are really motivating to take works in this direction forward which also exhibit the uniqueness of LIBS for such applications.

References

[1] D. A. Cremers and L. Radziemski, Handbook on Laser-Induced Breakdown Spectroscopy, Tucson: Wiley, 2006.ISBN: 9781119971122

[2] A. D. Giacomo, M. Dell'Aglio, R. Gaudiuso, c. Koral and G. Velenza, "Perspective on the use of nano-particles to improve LIBS analytical performance:Nano-Particle Enchanced LIBS," Journal of Analytical Atomic Spectroscopy, vol. 31, no. 8, pp. 1566-1573, 2016.

[3] F. Poggialini and V. Palleschi, "Green-Synthetized silve nanoparticles for NELIBS," Spectrochemica Acta Part B: Atomic Spectroscopy, vol. 141, pp. 53-58, 2018.

Detection of heavy metals in urea by surface-assisted LIBS method

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Laser-induced plasma spectroscopy (LIBS) is a technique for qualitative and quantitative elemental analysis of solid, liquid and gas samples. It is worth to mention that the elemental analysis of liquids samples is a great challenge for laser ablation. This technique requires minimal or no sample preparation, because ablation and excitation occur simultaneously at the same site. For quantitative analysis, LIBS technique usually uses calibration curves, which generally show a linear relationship between the intensity of emission lines vs. concentration from known reference samples. The present work was focus in the application of the surface-assisted laser induced breakdown spectroscopy (LIBS). In this work, we were devoted to the improvement of the accuracy of the measurements with simultaneous reduction of detection limits (LOD) repeatability, and sensitivity. In this work we have studied thin layers of synthetic urea, as the sediment formed after drying the liquid samples on a high reflective surface such as aluminum wafers and in agar gel, to perform the surface-assisted LIBS analysis. We have measured heavy metals in synthetic urea with different concentrations to determine their calibration curves. Also a validation sample has been employed to test the accuracy of the established calibration curves. The main objective of this work is to obtain the calibration curves of all the samples studied for a future determination of heavy metals contamination that can be determinate in real urine for human health diagnostics purpose.

References

[1] J. Bobckova, A. Marin Roldan, J. Yu, P. Veis, “ Potential use of surface-assisted LIBS for determination of strontium in wines”, Appl. Opt. 57, 8272-8278, (2018).

[2] Y. Tian, C. Yan, T. Zhang, H. Tang, H. Li, J. Yu, J. Bernard, L. Chen, S. Martin, N. Delepine-Gilon, J. Bocková, P. Veis, Y. Chen, J. Yu, “Classification of wines according to their production regions with the contained trace elements using laser-induced breakdown spectroscopy”,Spectrochim. Acta B 1

[3] J. Bockova, Y. Tian, H.Yin, N. Gilon, Y. Chen, P. Veis, J. Yu, "Determination of Metal Elements in Wine Using Laser-Induced Breakdown Spectroscopy (LIBS)", Appl. spectros. 1750-1759. (2017).

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PI_060

Analysis of TiB2 and Al2O3 thin films by LIBS

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Laser Induced Breakdown Spectroscopy (LIBS) has been recognized as a powerful, versatile technique for materials analyses. There is no need of sample preparation for solid, liquid, and gaseous sample analyses. Double pulse LIBS has been used for the analysis of TiB2 and Al2O3 thin films. Depth profile information was obtained from the spectra of consecutive laser pulses. TiI (334 nm), AlI (309) and SiI (288 nm) spectral lines were selected for depth profile analysis. There were no spectral interfaces at the position of lines. Low Z elements (N,O,B) in thin films can be detected by LIBS technique under normal atmosphere conditions. The Q-switched Nd:YAG laser with pulse width of 4.4 ns at 1064nm wavelength was used for the analysis. The laser is capable of maximum energy output up to 700 mJ and can be run at the maximum repetition rate of 20 Hz (see Figure below). The laser beam is focused by a fused slica lens with 150 mm focal length. The laser and spectrometers were triggered and syn

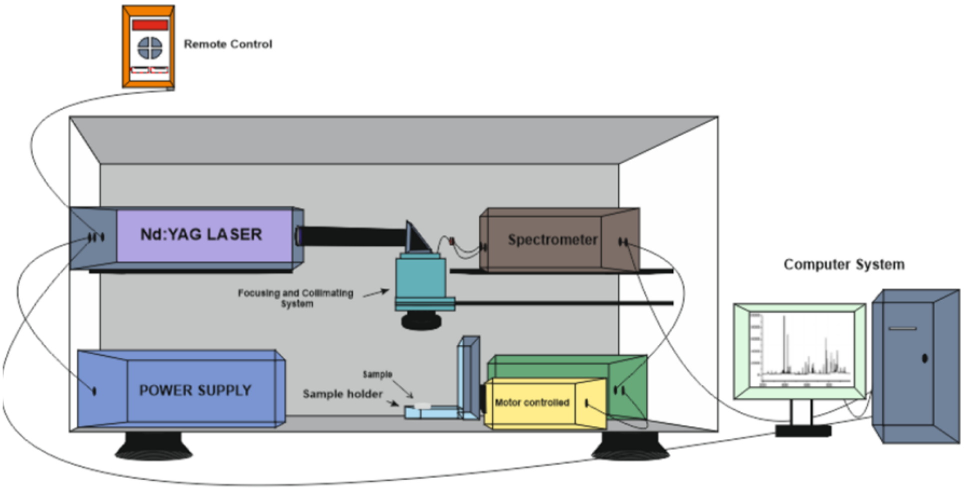

Fig. 1.: Figure 1: Exerimental setup.

PI_061

Analysis of Indium Tin Oxide thin films by using Laser Induced Breakdown Spectroscopy (LIBS) in the Vacuum Ultraviolet

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Depth profiling analysis by use of Laser-Induced Breakdown Spectroscopy (LIBS) has been shown to be a promising technology for the characterization of different types of materials exhibiting longitudinal variations in their compositional profile. A challenging area of application of LIBS depth-profiling is the characterization of very thin films due to the minimum ablation depth that should be achieved for ensuring fine profiling, while maintaining proper conditions for generating laser plasma that is analytically useful. To address these issues we propose an extending plasma emission observation in the vacuum ultraviolet (VUV). The fact that several elements display intense resonant emission lines in the range of 100 – 200 nm could offer enhanced analytical sensitivity that might counterbalance the experimental complexity. The present work focuses on the study of LIBS analysis of 100-150 nm thin films of Indium-Tin-Oxide (ITO). A Q-switched nanosecond laser is employed (□ = 266 nm, tpulse = 10 ns) for generating plasma on the surface of the sample housed in a small sample chamber with Ar as a background gas. The emission of the plasma plume is analysed by use of VUV spectrograph covering the spectral range from 100 – 300 nm, and recorded on an iCCD camera. Preliminary experiments demonstrate that it is indeed possible to obtain information of the compositional profile of the ITO films over the plastic substrate based on the varying intensity of several spectral lines of In, Sn and C. Critical to the success of the method is to a) run measurements at relatively low energy fluence levels that permit slow penetration of successive pulses through the film and b) increase collection efficiency of the plume emission into the spectrograph. Studies are currently underway to correlate emission intensity of In and Sn lines with film thickness as well as to extend this methodology to the analysis of similar films of different materials.

References

[1] V. Zorba, J. Syzdek, X. Mao, R. E. Russo, R. Kostecki, Ultrafast laser induced breakdown spectroscopy of electrode/electrolyte interfaces, Appl. Phys. Lett. 100, 234101 (2012); https://doi.org/10.1063/1.4724203

UV-Femtosecond Double-Pulse LIBS for the in-situ characterization of ITO-based thin films

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Performing compositional analysis and depth-resolved profiling of nanometer-scale samples (thin films) is a demanding task and requires the use of sophisticated techniques. Furthermore, if this type of analysis is to be done in the context of a production line in an industrial environment, additional requirements are imposed having to do with the speed of analysis and the ability to run such diagnostics in situ. For these reasons, Laser-Induced Breakdown Spectroscopy (LIBS) has been investigated as a potential technology for rapid analysis of materials at different depths of thin film structures [1]. A main challenge in this application is the need to achieve efficient analysis of each layered film with just a single sequence of pulses. This translates to the requirement of recording reliably good emission signals which arise from a single laser-plasma event that samples material volumes as low as 5 - 80 □m3 corresponding to elemental mass quantities down to 10 picograms. In an effort to maximally exploit the optical energy of each laser pulse for generating an intense plasma, hence enhancing the analytical capacity of the proposed method, we have examined the possibility of performing Double-pulse (DP) LIBS [2] which involves ablation of the sample with a pair of pulses temporally separated by a few tens of picoseconds. The current work concentrates on the use of UV-Femtosecond-DP-LIBS (□ = 248 nm, tpulse = 450 fs) for the characterization of multi-layered thin films, of relevance to industrial applications, exploring critical measurement parameters and attempting to establish optimum conditions for performing minimally invasive depth-profile analysis. The results on indium-tin oxide (ITO) films indicate increase of the emission by as high as a factor of 3-5, depending on pulse energy and spectral transition properties, when DP-LIBS is used in comparison to (single-pulse) SP-LIBS, demonstrating that the proposed double-pulse approach is a promising one for the characterisation of nanofilms.

References

[1] S. P. BANERJEE, T. SARNET, P. SIOZOS, M. LOULAKIS, D. ANGLOS, and M. SENTIS, Characterization of organic photovoltaic devices using femtosecond laser induced breakdown spectroscopy, Appl. Surf. Sci., 418, 542–547 (2017).

[2] V. PINON, D. ANGLOS, Optical emission studies of plasma induced by single and double femtosecond laser pulses, Spectrochim. Acta B, 64, 950–960 (2009).

Acknowledgement

This project has been supported in part by the International Associated Laboratory (LIA)MINOS between LP3 and IESL-FORTH. PS acknowledges support from the POLITEIA-II and HELLAS-CH projects (MIS-5002478, MIS 5002735, NSRF 2014–2020).

Depth profiling of tungsten layer on molybdenum substrate by Calibration free LIBS analysis

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Molybdenum and its alloys have been chosen as suitable materials for limiters and in some special cases as first wall materials for test operation of tokamak devices. For its good mechanical properties and thermal conductivity has been molybdenum also used as a base for tokamak-like samples. On the other hand, tungsten, for its low activation, has been chosen as divertor material for the ITER. The migration of tungsten and other elements in tokamaks is recently the subject of many studies. Sputtered material from the first wall is consequently deposited on the divertor components and vice versa. One of the suitable techniques for post mortem analysis of these parts is Laser induced breakdown spectroscopy (LIBS). In this work, we used calibration free (CF) LIBS approach as a diagnostic method for depth profiling of tungsten based mix layers on molybdenum substrate. LIBS spectra were measured under air atmospheric pressure and under argon and nitrogen flow as a shielding gas in a background of atmospheric air pressure. LIBS Plasma was created using Nd:YAG laser operating at the second harmonic (532 nm). Atomic and ionic spectral lines of Mo and W were selected from spectra and used for analysis. The evolution of plasma parameters (ne evaluated from Stark broadening of selected spectral lines and Te evaluated from the Saha-Boltzmann plots) has been observed by choosing different gate delays and gate widths. Finally, the quantitative determination of elements has been calculated by CF LIBS approach from Boltzmann and Saha-Boltzmann plots, from the known cross sections and integration of all main undisturbed lines of the element of interest. The results are showing depth dependence on decreasing tungsten and increasing molybdenum concentration. The measurements under argon flow causes slightly higher density and temperature of electron while measurements under nitrogen flow are very similar to atmospheric air measurements. The goal of this work is to choose the right set of molybdenum and tungsten lines for future CF LIBS in depth profile analysis, what can be applied for quantitative analysis of deposited material on the real divertor walls.

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Data signal fusion LIBS – LA-ICP-MS for thin film samples

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The chemical determination of alkali elements in LLZO (Li7La3Zr2O12) layers as well as Kesterit (Cu(In,Ga)Se2 (CIGS) and Cu2ZnSn(S,Se)4 (CZTSSe–kesterite)) thin film samples is a challenging analytical task [1]. An elaborate digestion process combined with an ICP-MS method is normally used. This is however not suitable for a spatially resolved and quantitative analysis for the purpose of process monitoring. By means of LA-ICP-MS it is possible to generate spatially resolved signals and accelerate the thin film layer analysis (<1min / measurement) since the digestion step is not needed. The problem with LA-ICP-MS quantification is the lack of matrix matched calibration standards and the large standard deviations >20% of the signals. To enhance the data quality LIBS is coupled to the LA-ICP-MS system. By combining the signals from LIBS and LA-ICP-MS, the influence of different surface textures and the behavior of the different analytes could be examined on NIST610. Finally LLZO thin films were analyzed using the simultaneous measurement method-ology LIBS / LA-ICP-MS. The signals of the main elements were combined by im-plementing a LIBS signal corrected normalization process. On the poster we present the results of the different measurements as well as the results of the normalization process. While LIBS shows a favorable depth resolution (200nm LA-ICP-MS / 50nm LIBS) the LA-ICP-MS stands out for its high detection Limit (e.g. LOD Li <2ppm).

References

[1] [1] Haass, S. G., Andres, C., Figi, R., Schreiner, C., Bürki, M., Romanyuk, Y. E., & Tiwari, A. N. (2017). Complex Inter-play between AbsorberComposition and Alkali Doping in High-Efficiency Kesterite Solar Cells. Advanced Energy Ma-terials

Microscopic depth profiling of layered structures by combined application of Raman spectroscopy and LIBS

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Non-destructive or minimal invasive analytical characterization of layered structures is a need in forensics, in the field of Cultural Heritage or in quality control of demanding industrial processes. The combination of Raman spectroscopy with Laser-induced Breakdown Spectroscopy provides an excellent means of gathering chemical information as well as information of the elemental composition of unknown samples. A newly developed instrument combines both methods together with a microscopic sample imaging enabling depth profiling at single points or at a grid of points. Raman measurements are performed with two lasers at 532 nm and 785 nm wavelength respectively. For LIBS measurements a nanosecond pulsed Nd:YAG laser at 1064nm is used. The focus diameter of the Nd:YAG laser of about 20 µm determines the lateral resolution for the analysis. The Nd:YAG laser energy is continuously adjustable thus allowing to adapt the rate of material removal to the sample type and layer thickness. In order to prove the applicability of this technique for forensics and quality control it was applied to the characterization of layers of automotive paint and electronic components. For Raman spectra classification based of spectral correlation a large commercial database was used. For LIBS spectra analysis advanced methods of elemental recognition as well as principal components analysis (PCA) were applied. Depth profiles of individual layer structures with thicknesses in the order of less than 5 µm have been identified.

References

[1] BOL'SHAKOV A. A., YOO J. H., LUI C., PLUMER J. R. a Russo R. E. Laser-induced breakdown spectroscopy in industrial and security applications. Appl. Opt. 49, C132-C142 (2010)

[2] Musazzi S., Perini U. editors. Laser-Induced Breakdown Spectroscopy. Springer Heidelberg New York Dordrecht London, 2014, ISBN: 978-3642450846

Advances in Thin-Film Microextraction - Laser-Induced Breakdown Spectroscopy methodology for trace elemental analysis in liquid matrices

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As already well known, LIBS analysis of liquid matrices is usually less sensitive and experimentally more problematic than that of solids. In addition, conventional spectrometric techniques are, nowadays, able to perform elemental analysis of liquid samples with better sensitivity and precision than LIBS. There are, however, some unique features that turn LIBS into a very attractive technique for liquid samples analysis, such as the ability to perform in-situ and/or on-line detection due to the field-operable and easily automated LIBS instrumentation. A possible way for improving the analytical performance of LIBS when applied to liquid samples, while maintaining its intrinsic in-situ and real time capabilities, is the use of hyphenated techniques combining easily automated sample preparation methodologies with LIBS detection. In particular, Thin-film microextraction (TFME) is a miniaturized, fast and efficient extraction method with high possibilities for automation, which can be easily coupled with LIBS to form a fully automated, portable and sensitive analytical system. By using TFME methodology, analytes in a liquid sample are adsorbed and concentrated on a very small quantity of solid adsorbent coated on the surface of a sheet-lake base material. After extraction, the analyte-enriched thin film is analyzed by LIBS, leading to a substantial sensitivity improvement. Nevertheless, when TFME is to be coupled with LIBS, studies of several parameters influencing both the extraction and detection steps are essential. Among others, the use of the most adequate solid sorbent and base material, and the selection of the best fabrication procedure for generating homogeneous and reproducible thin films, are critical for obtaining sensitive and precise results. In this work, the most recent advances in the development of a TFME-LIBS analytical procedure for trace elemental analysis in liquids are presented. Different strategies for the generation of reproducible and homogeneous thin films of carbon-based adsorbents are evaluated. The obtained results are shown and discussed.

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Restricted Boltzmann Machine Method for Dimensionality Reduction of Spectroscopic Data

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Multivariate data obtained using, for instance, Laser-Induced Breakdown Spectroscopy (LIBS) are quite bulky and complex. Advanced processing of spectroscopic data demands a multidisciplinary approach covering not only modern machine learning tools but also a deep understanding of underlying physical mechanisms. Strong non-linearities of those mechanisms are inducing problems in their processing using standard linear algorithms. Artificial Neural Networks (ANN) seem suitable for this task, and based on their success, they are given considerable attention within the spectroscopic community. We propose a new methodology based on Restricted Boltzmann Machine (ANN method) for dimensionality reduction of spectroscopic data and compare it to well known linear techniques such as PCA. Moreover, we apply this technique to the processing and mapping of very high-dimensional LIBS data.

Acknowledgement

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Investigation on Feature Selection and Extraction applied in Laser Induced Breakdown Spectroscopy

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Laser Induced Breakdown Spectroscopy (LIBS) is a potential technology in the field of spectral analysis. Due to the advantages of fast, simple operation, no sample preparation, real-time online and multi-element simultaneous detection, LIBS has been developed rapidly in recent years. Using LIBS combined with chemometrics models to classify and analyze the material is an important research field. The recognition results of these models were depended on the performance of model largely. In a meanwhile, the input variables of spectral data can also influence the classification result. The input variables of spectral data were largely depended on the feature selection and extraction methods. In hence, the feature selection and extraction methods were also an important factor to influence the recognition results of models. Therefore, it is necessary to investigate the relationship between the feature selection and extraction method and correct classification rate of models. The current research mainly focused on the effect of different feature selection and extraction algorithms on the LIBS spectral data of plastics and explosive. The research was performed with a few sample preparations. Each sample was ablated by laser pulse to generate plasma emission spectra related to their chemical compositions. Plasma spectra were collected and transmitted into computer by a two-channel gated charge-coupled device (CCD) spectrometer (AvaSpec 2048-2-USB2, Avantes). The classification accuracy of the support vector machine (SVM) model was used to evaluate these algorithms. The experiment compared three feature selection algorithms (ReliefF, F-Score, and Fisher score). Feature selection methods were to select features variables from the original variables. The new feature variables constructed facilitate the visual analysis of the sample distribution. The feature selection can remove redundant and unrelated information to improve the classification accuracy of models.

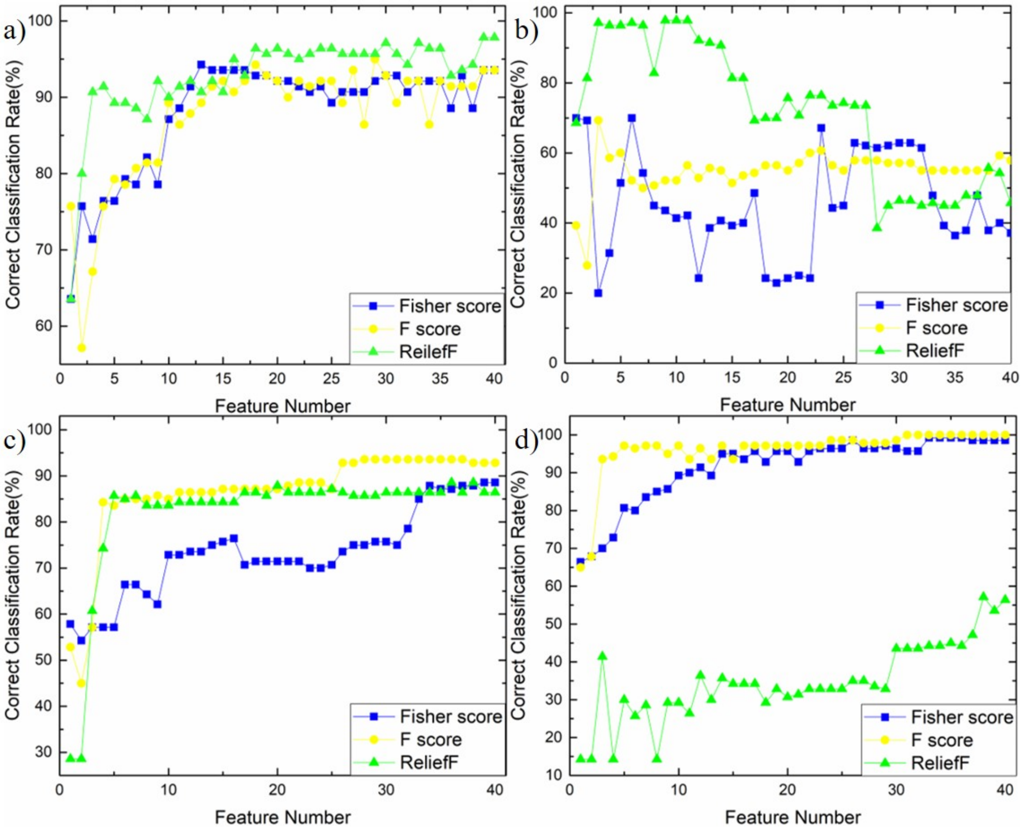

Fig. 1.: Fig. 1 Classification results of SVM model for spectral data selected by Fisher score, F score and ReliefF with a) autoscaling, b) mean-centering, c) normalization and d) SNV methods respectively.

References

[1] Wang Q, Teng G, Qiao X, et al. Importance evaluation of spectral lines in Laser-induced breakdown spectroscopy for classification of pathogenic bacteria[J]. Biomedical Optics Express, 2018, 9(11): 5837-5850.

[2] E. Vors, K. Tchepidjian, and J. B. Sirven. Evaluation and optimization of the robustness of a multivariate analysis methodology for identification of alloys by laser induced breakdown spectroscopy[J] Spectrochim. Acta. Part B, 2016,117:16–22.

[3] K. Liu, Q. Q. Wang, and H. Zhao. Application of laser induced breakdown spectroscopy in plastics classification[J]. Spectrosc. Spect. Anal. 2011, 31:1171–1174.

Acknowledgement

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Multivariate models for data library transfer in laser spectroscopy

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Laser-Induced Breakdown Spectroscopy (LIBS) serves as an exceptional platform for a fast sample analysis. Detected laser-induced plasma (LIP) spectrum is composed of unique information (i.e. chemical fingerprint) characterizing the sample from which it originates. A typical LIBS analysis, obtained with applying repetition rate, results in a great number of measurements (spectra). The size of the data matrix is intensified by the number of variables carried by each LIP spectrum. Therefore, the processing of given data matrix calls for sophisticated statistical algorithms. Chemometric (or Multivariate Data Analysis; MVDA) algorithms are becoming an inevitable part of the spectroscopic analysis [1]. A successful MVDA implementation is based on the well-balanced data pre-processing (outlier filtering, signal standardization, variable down-selection, etc.). First and the most common step is the dimensionality reduction and data visualization. This is consecutively followed by the model creation, further classification, and quantitative analysis. Nevertheless, data and related statistical models are not transferable among LIBS instruments. This is the main drawback of LIBS which limits its spread over applications (regardless of the great success of the Mars rover, Curiosity). We strive to deliver a feasibility study on the possibility of transfer of data libraries between LIBS systems. For this, we have created a novel multivariate algorithm that enables to alter the signal response of individual LIBS systems and to unify their respective data models, as schematically depicted in Figure 1.

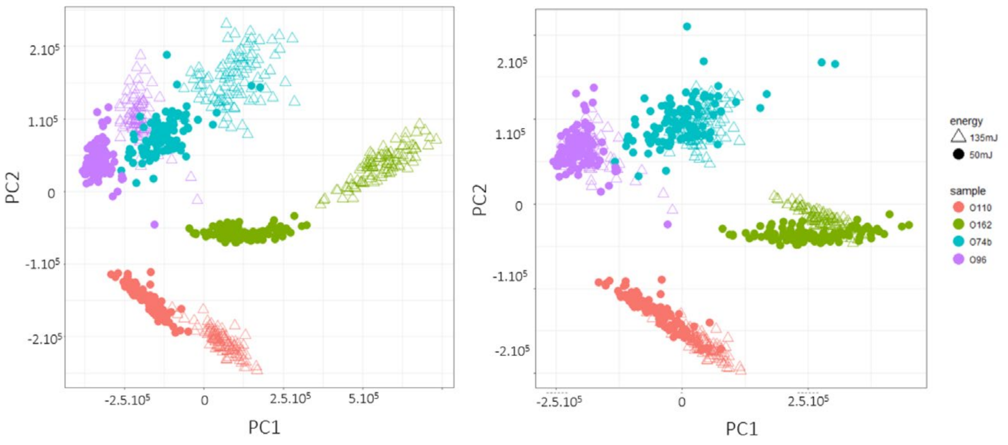

Fig. 1.: The figure shows the principal component space of untreated (left) and remodeled (right) data sets obtained using two different LIBS systems; in this case, two systems were substituted by the utilization of various laser pulse energy resulting in a signif

References

[1] POŘÍZKA, Pavel, Jakub KLUS, Erik KÉPEŠ, David PROCHAZKA, David W. HAHN and Jozef KAISER. On the utilization of principal component analysis in laser-induced breakdown spectroscopy data analysis, a review. Spectrochimica Acta Part B. 2018, 148, 65-82 [cit. 2019-05-20]. DOI: 10.1016/j.sab.2018.05.030.

Acknowledgement

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An Artificial Neural Network Software Package for LIBS Data Modeling

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Building accurate quantitative prediction models from LIBS data has been a challenging task due to various uncertainties observed in common LIBS data, such as strong inter-element interactions (e.g., matrix effects) and variations in plasma parameters (e.g., plasma temperature, electron density, amount of ablated material from the sample, etc) due to the instabilities of the LIBS instrument. In this work, we present an artificial neural network based AI approach and software code to address this hard problem. Comparative studies with conventional approaches will also be presented.

PII_071

Chemometrics for the analysis of cement-based materials

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The analysis of the chemical composition of cement-based materials like concrete is a crucial task in civil engineering. Concrete is a multi-phase material made of cement, water, aggregates, additives and admixtures. During the damage assessment of concrete structures, the external ingress of harmful species like chlorine, alkalis or sulfates needs to be determined. In order to provide a fast and precise analysis of concrete the application of LIBS offers unique possibilities as the technique can detect all elements at air atmosphere. To determine the condition of concrete, the information about the chemical composition, the ingress of harmful species as well as the evaluation of characteristic values like the used cement type or the type of aggregates are needed. This work presents the two-dimensional evaluation of concrete samples using LIBS and multivariate data analysis of atomic and molecular emission. For the evaluation of the main components different classification methods will be applied to identify the heterogeneity of the samples. With respect to their specific phase, different species will be quantified using multivariate regression (PLS) and important figures of merit will be presented. All results will be verified using standard procedure of wet chemistry (XRF, potentiometric titration and ICP-OES).

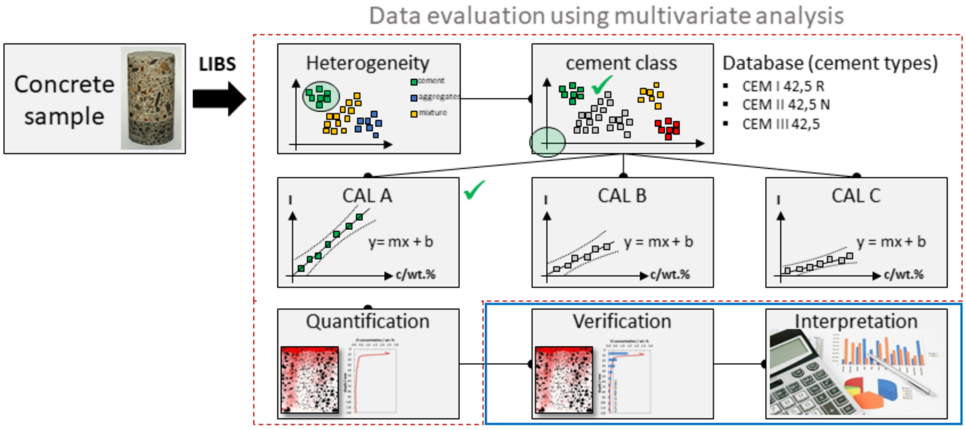

Fig. 1.: Fast concrete analysis using a combination of multivariate methods

References

[1] GOTTLIEB, C., MILLAR, S., GROTHE, S., WILSCH, G.: 2D evaluation of spectral LIBS data derived from heterogeneous materials using cluster algorithm. Spectrochimica Acta Part B: Atomic Spectroscopy 134 (2017), 58-68. https://doi.org/10.1016/j.sab.2017.06.005. ISSN 0584–8547

[2] Jolivet, L., Leprince, M., Moncayo, S., Sorbier, L., Lienemann, C.-P., Motto-Ros, V.: Review of the recent advances and applications of LIBS-based imaging, Spectrochimica Acta Part B: Atomic Spectroscopy 151 (2019), 41-53. https://doi.org/10.1016/j.sab.2018.11.008

[3] DOUCET, F.R., FAUSTINO, P. J., SABSABI, M., LYON, R.C.: Quantitative molecular analysis with molecular bands emission using laser-induced breakdown spectroscopy and chemometrics. Journal of Analytical Atomic Spectrometry. Issue 5 (2008), 694-701

Application of laser-induced breakdown spectroscopy for proximal soil sensing in precision agriculture

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The processes of soil development vary on the spatial and temporal scale, leading to an inhomogeneous distribution of soil properties. Uniform management of land often results in yield and quality losses and contributes to the waste of resources and environmental pollution. The concept of precision agriculture can remedy this situation by capturing the spatial variations within one field by a wide variety of sensors. A promising sensor technique is laser-induced breakdown spectroscopy (LIBS), which potentially allows the characterization of the element distribution on fields without the need for sample preparation. This advantage is contrasted by a strong matrix dependence of the LIBS signal which requires sophisticated data evaluation methods. In this work, different approaches for the evaluation of LIBS data, including two univariate and one multivariate method, are characterized. 139 soil samples collected on two different agricultural fields were measured by a handheld and a stationary LIBS instrument as well as by reference analysis. The first univariate method is based on calibration by the standard addition method on one soil sample and it is applied to the LIBS data of both fields. The second univariate method uses all sample points of the first field characterized by reference analytics for calibration. Then this calibration data is validated on LIBS data of the second field. The second method yields better calibration and prediction results because it better accounts for matrix effects. In partial least squares regression (PLSR) the LIBS spectra of the first field are used for training. Validation is based on LIBS data of the second field. PLSR yields better calibration curves but does not strongly improve the prediction. Beside the data treatment, the focus was on the characterization of both instruments for their application as sensor techniques. Finally, the optimized measurement and data treatment methods were transferred to in-field measurements.

Acknowledgement

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Multivariate Analysis of Moon Rocks using Laser Induced Breakdown Spectroscpy(LIBS) Spectra

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Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique used to classify and potentially quantify elements in complex hosts (or matrices). LIBS is a well-established technique for the analysis of different minerals and rocks spectrum. In this research Multivariate analysis is applied to analyse the LIBS spectra for the different Olivine and Plagioclase samples. For the LIBS experimental setup special vacuum conditions were practiced imitating the moon environment. LIBS spectra were analysed using PCA for the classification of different sets of data and PLS Regression method by making a set of reference samples to identify the unknown samples. Some other multivariate techniques were also explored to validate the prediction of the unknown samples. Multivariate Analysis is useful technique to predict the unknown samples of moon rocks and is very promising method for the remote space Instruments for the quick exploration of the complex space materials.

References

[1] X. Jiang, et al., Spectrochim. Acta B 86 (2013) 66

[2] X. Jiang, et al., Spectrochim. Acta B 86 (2013) 66

[3] S.M. Clegg et al. / Spectrochimica Acta Part B 64 (2009) 79–88

Spectral fingerprint analysis of forensic glass microsamples by LIBS

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Glass is an important forensic evidence wherewith a crime scene and a suspect, persons to each other and/or given locations can be linked. Splinters, glass microparticles (less than 1000 μm in length) can also be generated by incidents and these can occasionally fly more than 3 meters away from the source at the time of shatter, where they can be trapped by and persist in the clothing, shoes and hair of a suspect. During forensic investigations, glass samples are usually examined for their refractive index and by scanning electron microscopy. Complementary data may also be collected by μ-XRF or laser ablation ICP-MS or ICP-OES. Unfortunately, some of the presently applied analytical methods have limitations in terms of sample size and shape, sensitivity, cost and analysis time. For these reasons, we decided to test the potential of LIBS, which has already proven its utility in discriminant analysis of a variety of sample types [1-3], for the analysis of forensic glass microsamples. In our study, we collected and statistically evaluated LIBS spectra of about 400 samples originating from 6 groups (toughened, laminated, float, cathedral, headlamp and container glasses) by using an Applied Spectra J-200 tandem LA/LIBS instrument. Ablation craters in these glass samples were examined by contact profilometry, and the experimental parameters of LIBS analysis (e.g. laser wavelength, pulse energy, spot size, gas atmosphere) were optimized. By using NIST glass standard samples (No. 610, 612, 614, 1831), limits of detection for a number of trace elements were determined in order to assess from which concentration level upwards can trace contaminants influence the successful classification/identification of glass samples. Intra-sample variation of spectra/composition was also investigated. During chemometric evaluation, the open-source software package R, as well as Origin Pro was used, using conventional functions and self-developed scripts for PCA, LDA, ANN and SVM.

References

[1] A. Metzinger, D.J. Palásti, É. Kovács-Széles, T. Ajtai, Z. Bozóki, Z. Kónya, G. Galbács, Energy Fuels 30 (2016) 10306-10313.

[2] M.M. El-Deftar, N. Speers, S. Eiggns, S. Foster, J. Roberson, C. Lennard, Forensic Sci. Internat., 241 (2014) 46-54.

[3] J. M. Curran, Internat. Stat. Rev. 71 (2007) 497-520.

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Classification of archaeological samples using supervised machine learning algorithms

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Elemental composition of glass differs based on raw material and additives used during manufacturing process (Blomme et al. 2016).Manufacturing process differ across time as well as being affected by the availability of materials from the local area. Therefore, elemental analysis is one of the most important techniques used for classification of archaeological glass samples. Elemental composition is also influenced by the addition of small quantities of colorants, opacifiers and clarifiers to the glass melt (Henderson 1985). Major, minor and trace elements in glass beads from 3 different locations (Bavaria, Bohemia and Morava) were determined. LA-ICP-MS was used for elemental analysis. From an archaeologicalpoint of view, it is usually important to compare main oxides, such as K2O and MgO to differentiate soda-lime natron glass from plant ash glass. However, this study focusses on the use of machine learning algorithms to find patterns in trace elements of the glass beads. The aim of this study is to compare multiple machine learning algorithms for this data set. Its main purpose is to show the possibilities of complex algorithms, such as quadratic discriminant analysis (QDA), k-nearest neighbours(KNN), support vector machines (SVM), decision trees or random forest (RF). Anexploratoryanalysis was performed at the beginning to determine variables - elements with high distinguishing power. Principal component analysis (PCA) was used to achieve dimensionality reduction for visualisation. Programming language python with sci-kit learn (Pedregosa et al. 2011)library was used for data processing and classification.

References

[1] Blomme, A., Elsen, J., Brems, D., Shortland, A., Dotsika, E. and Degryse, P. 2016. Tracing the primary production location of core-formed glass vessels, Mediterranean Group I. Journal of Archaeological Science: Reports, 5: 1–9.

[2] Henderson, J. 1985. The raw materials of early glass production. Oxford Journal of Archaeology, 4(3): 267-291.

[3] Pedregosa, F., Varoquaux, G., Gramfort, A., Michel, V., Thirion, B., Grisel, O., Blondel, M., Prettenhofer, P., Weiss, R., Dubourg, V. and Vanderplas, J. 2011. Scikit-learn: Machine learning in Python. Journal of Machine Learning Research, 12(10): 2825–2830.

Acknowledgement

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Cluster analysis of spectroscopic data in the principal component space

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Laser-Induced Breakdown Spectroscopy (LIBS) is commonly used for mapping heterogeneous samples with unknown chemical composition. After adequate pretreatment of spectroscopic data and choosing the right chemometric methods, the visualization of individual matrices is obtained. However, the outcome from heterogeneous samples are blurred, non-distinct clusters. This phenomenon corrupts the possibility to distinguish individual matrices and provide proper clustering. The experiment is designed to simulate an interference, where two different matrices (or elements) meet. The ablation spot hits the boundary of these two compounds, in this case Iron (Fe) and Aluminium (Al), with controlled step and therefore known ablated Fe:Al ratio. The ratio between Iron and Aluminium is determined using Principal Components Analysis (PCA), clustering and computing the Euclidian distance between clusters. The data is pretreated using methods such as detecting and deleting outliers, different kinds of data standartization and several kinds of approximation.

Rapid identification of the plastics using laser-induced breakdown spectroscopy

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The extensive use of plastic in our daily lives is leading to an increase in pollution and raises more concerns over reusing/recycling albeit their identification is a primary step in recycling[1,2,3]. In this work, we present an efficient identification of ten types of plastics obtained from the local recycling unit using laser induced breakdown spectroscopy (LIBS) technique. A systematic study has been done with the aim of reducing the data acquisition and analysis time along with the cost of the LIBS system. For this investigation, the spectra has been recorded ten shot average and single shot mode. The spectral emissions were captured by two spectrometers simultaneously. The first one is an Echelle spectrograph equipped with ICCD. The second one is a low cost, compact and portable Czerny Turner CCD spectrometer. The principal component analysis (PCA) results have shown that an excellent discrimination can be achieved irrespective of the data considered for the analysis. Further, the individual identification accuracies up to 99 % were obtained with the artificial neural network (ANN). The average identification rates ~97.7 % were achieved for the total data acquired with ICCD in ten shot average mode. The performance is almost similar (average identification rate only lesser by ~ 2 %) for the data recorded CCD even in single shot mode. However it has resulted in reduction of data acquisition and analysis time by a factor of 10 and 7 respectively. The identification rates obtained from the single shot ICCD data is 5 % lesser compared to the CCD. Besides that the analysis time is 7 times to the CCD data. It is also worth to consider that (collection+ detector) size and overall cost (~ 10 times) can be reduced by employing the CCD spectrometer which realizes in making compact LIBS system. These results demonstrates that rapid identification with high accuracies can be achieved the compact portable spectrometer in a single shot.

References

[1] J. Anzano, B. Bonilla, B. Montull‐Ibor, J. Casas‐González, Plastic identification and comparison by multivariate techniques with laser‐induced breakdown spectroscopy, Journal of Applied Polymer Science, 121 (2011) 2710-2716.http://dx.doi.org/10.1002/app.33801

[2] R. Junjuri, C. Zhang, I. Barman, M.K. Gundawar, Identification of post-consumer plastics using laser-induced breakdown spectroscopy, Polymer Testing, 76 (2019) 101 108.http://dx.doi.org/https://doi.org/10.1016/j.polymertesting.2019.03.012

[3] V. Unnikrishnan, K. Choudhari, S.D. Kulkarni, R. Nayak, V. Kartha, C. Santhosh, Analytical predictive capabilities of laser induced breakdown spectroscopy (LIBS) with principal component analysis (PCA) for plastic classification, RSC Advances, 3 (2013) 25872-25880.http://dx.doi.org/10.1039/C3RA44946

Quantitative determination of lithium in granite rock-forming minerals by laser-induced breakdown spectroscopy (LIBS)

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There is a high global demand for lithium resources. From a geochemical perspective, the lithium-bearing minerals such as spodumene, lepidolite or petalite crystallize in the late-magmatic/pegmatitic period, producing granitic pegmatites. One such granitoid massif, about 1 km below the present surface in SE Hungary is located in the Battonya Unit. Here, the granitoids typically contain quartz, feldspar and micas, like biotite and muscovite. All these phases can incorporate a significant amount of lithium, thus may become a potential target of lithium mining. In order to test this hypothesis and to assess the true potential of these lithium resources, prospection by a suitable laser spectroscopy technique is needed for the in-situ screening of the lithium concentration of rock phases in a large number of granite samples. One such solid sampling atomic spectroscopy method is laser-induced breakdown spectroscopy (or LIBS). In the focus of the present work was the development of an analytical method which would allow the accurate quantitative determination of Li in the above rock phases. Drill samples, taken from different locations in the Battonya region, as well as commercially obtained grains of granitoid rock phases (e.g. feldspar, muscovite, quartz, biotite, chlorite) were used as samples during the study. NIST 610, NIST 612, and NIST 614 standards were tested for calibration due to their similarity in matrix composition (silicate). Prior to the analysis, each grain (ca. 200 µm in diameter) of the studied rock phases in the samples were identified by optical microscopy. Measurements were performed on an Applied Spectra J-200 LA/LIBS instrument used in the LIBS mode. Experimental conditions were optimized. We found that biotite and muscovite contain elevated levels of Li concentration, in excess of 1 mg/g, whereas quartz had negligible concentration, around 5 µg/g. A quality assessment of the analytical results was also carried out.

Acknowledgement

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Lithium bearing minerals differentiation using Laser-Induced Breakdown Spectroscopy

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Lithium (Li) has gained the spotlight for exploration and mining companies due to the high demand on Li compounds by the battery industry1. Although present in several minerals, there are only a few Li bearing minerals that are economically profitable to process when a large deposit is found, namely spodumene, petalite, and lepidolite2. Moreover, Li concentration and extraction efficiency depend on the type of Li mineral resulting in different conversion capacities to Li carbonate/hydroxide. Hence, to be able to successfully and accurately identify different Li minerals in the most expedite way is of uttermost importance. In this work, a Laser-Induced Breakdown Spectroscopy (LIBS) prototype with a new artificial intelligence patented software3, was used to successfully identify Li minerals. This new AI approach takes advantage of the highly structured LIBS spectra and interprets the structure/geometry of the spectral information spaces resulting in an accurate identification. Using LIBS elemental mapping, it was possible to visualize Li leaching in the border between Li minerals and the surrounding minerals. Accurate discrimination in the same sample between two Li minerals, spodumene and petalite, was also achieved. These results were corroborated by petrographic studies. This ground-breaking approach is highly disruptive for LIBS spectroscopy and Li industry, allowing to measure Li concentration while determining the mineral present in the sample. This might be a game-changer improvement, once it can assist with the escalating demand for Li hydroxide, used in better performance batteries, which is only extracted in a cost-effectively way from spodumene.

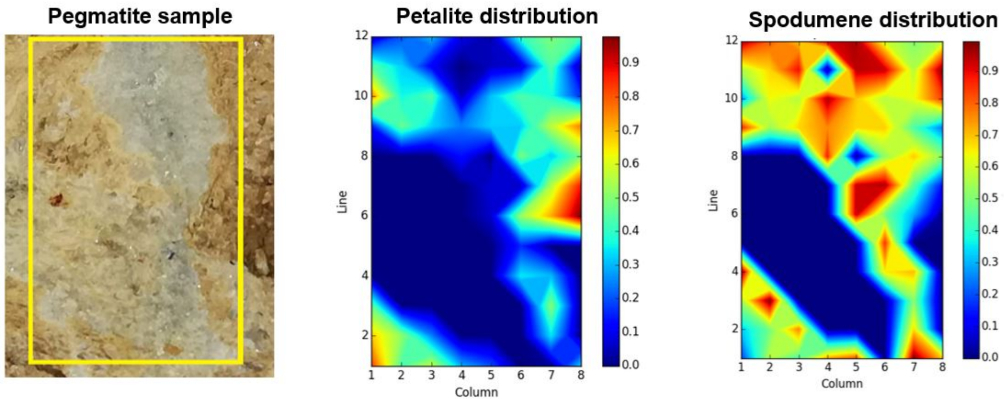

Fig. 1.: Mapping of Spodumene and Petalite in a Pegmatite sample.

References

[1] (1) Cheng, X. B. et al., "Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review," Chem. Rev. 117 (15), 10403–10473 (2017)

[2] (2) Meshram, P., Pandey, B.D. and Mankhand, T.R, “Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review.”, Hydrometallurgy 150, 192–208 (2014).

[3] (3) Martins, R. C., PPP 109644. Big data self-learning methodology for the accurate quantification and classification of spectral information under complex variability and multi-scale interference (2016).

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This work is funded by National Funds through FCT - Portuguese Foundation for Science and Technology within the scope of a PhD scholarship with the reference SFRH/BD/130680/2017 and the project under the reference PTDC/EEI-EEE/31165/2017 and FEDER funds through the COMPETE 2020 Programme under the project number POCI-01-0145FEDER-031165.

Quantification of minerals and valuable metals in complex drill cores from Finnish orogenic gold deposits

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Rapid and competitive drill core characterization and quantification of valuable components is a main goal in mineral exploration. Thereto, the development of appropriate drilling core analysis systems offers interesting possibilities. As part of the EU-funded project “ANCORELOG”, the quantification of major and minor elements in drill core samples from orogenic gold deposits is investigated with Laser Induced Breakdown Spectroscopy (LIBS) and Partial Least Square Regression (PLSR). The investigated sample material consists of different rock types showing different levels of complexity, from nearly homogenous to widely heterogeneous with complex structures. They were classified in 14 different lithologies with metamorphic imprints ranging from greywackes, intermediate metavulcanites and chlorite schists to amphibolites and skarns. The material was mapped with a resolution of up to 200µm with a LIBS drill core scanner (Nd:YAG 1064nm laser; laser spot size 200µm; high-resolution 285-964nm Echelle spectrometer). The resulting spectra were processed to get the intensity of multiple characteristic emission lines for 25 target elements. LIBS analysis of heterogeneous sample material is in particularly complicated by the severe plasma variations that occur due to chemically induced matrix effects. One way to reduce the problems with geologic material is to apply multivariate calibration with an extensive, carefully selected set of representative reference samples of known composition and textural structure. Therefore bulk XRF data as well as spatially resolved X-ray fluorescence data (µ-EDXRF) were applied and used for PLS Regression modeling. For fast drill core analysis, detailed mappings are time consuming and may not always productive. Therefore, a possible reduction of the data without loss of fundamental information is investigated. For different samples, reduced and detailed mappings were compared with respect to expenditure of time, validity and accuracy.

PII_081

Classification of copper-containing minerals by combined laser-induced breakdown and Raman spectroscopy

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The identification of minerals as constituents of rocks and as components of soils and sediments is an important prerequisite for understanding the genesis of rocks and, thus, for the geological exploration of valuable resource deposits (e.g. copper). The identification of minerals in the field is generally based on their physical properties (color, hardness, etc). A reliable identification by geologists is limited if the minerals have similar physical properties or are very fine-grained. Therefore, a spectroscopic method for in-field mineral identification is needed. Portable methods which do not require sample preparation include X-ray fluorescence, Raman and laser-induced breakdown spectroscopy (LIBS). LIBS and Raman spectroscopy are complementary spectroscopic methods. While LIBS provides informa¬tion about the elemental composition, structure information from characteristic vibrations can be obtained by Raman spectroscopy. In many cases, fusing information from both methods facilitates the distinction of similarly composed minerals. Furthermore, multivariate methods can be used for mineral classification. In this work, 200 minerals, of which 120 are separate copper-bearing minerals and the rest are of different provenance, were investigated by LIBS and Raman spectroscopy. The LIBS measurements were carried out by two LIBS spectrometers, a handheld instrument and a stationary instrument consisting of a double pulse laser and an ICCD equipped Echelle spectrometer. The focus of the LIBS measurements was on the characterization of the handheld instrument for mineral classification. Different excitation wavelengths as well as shifted□excitation Raman difference spectroscopy (SERDS) were tested for the suppression of mineral luminescence in Raman spectroscopy. Full LIBS and Raman spectra were used in multivariate methods for mineral classification. A set of different multivariate methods were tested for LIBS or Raman spectra and a combined data set.

Acknowledgement

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On the use of laser-induced breakdown spectroscopy for analysis of metals in ores

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Laser-induced breakdown spectroscopy was utilized to determine the metal content of ore samples. Ore certified reference materials (CRM) with varying chemical composition and different matrices were analyzed with a LIBS system that included a 1064 nm laser, a Czerny-Turner spectrometer (500 mm focal length) and an ICCD camera (265×1024 pixels). CRM are prepared from natural ore and rock samples sourced from deposits throughout several regions in the world. High homogeneity and accurate chemical composition are key characteristics of the CRMs analyzed. The samples were provided as pulverized material (crushing and milling to 99% minus 70 µm). 20 g of sample was deposited in aluminum cap and compressed (20-40 MPa) to form compact 32-mm diameter pellets for surface analysis. Metals such as Ag, Au, Ca, Co, Cr, Cu, Mg, Mn and Si were qualitative and quantitatively studied. Calibration curves were developed for quantitative analysis, while principal components analysis was utilized for matrix classification. This work presents a discussion on LIBS sampling characteristics and limits of detection considering analytes signal intensity, spectral noise, number of sampling shots, analytes physical characteristics and concentrations, and sample homogeneity.

Characterisation of iron type meteorites using simultaneous broadband and narrow- high-resolution laser induced breakdown spectroscopy (LIBS)

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Quasi non-destructive character, no or minimal sample preparation, detection and quantification of all elements in the periodic table (including light elements) make LIBS an ideal method for the analysis of precious samples (archaeological findings and artefacts, meteorites, sculptures or mosaics, artworks, etc.). The LIBS technique has been successfully used for the analysis of different types of meteorites [1,2]. Based on these advantages, we applied LIBS for the analysis, characterisation and evaluation of trace elemental contents (Ir, Ge, Ga) in the iron meteorite fragments found in the territory of Slovak republic. Iron meteorites are usually classified according to the content of iron (as a major element), nickel (as a minor element) and iridium, germanium and gallium (as trace elements). Due to the well-known fact that Fe has abundant emission lines in the observable spectral range (200-1000nm) which is more than 45 000 (Fe I-II) [3], the LIBS analysis of Fe rich samples are extremely difficult especially from the quantification point of view of trace elements. For this reason we performed simultaneous broadband and narrow high-resolution LIBS measurements of the meteorite fragments. Broadband spectra (200-975nm) were measured using the Mechelle ME5000 (Andor) spectrometer and used for the precise determination of the electron temperature (Saha- Boltzmann plots of Fe I-II and Ni I-II spectral lines). On the other hand, with an ultimate aim to obtain well-resolved LIBS spectra for the quantification of trace elements, a THR1500 spectrometer (Jobin Yvon) was utilized and used for the precise determination of the electron density (Stark broadening of spectral lines). Quantification of major, minor and trace elements was performed using the calibration free LIBS. From these studies, it is inferred that LIBS can be considered not only as a comparable technique but also a full-fledged well-established method like other standard techniques (ICP MS, EPMA, etc.).

References

[1] D. Ozdín et al., Meteoritics & Planetary Science 50 (2015) 864–879

[2] M. Hornackova et al., Eur. Phys. J. Appl. Phys. (2014) 66: 10702

[3] https://www.cfa.harvard.edu/amp/ampdata/kurucz23/sekur.html

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Towards Real time ore grading in ¡VAMOS! Underwater Robotic Mining system

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The shortage of critical raw materials created an urgent demand for new technologies, particularly those capable of “in-situ” and “real-time” identification and quantification of minerals and their elements, which will enable more efficient exploration and exploitation of new and old mineral resources. In this context, a new approach to re-mine flooded mines, with high efficiency and minimum human exposure to risk was proposed by H2020 Project ¡VAMOS! (Viable Alternative Mine Operating System) , where an Underwater robotic Mining system was demonstrated. One of the key components of a successful underwater operation is the ability to know, in real time, the quality of the extracted material, in order to better guide the system operation. During the project, the suitability of LIBS technology to be used as a real time ore grading system in the context of robotic mining operations was evaluated. A LIBS prototype was developed and evaluated for its capability to discriminate complex mineral samples in a mining context. A spectral database was built from pure minerals and reference materials, enabling the system to recognize target ores in complex scenarios. Different signal processing schemes and pattern recognition strategies were tested and compared with newly developed Artificial Intelligence method. The system was validated in real field trials, with samples from submerged mine pits in Lee Moor, UK, and Silvermines Ireland, as well as additional case studies with Lithium bearing minerals. Results will be presented giving an overview of the VAMOS system and showing the viability of LIBS technology to be used as a real time ore grading tool in complex mining scenarios.

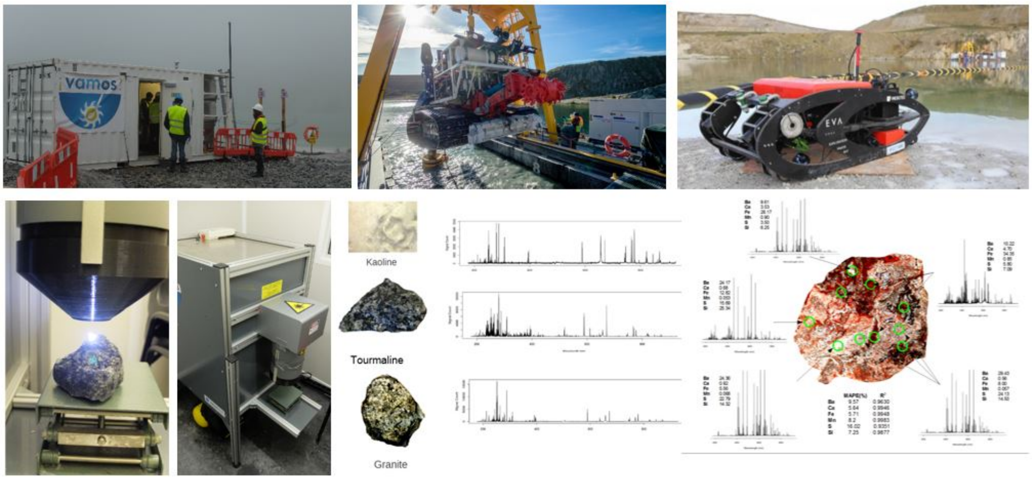

Fig. 1.: Using Libs for real time ore grading in ¡VAMOS! Underwater Robotic Mining system

Acknowledgement

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PII_085

A combined LIBS/Raman underwater system and its sea trial in the South China Sea

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In this presentation, a newly developed combined multi-optical spectroscopy system (CMOSS) was introduced and used for deep-sea investigation with the aid of a remotely operated vehicle (ROV). During the investigations, LIBS-Raman-fluorescence spectra can be taken using two separated laser spectrometers, i.e. Cmoss-LIBS and Cmoss-RFS (Raman & fluorescence spectroscopy). The former is used to take LIBS signal and both Raman scattering and fluorescence of the sea water can be recorded with Cmoss-RFS. In May 2019, a sea trial was taken place in the South China Sea, where an active cold seep system was discovered earlier. The CMOSS system was installed on the front and side bottom of ROV separately, as shown in Fig 1a. A total of five dives has been carried out in the sea trial with hundreds of thousands of LIBS/Raman combined spectra collected. Fig 1b shows the operation of Cmoss-RFS in an in-situ observation of the gas hydrate formation. The LIBS signal of carbonate rock in seawater at different depths were captured successfully, with a piece of carbonate rock was constrained in front of the probe of Cmoss-LIBS as shown in Fig 1c. Fig 1d is the typical LIBS spectra taken from carbonate rock sample. Its future development and possible applications to the geochemistry of hydrothermal system are also discussed in this presentation.

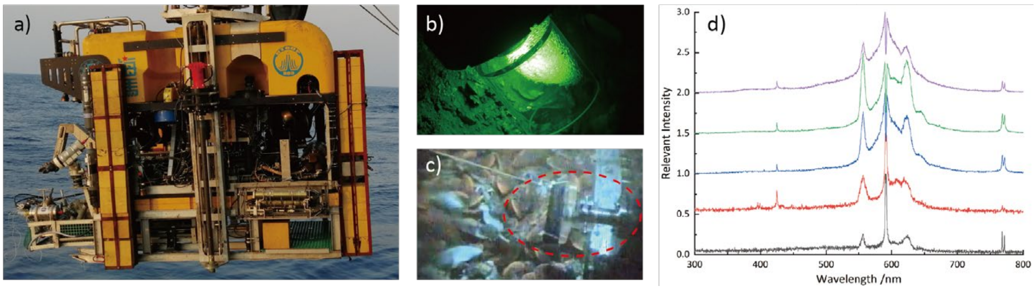

Fig. 1.: The photos of the CMOSS system equipped with “Haima” ROV for deep-sea investigation and its preliminary results of this sea trial.

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Developing LIBS applications for the mining and minerals industry

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In order to secure a sustainable future, there is a need to improve the efficiency of mining natural resources. Mining operations deal with huge quantities of excavated material with varying mineral concentrations and economic value. Increased knowledge about the composition of this material provides opportunities to improve the use of mineral resources through better stockpiling, sorting, and mineral processing. At SPECTRAL Industries we work together with the mining industry to develop LIBS-based sensor applications for the mining environment. Examples of applications are in-line conveyor belt analysis, scanning exposed rock surfaces, and scanning drill chips from blasthole drilling. We investigate the applicability of various spectrometers and different types of lasers, including fiber lasers, to develop the best LIBS setup for a specific application. One of the major challenges of using LIBS for characterizing the mineral quantity in rocks is the heterogeneity of this material. Rocks are typically composed of 5-10 different minerals with various grain sizes. Each mineral consists of several different elements and for some minerals the relative quantity of these elements can vary. Depending on the size of the mineral grains, a single LIBS measurement can represent one to several different minerals. This means that the influence of matrix effects on the acquired LIBS data is often significant. Development of advanced data processing techniques is therefore required in order to provide quantitative compositional information that meets the required accuracy. In this presentation we will show the results we obtained from testing LIBS on ore samples from active mining operations. These results show that LIBS can be used to provide the information that is needed to improve the efficiency and sustainability of future mining.

LIBS methodologies for the determination of halogen molecular species in gypsum from thermal power plants

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Pollutant emission control is one of the most pressing issues in today's industry. Specifically, this sector requires fast and efficient monitoring methods allowing a complete analysis of emissions in real time. LIBS technique represents a promising tool that meets these requirements since it allows online analysis of many types of industrial waste with minimal and non-polluting sample preparation. In recent years the detection of molecular excited species has been developed to improve the analytical capabilities of LIBS for halogen determination [1, 2]. This work applies LIBS in order to detect the presence of halogens in gypsum and ashes from thermal power plants since the feasibility of recycling these wastes depends on the halogen content. For this purpose, the emission signal of excited CaF and CaCl molecules has been evaluated as a spectroscopic source for the determination of F and Cl. Particularly, the temporal evolution of these emissions within the plasma, as well as several sample preparation procedures have been studied to optimize the detection of these elements.

References

[1] M. Gaft, L. Nagli, N. Eliezer, Y. Groisman, and O. Forni, Spectrochim. Acta - Part B At. Spectrosc. “Elemental analysis of halogens using molecular emission by laser-induced breakdown spectroscopy in air,” vol. 98, no. June, pp. 39–47, 2014.

[2] C. Alvarez-Llamas, J. Pisonero, and N. Bordel, Spectrochim. Acta Part B At. Spectrosc “Quantification of fluorine traces in solid samples using CaF molecular emission bands in atmospheric air Laser-Induced Breakdown Spectroscopy” vol. 123, pp. 157–162, Sep. 2016.

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- Government of the Principality of Asturias GRUPIN IDI/2018/000186
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Considerations on the formation mechanisms of emitting species from organic and carbon-containing inorganic compounds in CO2 atmosphere using LIBS

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Integration of LIBS instruments in the rover used for planetary exploration in an attempt to get multi-elemental information from rocks, minerals, and soils is a reality. Its great effectiveness has been demonstrated in many works from the research teams participating in the mission Mars Science Laboratory (MSL). However, the detection and discrimination by LIBS of organic compounds can be complex since, among other aspects; this technique is very sensitive to environmental conditions, such as the atmosphere composition and pressure [1-3]. The objective of this investigation is to assess the effect of the surrounding atmosphere (CO2) on the formation of emitting species in laser-induced plasmas of C-containing compounds in order to identify the possible both inorganic and organic sources. Moreover, the influence of molecular structures on the intensity of C, C2, CN, H, N and O emissions has been analyzed (Fig. 1). Four organic compounds (adenine, glycine, pyrene, and urea) were selected for their interest as possible indicators or precursors of life. A laboratory LIBS system coupled to a pressure chamber for simulating Martian environment was used for the analysis of pellet-shaped samples. Formation pathways of species coexisting in the plasma plume (C, C2 and CN, mainly) generated in air and in CO2 atmosphere have been considered. The ablation thresholds and the limits of detection of the organic molecules on inorganic matrices (CaCO3 and CaSO4 2H2O) have been established.

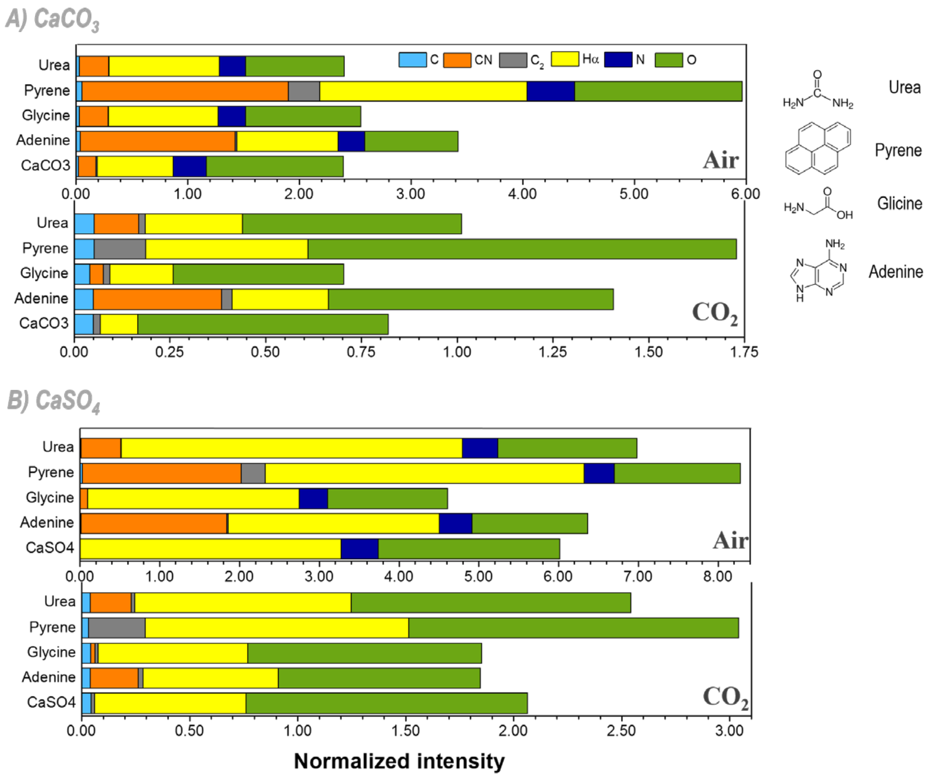

Fig. 1.: Comparison of the optical emission C-containing and non-C-containing species expressed as normalized intensity. The results were determined in pure inorganic matrixes mixed with a 10 % (w/w) of organic dopant, both in air and in CO2 atmosphere conditions.

References

[1] MOROS, J., EL FAHAM, M., LASERNA, J.J., Dual-spectroscopy platform for the surveillance of Mars mineralogy using a decisions fusion architecture on simultaneous LIBS-Raman data. Analytical Chemistry. 90 (2018) 2079–2087.

[2] DELGADO, T., VADILLO, J. M., LASERNA, J. J. Pressure effects in laser-induced plasmas of trinitrotoluene and pyrene by laser-induced breakdown spectroscopy (LIBS), Appl. Spectrosc. 68 (2014) 33–38.

[3] DELGADO, T., VADILLO, J.M., LASERNA, J.J., Acting Role of Background Gas in the Emission Response of Laser-Induced Plasmas of Energetic Nitro Compounds, Appl. Spectrosc. 70(8) (2016) 1364–1374.

Acknowledgement

This work was financially supported by the Programa Estatal de Fomento de la Investigación Científica y Técnica de Excelencia. Ministerio de Economia, Industria y Competitividad. Reference: CTQ2017-82137-P

A non-calorimetric study of hygrothermal aging of pyrotechnic material by using laser-induced breakdown spectroscopy

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The degradation of thermal properties such as burning rate and exothermic heat of reaction due to aging is a serious issue associated with a long-term storage of a pyrotechnic material. This study investigates the effect of the excessive exposure to moisture for the aging pyrotechnic delays, composed of metal fuel (Zr) and oxidizers (BaCrO4, KClO4). The laser-induced breakdown spectroscopy (LIBS) was used to effectively obtain both molecular and atomic signals by detecting the zirconi-um-oxygen (Zr-O) bonds. The rising trend of a distinctive molecular signal provides meaningful interpretation of the oxida-tion level for metal fuel. The additional complementary spectroscopic techniques such as x-ray photoelectron spectroscopy and scanning electron microscopy were used to investigate the chemical changes in oxidizers and the physical changes in the fuel, respectively. As a result, one enriches the understanding of aging mechanism from the calorimetric assessment together with the spectroscopic analyses for the underlying cause of aging.

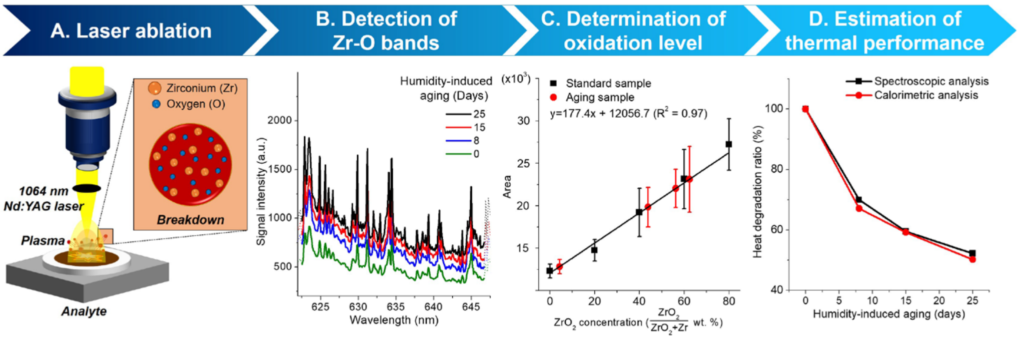

Fig. 1.: The experimental procedure utilizing LIBS for studying the aging mechanism.

Acknowledgement

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PII_090

Effect of IR laser energy on several polymers using LIBS analysis

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Polymers are frequently used in the prototyping platform in the research center of Algeria CDTA (Centre de Développement desTechnologies Avancées). For this reason, we investigated thermal effect of several polymers in order to show their thermal damage. The IR laser in nanosecond regime induce photo thermal effect than photochemical one [1, 2], this allows us to use the laser energy as a thermal source. The experiments is done in atmospheric ambiance using an Nd:Yag laser (□=1064 nm, t=10ns) to create the plasma and a echelle spectrometer (ARYELLE 200, LTB) to record the spectra. Five polymers are studied: Polyvinyl chloride (PVC), Teflon, polyimide, Bakelite and PolyOxymethylene (POM). C, Na, Mg, Ca atomic lines and CN molecular bands, characterizes all spectra of those polymers. The polymer's plasmas have been differentiated on the basic on the atomic lines related to additive compound; these components are added to polymers chains in order to improve their physical and mechanical properties. Wavelength Dispersive X-ray Fluorescence (WDXRF) analysis has also been done to determine and to confirm the qualitative polymers composition.

References

[1] M. Boueri, Laser-induced plasma on polymeric materials and applications for the discrimination and identification of plastics, in, Université Claude Bernard-Lyon I, 2010.

[2] D. Bäuerle, Laser processing and chemistry. 2011, in, Springer-Verlag: Berlin Heidelberg.

Analysis of HPHT diamonds by laser-induced breakdown spectroscopy during the laser-induced graphitization process

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HPHT method make it possible to grow large single-crystal diamonds both for the jewelry industry and technological applications. Synthetic diamonds contain various impurities and impurity centers in their atomic structure that affect the change in their physical and optical properties. Previously, two stationary stages of laser ablation during the laser-induced graphitization of the diamond surface were observed (Fig 1.). As a result, the appeal of using LIBS in combination with an increasing in the sensitivity of the method was found. It was also confirmed that the LIBS can be used to detect changes in the structural bonds of carbon atoms in samples that occurred due to changes in hybridization [1, 2]. Graphitization of the diamond surface already began after few laser pulses and was got noticed in a sharp increase in the emission intensity of the C2 molecular bands in the plasma spectra which was significantly different for the sectors with crystallographic orientations (100) and (111). Increase of intensity of the CN emission bands was also observed but turned out to be less significant. Based on the latest data obtained, it is possible to conclude that the plasma spectra of transition states of the surface during the process of laser-induced graphitization also are very important for analysis of diamonds and can help in their identification. Identification of diamonds, including real time[3], both can occur based on the detection of differences in content of H, O, N impurities (on basis of analysis of intensities of CN, H, O,N emission bands), and detecting differences in the structural disorder of carbon bonds, particularly in the relative change in the number of C=C bonds (on base of analysis of C2 emission bands). All these differences may be the result either of technological differences in the history of diamond synthesis, or the presence of additional post-growth diamond processing, or the presence of the multisectoral structure of the test sample.

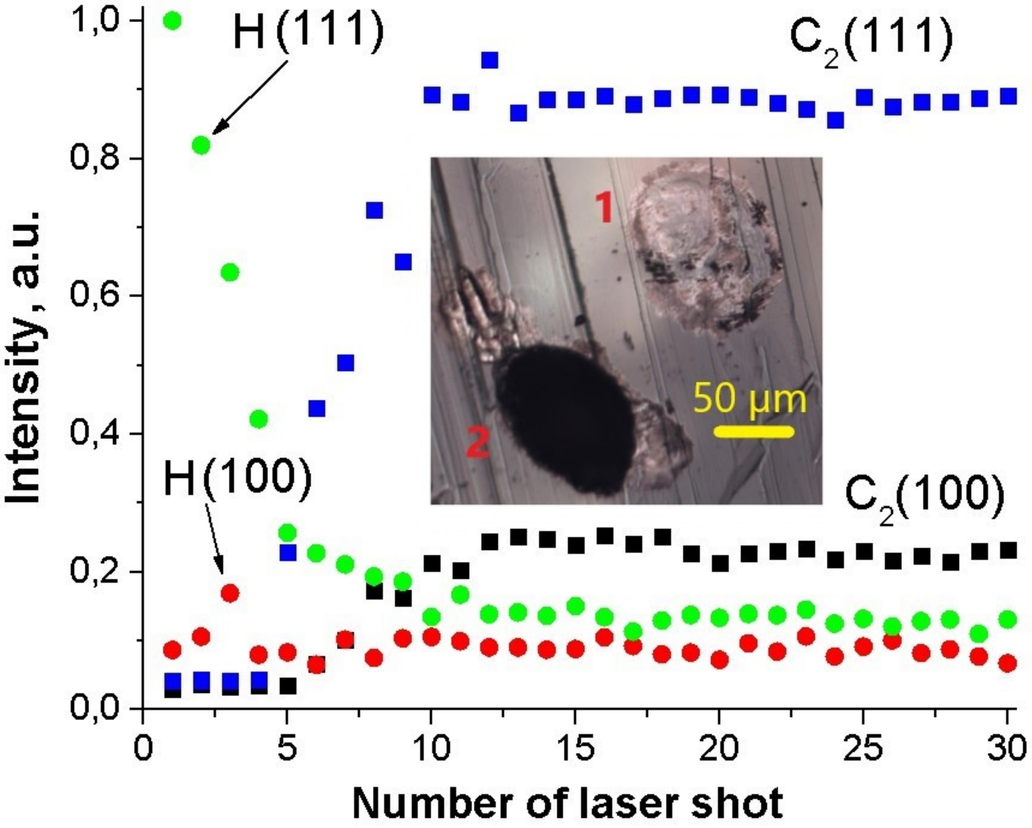

Fig. 1.: Dependences of intensities of C2 and H bands on the laser pulse number (inset: photo of spots after 5 laser pulses (1) and more than 15 pulses (2)). Energy of laser pulses is 234 mJ

References

[1] Lebedev, V.F., Pavlov, K.V., Koliadin, A.V., Quantum Electronics. 2018, v. 48(12), pp. 1171-1173.

[2] Lebedev, V.F., Rabchinskii, M.K., Kozlyakov, M.S. et al., J. Anal. At. Spectrom., 2018, vol. 33, pp. 240-250.

[3] Lebedev, V.F., Makarchuk, P.S., Stepanov, D.N., Spectr. Acta Part B, 2017, v. 137, pp. 23-27.

Nanoparticle analysis by LIBS and ICP-MS in industrial and environmental samples

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Along with the quickly expanding use of nanoparticles (NPs) in various products, the need for the development of analytical techniques for the detection and characterization of nanoparticles in industrial and environmental matrices also grows. Two applicable analytical techniques are LIBS and ICP-MS. Both of these sensitive and versatile techniques provide elemental compositional information. Based on the success of the application of LIBS in aerosol analysis, also in numerous in-field scenarios, this technique can be expected to be similarly useful in NP monitoring applications, such as the detection of NPs in liquid or gaseous matrices, or for the monitoring of the properties of NPs produced by physical generation methods (e.g. electrical discharges or laser ablation). ICP-MS on the other hand has already proven itself useful in the literature, both in the solution or single particle analysis (spICP-MS) modes, for the characterization of nanoparticles. In recent years we also reported about the successful development of several ICP-MS based analytical methods for the compositional and dimensional analysis of NPs (e.g. [1, 2]). In our present study, we investigated the potential of LIBS and ICP-MS for nanoparticle detection and characterization both in on-line (only for LIBS) or off-line (following collection on a filter) mode. Dispersions of various types of nanoparticles (e.g. monometallic, bimetallic, oxide, polymer) in simulated or real liquid and gaseous industrial and environmental matrices were measured. Some NPs were obtained commercially, while others were generated by in-house developed electrical (spark or arc) discharges. Additional and reference characterization of the nanoparticles were performed by electron microscopy (SEM, TEM) and scanning mobility particle sizing (SMPS). Size and mass detection limits were also calculated for on-line LIBS detection of nanoaerosols and for spICP-MS detection of NPs in aqueous nanodispersions.

References

[1] A. Sápi, A. Kéri, I. Kálomista, D.G. Dobó, Á. Szamosvölgyi, K.L. Juhász, Á. Kukovecz, Z. Kónya, G. Galbács,
J. Anal. At. Spectrom. 32 (2017) 996.

[2] A. Kéri, I. Kálomista, D. Ungor, Á. Bélteki, E. Csapó, I. Dékány, T. Prohaska, G. Galbács, Talanta 179 (2018) 193.

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PII_093

Application of LIBS for elemental analysis of composite nanoparticles in solutions

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In recent years, plasma-based techniques in liquid have been recognized as versatile and effective tools for fabrication of nanoparticles (NPs) including composite ones. Therefore the development of methods for rapid monitoring of the NPs composition is one of the most important tasks in modern nanotechnology.

Laser-induced breakdown spectroscopy (LIBS) has emerged as a promising technique suitable for rapid, *in situ*, and multi-element analysis. However, as for the quantitative LIBS analysis of liquids, there are still some drawbacks that limit its capabilities, such as poor repeatability and low sensitivity. One of the ways to overcome these difficulties is to convert the liquid into a solid phase by drying the colloid on the substrate. In the present paper we report on the experimental results demonstrating the feasibility of the LIBS for the control of the colloidal NPs elemental composition. As a rule, LIBS analysis requires calibration of the spectrometer using certified reference materials, whose range is extremely limited. Another approach is based on the optical diagnostics of laser produced plasma and is calibration free (CF-LIBS). The purpose of this work was to test CF-LIBS technique for the analysis of colloidal nanocomposites.

Sn/Ge, Si/Sn, Ag/Cu NPs as well as CoO/ZnO nanocomposites synthesized both by laser ablation and electrical discharge in liquids were analyzed using LIBS. The samples were prepared by drying a droplet of the colloidal solution (10 □l) on a glass substrate. Varying a number of drops of the colloidal solution makes it possible to vary the surface concentration of NPs in order to obtain sufficiently intense but optically thin spectral lines. LIBS experiments were carried out by using a Nd:YAG laser (LOTIS TII, LS2134D, Belarus), operating in a double-pulse mode at 1064 nm (energy 80 mJ/pulse, pulse duration 10-12 ns, optimal delay between laser pulses 2 µs). The laser beam was focused to a spot ~ 800 □m in diameter. Plasma emission spectra were detected using a grating spectrometer equipped with CCD linear array in the spectral range of 200–1060 nm.

The obtained LIBS spectra revealed that NPs can be identified and that the LIBS technique can be used to determine the NPs elemental composition. 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 particle components and calculating the elemental composition of the NPs. The results of LIBS analysis of CoO/ZnO, Sn/Ge, Si/Sn, Ag/Cu 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 the analysis of solutions consist in its simplicity, speed, small amount of solution needed (few □l), and a possibility of

NPs stoichiometry control during the production process.

Acknowledgement

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Evaluation of silver nanoparticles on indium-tin-oxide (ITO) type SERS substrates for nanoparticle-enhanced LIBS analysis of liquid samples

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Nanoparticle enhanced LIBS (NELIBS), introduced by de Giacomo et al. [1] is a noteworthy approach that promises LIBS signal enhancement as large as hundred-fold by employing properly sized and distributed (metallic) nanoparticles on the surface of a solid (preferentially conducting) sample, or on a similarly prepared solid substrate that carries a liquid sample [2]. Today, surface-enhanced Raman scattering (SERS) substrates are commercially available popular tools that provide strong signal enhancement (up to 108) in Raman spectroscopy [3]. They are essentially similar in construction to NELIBS substrates. In addition to this, good sample contact with the substrate, strong absorption of the laser light at the surface plasmon resonance peak are also similar preconditions in both applications. Based on this similarity, we decided to assess how commercial SERS substrates perform in NELIBS and whether they can be tuned also to be useful for NELIBS purposes or not. Should the applicability be proved, it would open up a possibility for the widescale application of NELIBS in routine liquid sample analysis. During this study, we used the popular indium-tin-oxide (ITO) coated glass with Ag nanoparticles as substrate (SERSitive Ltd.). Nd:YAG lasers with wavelengths 266 nm and 1064 nm and various spot sizes were utilized. The effect of a number of experimental parameters on the NELIBS signal enhancement and signal repeatability provided by the substrate for liquid samples dried onto the substrates were investigated. Among the studied experimental variables were: nanoparticle diameter, nanoparticle surface concentration, laser wavelength, laser fluence, methods of coating preparation from the sample liquid (e.g. droplet placement, dip-coating, etc.). The prepared substrates were also scrutinized by surface characterization tools. We also studied how the NELIBS effect would affect the background LIBS spectrum originating from the ITO and glass layers.

References

[1] A. De Giacomo, R. Gaudiuso, C. Koral, M. Dell’Aglio, O. De Pascale, Anal. Chem. 85 (2013) 10180.

[2] M. Dell'Aglio, R. Alrifai, A. De Giacomo, Spectrochim. Acta Part B, 148 (2018) 105.

[3] P.A. Mosier-Boss, Nanomaterials 7 (2017) 142.

Acknowledgement

Financial support of the project was provided by the National Development, Research and Innovation Office of Hungary under No. K_129063 and EFOP-3.6.2-16-2017-00005 (Ultrafast physical processes in atoms, molecules, nanostructures and biological systems).

Laser-Induced Breakdown Spectroscopy as a Novel Readout Method for Nanoparticle-Based Immunoassays

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Laser-Induced Breakdown Spectroscopy (LIBS) was examined as a novel method to provide the readout of microtiter plate immunoassays involving nanoparticles (NP). The so-called Tag-LIBS, i.e. a sensitive detection of specific biomarkers, was applied to detect the NP labels using the nanosecond ablation sampling. The NP labels were examined from the bottom of the standard 96-well microtiter plate. Thanks to the well-known flexibility in the LIBS instrumentation, the plasma emission collection as well as the focusing optics can be rebuilt into a collinear arrangement. The presented experiments proved the suitable detection of silver NPs from the microtiter plate's bottom without any negative effects on the NPs' qualitative and quantitative analysis. Subsequently, a sandwich immunoassay that detects human serum albumin was successfully developed, using streptavidin-coated AgNP labels. The assay provided a detection limit of 10 ng/mL, which is comparable with the fluorescence-based readout. The main advantage of LIBS readout is that it enables a detection of any type of NP labels independent on their fluorescence or catalytic properties. Owing to the immediate signal response, a relatively simple instrumentation enabling the automation, and the capability of multi-elemental analyses, LIBS technique offers a promising and fast alternative to other readout techniques allowing a multiplex detection of various biomarkers.

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Plasma relative emission efficiency for LIBS and NE-LIBS

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In this work, the correlation between plasma emission and ablation mass is investigated during LIBS (Laser Induced Breakdown Spectroscopy) and NELIBS (Nanoparticlecles enhanced LIBS) experiments. The aim of this study is to compare the relative emission efficiency, defined as the ratio between plasma emission on the ablated mass, as estimated by crater profiles, for different LIBS and NE-LIBS experiments. The experiments were performed on a titanium target using a Nd:YAG laser at 1064 nm with a pulse time duration of 6 ns. LIBS and NELIBS plasma emissions were acquired by employing different lasers spot sizes at constant fluence of 10 J/cm2. The obtained results have been finally compared to a set of LIBS measurements at constant spot size of 500 µm and different laser fluences. It has been observed that, even if the variation of the laser energy, holding constant spot size, does not affect notably the ablated mass, the energy increase leads to higher emission efficiency. This behavior suggests that the most of the energy is directly transferred to the plasma phase improving the sample atomization and excitation. On the contrary, for a given fluence, by increasing the laser spot size, the ablated mass notably increases as well, but the LIBS emission efficiency decreases. In this case higher signal is collected only because more sample is ablated but in the ablated material lower atomization and excitation can occurs. While at constant spot size LIBS and NE-LIBS have a similar trend with varying fluence, increasing the laser spot size keeping constant the fluence, increases the NELIBS emission efficiency. The latter observation shows a completely opposite NELIBS trend with respect to the LIBS one. This phenomenon has been ascribed to the additional energy transferred to the sample because of nanoparticles (NPs), as a consequence of the NPs plasmonic effect during laser-sample interaction.

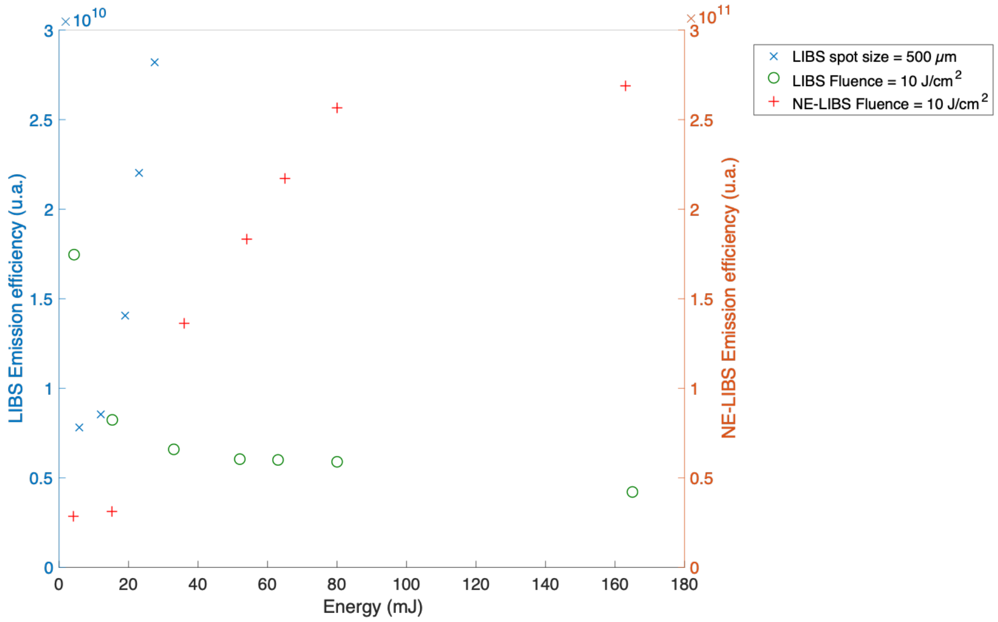

Fig. 1.: Emission efficiency, defined as integrated intensity divided by ablated mass for a single shot for LIBS and NE-LIBS as a function of the energy. Three different behaviors seem to appear, each one connected to the ionization state of the plasma.

Double-Pulse Nanoparticle-Enhanced LIBS (DP-NELIBS)

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Traditionally, the improvement of LIBS performances is based on the introduction of more powerful lasers, high sensitivity detectors or controlled environmental parameters. Several strategies have been effectively tested in the past to enhance the emission intensity, involving different experimental configuration, such as Double Pulse LIBS (DP-LIBS) or the use of a secondary electric pulse following the laser ablation. Besides multiple excitation schemes, alternative methods based on confining the plasma expansion have been also studied, for instance confining the laser plume in a steady or pulsed magnetic field. Recently, sample treatment has proven to be a viable and simple way to enhance the LIBS signal; in particular, the NELIBS methodology uses a deposition of metal nanoparticles (NPs) on the sample to greatly increase the emission of the LIBS plasma. In several works, enhancement of the LIBS signal up to two orders of magnitude have been separately reported either using DP-LIBS or NELIBS, with respect to single impulse LIBS on untreated surfaces. In this communication we will present and discuss the advantages of a new combined approach that allowed us to obtain, by applying minimal modifications to a standard collinear LIBS double-pulse setup, a substantial enhancement of the LIBS signal with respect to both conventional DP and NELIBS. The chosen set-up uses two offset and collinear laser pulses to ensure the activation of NPs during both pulses, while maintaining the low-pressure environment typical of DP-LIBS. The two laser beams are indeed spatially separated so that the second beam is focused within the plume of the first one. This configuration would allow for the exploitation of the advantages of both DP-LIBS and the enhancement provided by silver NPs deposited onto a metallic target (DP-NELIBS). DP-NELIBS can be particularly interesting in a number of analytical applications because of its capability of strongly enhancing the signal of otherwise weak

Enhancement of LIBS signals from a steel sample with Au nanoparticles on its surface

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One of the main drawbacks of Laser Induced Breakdown Spectroscopy (LIBS) in analytical applications is its rather low sensitivity and hence a high limit of detection as compared to the best techniques using optical emission spectra (e.g., ICP-OES). For solid samples, their surface preparation was found to help in ameliorating the LIBS performances. One of the ways is using nanoparticles deposited on the sample surface before the laser shots. The nanoparticles increase the intensity of spectral lines in the plasma plume emission, thus enhancing analytical signals of LIBS. Despite the rapid growth in the number of articles devoted to the nanoparticle use in LIBS, the factors that provide the enhancement are still not fully established. In the report, characteristics of the plasma plumes on a surface of the steel samples covered with Au nanoparticles have been studied and compared to the case with no nanoparticle deposition. The setup used for the measurements consists of a Nd:YAG laser generating the fundamental harmonic at 1064 nm with pulses of 6-8 ns duration and 10 Hz repetition rate. Laser plumes were imaged 1: 1 on the end of a quartz optical fiber using an achromatic lens of 20 mm focal length. A Cherny-Turner spectrometer has been used with the focal length and aperture of 380 mm and 1: 4.7, respectively, with a grating of 600 lines/mm. The emission spectra were recorded within 200 – 1000 nm by a CCD detector of 2048 pixels. The spectra, as well as images of the plumes and the laser erosion craters have been analyzed depending on power density of the laser pulses and space zones of the laser plumes with and without surface deposited nanoparticles. The spectra lines have been used to evaluate optical density, electron concentration and elemental composition of the plasma. It has been found that the nanoparticles increase the volume of the plasma and the concentration of electrons, but it does not lead to an increase in the erosion of the sample material. In this case, an increase in the intensity of the emission of spectral lines is observed, the relative magnitude of which depends on spatial zones of the plasma plume emission. For the areas remote from the sample surface, the signal relative gain is significantly higher. Also, an influence of ambient atmosphere on the plasma composition and thus its stoichiometry compared to the sample has been observed. With the nanoparticles, concentration of nitrogen decreases being forced out by the sample metal, which can be one of important reasons of the observed enchancement of analytical signals.

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Nanoparticle-enhanced laser ablation coupled with ICP-MS

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Nanoparticles (NPs) applied to the surface of some solids can increase signals in LIBS [1-2] and also in inductively coupled plasma mass spectrometry (ICPMS) [3]. Drops containing nanoparticles of Ag and/or Au in the size range of 10 to 200 nm were deposited on metallic and ceramic/glass samples, and after being dried, both the samples treated with NPs and plain targets were ablated by one pulse per spot. The laser ablation ICPMS (LA-ICPMS) signals were enhanced for metallic samples modified with NPs in comparison to signals produced at the plain, untreated surface.

Maps of LA-ICPMS signals recorded for several laser fluences show that the NP-induced signal enhancement exceeds even 2 orders of magnitude for metallic samples. No enhancement was achieved for nonconductive samples. This enhancement is limited to the peripheral annular region of the dried droplet area where NPs are concentrated due to the “coffee stain” effect. Ablation crater profilometric inspection revealed a more uniform material rearrangement over the NP-treated surface compared with the ablated plain target. However, besides a smoother crater bottom, no other evidence of an NP-enhancing effect was noticed, although an increased ablation rate was anticipated. Limits of detection dropped by 1 order of magnitude for the minor elements in the presence of NPs. Observed phenomena depend only on the NP surface concentration but not on the material or size of the NPs. An electron microprobe study of the collected ablation aerosol has shown that aerosol particles consisting of the target material are aggregated around the NPs. The particle size distribution of aerosol measurement showed an increased number of transported particles in case of nanoparticle-enhanced LA. The combination of changes in particle size distribution and particle number leads to better transport/vaporization efficiency, thus enhancing signals of measured analytes.

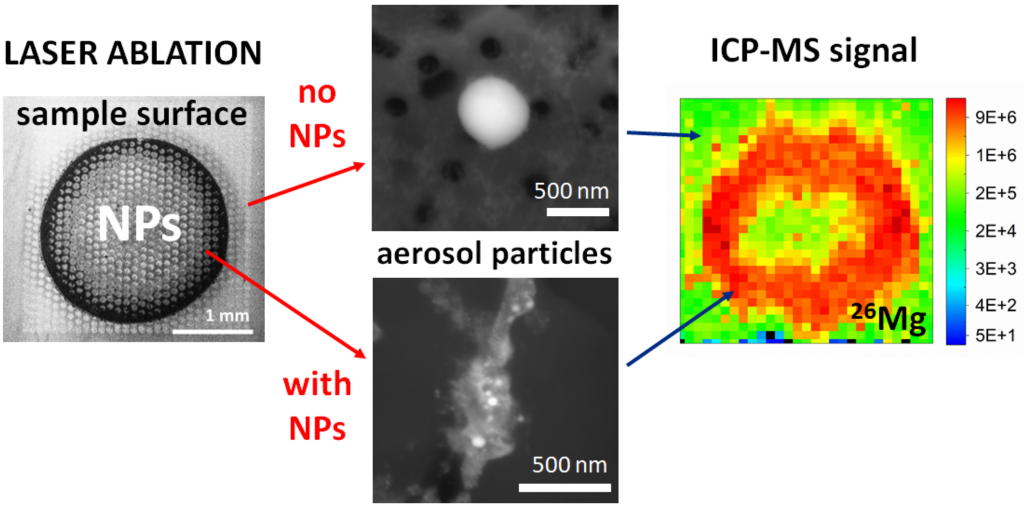

Fig. 1.: Schema of nanoparticle-enhanced laser ablation ICPMS principle.

References

[1] SLA□DKOVA□, L., PROCHAZKA, D., POR□ÍZKA, P., S□KARKOVA□, P., REMES□OVA□, M., HRDLIC□KA, A., NOVOTNY□, K., C□ELKO, L., KAISER, J.: Spectrochim. Acta, Part B 2017, 127, 48–55.

[2] HOLA□, M, SALAJKOVA□, Z.,HRDLIC□KA, A.,POR□ÍZKA, P.,NOVOTNY□, K., C□ELKO, L., S□PERKA, P., PROCHAZKA, D., NOVOTNY□, J., MODLITBOVA□, P., KANICKY□, V., KAISER, J.: Anal. Chem. 2018, 90, 11820–11826

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Study of the feeding effect on recent and ancient bovine bones by nanoparticle-enhanced laser-induced breakdown spectroscopy and chemometrics

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This study aimed to exploit laser-induced breakdown spectroscopy, enhanced by nanoparticles (NELIBS), as a fast, sensitive and low-cost technique, to correlate the elemental composition of recent and ancient bovine bone with the elemental composition of the fodder that has been fed to the cattle throughout their life. Biosynthesized silver nanoparticles (BS- Ag NPs) were used to enhance the emission intensity of the spectral lines in the LIBS spectra of contemporary and ancient bovine bones and fodder samples. The ancient bones are more than 4600 years old and belong to the 3rd dynasty of the old Egyptian Kingdom. Ag NPs were biosynthesized in a simple and inexpensive manner using potato (Solanum tuberosum) extract. As a validation technique for the NELIBS results, EDX spectra were successfully used, and scanning electron microscopy (SEM) clearly discriminated between recent and ancient bovine bones. Additionally, principal component analysis (PCA), as a multivariate analysis technique

Laser-induced breakdown spectroscopy: a characterization tool in the restoration field related to protective nano-biocides

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In this work the penetration depth of four biocidal treatments based on nanoparticles has been characterized and compared by laser-induced breakdown spectroscopy (LIBS) technique. In particular, limestone from Novelda quarry (Alicante, Spain), widely employed in historical and contemporary buildings in Spain, was treated with four different nano-biocides based on silver nanoparticles, combined in some cases with titanium dioxide nanocomposites. These biocidal nanoparticles are being studied to be employed in historic buildings and stone monuments due to their capability to inhibit the growth of biofoulings, and the biocidal effectiveness of the treatment depends on the penetration depth of the nanoparticles. For this reason, depth analyses were carried out by LIBS to determine and to compare the penetration depth of the four treatments. The emission line of Ag at 338.289 nm was monitored as an evidence of the presence of the silver nanoparticles and derived nanocomposites in the limestone and LIBS depth profiles of the Ag net signal were generated. Both, the in-depth spectra sequences and the depth profiles exhibited the decrease of Ag signal with depth, in agreement with the diffusion of the treatments in the limestone matrix. In addition, the results evidenced penetration differences between the four bactericidal treatments which were explained by differences in the hydrodynamic diameter of the nanoparticles that would affect their diffusion in the limestone pore. This study demonstrates the capability of LIBS technique for the characterization and comparison of nano-biocidal treatments effectiveness from the analysis of the penetration depth of the nanocomposites and the potential of the technique as a characterization tool in the restoration field related to protective nano-biocides.

Application of LIBS in the recycling and sorting of aluminum scrap

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Aluminum alloys are the most widely used non-ferrous metallic structural materials in the aviation industry. A large number of aluminum alloys wastes need to be recycled. Aluminum alloys are used on different position of industrial equipment and largely vary in prices due to their chemical compositions. Therefore, classified recovery is needed. In this paper, the on-line sorting system of aviation aluminum scrap is designed. The laser focused light path is focused at a long focal length, so that samples of different thicknesses can be effectively bombarded; According to the different shapes and heights of aluminum scrap, a high-focus coaxial optical system with a wide range of heights is designed to solve the problem of spectral focal plane shifted of actual samples. The sample recognition system uses image recognition technology to identify samples of different sizes, Combined with the hardware synchronous trigger control system to excite the sample precisely; Combined with the sorting samples a variety of classification algorithms are designed. The results show that the accuracy of three kinds of aluminum alloy sorting can reach above 90% and sorting speed is no less than 90 pieces per minute. In a word□LIBS combined with classification algorithms by machine learning can classify aluminum scrap rapidly and accurately, and it can also be used in the recycling of other metal materials, thus has important application and popularization value.

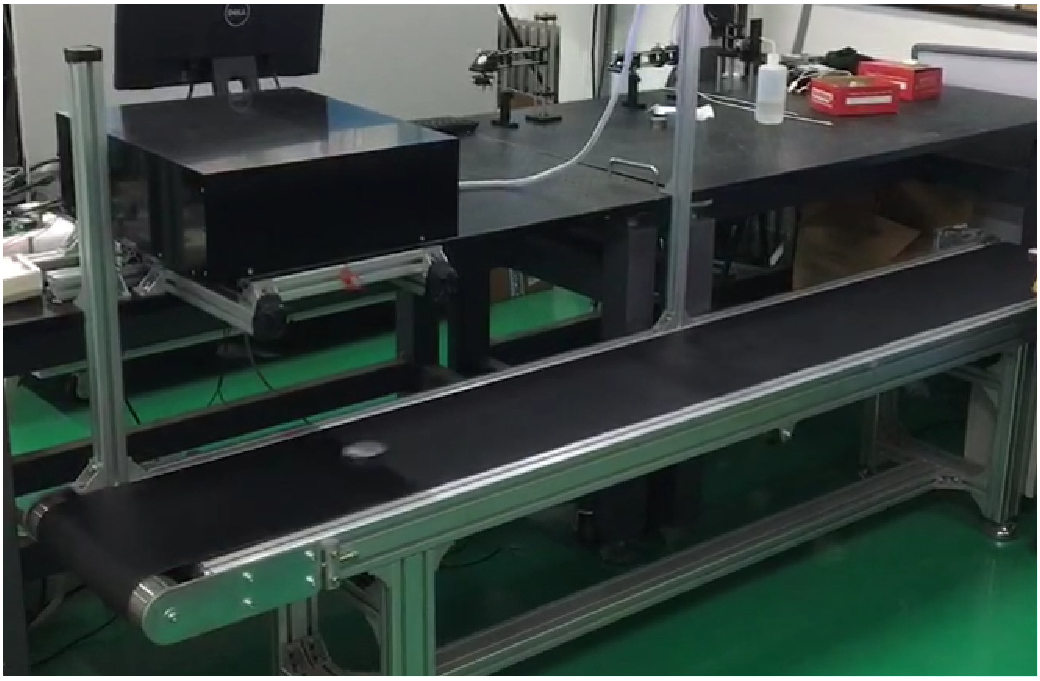

Fig. 1.: LIBS Sorting System

References

[1] Bigne F B. Applied Spectroscopy, 2007, 61(3):333

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Advantages and limitations of Laser-induced breakdown spectroscopy (LIBS) for direct e-waste analysis

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Over the years, the amount of waste of electrical and electronic equipment (WEEE) is growing in several countries due to alarming levels of disposable income and urbanization. There are elements of industrial and strategic importance in WEEE, being a source of resources for recovery [1]. In order to characterize this material, analytical techniques are used, where LIBS is an alternative in which it is possible do the direct solid analysis. But direct analysis presents some difficulties in the reproduction of the data due to, sampling, ablation process, microheterogeneity and matrix effects, which can be minimized combining the LIBS spectra with chemometrics [2]. In this study, one printed circuit board (PCB) from hard disk (HD) was cut in 77 small fragments (1 by 1 cm) in order to simulate a crushing machine in industry [3]. Each solid fragment was analyzed by LIBS, followed by acid digestion and analysis using ICP OES in order to acquire reference values. For LIBS (Applied Spectra, model J200), a fluence of 1270 mJ/cm2, 1 µs of delay time and 5 Hz of frequency were used, and a matrix of 4 rows and 4 columns was made in each fragment and 10 pulses in each point of the matrix (160 spectra per fragment). The great challenge of the study is to correlate these 160 spectra with one reference value obtained by ICP OES, because while LIBS is a punctual technique, for ICP OES the result is for whole sample (fragment). On the one hand, the LIBS may reach a specific point with a certain composition, but in ICP OES it is not that actual point that is analyzed, but rather the whole fragment. Hence the correspondence between the LIBS and ICP OES measurement may be a significant problem. Therefore, to find a solution to solve this challenging problem some chemometrics approaches were tested, using a classification models for Au as an example. Despite the problems mentioned, good classification results are being obtained using partial least squares discriminant analysis (PLS DA).

References

[1] Balde, C. P., Forti, V., Gray, V., Kuehr, R., Stegmann, P. The Global E-waste Monitor 2017, Quantities, Flows and Resources. United Nations University. Geneva, Bonn, Vienna – November 2017

[2] Zhang, T.; Tang, H.; Li, Hua. Chemometrics in laser-induced breakdown spectroscopy. Journal of Chemometrics. 2018, 1-18.

[3] Noll, R.; Fricke-Begemann, C.; Connemann, S.; Meinhardt, C.; Sturm, V.; LIBS analyses for industrial applications – an overview of developments from 2014 to 2018. J. Anal. At. Spectrom. 2018, 33, 945-956.

Acknowledgement

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On-line LIBS analysis for the classification of metal alloys and plastic scrap. From lab environment to conveyor belts.

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The purpose of the work is to develop stable and accurate algorithms for the analysis of LIBS data of metal alloys and plastics in view of their rapid identification and sorting at industrial recycling facilities. One requirement for machine learning (ML) approaches is to have a large representative test set in order to ensure that the model is based on signals originating only from the material of interest. In this view, we have performed extensive measurement campaigns for plastic and metallic scrap-material both at our in-house test bed and at several industrial facilities. This provided us an extensive sample set made up of several independent measurements of real scrap pieces, on which we could test different ML algorithms. The methods include decision tree, artificial neural networks, and principal component analysis-based techniques. The performance of each algorithm in terms of classification accuracy and robustness and the influence of data-preprocessing are presented. For the classification of plastics and identification of additives, the requirement for a large and statistically training and test sets is even more important to get reliable results. The composition of additives can vary dramatically for material of different origin and interfere strongly with the LIBS-signals of the polymers.1,2 We carried out several independent LIBS measurements on different black plastics including PP, PE, PS, ABS, MEP and in particular the positive identification of non-halogenated plastics is of interest for the recycling industry. Soft-independent modelling of class analogy (SIMCA) was then used to classify the polymers. The constructed model gives promising results for these validation samples in term of classification accuracy. Finally, real plastic scrap pieces collected at industrial facilities are being measured with LIBS on an in-house conveyor belt to evaluate the stability of the SIMCA algorithm.

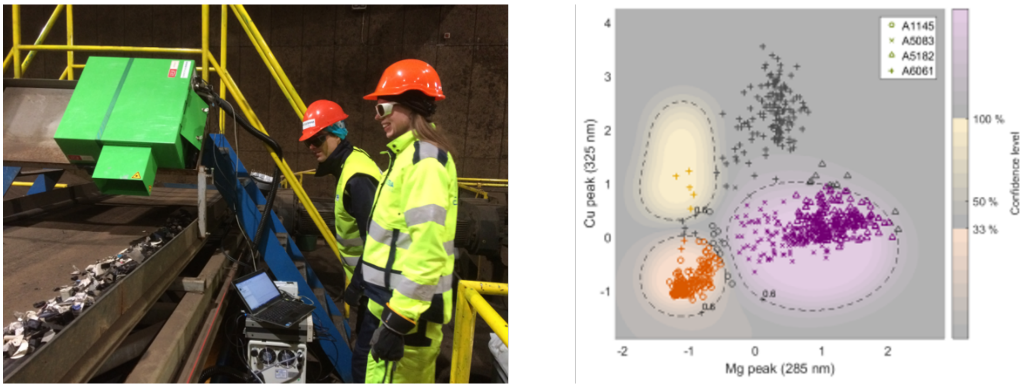

Fig. 1.: (left) Plastic scrap at recycling facility (right) implementation of SIMCA-analysis for classification of aluminium alloys

References

[1] Guo et al. Optics Express, 2014, 22, 3895-3901.

[2] Pereira-Filho et al. Polymer Testing, 2017, 59, 390-395.

Handheld LIBS Analyzer with Miniature Echelle Spectrometer for Analysis and Grade Identification of Alloys

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The very first, commercially available, Handheld LIBS analyzer was introduced in early 2013. Since that time several manufacturers entered with their offerings thus marking the successful migration of Laser Induced Breakdown Spectroscopy from the laboratory to field and industrial environments. Such progress has been made possible by development of small size and small power, pulsed, solid state lasers which could run on battery power. These Handheld LIBS analyzers are primarily built and configured for analysis of metallic alloys. However, the analytical performance of these new instruments (accuracy and precision) is still not as good as that offered by the Handheld X-Ray Fluorescence1), an industry accepted benchmark. One of the reasons for inferior performance is rather limited spectral resolution of spectrometers used in Handheld LIBS devices. Typical HHLIBS instrument is equipped with Czerny-Turner Spectrometer with spectral resolution on the order of 0.15 nm within the 200 to 450 nm range. Many emission lines are not resolved, thus significantly limiting number of lines suitable for analysis. In this paper we introduce a first of its kind, miniature Echelle spectrometer which offers practical spectral resolution of 0.03 to 0.05 nm within the 200 to 450 nm range (Fig. 1). With its small size of 126 x 60 x 71 mm and weight of about 400 grams, it can be easily built into a handheld LIBS analyzer. Improved spectral resolution increased significantly number of available analytical lines and made feasible quantitative analysis of certain elements present in steels at low concentrations. Examples will be shown of how the new spectrometer improves the limits of detection for alloying elements in steels and other alloy families and allows for their quantification at concentration levels below 0.1%. We will also discuss the performance of the spectrometer in LIBS analysis of carbon content of various steel grades. We will show that using protective atmosphere of helium rather than argon helps not only in analysis of carbon but also benefits quantification of other alloying elements. Improved overall analytical performance with added capability of analysis of carbon, silicon, magnesium, boron and lithium has potential to make HHLIBS an alternative to HHXRF method.

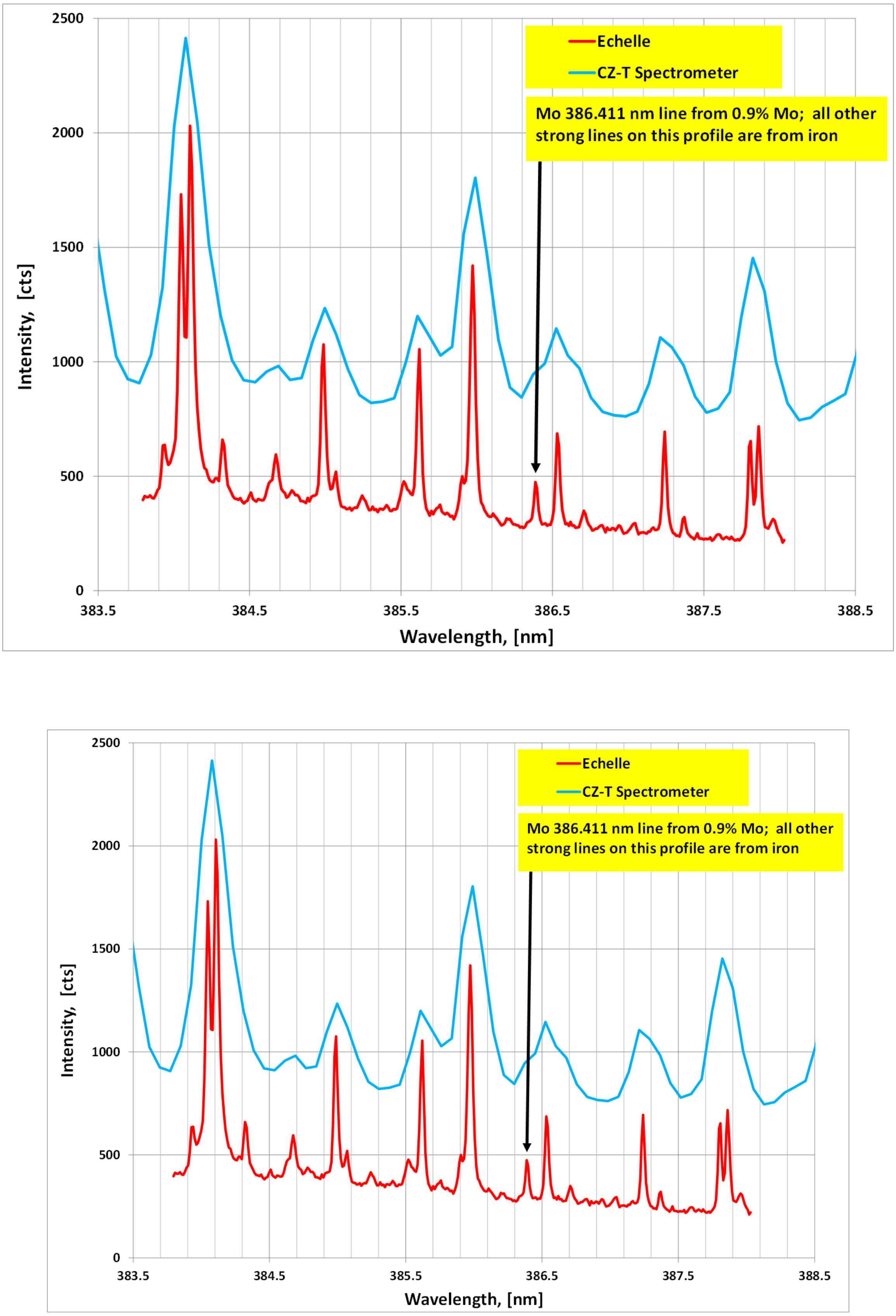

Fig. 1.: Fig. 1. Spectral resolution of two spectrometers. Shown are two LIBS spectra of Cr/Mo steel containing 0.9% molybdenum.

References

[1] S.Piorek, "Performance Comparison of Handheld LIBS and Handheld XRF Analyzers in Analysis and Grade Identification of Metallic Alloys", Presented at EMSLIBS 2017 Conference, June 11-16, Pisa, Italy.

On-line analysis of molten slag using Laser-induced breakdown spectroscopy

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The purpose of this work is to develop a technique for making quantitative analysis of the chemical composition of molten slag, with no or minimal sample preparation and short time from sampling to result. The motivation is both to be able to control the steel-making process and to be able to better use the slag as secondary raw material. Significant achievements in this direction will be presented. The method is based on Laser induced breakdown spectroscopy (LIBS) which has the potential to fulfill these needs of fast measurements and minimal sample preparation (compare with the grinding and molding that is required for an accurate XRF analysis). We have already demonstrated such experiments on solid slag samples that were analyzed with coarse crushing as the only sample preparation. The results obtained with our LIBS set-up compared very well with the XRF reference measurements; repeated measurements gave very similar relative standard deviation for both methods, approx. 1-2 % for the main elements. Quantitative measurements on molten slag in ladles after tapping have been demonstrated by Sturm et al. An important step towards a quantitative analysis of molten slag for process control is the ability to calibrate the LIBS-system with solid reference samples. We have experimental results on hot slag that show a significant correlation between the LIBS signals and the temperature. This has also been demonstrated in work by Lopéz-Moreno et al. and interestingly the signals for Si/Ca shows opposite behavior with temperature for the two studies. This shows that the calibration is not straight-forward since LIBS-signals are very sensitive to varying experimental conditions. However, it indeed shows that it is possible to obtain a calibration for molten slag using solid reference samples and this enables a correct calibration to be maintained for a long period of time which is required for the system to be implemented in the metallurgical process.

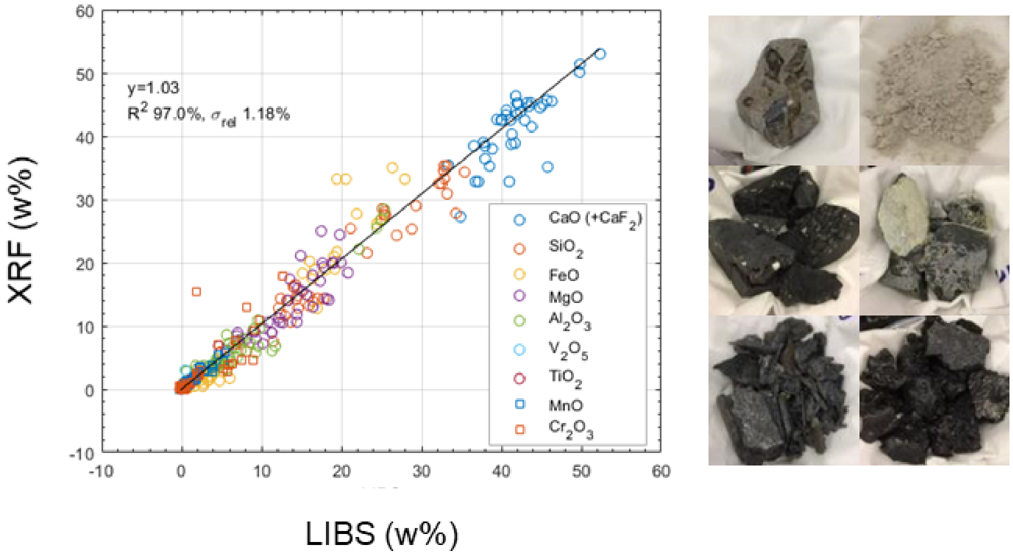

Fig. 1.: (left) chemical composition obtained with LIBS vs XRF. (right) typical composition of samples that were analyzed

References

[1] V. Sturm, R. Fleige, M. de Kanter, R. Leitner, K. Pilz, D. Fischer, G. Hubmer and R. Noll, Anal. Chem., 2014, 86, 9687–9692.

[2] C. López-Moreno, S. Palanco, J. J. Laserna, Spectrochimica Acta Part B, 2005, 60, 1034 – 1039

Classification of cement pastes with laser-induced breakdown spectroscopy

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In civil engineering, the investigation of existing infrastructure is of major importance for maintaining and ensuring stability of the structures. To ensure durability, uniform regulations and standards apply e.g. the European standard EN 206-1. In some countries, the EN-standard is supplemented by additional standards, as in Germany with DIN 1045-2. Here, specific application rules are described, e.g. for the cement type, to ensure the resistant to different exposures. Therefore, the knowledge of the materials originally used is important in assessing the condition of existing concrete structure. Unfortunately, these are often unknown and must be determined retrospectively. Therefore, we present the application of the laser-induced breakdown spectroscopy to distinguish between different types of cement. Spectral information's are used to build a classification model. First, the accuracy of the classification is analyzed on ten pure laboratory cement samples. To investigate possible sources of error, the model was then applied to cement samples with different moisture content. The study shows that LIBS is a promising tool for distinguishing between cement types. For further industrial application, however, factors influencing the LIBS signal must be included to ensure a robust model.

Laser-Induced Breakdown Spectroscopy: An essential technique for direct analysis of refractory wastes from steelmaking processes

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Refractories are primary materials that are able to withstand temperatures from 260°C – 1850°C used by the steel industry. A typical steel plant uses hundreds of types of refractories, each engineered for specific applications. Over a great many years, because of the abundance and low cost of virgin raw materials as well as the no or minimal disposal costs of the, scant attention has been given to recycling tasks of refractories. However, during the last years, difficulty in having high quality raw materials because their increasing global scarcity and the rising prices has led the much of refractory industry to turn attention to the recycling of spent refractories. This is why several technological innovations (including LIBS-based strategy) for refractory wastes reusing, remanufacturing and recycling, towards a circular economy adopted as the development model, are ongoing [1-2]. The goal of the present work focuses on the implementation of an efficient algorithm able to classify with great accuracy the nature of the refractory materials from their emission spectral information. A total of 11 samples from the various characteristic parts of a steel ladle have been assayed. Strategy begins with the identification and statistics evaluation of the spectral signals associated to Al and Mg, and the graphing, on 3D subspaces involving emission intensity ratios from some of those spectral signals as coordinates. Thus, the MgO-based and Al2O3-based refractories can be discriminated. Strategy has proven to yield satisfactory results to the sorting of "clean" (before-service) refractories. However, more adjustments are required (laser-cleaning, spectral data filtering ...) to a good performance of the strategy on the analysis of the refractory scraps because of the physical and chemical post-mortem (after operating) changes of the materials to permit LIBS to take one step forward in its progress towards the consolidation as a sorting tool.

References

[1] HORCKMANS, L., NIELSEN, P., DIERCKX, P., DUCASTEL, A. Recycling of refractory bricks used in basic steelmaking: A review, Resour. Conser Recy. 140 (2019) 297–304.

[2] NOLL, R., FRICKE-BEGEMANN, C., CONNEMANN, S., MEINHARDT, C., STURM, V. LIBS analyses for industrial applications – an overview of developments from 2014 to 2018, J. Anal. At. Spectrom. 33 (2018) 945–956

Acknowledgement

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Project website: https://www.life5refract.eu/es/

Copper and nickel elemental composition analysis by Laser-Induced Breakdown Spectroscopy (LIBS) in metal recovery chelating resin

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The recovery of valuable compounds from industrial wastes provide economic and environmental benefits. Particularly, the selective recovery of metals from wastewaters is an important strategy to minimize the raw material and natural resources consumption, as well as to avoid the environmental contamination. Acidic effluents containing nickel, copper and iron in sulphate media were provided by a local waste management industry. The selective removal and recovery of the target metals, nickel and copper, were performed by using the chelating resin MTS9600® (bis-picolylamine functionalization). In this preliminary work, we propose the use of the Laser-Induced Breakdown Spectroscopy (LIBS) technique to perform a chemical analysis of copper and nickel in the spherical particles of the resin. To understand the spatial distribution of the target elements in the resin's spheres, artificial effluents with different concentrations and combinations of metals have been treated. Superficial and inner measurements were performed in the resulting resin samples. The LIBS setup includes a Nd:YAG laser (Lotis LS-2147) at 1064 nm and 10 Hz repetition rate. The spectrometer used to perform the analysis is an Avantes ULS2048-USB2-RM. The setup is fully automated with a XYZ positioner, through-lenses imaging and an autofocus system based on image processing to deal with non-flat surfaces. The relative concentration of Copper, Nickel and Iron has been determined form the captured spectra.

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Analysis of major and minor elements in coal by laser-induced breakdown spectroscopy

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In this work, laser-induced breakdown spectroscopy (LIBS) measurements are performed on coal reference materials to determine the efficiency of this method concerning the detection of major and minor elements in coal. Cylindrical pellets are pressed from the reference coal powders and LIBS spectra are measured by Nd:YAG laser ablation and by the detection of plasma radiation using an Echelle spectrometer and intensified CCD camera. The experimental parameters (spectrometer timing, laser pulse energy) are optimized to measure emission line intensities with high signal-to-background and signal-to-noise ratio. LIBS calibration curves for the relevant chemical elements are created from the measured emission line intensities and the reference concentration values. Our results show that the major elements Si, Al, Fe, Ti, Ca, Mg, and C (exceptions are potassium and sulfur) can be clearly detected. The calibration curves show good linearity with high R^2 values, e.g. R^2 = 0.99983 for Ti. The minor elements are harder to detect but also exhibit very high R^2 values. Our next LIBS measurements will focus on the quantification of relevant elements in industrial coal samples.

Acknowledgement

Financial support by the Austrian Research Promotion Agency FFG is gratefully acknowledged (K-project PSSP 871974).

Following the cementation in steel with LIBS

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Carburizing is used to increase the surface hardness of low carbon steel workpieces. It modifies the iron phases from austenite to martensite while the core remains a ferritic and/or pearlite microstructure.So far with the classic technics, its control is slow and destructive. Cetim Grand Est and Holo3 are working together on a Region Grand Est project whose aims to build a fully automatic demonstrator able to assure the quality of the treatment of all the workpieces. Such a system could be integrated in a production line. Based on the LIBS and 3MA (Multi-parameter Micro magnetic Microstructure stress Analyzer) technics, it collects several information to ensure the analysis of the workpiece. Thus to control the quality of this treatment by LIBS, we measure the carbon concentration on the surface / subsurface.

In the literature, measuring C in steel by LIBS has shown various setup combining laser-spectrometer-gaz. For a long time, most of the setup were expensive (double laser (1), Paschen Runge spectrometer (2)) and only more recently smaller spectrometers (3) had been used and even now mobile LIBS device dedicated for this application also exists (SciAps). In this project, we tried to optimize the cost, the efficiency, the automation and the integration of the LIBS system with another technology (3MA).

References

[1] LI, J., ZHU, Z., ZHOU, R., ZHAO, N., YI, R., YANG, X., LI, X., GUO, L., ZENG, X., LU, Y. Determination of carbon content in steels using laser-induced breakdown spectroscopy assisted with laser-induced radical fluorescence. Analytical chemistry. 2017 Jul 13;89(15):8134-9.

[2] STURM, V., PETER, L., NOLL, R. Steel analysis with laser-induced breakdown spectrometry in the vacuum ultraviolet. Applied Spectroscopy. 2000 Sep 1;54(9):1275-8.

[3] PAN, C., DU, X., AN, N., ZENG, Q., WANG, S., & WANG, Q. Quantitative analysis of carbon steel with multi-line internal standard calibration method using laser-induced breakdown spectroscopy. Applied spectroscopy. 2016. 70(4), 702-708.

Acknowledgement

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Measurement of major and minor elemental composition of exhaust emissions from in-use Diesel engine passenger vehicles by LIBS

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In this study we apply Laser Induced Breakdown Spectroscopy technique for qualitative and quantitative spectrochemical analysis of Diesel Particulate Matter (DPM) emitted from in-use Diesel combustion engine exhaust emissions. Here we analysed collected particulate matter from sixty-seven different Diesel engine passenger vehicles of EU car producers used in daily life environment. The aim of this study is to compare Particulate Matter (PM) matrices composition, mainly major and minor chemical elements agglomerates in PM. Special attention is given to analyse different PM and perform a quantification and calibration of LIBS spectral signal. The presence of agglomerate chemical elements in Diesel exhaust emissions are due to different processes involved within the combustion. These are mainly related to the Diesel fuel, fuel additives, engine performance, catalytic reactions and Diesel particulate filtering techniques.

Acknowledgement

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Laser induced breakdown spectrometry for online multielement analysis of metal powder jet during coaxial laser cladding

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Additive manufacturing is a promising technology that allows to create parts with unique characteristics and properties. For aviation industry, industrial engineering plays a major role production parts with designed gradients of elemental composition [1]. Therefore, synthesis of compositional graded parts requires rapid elemental analysis. However, high reproducibility of the product's properties is difficult to achieve. Real time monitoring of metal powder feedstock used in additive manufacturing will be good for possible failures detection during metal processing part. In our study, laser induced breakdown spectroscopy (LIBS) has been used for elemental analysis of metal powder jet during coating synthesis by coaxial laser cladding. Coaxial laser cladding is an additive manufacturing technology (laser direct metal deposition) based on part build-up process with metal powder melting by powerful continuous wave laser. A compact and lightweight LIBS probe has been designed to equip the laser cladding head installed on an industrial robot [2]. The emission of laser plasma induced at powder particles was significantly lower compared to that for bulk sample. LIBS signals reproducibility for metal particles was also poorer compared to conventional ablation of metal target. LIBS sampling was carried out at different areas of gas-powder jet at coaxial nozzle but greater intensity and better signal reproducibility was achieved at jet waist. Spectral range, plasma emission gating and spectra averaging were selected to improve the LIBS signal reproducibility. Samples of wear resistant coatings (nickel alloy matrix reinforced with tungsten carbide particles) synthesized with variable proportions of powder flows were deposited while LIBS analysis was carried out. Solid clads were cooled, cut off and analyzed by X-ray fluorescence spectroscopy in laboratory conditions. The LIBS system was calibrated for quantitative analysis of major components.

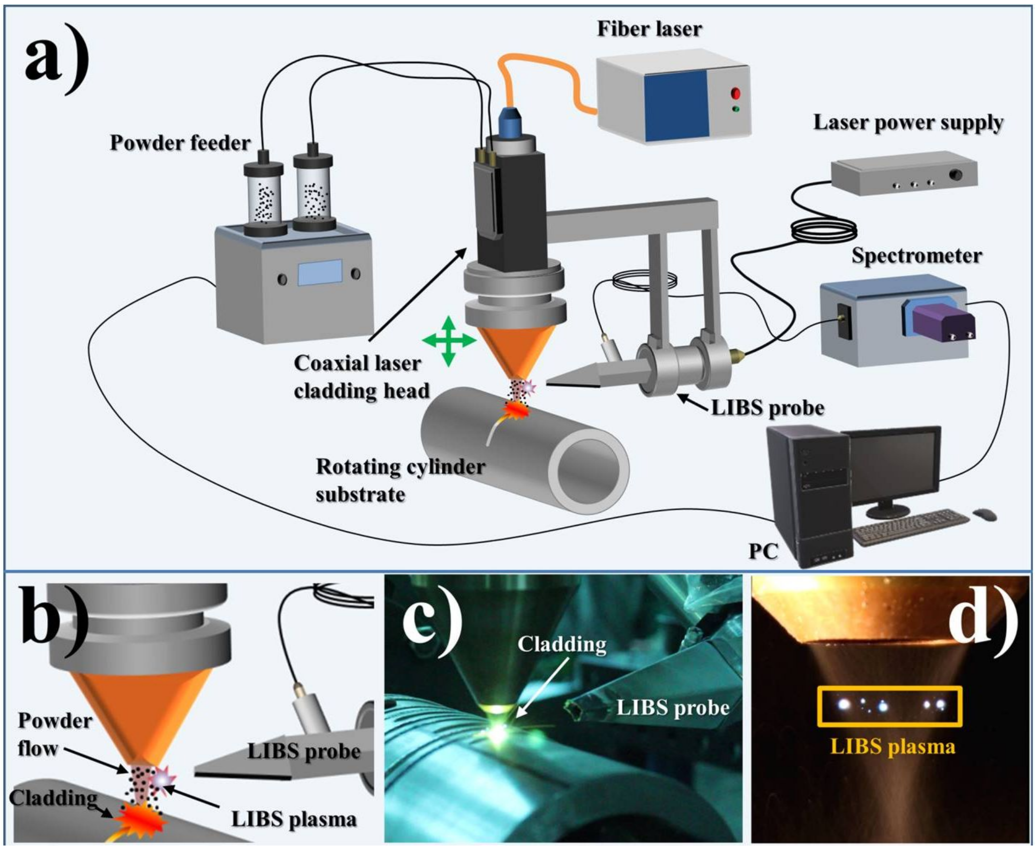

Fig. 1.: Scheme (a,b) and photo (c) of the coaxial laser cladding setup equipped with the laser induced breakdown spectroscopy (LIBS) system for analysis of metal powder flow. LIBS plasma photo (d) on metal powder flow.

References

[1] D. C. Hofmann, J. Kolodziejska, S. Roberts, R. Otis, R. P. Dillon, J.-O. Suh, Z.-K. Liu, and J.-P. Borgonia, “Compositionally graded metals: A new frontier of additive manufacturing,” J. Mater. Res. 29(17), 1899–1910 (2014).

[2] V. N. Lednev, A. E. Dormidonov, P. A. Sdvizhenskii, M. Ya. Grishin, A. N. Fedorov, A. D. Savvin, E. S. Safronova, and S. M. Pershin, “Compact diode-pumped Nd:YAG laser for remote analysis of low-alloy steels by laser-induced breakdown spectroscopy,” J. Anal. At. Spectrom. 33(2), 294–303 (2018).

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PII_114

Mechanical stirring: a novel engineering approach for in situ spectroscopic analysis of molten metals

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This study proposes a novel engineering approach to control silicon melt purification to satisfy photovoltaic application requirements. The efficiency of purification is related to the decrease of impurities concentrations in the melt. To reduce analysis time and cost, in-line analysis techniques are more advantageous as they provide real-time information about silicon melt composition. For this reason, recent research works focus on the development of new devices based on LIBS (Laser Induced Breakdown Spectroscopy) taking into account silicon behavior in a liquid phase as a molten metal at high temperature. These devices allowed to analyze impurities inside molten metals with great performances, however, improvements related to the immersion probe conception are still required [1]. Indeed, the previous design used bubbling inside the melt, leading to spatial instabilities of the silicon surface analyzed by LIBS, hence to undesirable signal fluctuations. The solution presented here is mechanical stirring [2] by innovative rotary blades which will be a part of an immersion LIBS probe. Their rotation will generate a representative, renewed and stable surface that will be targeted by LIBS laser for an in-situ silicon analysis at high temperature. This solution was validated using experimental tests based on particle imaging velocimetry (PIV) in water then applied on silicon melt for impurities detection.

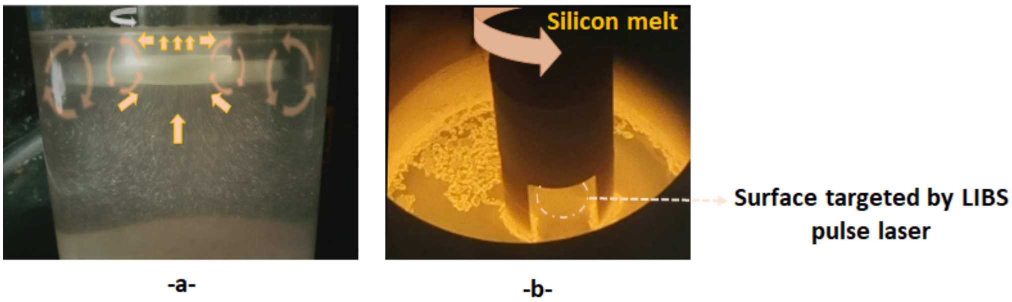

Fig. 1.: Liquid flow generated (-a-) to obtain a stable, renewed and representative targeted surface by LIBS in silicon melt (-b-)

References

[1] PATATUT, L. Développement d'un dispositif de LIBS pour l'analyse quantitative en ligne des procédés de purification du silicium fondu, PhD thesis, 2015, Univ. Grenoble Alpes

[2] BENMANSOUR, M., BENRABBAH, R., GARANDET, J. P., MORVAN, D. Device for analyzing an oxidisable molten metal using a libs technique, 2015, patent US9933368B2

Acknowledgement

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LIBS for identification of valuable materials in electronic components

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Waste electrical and electronic equipment (WEEE) contain a significant amount and variety of valuable elements. In spite of their economic, technical and strategical importance for the European economy, a serious number of valuable elements are not recovered by current recycling technology. This applies to elements such as tantalum, neodymium and tungsten. In order to improve the recovery of such materials from WEEE, it is desired to extract and accumulate individual components containing a particular, valuable material into a sorting fraction. Those fractions enable an economic recovery of raw materials by metallurgical methods, for example. In a joint project of R&D and industrial partners an automated analysis, disassembly and sorting system for electronic components on printed circuit boards (PCBs) from end of life electronics was developed. PCBs from different sources, e.g. mobile phones and server boards, are processed to extract individual electronic components from the PCBs selectively, depending on their composition. In order to generate sorting fractions with enriched content of a certain element, the approximate element content of the electronic components must be determined. In this work, LIBS is employed to detect the presence of the element of interest. Electronic components have an inhomogeneous internal structure, of which only some parts contain the target elements and which is usually surrounded by a housing. An operational concept was worked out to use a single laser source firstly to remove the housing and covering layers and secondly to excite the LIBS plasma. The approach allows, for example, to identify tantalum containing capacitors among other electronic components of the same mounting form. In field tests on an industrial scale, WEEE is processed and electronic components are analyzed with LIBS. To gain reproducible results for a wide range of electronic components and structural shapes, generalized measurement strategies are employed and evaluated.

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In situ Tungsten Inert Gas Welding Monitoring by LIBS Measurements

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TIG welding process was monitored using LIBS for the in situ measurement of chemical compositions in austenitic stainless steels. This research aims to prototype a real-time chemical composition analysis system for welding applications and prove the feasibility of such a quality control loop. The chemical compositions of the weld pool, considering the welding metallurgy, is the most critical parameter for any occurring weld defects, e.g. hot cracking[1]. Hence, controlling the weld pool chemical composition allows governing of the weld pool solidification behavior by monitoring and adjusting the respective welding parameters, e.g. welding current. LIBS measurements were conducted during a TIG-welding process. The effect of the welding plasma on the LIBS signal was thoroughly investigated by varying various LIBS settings, e.g. delay and exposure time. Quantification of the main alloying elements Cr and Ni in the weld pool during welding was achieved by univariate calibration procedure.

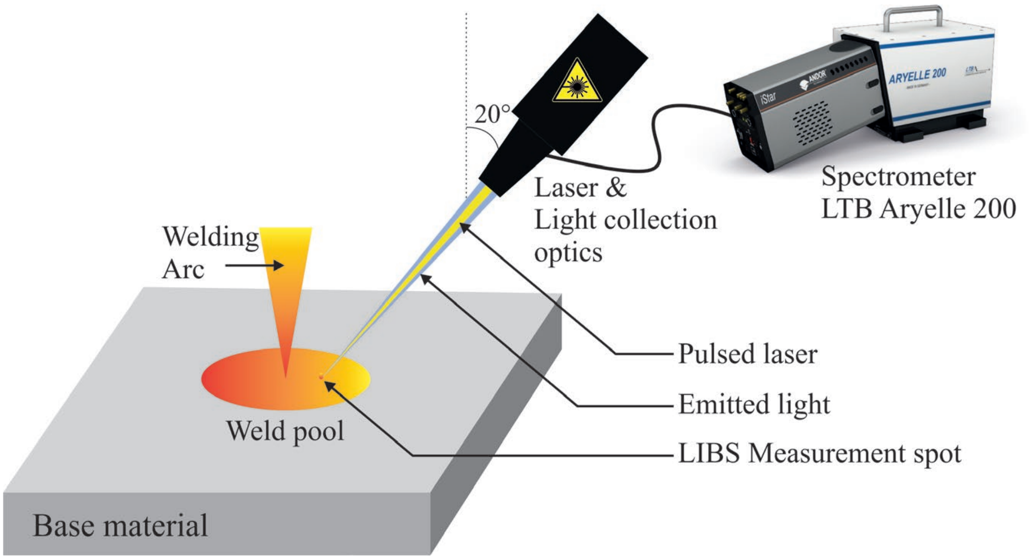

Fig. 1.: Experimental set-up of the LIBS monitored welding system

References

[1] Taparli et. al. Spectrochim. Acta, Part B, 2018, 139 , 50-56

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Absolute Depth LIBS-Stratigraphy with NoScSiSp-OCT

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LIBS is a proven method for elemental analysis. It needs little to no sample preparation and relies soleyly on optical access to the sample.
LIBS has therefore been handled as a promising analytic method for layered or structured samples with the potential to replace metallurgic cross-sections followed by SEM/EDX raster screenings.

Due to the strong dependency of the ablation process on changing crater geometries, laser fluence and plasma dynamics (e.g. self-absorption, material dependent optical depths, reflecting coefficients, scattering processes, etc), attributing an absolute depth to the number of laser pulses applied to the sample is not trivial.

In this work, we show absolute depth recognition based on single-spot, non-scanning optical coherence tomography on LIBS craters produced with a standard LIBS setup. Also we verify these results with the use of ex-situ (electrun-microscopic techniques.

We further discuss it's potential application for density and hence porosity probing in LIBS-stratigraphy for fast QC/A in the production line. This enables the quantification of key properties in porous samples, e.g. thermal-barrier coatings (TBCs) , used in the hot section of state-of-the-art aircraft jet engines.

Analysis of the reinforced concrete structures with various degree of deterioration by LIBS

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Chemical corrosion of concrete for decades remains one of the main problems of the construction industry and transport infrastructure. The corrosion should be controlled by the periodical diagnostics and determination of the type of chemical corrosion. In recent years, laser-induced breakdown spectroscopy (LIBS) is considered for in-situ elemental analysis of concrete. However, the particular content of corrosion-active components responsible for the degradation of concrete (chlorine, sulfur and carbon) can be insufficient to characterize the degree of corrosion of concrete. Thus, the revealing the additional signal and parameters characterizing the material changes due to corrosion would be beneficial for concrete structures diagnostics. It was proposed to use the signal of the iron oxide originated from rebar and optoacoustic response during laser ablation to enhance diagnostics. We have considered 6 samples, which imitate different degree of degradation.

Acknowledgement

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Archaeometallurgical study of the gilding technique of two iron spurs by means of LIBS depth profiling.

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In 2013, during the conservation treatment of two ceremonial iron spurs (dated in the 13th century and found in 2010 at the Monastery of Corias, Asturias), a gold layer was noticed in both sides and pricks (fig.1). The capabilities of LIBS to carry out deep profiling analysis with minimum sample erosion constituted a unique opportunity to study the stratigraphy of these spurs. The aim of this work is to find out the gilding procedure of the spurs studying the in-depth distribution of some metals (Au, Hg and Ag). For this purpose, the intensity of selected emission lines of Au, Hg and Ag has been recorded versus consecutive laser shots in two spots. The results show the presence of three layers, a gold external coating followed by a mercury layer and an internal one of silver over the iron nucleus. The manufacture technique comprises mercury gilding, a method based on the mixture of mercury and gold to form an amalgam that can be applied to the metal surface, which will then be heated: as most of the mercury evaporates, it leaves a gold layer behind. The atypical presence of an inner silver layer relates to another set of medieval spurs, discovered at the archaeological site of Ereñozar (Biscay) [1].

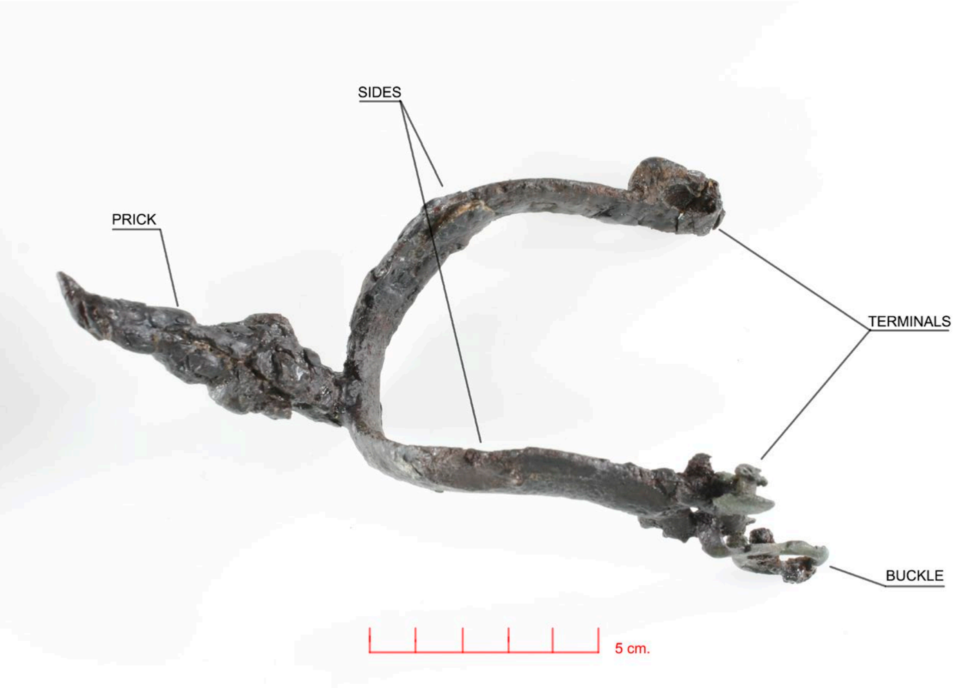

Fig. 1.: Parts of the medieval spur.

References

[1] García-Boullosa, L., Aramendia, J., Veneranda, M., Fdez-Ortiz de Vallejuelo, S., Neira, M., Castro, K., Madariaga, J.M., García-Camino, I. Estudio y conservación de objetos metálicos procedentes de una necrópolis medieval costera (Castillo de Ereñozar, Bizkaia). MetalEspaña 2015.

Halides detection in Pompeian wall paintings through the use of LIBS molecular emission bands.

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Halides are known to cause the degradation of both mortars and pigment layers in mural paintings. Therefore, it is recommendable to assess their presence in a fast and non-invasive way without sampling. Widely used portable techniques, such as p-XRF, do not allow the detection of fluoride. The use of p-LIBS can overcome this limitation. The layers of ash and pumice that covered Pompeii after the 79 AD eruption of Mt. Vesuvius acted as a protective layer of the wall paintings until their excavation. Nonetheless, tephra deposits are a source of halides, specially fluoride and chloride. Thus, in this work, we present the application of a commercial portable LIBS equipment (EasyLIBS, IVEA) to detect the main areas of halides accumulation in wall paintings and their efflorescences at the House of the Gilded Cupids and the House of Ariadne (Archaeological Park of Pompeii). Molecular emission bands were used to determine the position and distribution of these halides in the mural paintings [1]. On the other hand, thanks to previous leaching experiments, it was established that sodium and potassium correlate with halides in volcanic strata. To verify if p-LIBS would also be capable of determining the association of these cations with the halides, their distribution along the wall paintings was monitored through this technique. This information could also assist the identification of additional inputs of salts, which constitutes one of the main goals of the archaeologists and restorers of the Archaeological Park of Pompeii.

References

[1] Gaft, M.; Nagli, L.; Eliezer, N.; Groisman, Y.; Forni, O. Elemental Analysis of Halogens Using Molecular Emission by Laser-Induced Breakdown Spectroscopy in Air. Spectrochim. Acta Part B At. Spectrosc. 2014, 98, 39–47.

Acknowledgement

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Elaboration of chemical and tomographic data by the principal component analysis method for archaeological applications

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Using large datasets is becoming more and more common in every discipline. Today's biggest task is to find a tool which would reduce effectively their dimensionality. By the word effectively here it is meant to keep the loss of information within datasets to a minimum, thus maintaining the interpretability of data at a maximum possible level. An example of disciplines where large datasets are handled on a daily basis is X-ray Computed Tomography (XCT) and Laser-Induced Breakdown Spectroscopy (LIBS). The combination of these two techniques allows complex analyses of the inner structure of materials. These types of analyses could also help to solve one of the current tasks that archaeologists deal with. This task concerns the study of ancient technology, raw materials and possible origin of the artefacts, such as pottery. Such information are useful to reconstruct ancient manufacturing processes, exchange systems and trade. This method has been tested on samples which came from an extensive investigation carried out between 2015 and 2018 at the UNESCO site of Al-Khutm (Bat, Oman). From the archaeological site, about 20 selected samples have been investigated using a multi-analytical approach in order to characterise their microstructure and chemical composition. The results obtained by using different techniques, providing a detailed description of pottery fabrics, allowed recognising local vs non-local raw materials.

Acknowledgement

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Depth profiling of elemental composition of mollusk shells by Laser-Induced Breakdown Spectroscopy (LIBS)

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The chemical composition of mollusk shells is an archive of the environmental conditions during the mollusk' lifespan [1]). It can be used to monitor the presence of trace elements like heavy metals, or to infer the seawater temperature and salinity from the concentration of some elements (Magnesium, Strontium, Lithium…) in the calcium carbonate matrix. Due to the durability and stability of this biogenic material, the shells offer valuable information of the past with archaeological and paleoclimatic implications. The typical measurement procedure involves cutting the shell in two halves and sampling the material at different spatial points along a path over the section surface, that is species-dependent and must be manually decided. Here, we propose the use of the LIBS technique to perform a chemical depth profiling in the apex area of shells of common limpets (Patella vulgata). This area has spatially compressed layers of calcite covering the entire lifespan [2]. The elemental analysis in this specie, however, is typically performed on the much larger "m+2" outer calcite layer exposed in the cut section [2], because the relationship between the seawater temperature and composition in this layer has been already confirmed [3]. The depth profiling through the apex using LIBS open the possibility of fast measurements with no sample preparation at all. The LIBS setup includes a Nd:YAG laser (Lotis LS-2147) at 1064 nm, and an Avantes ULS2048-USB2-RM spectrometer. The setup is fully automated with a XYZ positioner, through-lenses imaging and an autofocus system. From the captured spectra, the concentration of Magnesium, Strontium and Lithium relative to the calcium carbonate matrix has been obtained. The proposed "vertical" measurements method based on depth profiling is compared with traditional "horizontal" measurements along the surface of the exposed section, both at the "m-2" inner calcite area (near the apex) and the traditional "m+2" outer calcite area.

References

[1] Andrus, C.F.T., 2011. Shell midden sclerochronology, Quaternary Science Reviews 30, 2892-2905.

[2] Fenger, T., Surge, D., Schöne, B., Milner, N., 2007. Sclerochronology and geochemical variation in limpet shells (Patel-la vulgata): A new archive to reconstruct coastal sea surface temperature, Geochemistry, Geophysics, Geosystems 8.

[3] García-Escárzaga, A. et al , 2018. Mg/Ca profiles within archaeological mollusc (Patella vulgata) shells: Laser-Induced Breakdown Spectroscopy compared to Inductively Coupled Plasma-Optical Emission Spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy 148, 8-15.

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Micro-LIBS mapping of marine mollusk shells enables reliable use of Mg/Ca as a temperature proxy

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Mollusc shells constitute valuable biogeochemical archives based on seasonal variability records imprinted in their growth increments as elemental composition or isotope variations. Their availability along modern and ancient shorelines as well as their good preservation facilitate climatic analyses at a high temporal and spatial resolution. They are commonly analysed using oxygen isotope ratios (□18□) or elemental ratios (e.g. Mg/Ca, Sr/Ca, Ba/Ca) which are correlated to the variations of environmental temperature. However, the lack of fast methods limits analysis to low numbers of shells, and thus reduces significantly the statistical value of results. The use of micro-LIBS mapping facilitates acquisition of spatially extensive elemental maps and opens up prospects for handling large numbers of samples. [1] In these studies, we have employed a custom-made LIBS microscope and concentrated on recording Mg/Ca ratio maps across sections of aragonitic or calcitic shells. Maps provide information regarding the season of death, as well as season dependent annual minima and maxima, but furthermore enable one to understand whether the recorded variations are specific to research location or individual specimens and thus avoid misinterpretations. Still obtaining absolute estimates of temperature based on Mg/Ca ratios is not straightforward. However, combining these high resolution data from samples that show meaningful seasonality patterns with one or two measurements of oxygen isotope analysis (performed on the same sample) gives rise to true temperature variation mapping and provides the means to access previously uninterpretable climate proxies on a large scale. [2]

References

[1] Cáceres, J. O., Pelascini, F., Motto-Ros, V., Moncayo, S., Trichard, F., Panczer, G., Marín-Roldán, A., Cruz, J. A., Coronado, I., Martín-Chivelet, J. Megapixel multi-elemental imaging by Laser-Induced Breakdown Spectroscopy, a technology with considerablepotential for paleoclimate studies, Scientific Reports 7, 5080 (2017)

[2] Hausmann N., Prendergast A. L., Lemonis A., Zech J., Roberts P., Siozos P., Anglos D., Extensive elemental mapping unlocks Mg/Ca ratios as climate proxy in seasonal records of Mediterranean limpets, Scientific Reports, 9, 3698 (2019)

Acknowledgement

This study was funded in part by the EC H-2020 Program through the Marie Skłodowska-Curie Individual Fellowship project ‘ACCELERATE’ (Grant No. 703625). IM and PS acknowledge support from the POLITEIA-II and HELLAS-CH projects (MIS-5002478, MIS 5002735, NSRF 2014–2020).

Impact of LIBS implementation on the characterization of archaeological ferrous metals

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Archaeometallurgy consists of studying metallurgies for determination its quality: the nature of materials, the production process, finding the original product place after trading, etc. For ferrous metals, it requires the identifications of the heterogeneities of composition. Carbon content is one of the important parameters in metallographic studies. However, its analysis is difficult for old ferrous alloys because of the multifarious carbon distribution in the material. At present, the most effective method in terms of cost / sensitivity is metallographic analysis by optical microscopy after Nital attack. Unfortunately, this method is laborious, time-consuming and very cumbersome to implement for in-situ observations. In addition, it lacks special precision for some non-equilibrium structures. Moreover, on a macro-scale view, a preliminary sampling is required to observe the objects in situ in order to locate the high carbon zones for the further analysis and on a micro-scale view, the carbon content and its variation in the object should be precisely and locally determined, even on non-equilibrium structures. Thus, LIBS technique is proposed to give a fast measurement without samples preparation and to carry out in situ. In this work, we focus on the LIBS implementation in order to establish a protocol for qualitative and quantitative analysis of carbon composition. We propose the use of a "macro-LIBS" with a laser spot diameter of several hundred micrometers as the similar size of carbon fragment, so the carbon concentration can be obtained. And "micro-LIBS" with a spatial resolution of about 10 micrometers will be applied to have a high potential for detecting the different carbon zones and potentially make mapping equivalent to a metallographic observation as well.

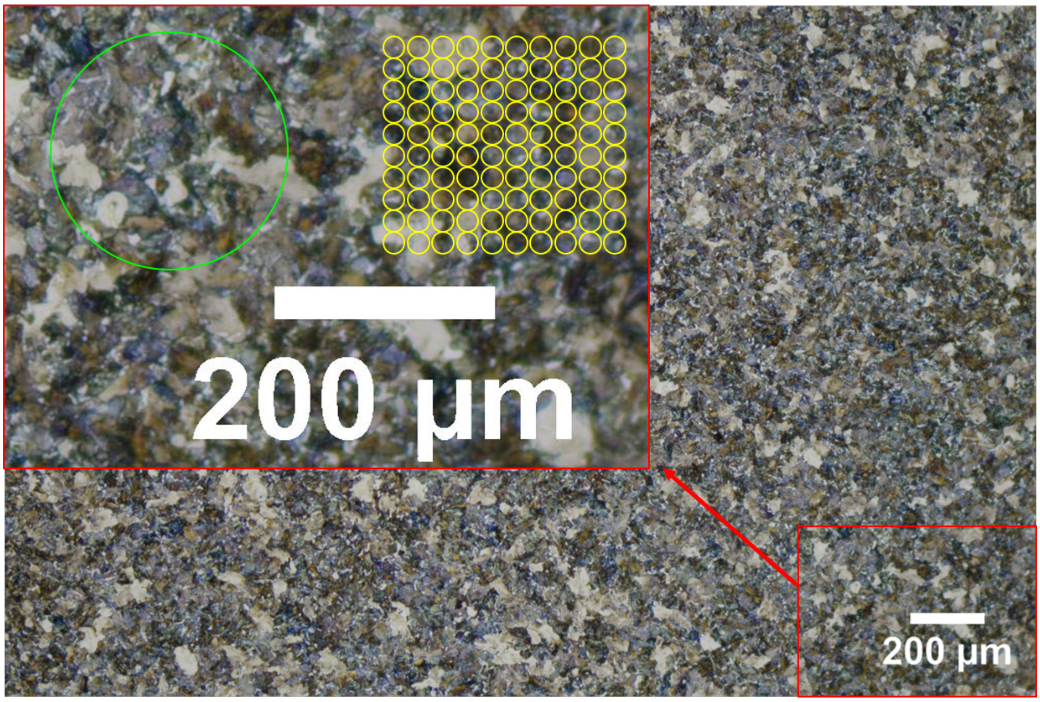

Fig. 1.: Figure 1 Optical microscopic image of a steel slice of 0.85% carbon concentration. Green circle of 200 µm diameter shows the macro-LIBS analyzing area and yellow circles shows the micro-LIBS mapping zone with a resolution of 20 µm.

Exploration of LIBS depth profiling of archaeological ceramics by means of X-ray computed tomography

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Many objects with various layers can be found and investigated in the field of cultural heritage. Laser-induced breakdown spectroscopy (LIBS) as a depth-resolved analysis provides the information on the chemical composition of individual layers of the analyzed objects, allowing their differentiation, with minimum damage. A detailed exploration of the ablation craters formed during the LIBS analysis is, however, a complex issue. The craters tend to be deep and narrow, and the depth-measuring techniques based e. g. on microscopy might provide biased results [1]. The utilization of the X-ray computed tomography (CT) as a tool for an examination of the LIBS craters on a sample of glazed archaeological ceramics is suggested in this work. The glazes used on the archaeological ceramics often contain a significant amount of Pb, which makes them distinguishable from the bulk material by the CT technique. CT enables not only to differentiate the glaze layer and to determine its thickness, but also to measure precisely the depths of the craters and to obtain detailed information on their shape in 3D. Moreover, the structure of the analyzed object including various defects (e. g. cracks, bubbles, etc.) can be thoroughly examined. By comparing the state of the sample before and after the analysis, several effects occurring during the LIBS measurements might be better explained.

References

[1] POSPÍŠILOVÁ, E. et al. Depth-resolved analysis of historical painting model samples by means of
laser-induced breakdown spectroscopy and handheld X-ray fluorescence. Spectrochimica Acta Part
B: Atomic Spectroscopy, v. 147, p. 100-108, 2018/09/01/ 2018. ISSN 0584-8547.

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This research was carried out under the project CEITEC 2020 (LQ1601) with financial support from the Ministry of Education, Youth and Sports of the Czech Republic under the National Sustainability Programme II and CEITEC Nano Research Infrastructure (MEYS CR, 2016–2019). Student Project Grant at MU (Specific Research, Rector's Programme) MUNI/A/1375/2018 is also highly appreciated.

Semi quantitative Elemental Analysis of Volcanic Ashes from Populations Surrounding the Tungurahua Volcano of the Eruptive Period 2008-2010, Using the LIBS Spectroscopy (Laser-Induced Breakdown Spectroscopy)

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The geochemical characterization of volcanic ash is of great scientific interest since, it allows to clarify the mechanisms that dominate the behavior of the eruptions of the volcano, and to know in more detail the products generated and processes involved in each eruptive phase, in order to distinguish changes in their activity patterns. This work was carried out in the Spectroscopy laboratory of the Physics Department of the National Polytechnic School, applying the Laser-induced Breakdown Spectroscopy (LIBS) technique to determine the elemental chemical composition in 18 ash samples from the Tungurahua volcano collected from nearby populations. In this work we propose suitable preparation methods of volcanic ash to guarantee the homogeneity of the sample. Qualitative and quantitative elemental analysis was performed in two different environments for the taking of spectra, common air and atmosphere saturated with argon. For the quantitative analysis of the elements present, Calibration-free LIBS (CF-LIBS) is used, a technique used to determine the elemental composition of an arbitrary sample using statistical distributions of Saha-Boltzmann and Boltzmann. The instrumental response function of the LIBS equipment of the EPN was determined, adjusting each of the intensity values measured in a LIBS spectrum by a factor that represents the relative response of the instrument in that value. This correction was used for the analyzed samples, in combination with software appropriate for the CF-LIBS analysis, in which the corresponding Saha-Boltzmann and Boltzmann graphs are analyzed, thus quantifying the temperature, and the electronic density of the plasma.

References

References

[1] P. Samaniego, J. Le Pennec, C. Robin and S. Hidalgo, "Petrological analysis of the pre-eruptive magmatic process
prior to the 2006 explosive eruption at Tungurahua volcano (Ecuador)," Journal of Volcanology and Geothermal
Research, vol. 199, pp. 69-84, 2011.

[2] S. Arellano, M. Halla, J. Samaniego, L. Le Pennec, A. Ruiz, I. Molina and H. Yepez, "Degassing patterns od
Tungurahua volcano (Ecuador) during the 1999-2006 eruptive period, inferred from remote spectroscopy measurements od SO2 emissions," Journal of Vulcanology and Geothermal research, 2008.

[3] D. Bujalic, M. Corsi, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti and E. Tognoni, A new Self Calibrated
Method for precise Quantitative analysis by Laser- Induced Breakdown Spectroscopy, Pisa: Instituto di Fisica Atomica e Moleculare del CNR.

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Optimization of DP-LIBS sensitivity for tungsten detection in the nuclear fusion applications

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Tungsten is a material of the crucial importance for MCF (Magnetic Confinement Fusion) since it is foreseen that it will be used for the divertor of the next-step fusion reactors. To monitor the erosion and deposition on the divertor surface, LIBS was proposed as a remote method providing no interference with the main system and the capability of operation in harsh tokamak conditions. Furthermore, it has been shown that DP-LIBS (Dual Pulse Laser Induced Breakdown Spectroscopy) facilitates the measurements by improving the sensitivity [1]. Research described in this paper is focused on the analysis of the DP LIBS performance for tungsten in low pressure conditions for the optimization of the method in terms of the inter-pulse (IP) separation and improvement of understanding of its mechanisms, hitherto not fully investigated. For the pulses with power density in the range of 109 W/cm2 and the IP in range from a quasi-single pulse to 250 ns spectra have been recorded in kinetic series of 100 frames per each IP value. The single observation time was 50 ns and the gate delay step was 25 ns. As the auxiliary diagnostics ion collectors have been applied to provide the information on ion velocity distribution. The experiment showed substantial increase in the time-scale of the phenomena and allowed for the optimization of the IP delay in terms of its sensitivity for tungsten.

References

[1] S. Almaviva, L. Caneve, F. Colao, P. Gasior, M. Kubkowska, M. ??epek, G. Maddaluno, Double pulse Laser Induced Breakdown Spectroscopy measurements on ITER-like samples, in: Fusion Eng. Des., 2015: pp. 848–851. doi:10.1016/j.fusengdes.2015.02.068.

Laser-induced breakdown spectroscopy of uranium in the vacuum ultraviolet

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Quantitative analysis of impurities in nuclear materials is necessary in a number of areas, including process control during manufacturing, quality control of products, or for nuclear forensics purposes. Due to the important handling constraints induced by the samples radioactivity and their containment inside airtight enclosures, optical analytical techniques have great advantages over standard ones that require sample preparation, like ICP-based techniques. Therefore, laser-induced breakdown spectroscopy (LIBS) is developed for fast quantitative analysis of impurities in uranium. Actinides are well-known to have a huge number of emission lines in the UV-visible spectral range, hence making the detection of trace or minor elements a real challenge. Therefore, in this study we explored the vacuum ultraviolet range (VUV), i.e. below 200 nm, in order to investigate if this spectral region is more favorable for elemental analysis of uranium by LIBS. As practically no data on VUV spectroscopy of uranium are available, we first analyzed the spectra obtained in view of the spectral density of uranium lines, both in the UV and VUV. Then the plasma generated in the vacuum was characterized, its electron temperature and density were determined using standard spectroscopic approaches. Finally, the detection limit of two elements, carbon and vanadium, were estimated. We found that in spite of a less dense and less intense uranium background in the VUV, this spectral region is not relevant for metal impurities whose spectroscopy is not favorable in the VUV. Conversely, for non-metals having intense lines in the VUV, the detection limit can be significantly better than in the UV. This was already known for non-nuclear samples. This study extends that conclusion to nuclear materials and has important practical consequences on the implementation of a LIBS analyzer in a nuclear facility.

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Identification of Radioactive Materials at the Site of Dirty Bomb Attack Using Laser-Induced Breakdown Spectroscopy

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A radiological dispersal device, known as an RDD or a dirty bomb, is the most possible type of nuclear terrorism. It is designed to employ radioactive material by spreading it to contaminate the target area, create panic and fear, and cause long-term health effects and major financial loss. The key to minimize damage in the event of a dirty bomb terrorist attack is to quickly identify what radioactive material is used, which makes the contaminated area predictable and enables appropriate treatment for patients exposed to radiation. LIBS is considered suitable for use in radiological terror sites since it can accurately detect target materials in a very short time. In this study, LIBS was employed to analyze the sample containing radioactive materials, and its performance was evaluated by LOD measurement. In order to simulate the real scene, the sample was made by dissolving target materials into highly purified water and spreading it onto diverse matrices using a sprayer. At the same time, matrices were heated to 130 ▯ to make sprayed droplet evaporated continuously without lumping. This process prevented the coffee-ring effect and therefore increased the homogeneity of the target materials on the surface of the matrices and reproducibility. Target materials were selected as powder of SrCl2, CsCl, Co, and Ir, which are sealed source chemical forms of isotopes of interest for RDDs. Since terrorism is likely to occur in densely populated urban areas, matrix was selected as aluminum. Even though there were small LOD differences between each sample, radioactive materials were identified with reasonably low LODs in all samples. These results demonstrate the feasibility of LIBS being used in the early phase of the dirty bomb attack and provide the information of which matrix is best for detection.

References

[1] Martin, M. Z., Allman, S., Brice, D. J., Martin, R. C., & Andre, N. O. (2012). Exploring laser-induced breakdown spectroscopy for nuclear materials analysis and in-situ applications. Spectrochimica Acta Part B: Atomic Spectroscopy, 74, 177-183.

[2] Bhatt, B., Angeyo, K. H., & Dehayem-Kamadjeu, A. (2018). LIBS development methodology for forensic nuclear materials analysis. Analytical Methods, 10(7), 791-798.

[3] Peterson, J., MacDonell, M., Haroun, L., Monette, F., Hildebrand, R. D., & Taboas, A. (2007). Radiological and chemical fact sheets to support health risk analyses for contaminated areas. Argonne National Laboratory Environmental Science Division, 133.

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Monitoring of Liquid Radioactive Waste Treatment Process using Laser-induced Breakdown Spectroscopy

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Since the LIBS can measure a target rapidly and remotely, it is the most promising technique for monitoring and analyzing radioactive materials [1-3]. To protect workers and collect information on liquid waste treatment process with radioactive materials, LIBS has been considered. However, liquid analysis by LIBS is complicated due to splashed droplets by a shock wave from the generation of plasma. This splashed samples would be deposit optical parts, thereby distorting the laser light. To overcome this problem, some trials such as solidification and aerosols have been tried. However, these approaches make another problem. For the solidification, it has a representative problem due to the non-homogeneity. For the aerosol system, a null shot can occur and the number of samples in the plasma can change easily. In this study, we suggested two approaches to measure the targets in the liquid radioactive waste treatment process. To minimize that splashed sample deposit to optical parts, single-shot LIBS and multiple shots with the installation of the gas protective layer are discussed and compared. For this purpose, SrCl2 that is one major source of liquid radioactive waste is dissolved in pure water with various concentration as a sample. Two trials have the same experimental setup, but the gas protective layer has additional parts of injector combined with a regulator. The injective gas is air and blows the splashed sample, thereby eliminating contamination of the optical lens. RSD of single-shot LIBS has about 30%. In this case, the LOD for single-shot LIBS is about 245 ppm. However, accumulating 80 laser pulse can reduce the RSD as 6% without contamination of optical parts. Accordingly, the LOD for accumulation 80 laser pulse with a gas protective layer is about 15 ppm. These preliminary results may support that LIBS will be considered to monitor the process of the liquid radioactive waste treatment process with simple experimental setup instead of complicated setups.

References

[1] A.M. Popov, A.N. Drozdova, S.M. Zaytsev, D.I. Biryukova, N.B. Zorov, T.A. Labutin, Rapid, direct determination of strontium in natural waters by laser-induced breakdown spectroscopy, Journal of Analytical Atomic Spectrometry, 31 (2016) 1123-1130.

[2] M.Z. Martin, S. Allman, D.J. Brice, R.C. Martin, N.O. Andre, Exploring laser-induced breakdown spectroscopy for nuclear materials analysis and in-situ applications, Spectrochimica Acta Part B: Atomic Spectroscopy, 74-75 (2012) 177-183.

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