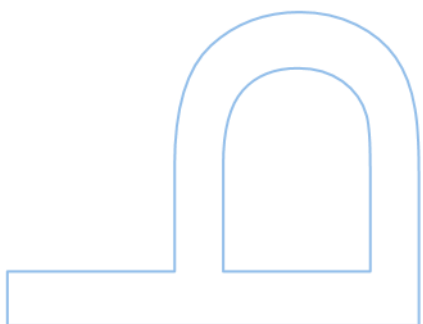




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Development of Laser-induced Breakdown Spectroscopy
Systems for Industrial Applications

Miguel Fernandes Soares Ferreira

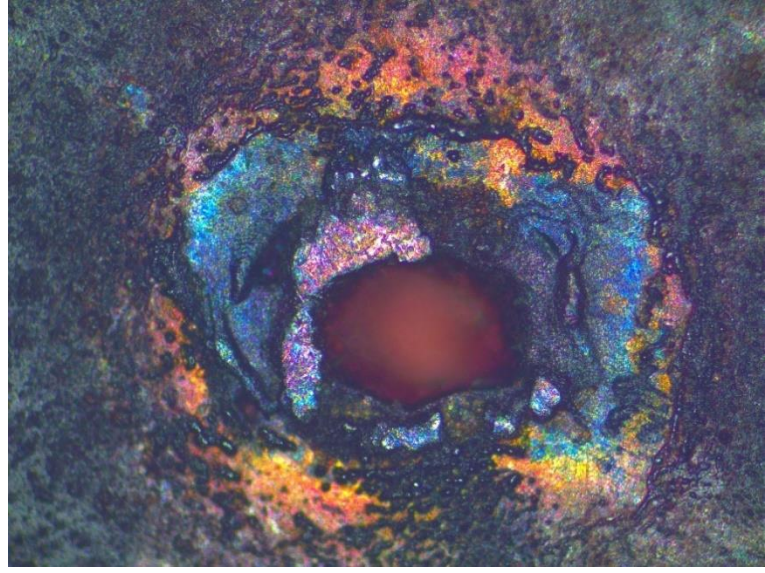


Universidade do Minho

Development of Laser-induced Breakdown Spectroscopy Systems for Industrial Applications

Miguel Fernandes Soares Ferreira

Thesis carried out as part of the Doctoral Program in
Physics MAP-Fis
Faculty of Sciences of the University of Porto, University of Aveiro and
University of Minho
2024



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Miguel Fernandes Soares Ferreira

Thesis carried out as part of the Doctoral Program in
Physics MAP-Fis
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2024

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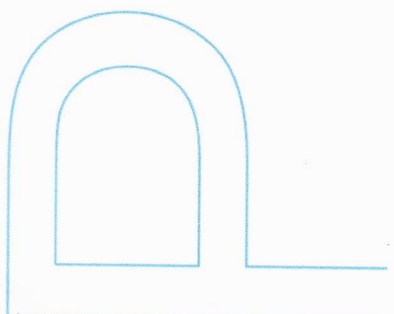
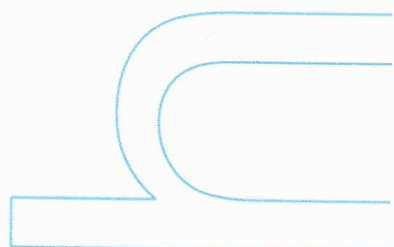
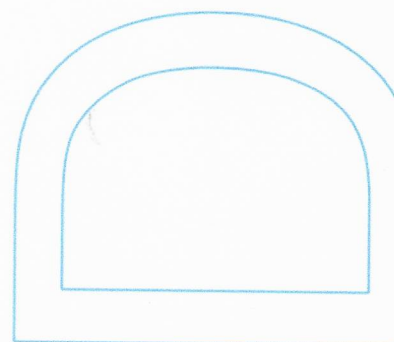


All the corrections determined by
the jury, and only those, were
made.

The Supervisor,

Señor Alberto Hilary

Porto, 13 / 12 / 2024





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In memory of:

Beatriz Guimarães Guedes

May you never be forgotten

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Resumo

Esta tese explora o desenvolvimento e aplicação de sistemas de Espectroscopia de Plasma Induzido por Laser (LIBS) em várias indústrias, motivada pelo potencial do LIBS para análise elementar em tempo real e in-situ, sem a necessidade de preparação extensiva de amostras. A investigação visa aprimorar as capacidades e aplicações da tecnologia LIBS através da criação de sistemas robustos e de alta resolução.

Parte I: Introdução define o contexto com uma visão geral da tese, incluindo a motivação, objectivos e uma estrutura detalhada. O capítulo "Dos fundamentos às inovações da técnica LIBS" fornece uma revisão abrangente da literatura, discutindo a evolução histórica, os princípios fundamentais do LIBS e o estado da arte actual.

Parte II: LIBS para Aplicações em Mineração aprofunda-se no desenvolvimento de um sistema LIBS robusto, especificamente projectado para amostras de mineração. "Um sistema LIBS robusto para amostras de mineração" detalha as especificações técnicas e melhorias do sistema, demonstrando o seu desempenho aprimorado e aplicações expandidas. "Avaliação de concentrações de lítio em amostras de mineração usando LIBS" foca-se nos procedimentos experimentais e métodos numéricos usados para quantificação de lítio, destacando a eficácia de abordagens não-lineares em relação aos métodos lineares tradicionais e apresentando melhorias significativas na quantificação de concentrações de lítio em amostras reais de mineração.

Parte III: LIBS para Imagem Elementar de Alta Resolução introduz um sistema LIBS baseado em laser de fibra, destinado a obter imagens de alta resolução. O capítulo "Implementação de LIBS baseado em laser de fibra" discute o design, caracterização e aplicações deste sistema avançado, enfatizando a sua capacidade de realizar mapeamento elementar detalhado com alta resolução espacial. A aplicação bem-sucedida do sistema LIBS baseado num laser de fibra para a geração de imagens de alta resolução de amostras geológicas marca um avanço significativo no campo.

Parte IV: Aplicação de LIBS na Indústria de Cortiça apresenta a aplicação da tecnologia LIBS na análise industrial de rolhas de cortiça. "Protótipo industrial de LIBS para análise de rolhas de cortiça" descreve o sistema protótipo desenvolvido para este propósito, demonstrando a sua eficácia na análise da uniformidade e composição de revestimentos de superfície em rolhas de cortiça. Esta aplicação inovadora, conhecida como CorkSurf, representa uma abordagem revolucionária no controlo de qualidade de produtos de cortiça e está actualmente em processo de industrialização. "Optimização

do sistema e desenvolvimento de métricas para análise de revestimentos" cobre os métodos usados para otimizar o sistema e desenvolver métricas para avaliar a uniformidade e a espessura dos revestimentos, potencialmente levando a uma melhoria no controlo de qualidade na produção de rolhas de cortiça.

Parte V: Conclusão fornece uma análise retrospectiva do trabalho, discutindo o impacto e as contribuições da investigação realizada. "Análise retrospectiva, impacto e perspectivas futuras" resume as principais descobertas, destaca as implicações académicas e industriais, e delinea potenciais desenvolvimentos futuros na tecnologia LIBS. Este capítulo enfatiza a criação de três sistemas LIBS distintos, contribuições significativas para técnicas de quantificação de lítio, avanços na imagem elementar de alta resolução e aplicações industriais bem-sucedidas.

No geral, esta tese demonstra a versatilidade e o potencial do LIBS como uma poderosa ferramenta analítica em contextos académicos e industriais, abrindo caminho para futuros avanços e aplicações. A investigação resultou em três publicações como primeiro autor, oito co-autorias e várias apresentações em conferências. Além disso, foi submetida uma patente para o sistema LIBS desenvolvido para a análise de amostras revestidas. Os protótipos práticos criados para análise de mineração e rolhas de cortiça sublinham o potencial da tecnologia LIBS para abordar eficazmente desafios do mundo real, com a aplicação CorkSurf representando uma inovação significativa agora em processo de implementação industrial.

Palavras-chave: Espectroscopia de plasma induzido por laser, mineração, mapeamento elementar, quantificação, laser em fibra, rolhas de cortiça, revestimentos

Abstract

This thesis explores the development and application of Laser-induced Breakdown Spectroscopy (LIBS) systems across various industries, motivated by LIBS's potential for real-time, in-situ elemental analysis without the need for extensive sample preparation. The research aims to enhance the capabilities and applications of LIBS technology through the creation of robust, high-resolution systems.

Part I: Introduction sets the stage with an overview of the thesis, including the motivation, objectives, and a detailed structure. The chapter "From basics to breakthroughs of the LIBS technique" provides a comprehensive literature review, discussing the historical evolution, the fundamental principles of LIBS and the current state-of-the-art.

Part II: LIBS for Mining Applications delves into the development of a robust LIBS system specifically designed for mining samples. "A robust LIBS system for mining samples" details the technical specifications and upgrades of the system, demonstrating its enhanced performance and expanded applications. "Assessing lithium concentrations in mining samples using LIBS" focuses on the experimental procedures and numerical methods used for lithium quantification, highlighting the effectiveness of non-linear approaches over traditional linear methods and presenting significant improvements in quantifying lithium concentrations in real mining samples.

Part III: LIBS for High-resolution Elemental Imaging introduces a fibre laser-based LIBS system aimed at achieving high-resolution imaging. The chapter "Implementation of fibre laser-based LIBS" discusses the design, characterisation, and applications of this advanced system, emphasising its ability to perform detailed elemental mapping with high spatial resolution. The successful application of the fibre laser-based LIBS system in generating high-resolution images of geological samples marks a significant advancement in the field.

Part IV: LIBS Application in the Cork Industry presents the application of LIBS technology in the industrial analysis of cork stoppers. "Industrial LIBS prototype for cork stoppers analysis" describes the prototype system developed for this purpose, demonstrating its effectiveness in analysing the uniformity and composition of surface coatings on cork stoppers. This novel application, known as CorkSurf, represents a groundbreaking approach in the quality control of cork products and it is currently in the process of industrialisation. "System optimisation and development of metrics for coating

analysis" covers the methods used to optimise the system and develop metrics for assessing the uniformity and thickness of coatings, potentially leading to improved quality control in cork stopper production.

Part V: Conclusion provides a retrospective analysis of the work, discussing the impact and contributions of the research. "Retrospective analysis, impact, and future prospects" summarises the key findings, highlights the academic and industrial implications, and outlines potential future developments in LIBS technology. This chapter emphasises the creation of three distinct LIBS systems, significant contributions to lithium quantification techniques, advancements in high-resolution elemental imaging, and successful industrial applications.

Overall, this thesis demonstrates the versatility and potential of LIBS as a powerful analytical tool in both academic and industrial settings, paving the way for future advancements and applications. The research has resulted in three first-author publications, eight co-authored publications, and several conference presentations. Additionally, a patent has been submitted for the LIBS system developed for analysing coated samples. The practical prototypes created for mining and cork stopper analysis underscore the potential of LIBS technology to address real-world challenges effectively, with the CorkSurf application representing a significant innovation now moving towards industrial implementation.

Keywords: Laser-induced breakdown spectroscopy, mining, elemental mapping, quantification, fibre laser, cork stoppers, coatings

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List of Abbreviations

ANN	ARTIFICIAL NEURAL NETWORKS
ASE	AMPLIFIED SPONTANEOUS EMISSION
ATR-FTIR	ATTENUATED TOTAL REFLECTANCE-FOURIER TRANSFORM INFRARED
CCD	CHARGE COUPLED DEVICES
CMOS	COMPLEMENTARY METAL–OXIDE–SEMICONDUCTORS
DDG	DIGITAL DELAY GENERATOR
DLL	DYNAMIC-LINK LIBRARY
EMSLIBS	EURO-MEDITERRANEAN SYMPOSIUM ON LASER-INDUCED BREAKDOWN SPECTROSCOPY
EU	EUROPEAN UNION
FCUP	FACULTY OF SCIENCES OF THE UNIVERSITY OF PORTO
FWHM	FULL WIDTH HALF MAXIMUM
HDF	HIERARCHICAL DATA FORMAT
HSI	HYPERSPPECTRAL IMAGING
ICCD	INTENSIFIED CHARGE COUPLED DEVICES
ICP-MS	INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY
IQR	INTERQUARTILE RANGE
IR	INFRARED
KNN	K-NEAREST NEIGHBOURS
LA-ICP-MS	LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY
LASER	LIGHT AMPLIFICATION BY STIMULATED EMISSION OF RADIATION
LDA	LINEAR DISCRIMINANT ANALYSIS
LED	LIGHT-EMITTING DIODE
LIBS	LASER-INDUCED BREAKDOWN SPECTROSCOPY
LIF	LASER-INDUCED FLUORESCENCE
LIPS	LASER-INDUCED PLASMA SPECTROSCOPY
LOD	LIMITS OF DETECTION
LSS	LASER SPARK SPECTROSCOPY
LTE	LOCAL THERMODYNAMIC EQUILIBRIUM
MAE	MEAN ABSOLUTE ERROR
MAPE	MEAN ABSOLUTE PERCENTAGE ERROR

MCC	MULTIVARIATE CALIBRATION CURVE
MOPA	MASTER OSCILLATOR POWER AMPLIFIER
ND:YAG	NEODYMIUM-DOPED YTTRIUM ALUMINIUM GARNET
NIR	NEAR INFRARED
NIST	NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
OD	OPTICAL DENSITY
PCA	PRINCIPAL COMPONENT ANALYSIS
PDG	PULSE DELAY GENERATOR
PLC	POWER LINE COMMUNICATION
PLS	PARTIAL LEAST SQUARES
PLS-DA	PARTIAL LEAST SQUARES DISCRIMINANT ANALYSIS
RAM	RANDOM-ACCESS MEMORY
RC	REVERSE CIRCULATION
RF	RANDOM FORESTS
RS	RAMAN SPECTROSCOPY
RS-232	RECOMMENDED STANDARD 232
SCMOS	SCIENTIFIC COMPLEMENTARY METAL–OXIDE– SEMICONDUCTORS
SNR	SIGNAL-TO-NOISE RATIO
SVM	SUPPORT VECTOR MACHINES
TRL	TECHNOLOGY READINESS LEVEL
UCC	UNIVARIATE CALIBRATION CURVE
UPS	UNINTERRUPTIBLE POWER SUPPLY
USB	UNIVERSAL SERIAL BUS
UV	ULTRAVIOLET
XRF	X-RAY FLUORESCENCE

Part I

Introduction

Chapter 1

Motivation and overview

1.1. Introduction

The ability to detect the presence of chemical elements in an accessible and fast manner encloses a strong potential for various fields of knowledge from fundamental and applied research to industry, empowering the user at the decision level. In this context, laser-induced breakdown spectroscopy (LIBS) stands as one of the most promising and versatile chemical analysis technique, allowing to assess the elemental composition of a spot on a sample with a simple and versatile optical-based setup.

Indeed, and in direct comparison with other competing techniques, like X-Ray Fluorescence Spectroscopy (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Raman Spectroscopy (RS), the LIBS technique presents a unique array of advantages. Among the most significant, and without entering into much detail, it may be included the minimal sample preparation and damage, the ability to detect most of the elements (including lighter ones such as hydrogen (H), beryllium (Be), lithium (Li) and carbon (C), impossible to detect with XRF and of high demand by the mining and battery industry[1] for example), the portability of the solution and capability of remote operation, and the localised analysis capability[2], that enables the ability to map chemical elements on surfaces of considerable dimensions (several centimetres) and with spatial resolution down to the micrometre scale[3–8].

Building on these advantages, applications of LIBS are now encountered across the most diverse topics from geological samples[9–11] and metallic alloys[12,13], to biology[14,15], food safety[16], medicine[14,17], forensics[18,19], environmental monitoring[20,21], archaeology[22,23] and military defence[24,25], just to name a few examples. But looking from a broader perspective, these advantages have established a unique and lively ecosystem of strong cross-disciplinary research, fostered by a major market pull during the last decade. It was also in this unique and lively environment where this thesis emerged.

1.2. A Local Context

A reader that casually flips through the pages of this thesis would most likely be surprised to observe that it encloses topics from minerals to electrodes and even cork stoppers. Therefore, along with the broader context presented above, it may also be interesting to discuss the local context that set the stage for this work at the Centre for

Applied Photonics at INESC TEC. Indeed, this work surged along a new research field and team at the Centre – Spectral Imaging – in a symbiotic manner, providing support but also being nurtured by a rich myriad of projects and collaborations that we had the opportunity to work in the last 7 years (Figure 1.1).

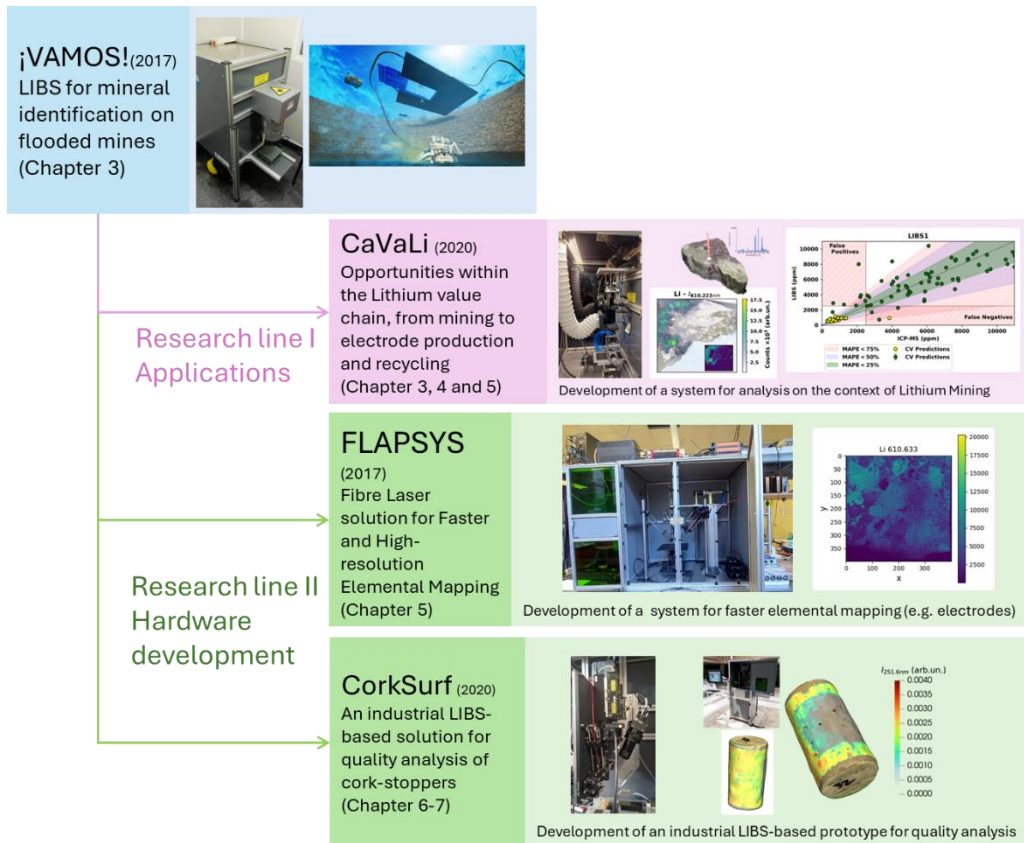


Figure 1.1 – Diagram representing the branching from the iVAMOS! project to the topics of this thesis.

Prior to the beginning of this thesis, our team participated in the project iVAMOS! (2017), that, among other activities, explored the potential of LIBS for mineral identification in the context of flooded mine explorations. At that time, our team built a first LIBS prototype to operate at a mining site identifying minerals that were being extracted from simple elemental signatures[9]. With the end of the project, the LIBS prototype was released from the mining site and building on the positive results in the project iVAMOS!, the team was motivated to explore new topics, dividing it into two concurrent strategic lines: i) research applications and case studies and ii) hardware development.

From the side of applications and case studies, and following our previous collaborations with the geology department at the Faculty of Science of University of Porto (FCUP), the applications involving mineral identification and characterisation

presented a straightforward yet promising opportunity. In particular, leveraging on the potential of LIBS to detect light chemical elements with the expertise of our collaborators, the research quickly tended to problems involving lithium-bearing minerals since its earlier stages[26]. With an almost perfect timing with the increasing market demand for lithium exploration and exploitation of the last decade, the potential of our research materialised not only in impactful research but also in novel research opportunities. Notably, this included a comprehensive project on the entire lithium value chain (CaVaLi, 2020), which established a perfect setting for two for the case studies that will be presented later in this thesis.

Along the second strategic line, i.e. hardware development, our first approach as newcomers in the topic was to look into opportunities within the areas of expertise of the research centre. In particular, leveraging on the long-tradition of INESC TEC in the topic of fibre optics, we first focused on the potential of using a fibre laser to overcome some limitations of the more standard Nd:YAG (neodymium-doped yttrium aluminium garnet, $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$) laser of the original system[27,28]. Indeed, with a high beam quality (M^2 close to 1), high repetition rates, basically maintenance-free and compactness, this type of laser could open the gates to numerous applications, in particular, high-resolution LIBS imaging, as explored in the context of project FLAPSYS (2017).

In a concurrent manner and driven by an ambition to explore the commercial potential of our solutions and systems, we undertook a product development opportunity alongside a local engineering company EGITRON that targeted the cork industry sector. In particular, we focused on the development of a full-stack solution to analyse the uniformity of surface treatment coatings deposited on cork stoppers, a problem of major interest for a national strategic economic sector. Indeed, using LIBS's micro-destructive nature and its unique versatility, our preliminary studies showed that a depth analysis could be performed using multiple shots at the same spot[29,30], making LIBS an ideal candidate for the analysis of such coatings. This potential inspired the CorkSurf project (2020) and materialised into the development of a fit-for-purpose LIBS system, specifically designed to analyse cork stoppers in an industrial environment, that will also be covered in this thesis.

1.3. Motivation and Objectives

At a conceptual level and in retrospective, we can identify three major reasons that motivated the work in this PhD thesis in the broad topic of LIBS and that strongly align with the strategic objectives of the research team at INESC TEC:

1. To improve past work and ignite cross-disciplinary applications, by exploring the potential of LIBS within our collaboration network and research interests with new case studies;
2. To enable hardware solutions that can improve the performance over standard solutions, in particular exploiting new laser sources with distinct capabilities;
3. To explore industrial applications for the LIBS technique within the local industry ecosystem, harnessing the technique with fit-for-purpose hardware and software solutions.

Towards these broader goals, the operational side of this dissertation focuses on the design and development three different laser-induced breakdown spectroscopy systems using Nd:YAG and fibre lasers to study their capabilities and applications in industries, aiming for real time analysis of element composition. The operational objectives established were:

1. Readapt a previously built LIBS system that uses a high energy Nd:YAG laser to laboratory operation and research its applications in mining;
2. Build a fibre laser-based LIBS system and explore the uses of high repetition rate and high beam quality for mapping;
3. Develop a LIBS system to analyse the quality of coating deposition in corks for industrial application.

1.4. Structure of the Thesis

This dissertation contains 8 chapter, divided into five parts, one of which is the introduction and another, at the end, the conclusion and future work. Three parts present experimental work throughout this thesis:

Part I is an introduction to this thesis. Chapter 1 comprises the motivation of this thesis, its objectives and, finally, the list of publications resulting from this work. Chapter 2 follows with an introduction of the LIBS technique, which this thesis is based on, dwelling on its state-of-art and fundamentals.

Part II contains the first LIBS system and its work. In Chapter 3, a description of the system is presented along with its past and its upgrades over time, following with some applications. Then, in Chapter 4, it is performed a comparison of numerical methods applied to LIBS data obtained with the system from Chapter 3 and commercial portable LIBS system for quantification of Li in samples from a real mining site.

Part III is dedicated to a fibre laser, the LIBS system that it is based on and the applications found for it. Chapter 5 presents the LIBS system, with a focus on the

characteristics of the fibre laser, including its strengths and weaknesses, followed by its characterisation, before finally dwelling on the application that better suits the system, high-resolution imaging.

Part IV focus on a new application for LIBS in the cork industry. Chapter 6 presents a new LIBS system dedicated to analysing coatings deposited on cork stoppers, resulting from surface treatments, in an industrial setting. The system is first described and then characterised before testing its viability by imaging regions shielded from the treatment. Chapter 7 then turns to depth analysis of the coatings, with attempts to find metrics to estimate the thickness and uniformity of the coatings.

Lastly, Part V ends this dissertation with Chapter 8. It presents the concluding remarks of this work, where the impact of the work of this PhD. is discussed, followed by future work possibilities.

1.5. Outputs

The work in this PhD. resulted in 3 publications in international scientific journals and 2 proceedings in international conferences as the first author and 5 oral communications in international conferences as the speaker. Apart from these, other 8 publications in international scientific journals and 6 proceedings of an international conference were published as a co-author stemming from cooperative work within the reach of this thesis along with 5 oral presentations in conferences as a collaborator. A total of 23 poster communications also resulted from the work in this PhD. Finally, 1 patent was submitted and it is currently in study for publication.

1.5.1. Patents

1. Rui Miguel da Costa Martins, Pedro Alberto da Silva Jorge, Paulo Vicente da Silva Marques, Diana Filipa Carmo Guimarães Dias Guedes, **Miguel Fernandes Soares Ferreira**. Sistema e método para a caracterização de uma peça revestida. Portuguese Patent PT 116928 A. Publication study in progress: 2022.08.18.

1.5.2. Publications in Peer-Reviewed International Journals

1.5.2.1. 1st Author

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7. Tomás Lopes, Diana Capela, **Miguel F.S. Ferreira**, Diana Guimarães, Pedro A.S. Jorge, and Nuno A. Silva Identification of Relevant Spectral Ranges in

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6. Tomás Lopes, Diana Capela, **Miguel F. S. Ferreira**, Joana Teixeira, Catarina Silva, Diana F. Guimarães, Pedro A. S. Jorge, and Nuno A. Silva, Multimodal Knowledge Distillation in Spectral Imaging. In *Optical Sensing and Detection VIII*; SPIE, 2024, Vol. 12999, p. 218-223.

1.5.4. Oral Communications

1.5.4.1. Speaker

1. **Miguel F. S. Ferreira**, Diana Guimarães, Cátia Dias, Ricardo Ribeiro, Alexandre Lima, Rui C. Martins, Pedro A. S. Jorge, Laser induced breakdown system optimization and its applications. In *3rd Doctoral Congress in Engineering (DCE 2019)*, FEUP, Porto, Portugal, June 2019.
2. **Miguel F. S. Ferreira**, Nuno A. Silva, Diana Guimarães, Rui C. Martins, Pedro A. S. Jorge, Effects of pulse duration in laser-induced breakdown spectroscopy. In *4th Doctoral Congress in Engineering (DCE 2021)*, FEUP, Porto, Portugal, June 2021.
3. **Miguel F. S. Ferreira**, Diana Capela, Nuno A. Silva, Alexandre Lima, Filipe S. Gonçalves, Diana Guimarães, Rui C. Martins, Pedro A. S. Jorge, Lithium quantification using LIBS: comprehensive comparison of linear and non-linear quantification methods for geological samples. In *11th Euro- Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2021)*, Gijón, Spain, 29th November to 2nd December 2021
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5. **Miguel F. S. Ferreira**, Rafaela Oliveira, Diana Capela, Tomás Lopes, José Marrafa, Pedro Meneses, Armindo Oliveira, Carlos Baptista, Tiago Gomes,

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1.5.4.2. Collaborator

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3. Lopes, Tomás; Capela, Diana; **Ferreira, Miguel**; Guimarães, Diana; Jorge, Pedro; Silva, Nuno, Collaborative opportunities in Multimodal Sensor Fusion. In *16.º Encontro de Investigação Jovem da U.Porto (IJUP 2023)*, Porto, Portugal, June 2023
4. Nuno A. Silva, Tomás Lopes, Diana Capela, Catarina Silva, **Miguel Ferreira**, Diana Guimarães, Pedro A.S. Jorge, Harnessing Multimodal Spectral Imaging: from sensor fusion to autonomous supervisors. In *12th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2023)*, Porto, Portugal, September 2023.
5. Tomás Lopes, Diana Capela, **Miguel F. S. Ferreira**, Joana Teixeira, Catarina Silva, Diana F. Guimarães, Pedro A. S. Jorge, and Nuno A. Silva, Multimodal Knowledge Distillation in Spectral Imaging. In *SPIE Photonics Europe*, Strasbourg, France, April 2024.

1.5.5. Poster Communications

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2. D. Guimarães, M. F. S. Ferreira, R. C. Martins, P. Jorge, A. Lima, Performance assessment of portable XRF for measuring K and Rb in

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12. P. A. S. Jorge, R. C. Martins, **M. F. S. Ferreira**, D. Guimarães, J. Almeida, A. Martins, S. Kapusniak, E. Silva, Towards Real time ore grading in iVAMOS! Underwater Robotic Mining system, In *10th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2019)*, Brno, Czech Republic, 8-12 September 2019.
13. Diana Capela, Nuno A. Silva, **Miguel F. S. Ferreira**, Rui C. Martins, Pedro A. S. Jorge, Diana Guimarães, Exploring adaptative mesh algorithms for intelligent element mapping, In *11th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2021)*, Gijon, Spain, 29th November to 2nd December 2021
14. Tosin, R., Silva F., Pereira M. R., Testa V., Jorge P., **Ferreira M.**, Santos F., Sandro M., Moura P., Aguiar A.S., Cunha J.B., Cunha M., Martins R.C. Laser Induced Breakdown Spectroscopy for monitoring Vitis-Vinifera Nutritional Uptake and Grape Maturity Evaluation. In *11th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2021)*, Gijon, Spain, 29th November to 2nd December 2021
15. **Miguel Ferreira**, Tomás Lopes, Pedro Rodrigues, Rafael Cavaco, Diana Capela, Nuno A. Silva, Pedro A. S. Jorge, Interactive three-dimensional chemical element maps with Spectral Imaging and photogrammetry. In *16th Mediterranean Workshop and Topical Meeting "Novel Optical Materials and Applications" (NOMA 2023)*, Cetraro, Italy, June 4–10, 2023.
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Chapter 2

From basics to breakthroughs of the LIBS technique

2.1. Introduction

Laser-induced breakdown spectroscopy, or LIBS for short, is an analytical technique that allows to assess elemental information of samples through the spectroscopic analysis of laser-induced plasmas. Also known as laser-induced plasma spectroscopy (LIPS) and more rarely as laser spark spectroscopy (LSS), this technique features unique advantages that have fuelled its fast development over the last two decades. In particular, offering almost instantaneous results, LIBS can theoretically detect any element, including the lighter ones, independently of their physical state which provides a high degree of versatility[2].

When a laser pulse is focused onto a sample, it initially causes material ablation, ejecting atoms and molecules from the surface. If the laser pulse continues to impact the sample, it excites the resulting gas plume, further increasing its temperature. This intense energy may eventually lead to the ionisation of the gas, forming a plasma in a process known as laser-induced breakdown. During the plasma decay, photons are emitted from the deexcitation of atoms and ions, each with a specific wavelength defined by the energy differences between atomic or ionic energy levels. Because these energy levels are unique to each element, the wavelengths of the emitted photons are also unique, enabling precise determination of the elemental composition of the sample when collected and further analysed with a spectrometer.

This chapter presents an overview of the LIBS technique, from its underlying principles to the innerworkings of the most common applications, aiming to establish a comprehensive landscape of the topic in order to support the discussion in the subsequent chapters. It will start with a brief historical note and proceed with a summary of the most important LIBS concepts and underlying physics. It will then advance to introduce the most common setups and possible variations within it. Finally, and taking into account the complexity of providing a complete review of the state-of-the-art for a topic that generates hundreds of research manuscripts every year, the focus turns to a comprehensive and critical perspective of the major applications, trends, and open research challenges of three complementary directions: i) Qualitative analysis, ii) Quantitative analysis, and iii) Spectral imaging.

2.2. A brief historical note

In retrospective, it is not that surprising that the first laser-induced plasma was observed[31] a mere two years after the invention of the laser itself in 1960[32]. Besides, and considering that the foundations of spectroscopy (in particular using spark and arc discharges) were already established through early studies of atomic emission and absorption spectra in the 19th century. It is also not surprising that one year later, in 1963, a first study on the spectrochemical analysis of surfaces with LIBS was published authored by Debras-Guédon and Liodec[33], marking what can be considered as an official date of birth for the technique. Through the rest of the decade, a myriad of studies covering the capacity of generating laser-induced plasmas not only in solid samples but also in air and liquids were reported[34–37].

The turn of decade brought an increasing comprehension and motivation to study the underlying physics of plasma formation and its properties. To this contributed much the introduction of time-resolved laser plasma spectroscopy[2], with the pivotal work in the early 1970s by Schroeder *et al.*[38] exploring electronic gating and signal averaging from several plasmas, reshaping the technique into a form closer to its modern operation procedure and providing new and rich insights. A few years later, the work of Griem in 1974 established a landmark study on spectral line broadening by plasmas with accurate calculations on spectral lines broadening and spectral shift for many atoms and ions that are still used to this date[39]. In hindsight, the decade also marked a paradigm shift for the technique towards emergent applications, with the first investigations in biological material, with the works of Marich *et al.*[40] and Treytl *et al.*[41], and in aerosols, with the studies by Lencioni[42], Belyaev *et al.*[43] and Edwards and Fleck[44].

With the advent of the '80s, the term LIBS began to appear in the works of Loree and Radziemski[45], in particular in the work reporting the detection of sodium (Na) and potassium (K) in a coal gasifier product stream, of phosphorus (P), sulphur (S) and chlorine (Cl) in organic molecules and of airborne beryllium. This work seeded a series of studies researching the detection of toxic and hazardous materials throughout the decade[46–51]. The decade was also marked by the first studies on the acoustic signals resulting from the plasma-generated shockwaves, their strength being related to the energy deposited in the medium[2,52].

Entering the 90s, the field started to develop quite rapidly with useful reviews[53–55] and with new research groups surging all around the world[56–59] working in multiple directions. First, motivated by the advantages against competing techniques (later detailed in this chapter), there was a strong push for quantitative analysis with LIBS, with

several studies attempting to investigate or improve its performance[59–69]. In-between these studies, the calibration-free analysis was developed[61], which uses the spectral lines of the elements that represent the sample to determine the concentration of the element of interest, assuming a thermodynamic equilibrium. On a second direction, the first reports of spatially resolved LIBS began to appear[70–75], seeding a research topic which was later rebranded as LIBS imaging. Instrumentation also received some improvements with the introduction of compact echelle spectrometers combined with charge coupled devices (CCD) detectors or intensified CCDs (ICCD)[76]. As they became available, new parameters, such as different wavelengths and temporal pulse length, were tested for LIBS applications[77–82]. Finally, with the advent of machine learning and artificial intelligence, novel solutions for qualitative[83] and quantitative[84] analysis led to high-performance applications over the most diverse fields, now being one of the most relevant research lines in LIBS research.

A final topic that is worth mentioning when discussing the history of LIBS are its applications in harsh environments, from deep-sea to extra-terrestrial applications. Focusing on the latter, ideas to take LIBS out of Earth were first mentioned in 1992[85,86], getting traction again a few years later[87] into the new millennium, with a LIBS prototype being placed in a prototype Martian rover for preliminary tests in the Nevada desert[88]. Successful results eventually led to the insertion of LIBS instrumentation into two Mars rovers, Curiosity and Perseverance, within the ChemCam[89] and SuperCam[90] instruments. These present one of the most important achievements of LIBS as a research topic.

In the last few decades, publications in LIBS have been growing exponentially (Figure 2.1), with a variety of new reviews and books[2,91–94], taking a hit after 2020, most likely due to the effects of the Covid-19 pandemic. The interest in the technique has led to the organisation of several LIBS conferences worldwide, with the XIII World Conference on Laser-induced Breakdown Spectroscopy, which occurs this year, and other continental-centric versions, like the Latin-American Meeting on Laser-induced Breakdown Spectroscopy (LAMLIBS), the Asian Symposium on Laser-induced Breakdown Spectroscopy (ASLIBS) and Euro-Mediterranean Symposium on Laser-induced Breakdown Spectroscopy (EMSLIBS), the latter having the most iterations, last year reaching the 12th edition (in Porto, Portugal, hosted by INESC TEC team).

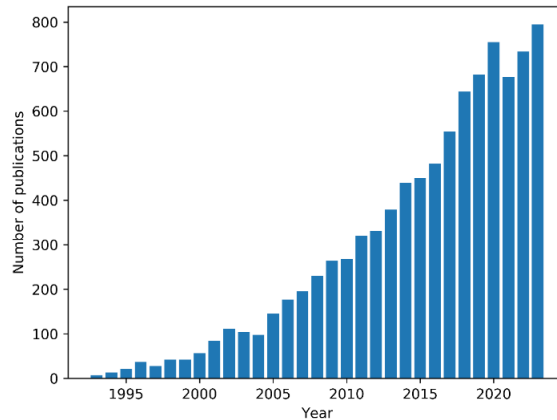


Figure 2.1 – Number of publications on Scopus from 1993 to 2023 obtained with the terms “laser induced breakdown spectroscopy”.

2.3. Fundamentals of LIBS

LIBS is a spectroscopy technique that is based on the analysis of light emitted from a plasma generated by a focused pulsed laser. These plasma emissions contain spectra information in the form of discrete lines that are specific to certain elements allowing to obtain the elemental composition of samples. When compared against other techniques, LIBS displays many advantages with particular highlight to:

- Can theoretically detect all elements;
- Fast and localised analysis;
- Simple setup implementation;
- Operation in laboratory or in-situ;
- Sample preparation is optional;
- Can perform remote measurements;
- Micro-destructive.

As every element has their own emission lines, every element should be detectable by LIBS, barring hardware limitations, meaning access to light elements that techniques such as XRF struggle with. The plasma lifetime lasting tens of μs makes LIBS analyses almost instantaneous and the focusing aspect leads to a very localised analyses instead of obtaining averages of larger areas. These two combined permit a quick study of large areas with high resolution. A basic LIBS setup is also quite simple to assemble and implement, it can also be enhanced in a variety of ways for more detailed studies in a laboratory setting or readapted to a portable version for in-situ operations. It can also be modified to perform remote measurement for hard to reach or dangerous samples or environments. The latter two aspects are further validated as the technique does not require any sample preparation, but, at the same time, it can also benefit from it,

enhancing laboratory results. While damaging samples, even if at a μm scale, is not ideal for all cases, in some cases it is negligible enough to be acceptable. Not only that, this apparent small disadvantage can be used favourably to produce depth analyses, as each consecutively shot will open a new layer as the previous one is ablated. Nevertheless, LIBS is not foolproof, with its main limitations including lower accuracy and relatively high limits of detection[2].

2.3.1. Plasma formation and spectral information

Plasma, commonly referred as the fourth state of matter, is a local assembly of atoms and/or molecules, ions and free electrons, which is overall electrically neutral. Physically speaking, a plasma can be characterised by a series of parameters namely the degree of ionisation, the plasma's temperature and its electron density. Laser-induced plasmas, like the ones created in LIBS, are considered weakly ionised plasmas as their ratio of free electrons to other species is lower than 10%. Their temperature is usually in the order of 10^4 K while the electron density roughly ranges between 10^{23} and 10^{25} m^{-3} [2].

Laser-induced plasmas are formed when short high-power laser pulses are focused just enough on a sample for the irradiance to breach its breakdown threshold. This process can occur in gases, liquids and solids, the latter two being preceded by the ablation of the surface (Figure 2.2). Their breakdown threshold heavily depends on a myriad of factors, ranging from 10^8 to 10^{14} W/cm^2 , with solids being in the lower range and gases at the higher[2]. These factors include the characteristics of the sample, such as its elemental composition, molecular structure and the already mentioned state of matter, the laser parameters, such as its wavelength and the pulse's duration, and combination of both, like sample's absorptivity of the laser's wavelength, among others.

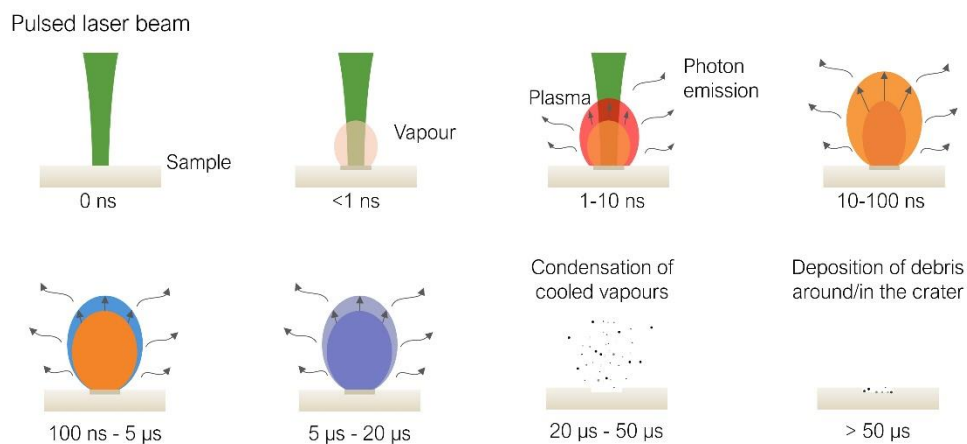


Figure 2.2 – Plasma lifetime stages for a ns laser focused on a solid surface. A laser pulse hits a sample, vaporising it and forming a plasma, which emits photons. After the laser pulse, the plasma cools down, condensates and leaves particles in the affected area.

When the laser irradiance is high enough, it will ignite a plasma. The ignition process is dependent on the state of matter of the sample and type of laser[2,91,94]. In the specific case of solids and nanosecond lasers, it comprises ablation, bond breaking, ionisation and plasma shielding. The process is dominated by thermal effects as the temporal length of the pulses is larger than the electron-lattice heating time, approximately 10^{-12} s. The laser pulse will melt and vaporise the irradiated surface of the sample, which will then ionise with the temperature increase forming the plasma. The plasma will then begin to expand, creating a shockwave that is dependent on the surrounding pressure. During this, part of the laser energy will continue to ablate the surface while some will be absorbed by the plasma, heating it further. If the energy is large enough, a plasma shielding effect can occur, where the plasma turns opaque to the laser radiation, shielding the sample's surface. The plasma will then continue to expand and start cooling down. Figure 2.3 presents a scheme of the lifetime of a LIBS plasma, while Figure 2.4 represents the electron transitions that occur during that period.

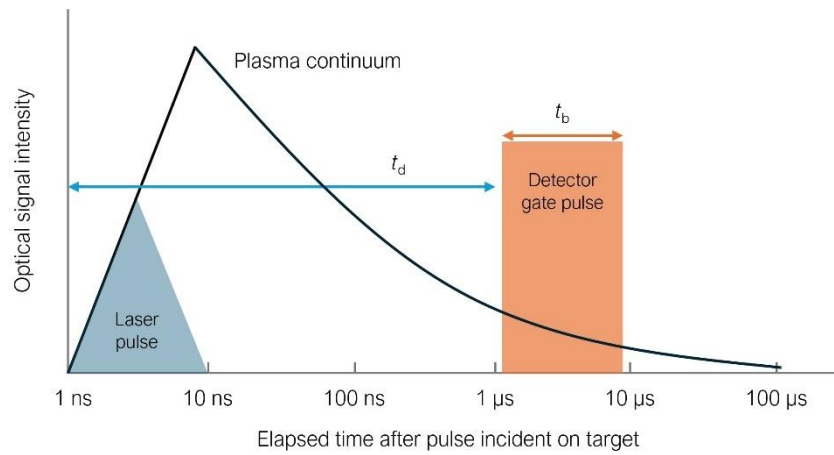


Figure 2.3 – Scheme of a laser-induced plasma lifetime along with an integration delay and integration time for LIBS.

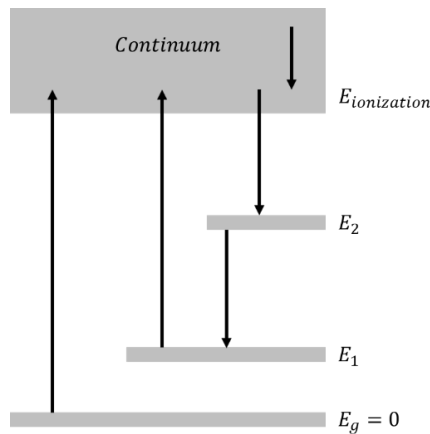


Figure 2.4 – Typical electron transitions in an atom or ion. From left to right: ionisation from the ground state, ionisation from an excited state, bound–bound, free–bound and free–free.

Light emission from a plasma can be separated into two categories, continuum and spectral line emission. The former has two origins, bremsstrahlung and recombination, while the latter occurs due to deexcitation. At the early stages of a laser-induced plasma, light emission is primarily composed of bremsstrahlung radiation, a type of photon emission that occurs due to kinetic energy loss of free electrons from collisions with other particles (free-free), and recombination, where photons are emitted due to electrons being capture by ions (free-bound). These processes decay faster than the deexcitation process, which dominates at later stages of the plasma lifetime. During deexcitation, the photon emitted have energies related to the differences of two energy levels between which electrons dropped from the more to the less energetic. The photons emitted from these processes are characterised by

$$\nu = \Delta E / h \quad \lambda = c / \nu, \quad (2.1)$$

where ν is the frequency of the photons, ΔE is the difference between energy levels, h is the Planck constant, λ is the wavelength and c is the speed of light.

Since each element has its own specific energy levels, spectral lines will relate to specific elements and thus, by analysing the wavelengths of the lines present in a spectrum, the elemental composition of a sample can be obtained. To help with that task databases such as the one from the United States' National Institute of Standards and Technology (NIST)[95] can be used to connect the spectral lines to their corresponding elements.

Additionally, molecular emissions can be observed from some samples apart from the elemental emissions. These occur from simple molecules that originate from atoms in high concentrations that recombine in the cooling plasma, resulting in emissions late into the plasma's lifetime[2].

While elements have very specific wavelengths, some effects lead to plasma emitting spectral lines with two-dimensional profiles and even shift[2]. The profile of a spectral line is dependent on the dominant broadening effects, Doppler broadening results in a Gaussian profile, while effects like natural line broadening and collision broadening result in a symmetric Lorentz profile. Often the resulting shape is the convolution of both, a Voigt profile. Stark effect is another effect that introduces broadening and wavelength shifts and it is one of the largest contributors to the line width alongside the Doppler broadening.

A plasma characteristic that can also affect a spectra line's profile is its opacity. Since an emitting element can also be an absorbing element there are some instances of

reabsorption that determine if a plasma can be considered as optically thin or not. Experimentally, reabsorption become noticeable when spectral lines are detected with a flat-top like profile, meaning self-absorption, or a dip at the central frequency, indicating self-reversal[96].

Assuming a local thermodynamic equilibrium (LTE), which requires some criterions to be met[97], the spectral line intensity is given by[2]:

$$I_{ij} = \frac{hcNg_iA_{ij}}{4\pi\lambda_{ij}Z(T_p)} \exp\left(-\frac{E_i}{k_B T_p}\right), \quad (2.2)$$

where h is the Planck constant, c is the speed of light, N is the number density of the species, λ_{ij} is the emission wavelength, A_{ij} is the transition probability, g_i is the degeneracy, E_i is the energy of the upper level k_B the Boltzmann constant and T_p the plasma temperature and $Z(T_p)$ is the partition function[2]. By taking the logarithm of that equation, one can rewrite it in a linear form ($y = mx + b$):

$$\ln\left(\frac{I_{ij}\lambda_{ij}}{g_iA_{ij}}\right) = -\frac{1}{k_B T_p} E_i + \frac{hcN}{4\pi Z(T_p)}, \quad (2.3)$$

where the slope $m = -\frac{1}{k_B T_p}$, which can be obtained by plotting E_i against $\ln\left(\frac{I_{ij}\lambda_{ij}}{g_iA_{ij}}\right)$, named Boltzmann plot, and used to calculate the plasma's temperature. Another method of calculating the plasma's temperature is using the Saha–Eggert) equation[2]:

$$\frac{N^I N_e}{N^{I-1}} = \frac{2(2\pi m_e k_B T_p)^{\frac{3}{2}}}{h^3} \frac{Z^I(T_p)}{Z^{I-1}(T_p)} \exp\left(-\frac{E_{ion}}{k_B T_p}\right), \quad (2.4)$$

where I and $I - 1$ represent an ionised state and the next lowest state of ionisation of the same element, respectively, m_e is the mass of an electron and E_{ion} is the ionisation energy of the element at the state $I - 1$. This equation gives a relation between two populations at different states of ionisation allowing for the use spectral lines from both cases to calculate the plasma temperature[2]. Besides, depending directly on the number density of atomic and ionised species, these relations are also the motivation for the quantification applications of LIBS, enclosing also its inner complexity as discussed later in this thesis.

2.3.2. Experimental setup

Contrary to the complexity of its physics, a LIBS system is reasonably straightforward to implement. As schematically represented in Figure 2.5, the system requires a pulsed laser as a source, a focusing lens to focus the laser pulse onto the sample, a light collection system, usually an optical fibre, a spectrometer to acquire the spectra and a computer to save and interpret the data.

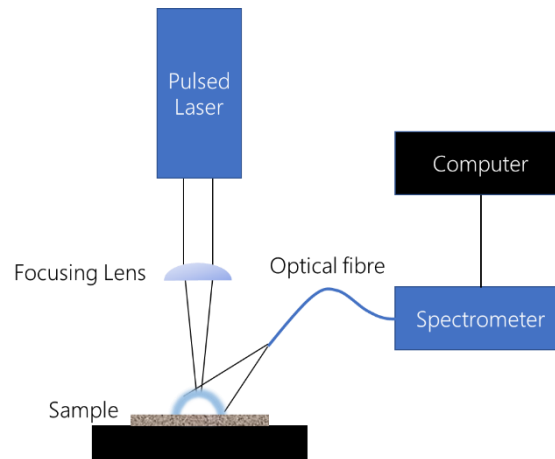


Figure 2.5 – Scheme of a basic LIBS setup. A laser emits a pulse through a focusing lens into a sample, generating plasma. Its emissions are collected by an optical fibre to a spectrometer, which then transmits the measurements to a computer.

Even in its most basic components, there are quite a few alternatives when implementing a LIBS system.

2.3.2.1. Laser sources and focusing optics

Starting with lasers, options include wavelengths from ultraviolet (UV) to far infrared (IR)[11,98–100] and pulse durations from ns to fs scales[11,15,99] with the optimal choice depending on the intended application. The Nd:YAG laser is the most commonly used laser in LIBS, working at its fundamental wavelength, 1064 nm[11,29,99,101], or at its harmonics, 532[99], 355[11] and 266 nm[98]. Other explored lasers include excimer lasers such as ArF (193 nm)[102], KrF (248 nm)[11] and XeCl (308 nm)[10], N₂ lasers (337 nm) [75], Ti-sapphire lasers (800 nm)[15], CO₂ lasers (10.6 μm)[103], microchip lasers[104] and fibre lasers[27,28]. All these include their share of advantages and disadvantages:

- Nd:YAG lasers are the most versatile to utilise in LIBS. They have high energy pulse, allowing for the formation of plasma without needing much precision in the optical system. They can access harmonic wavelengths, may have dual pulse capabilities and good beam quality can be achieved. These lasers are compact, but are dependent on their coolers, which, depending on the type, may severely increase its size and require maintenance, affecting their portability. Besides, the repetition rate of the pulses is one of the slowest, making it rather slow for some applications;
- Excimer lasers work in the UV range. Compared to the Nd:YAG laser, the beam quality is poorer and the need for periodic gas changes causes some restrictions for field operation;

- N₂ lasers operate at 337 nm. These lasers require molecular nitrogen to work and are more efficient when the gas is cold than when it is hot, meaning they require temperature control;
- Ti-sapphire lasers have femtosecond pulses at their disposal. These ultrashort pulses allow for a more efficient ablation and the avoidance of shielding effects from the plasma. However, these lasers are expensive and are not compact;
- CO₂ lasers, as the excimer ones, have poor beam quality compared to the Nd:YAG lasers and also need periodic gas changes. While their wavelength, 10.6 µm, have some applications, it does not couple well with some metals;
- Microchip lasers have good mode and beam quality allied with a high shot-to-shot pulse stability.
- Fibre lasers are known for their long lifetimes and are lasers with a high efficiency. Their pulses have a good beam quality ($M^2 < 2$) and can have their pulse width changed. They can operate from single shot up to hundreds of kHz which open the possibility of working with double or multi-pulse LIBS. These lasers have a compact size and moderate weight, making it suitable for a portable version.

Normally, to generate a plasma, the collimated beam from the laser needs to be focused in order to increase the beam's intensity above the sample's plasma threshold. Apart from the laser pulse's energy and temporal width, the intensity of the focus is dependent on spot size, which, in LIBS, is typically dependent on diffraction (Figure 2.6).

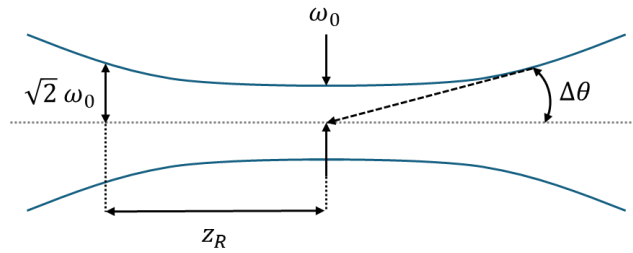


Figure 2.6 – Focused gaussian beam.

w_0 is the beam waist at the focal point and z_R is the Rayleigh range and, when taking into account the beam's quality, they can be described as:

$$\omega_0 = M^2 \frac{f\lambda}{\pi D/2}, \quad (2.5)$$

$$z_R = \frac{\pi \omega_0^2}{\lambda M^2}, \quad (2.6)$$

where f is the focal distance, λ is the wavelength, D is the diameter of the collimated beam and M^2 is the beam propagation ratio, related to the beam's quality, being 1 for a

theoretical gaussian beam. This means that the characteristics of the focusing lens are crucial in determining the spot size. A shorter focal length results in a smaller spot size, while a longer focal length provides a greater focal depth. This can be further explored with more complex focusing systems, like a beam expander placed prior to the focusing optics to further decrease the spot size, replacing the focusing lens with another focusing optics like a microscope objective or even a cylindrical lens to create a long but thin plasma.

2.3.2.2. Spectrometers and collection optics

To measure the emitted light from the plasma, spectrometers are the most commonly used device in LIBS. The performance of a spectrometer is tied to its components and configurations, affecting light acquisition, spectral range, wavelength resolution and integration parameters. The two most utilised spectrometer configurations are Czerny-Turner[105–107] and Echelle[105,108,109], but others such as Paschen–Runge[110] and Littrow[111] have been used. Depending on the application, different types of detectors have been used in LIBS. Photomultiplier tubes[112] can be used to measure light intensity without spectra decomposition. To obtain spectral decomposition, photodiode arrays could be used for time-resolved measurements[10], but they have been replaced by CCDs[98,113] for several applications, with ICCDs[105,114] offering higher signal-to-noise ratios (SNR) and better time-resolved detection with ns integration times. Lately, complementary metal–oxide–semiconductors (CMOS)[115,116] and scientific CMOS (sCMOS)[117,118] have been utilised instead of CCDs and ICCDs, respectively.

The most common way to collect and redirect light to the spectrometers is through the use of one or multiple optical fibres, usually placed close to the region of plasma formation to obtain as much plasma emission as possible[11,119]. Integrated optics is, however, another utilised option, where the light is redirected to the detector through the use of mirrors and lenses[10].

2.3.2.3. Advanced control and other setups

From this point, a LIBS system can be upgraded in several ways (Figure 2.7). The simplest methods include mirrors to better position the laser pulses through the focusing lens, collimators for the optical fibre to increase the amount of light captured and translation stages to move the samples or sometimes the optical system itself, the latter enabling elemental mapping. To take the technique further, one can add a digital delay generator (DDG) to better synchronise the timings between the pulse emission and the

gating of the spectrometer, obtaining a precise time control allowing to select or avoid specific plasma lifetime stages and enhancing the desired spectral signatures[2]. Moreover, due to the ablation process of the technique, there is an inevitable dispersion of particles that can affect the efficiency of the technique, for which incorporating a gas flow can be the solution[120].

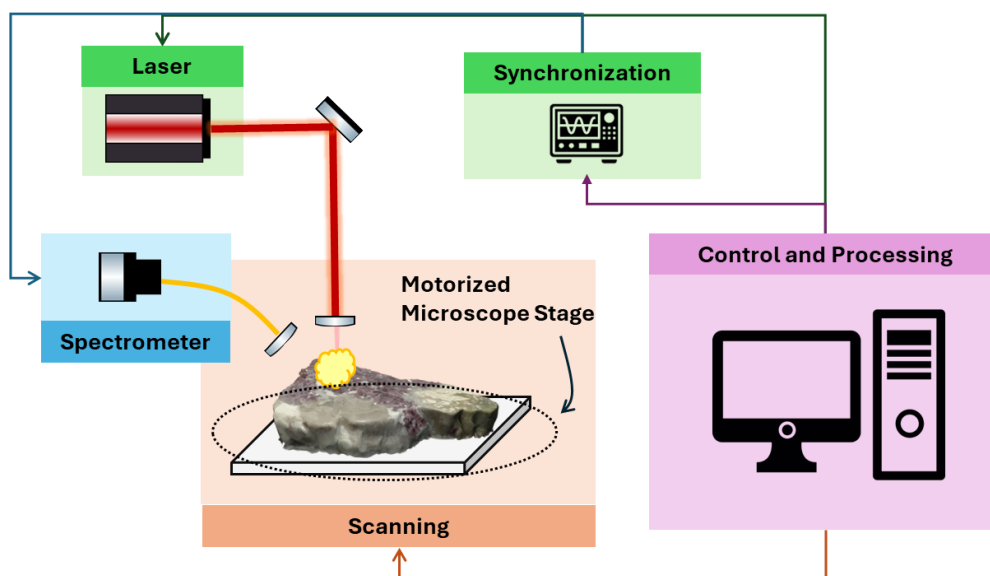


Figure 2.7 – Scheme of a LIBS system with synchronisation control and motorised stages for sample manipulation.

A more complex modification to a LIBS setup is the addition of a controlled surrounding medium. Altering the atmospheric pressure, usually reducing it by a certain amount, or the overall composition of the air that surrounds the sample, like He, N₂, Ar or CO₂, can enhance the LIBS spectra by increasing the SNR and reduce line broadening[121,122]. Alternatively, this kind of modification to a LIBS setup can be used to simulate conditions of extreme environments such as underwater or Martian atmosphere[114,123,124].

Lastly, there is also the double pulse LIBS, which often uses two distinct lasers, that may differ in wavelength, pulse duration, pulse energy and more[125]. This variation has two main configurations, orthogonal[105,126,127] and collinear[109,128]. In the orthogonal case, the beams are set perpendicular to each other with two possible operations. In orthogonal pre-ablation[127], the first pulse is parallel to the sample's surface and creates a plasma above the surface while the other ablates it. In the re-heating mode[105], the first laser is the perpendicular to the surface and ablates the sample, while the second pulse re-heats the plasma. In the collinear configuration, both beams travel along the same axis perpendicular to the sample's surface, with a similar operating principle to the previous one.

2.4. Current trends and research roadmap

Nowadays, LIBS has grown to be a very dependable technique, having expanded to a significant variety of fields[94,129]. Nevertheless, investigations into the fundamentals of the technique are still ongoing, with a recent study attempted to model a plasma with two homogeneous zones which made it possible to describe both atomic and ionic lines with a good match to experimental results, even the ones subjected to self-reversal[130]. Another study turned its attention to self-absorption, simulating spectra containing that effect to examine its dependence on plasma parameters[131].

Applications for the technique keep expanding. In terms of mining and geological samples, the interest in exploring Li keeps growing[132–134]. Studies on biomedical applications have shown LIBS as a possible tool for diagnosing lung diseases[135] and ovarian cancer[136]. LIBS micro-destructive nature does not deter its use in heritage, with a study of black resin and gold used by ancient Egyptians in embalming[137]. Recent studies also present LIBS as a tool to detect food fraud[138], metal contamination in flowers[139] and determination of the imidization degree of polyimides[140]. In the nuclear field, research has been performed to use LIBS to analyse walls of nuclear reactors[141,142]. With the Perseverance rover landing in Mars in 2021, the LIBS inserted in the SuperCam has been used for a variety of studies related to the exploration of Mars[143–146].

Alongside scientific development of the LIBS technology, commercially available systems have also evolved greatly in the last few years. A multitude of options are available nowadays with different markets and applications in mind. In addition to bulky systems that offer lower limits of detection (LOD) and greater spatial resolution, with the possibility of mapping samples[147–153], portable versions are also available. These versions, showcase the potential of LIBS as a resilient technique, able to be used in field applications. Portable systems are currently marketed for the analysis of ores, alloys, agro-food, cultural heritage and other applications[151–153].

The output of a LIBS process is an emission spectrum, characterised by spectral lines corresponding to the spectral fingerprints of atoms, ions, and molecules (Figure 2.8). With LIBS, analysis can be categorised into three major families: qualitative analysis, quantitative analysis, and spectral imaging.

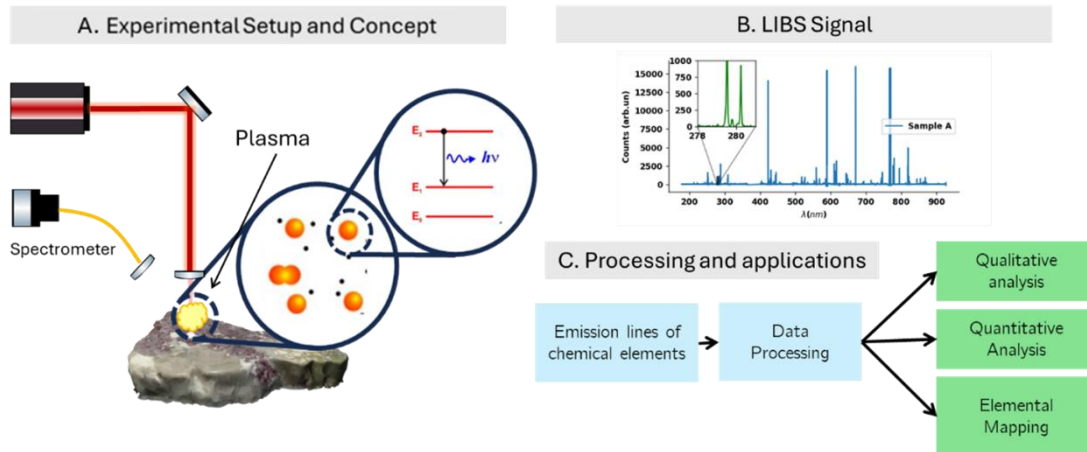


Figure 2.8 – Illustration of steps for LIBS analyses.

2.4.1. Data pre-processing

Before performing any kind of analysis, there is normally a pre-processing step to reduce uncertainty and improve SNR. In literature, denoising[154,155] and background subtraction[156–158], also known as baseline removal, are two common methods to improve SNR. Normalising the spectra is another pre-processing step often used as it reduces the signal uncertainty. This step, however, has many variations. From these, the commonly used methods are spectra area normalisation[159,160], background emission normalisation[161,162] and normalisation to an internal standard[163,164], but others have also been used for LIBS[165,166]. Other pre-processing methods include variable selection[167], to reduce redundancy, and generalised spectrum[168], to reduce fluctuations related to experimental conditions.

2.4.2. Qualitative analysis

Qualitative analysis in LIBS entails determining the presence or absence of specific elements within a sample. This is accomplished by comparing the emission lines observed in the LIBS spectra to established atomic spectra from reference databases[2], such as those provided by NIST.

Qualitative LIBS is often used in a variety of areas, including geomaterials[169,170], metals[171,172], biological samples[173,174], food[175,176], forensics[177] and polymers[178,179].

Built into the SuperCam of the Perseverance rover currently on Mars, LIBS has participated in an assortment of studies including for detection of carbonates[145] and ore identification[146], which also exemplify the concept of combining LIBS with other techniques such as Raman spectroscopy.

Unlike quantitative methods, this analysis does not necessitate calibration or reference standards. Instead, it typically utilises numerical algorithms to identify spectral peaks. Moreover, machine learning techniques, particularly classification algorithms, are employed to differentiate among various sample types or distinct regions within samples.

2.4.2.1. Methodologies

The simplest form of qualitative analysis is element identification. Usually, this is dictated by the presence of the element's corresponding spectral lines in a spectrum, which, depending on the sample's composition and spectral resolution, may vary in difficulty due to overlaps. In an attempt to correctly identify elemental lines, several considerations can be made. These include the likelihood of lines corresponding to elements known to be present in high concentrations in the sample, the presence of stronger, corroborating lines for the element in question with reasonable relative intensities, and the understanding that emissions from higher ionised species are less likely to occur compared to those from singly ionised or neutral species. Additionally, it is important to consider how the experimental conditions may influence the presence of ionised species.

Of course, in theory, looking at a broader picture, it should be possible to distinguish between different samples from the examination of the spectral features and group the ones that are similar. For this task, algorithms have been used to perform classification in LIBS as to determine what spectral features discriminate between classes, grouping similar samples together, naming a few:

- Linear discriminant analysis (LDA)[180–182], one classification technique that attempts to create linear boundaries that separate classes assuming they have normal distributions and the same correlation structure[183]. It does struggle with cases where the number of dimensions is larger than of the samples, a limitation that can be overcome using Principal component analysis (PCA)[184]. This method reduces the dimensionality of the data through a linear projection. It is able to handle the high dimensionality of the LIBS data and provides information through the principal components.
- Partial least squares discriminant analysis (PLS-DA)[172,185], it is a technique that combines partial least squares (PLS) and linear discrimination[186]. PLS aims to reduce the dimensionality of the data by performing a projection into a basis of the feature space[187], which is chosen based on the directions that maximise the correlation of the data with the sample's characteristics. Like PCA, it is capable of

handling LIBS spectra's high dimensionality while providing information through the latent variables.

- K-nearest neighbours (KNN)[188,189], it is a simple non-linear methodology that can be used for classification by identifying a sample's k nearest neighbours in the training data and assuming similarity based on distances in a multivariate space[190]. In the case of LIBS, this space consists of the spectral wavelengths, with the distances being calculated based on the intensities at these wavelengths.
- Support vector machines (SVM)[191,192], it is a non-linear methodology that attempts to create a hyperplane, controlled by support vectors, to separate two classes, while maximising the distance between that hyperplane and the training observations from both classes[193].
- Random forests (RF)[194,195], it is another non-linear technique that designs a classifier by combining decision trees, which are trained by dividing the multivariate space into subspaces that best separate the classes[196].
- Artificial neural networks (ANN)[197], it is group of complex algorithms that consist of multiple processing elements, which receive inputs and send outputs depending on the predefined activation functions[198].

Recent years have seen an increase in the use of machine learning methods, with goals such as classification of aluminium (Al) scrap metal[12,199]. Recent advancements have also explored the use of unsupervised clustering methods to classify different mineral types using LIBS[200].

2.4.3. Quantitative analysis

Even with the many advantages that LIBS possesses over other spectroscopic techniques, its performance in quantification can be regarded as its Achilles' heel[201,202]. While it had a few successes[203–205], LIBS still struggles to reach a quantitative level due to a variety of factors. These factors include effects that the technique is prone to, like matrix effects, properties of the experimental system, like the fluctuations of the laser pulse's energy, and even external conditions, like humidity, which all greatly contribute to the variability of the results.

Despite these problems, quantitative LIBS is a well-sought out analysis in a variety of fields such as metallurgy[206,207], minerals[10,208,209], heritage[210,211] and environmental[212,213], among others[214–216]. Also, with a LIBS inserted into the SuperCam, in the Perseverance rover, element quantification has also been performed on samples on and from Mars[143,144].

Being the technique's weakest spot and to ensure that LIBS is in the right path to being established as a quantification tool, a recent work brought a new perspective on how to statistically evaluate the performance of models in quantitative analysis with LIBS[217], models which can be divided into calibrations using numerical methods[201] and calibration-free LIBS[202].

2.4.3.1. Calibration models

Considering the field of LIBS, a calibration curve should provide the relation between the concentration of a particular element on a given sample to the spectrum resulting from a LIBS analysis. Since the calibration is often data-driven, the performance of the resulting curve will heavily depend on the training set, meaning that a training set that fails to represent the samples of a real case scenario will underperform independently of the used numerical methods.

After performing data pre-processing, a numerical model can be trained. Among others, some of the algorithms mentioned for qualitative LIBS have been used:

- PCA[10,218], it is able to handle the high dimensionality of the LIBS data, However, it does not consider the response information and does not perform well with non-linear behaviour like LIBS often has;
- PLS[219–221], it is capable of handling LIBS spectra's high dimensionality, but, similar to PCA, its performance degrades if the LIBS behaviour is highly non-linear;
- SVM[222,223], it can handle non-linear behaviour from data with high dimensionality even with a small sample size, but lacks interpretability;
- ANN[224,225], it is capable of managing complex non-linear data and it is appropriate for large scale data processing. However, it tends to overfit, lacking a way to interpret the model and requires a high computational power.

It is worth mentioning the increasing tendency to use of deep learning and other machine learning methods for quantification, with recent examples being quantification of major and minor elements in aluminium scrap metal and steel[116,226] and line analysis of coal[227].

2.4.3.2. Calibration-free method

First reported in 1999[61], calibration-free LIBS is a methodology that does not require any type of calibration. With the classic version, the concentration of a given species is determined by the Boltzmann plot with the plasma temperature being calculated with equation 2.3 using the spectral lines of that same species. In the case of there not being

enough atomic lines, but ionic lines being present, this method can be assisted by the Saha-Eggert equation (equation 2.4).

However, to use this method some conditions need to be met[2]:

- The stoichiometry of the sample is retained between the sample and plasma;
- The plasma is in LTE;
- The plasma is optically thin;
- The plasma is spatially homogeneous;
- The number density of neutral atoms and ions can be obtained;
- All elements of the sample have lines in the spectral region of the spectrometer.

These conditions, however, are seldom reunited, which hurt the performance of the method. Several improvements have been suggested throughout the years including self-calibrated LIBS[228], calibration-free inverse method[229], one point calibration LIBS[230], calibration-free LIBS with the standard reference line[231] and combination with machine learning[232], among others[233,234].

Lastly, this method has been applied in a variety of fields, including metallurgy[206,207], minerals[208,209], heritage[210,211] and environmental[212,213], among others[214,215].

2.4.4. LIBS imaging

One of the many LIBS capabilities is to perform imaging. LIBS imaging takes the concept of a single LIBS measurement to obtain the elemental composition of a μm -sized spot to a series of measurements at different positions covering the entirety of a region of interest allowing for the creation of elemental maps[92,235]. The first reports of spatially resolved LIBS date back from the 1900s[70–75] and LIBS-based imaging has gotten increasingly more interest over the years and it is currently one of LIBS main sub-fields.

2.4.4.1. Methodology and instrumentation

Two different methods of performing LIBS imaging have been reported in literature, those being point by point[236–238] and continuous[122,239–241] scans (Figure 2.9). In the former case, the system stops at each analysed point to deliver the laser shots, moving between them in a step by step manner, while on the latter, the system is synchronised to deliver a line by line analysis, where, for each line, the system does not stop for each individual point analysis but the laser and translation stages are synchronised to deliver shots at consistent physical intervals, before finally moving to the

next line. The main advantage of using a continuous scan over a point by point one is the speed of operation as no time is wasted for stopping at every single spot. On the other end, the point by point scanning allows for more versatility, as cleaning shots can be used and a 3-dimensional analysis can be performed[242]. In any case, the step size is what determines the resolution of the image, with each point representing a pixel, and it should be larger than the crater size to avoid overlap between analysed spots.

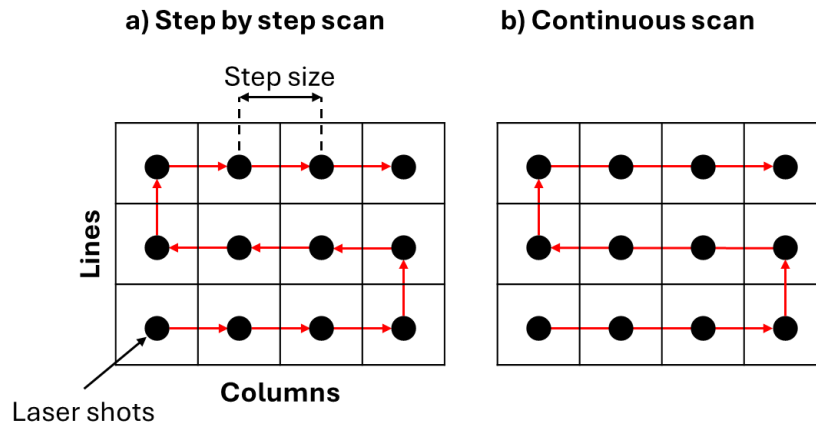


Figure 2.9 – LIBS scanning with a) step by step and b) continuous methods.

Crater size is critical to obtain a good resolution. Their size is dependent on the focusing systems and the parameters of the lasers, such as beam quality, wavelength, pulse energy and pulse width. The most significant contribution comes from the focusing systems, which are nowadays distinguished between macroscopic[243,244], with craters in the hundreds of μm and microscopic[245,246], reaching a few μm of resolution and often using microscope objectives. To improve the signal of the spectra, a constant gas flow can be directed at the sample, argon (Ar) being usually utilised[122,245], with alternatives such as helium (He)[247] and mixtures of Ar and He[248].

The vast majority of experiments utilises ns Nd:YAG lasers in either their fundamental level[241,249,250] or in their second harmonic[251,252]. However, there has been some interest in using fs lasers, as they provide a better control of the ablation process reaching very few μm of resolution[253,254]. Another approach that has been gaining attention, in this case to improve the SNR, is the use of double pulse[255,256].

Signal acquisition-wise, Echelle spectrometers are often used for their broad spectral range with ICCDs[237,257,258], but these spectrometers have low acquisition speeds and sensitivity when compared to other options. Czerny-Turner on the other hand have greater sensitivity and, when paired with ICCDs, they can reach 100 Hz[239], but usually

have a limited spectral range[259,260]. To overcome this, some studies use several Czerny-Turner spectrometers to attain a wider range[239,240], which in turn greatly increases costs. Another alternative is the use of cost-effective Czerny-Turner spectrometers, sacrificing resolution for a larger range at a smaller cost[250,261]. Paschen–Runge spectrometers are also an option[110,262], offering the most sensitivity and fastest detection speeds, though at a higher monetary cost and physical limitations. Lastly, focusing on the spectral region, some works have explored the detection in the vacuum ultraviolet range[3,263], requiring operating under vacuum conditions and purging the light collection system and spectrometers with inert gases.

Keeping a constant distance between the sample's surface and the focusing system throughout an entire LIBS scanning is crucial to guarantee reproducible ablations, especially when using microscopic objectives. Sample preparation such as polishing is usually used to obtain a flat surface to scan and it is usually enough for small samples. However, when dealing with large samples, the difficulty to obtain a flat enough surface increases and sample tilting will be more noticeable, therefore some studies have reported the use of an autofocus to deal with this issue[239,255,261].

Finally, LIBS can also be coupled with other techniques. Combining it with something as simple as a conventional camera can assist sample positioning, including focusing, and even allowing for stacking optical images with elemental maps[5,243,264]. However, greater value can be achieved by combining LIBS with techniques such as Raman spectroscopy[265], laser-induced fluorescence (LIF)[266] and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)[267].

2.4.4.2. Data processing

Apart from methods aiming to speed up the LIBS scanning process, data processing is increasingly requiring advanced methodologies to handle the massive datasets, which can reach scales up to 10 million pixels[268]. This, coupled with the fact that each pixel contains a spectrum with thousands of wavelengths, leads to data exceeding several GB just for a single sample, requiring an extensive time for processing.

The most common data processing method for LIBS imaging is the use of individual spectral emission lines to extract information from the elements of interest[4,269,270]. One approach can be using the line intensity after performing a baseline removal[269], but for more complex samples, with several phases and different matrices, the sample's dataset can be broken into smaller datasets comprising different phases[4].

Another approach being used is making a quantification-like analysis, performing a calibration using external methods. The most common tactic uses reference materials similar to the sample, which have known concentrations and compositions[247,267]. When unavailable, another possibility is to use complimentary techniques, like inductively coupled plasma optical emission spectrometry[271] and electron probe micro-analysis[8], to obtain the global elemental composition of the sample and use it to calibrate the LIBS imaging.

The complexity of some samples and the large datasets obtained with LIBS can also invite the use of chemometric tools. These tools can also provide a quantitative analysis, contributing in calibrations, but can also be used for classification[94] and signal unmixing[235]. Some methodologies used include PCA[241,272] and PLS[221,273], among others[174,274,275]. Finally, in more recent years, works exploring neural networks methodologies have begun to appear[276–278].

2.4.4.3. Applications and recent studies

LIBS imaging has already been applied to a variety of areas. One popular application where it is often used is the analysis of geological samples, being applied in mineralogy[279–281], cement and concrete[282,283], archaeology[253,284] and paleoclimate studies.[285,286].

Fields for applications in industry are quite varied. One of the most known is metallurgy[287,288], followed by electronics, with the analysis of examples such as batteries[289], semiconductors[290] and piezoelectric crystals[291]. Less well-known fields include catalysis[292,293] and nuclear field[294,295].

One of the most promising areas seems to be biology as, in the last few years, LIBS imaging has shown to be capable of assisting the medical field[135,174]. While not as vital, it has also shown its use with vegetal materials[296,297]. LIBS imaging has also seen its use in forensic science, being utilised to analyse gunshot residue[298] and fingerprints[299].

As mentioned before, this technique has reached fast imaging of samples with pixel acquisition rates in the kHz range with maps with 10 million pixels[268], but has also achieved spatial resolutions down to a few μm [300].

To finish, some effort has been put into improving LIBS imaging, with a recent work using chemometric tools to diagnose and correct spectral interferences to improve LIBS imaging[301] and another work combining it with hyperspectral imaging (HSI) for mineralogical analysis of copper (Cu) concentrates[302].

2.5. Concluding remarks

This chapter provided a comprehensive understanding of the fundamentals and evolution of Laser-Induced Breakdown Spectroscopy, commonly known as LIBS. The core mechanism involves using a high-power laser pulse to generate plasma, enabling elemental identification based on characteristic spectral lines. The inherent flexibility of LIBS was demonstrated through various system configurations and modifications, highlighting its adaptability to different applications.

Additionally, this chapter addressed the technique's capabilities in both qualitative and quantitative analysis, acknowledging key challenges and ongoing advancements aimed at improving accuracy and reliability. The concept of LIBS imaging was also introduced, emphasising its value in generating detailed elemental maps for complex samples and its growing importance in modern applications.

With this foundation in place, the upcoming chapters will delve into the specific LIBS systems developed in this work and explore their applications, optimisations, and contributions to advancing analytical capabilities.

Part II

LIBS for Mining Applications

Chapter 3

A robust LIBS system for mining samples

3.1. Introduction

A decade ago, despite advancements in recycling technologies and material sciences, the dependency of the European Union (EU) industry on metal imports was increasing each year. The EU consumed 25 to 30% of the world's metal production[303]. It was estimated that approximate 100 billion euros worth of unexploited mineral resources were located in Europe at depths ranging from 500 to 1000 m[304]. To address the challenges of rising metal import dependency and underutilisation of domestic mineral resources, a research and innovation program was established to develop new mining technologies.

One significant project resulting from this initiative was ¡VAMOS![305], funded by the European Union's Horizon 2020 research and innovation program. The ¡VAMOS! project aimed to develop a prototype underwater mining system to extract raw materials from flooded open pit mines, with minimum human exposure to risk, and it included autonomous mining systems, also integrating a LIBS system for real-time grade control of the slurry.

LIBS technology, known for its fast analysis, capability to detect light elements[2], and lack of sample preparation has been extensively used in the analysis of geological samples[10,11,101,119]. Its simple setup and minimal component requirements, despite the complex underlying physics, make it suitable for real time analysis in both laboratory and field setting. These features have made LIBS appealing for various application including mining, where it provides valuable data such as element identification, quantification and spatial mapping[10,115,306]. Moreover, LIBS has proven effective in more complex and challenging environments including underwater[307] and extra-terrestrial settings[89,90,143,308].

In the ¡VAMOS! project, a transportable and robust LIBS system prototype was developed to operate in-situ at mining sites (Figure 3.1). During field trials at a flooded open-pit mine in Lee Moor, Devon, UK, the LIBS system, alongside the main underwater robotic mining system, successfully classified different types of kaolin and granites, proving its usefulness in operational scenarios[9]. Following these successful trials, the system was transitioned from field deployment to a laboratory setting. This transition not only removed the constraints of in-situ operation but also allowed for a series of

customised upgrades, enabling the LIBS system to deliver more precise and reliable results under controlled conditions.



Figure 3.1 – Transportable LIBS system for in-situ operation made for project ¡VAMOS!.

In this chapter, the readaptation of the ¡VAMOS! LIBS system to a laboratory setting will be described. It begins with an explanation of the elements that comprise the system, with a more detailed look into the laser, focusing and collection optical systems, and the spectrometer. This is followed by a discussion of the upgrades added to the original setup, which have further increased its versatility, expanding its applications. A detailed characterisation of the system's operation and performance is given, based on a reference sample of an iron (Fe) sputtering target. A variety of representative applications of the upgraded LIBS system will be described, demonstrating its versatility. The chapter ends with some concluding remarks discussing the successes and limitations of the system.

3.2. LIBS system

The original LIBS system deployed in the ¡VAMOS! field tests, which is displayed in Figure 3.1, was divided into four sections. The main body of the system consisted of three levels, each housing different instrumentation as described below. Extending from this main body were a rectangular casing and a tubular casing that protected the optics responsible for delivering the laser excitation and collecting the plasma signals. The top level contained the spectrometer and the fibres that connected it to the collection optical

system. These fibres passed through the middle level, which contained the laser head, extending to the external tubular housing that contained both the focusing and the collection optical systems. The laser head was connected to the laser's cooling system, located on the bottom level, along with the system power supply and an additional uninterruptible power supply (UPS), that powers and protects the entire system from power outages and current spikes. Figure 3.2 presents a simplified 3D drawing of the system.

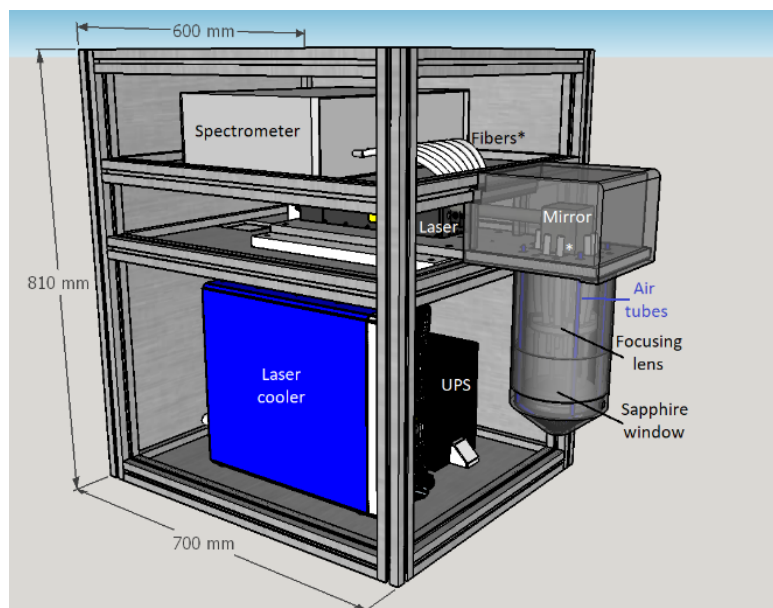


Figure 3.2 – Simplified 3D drawing of the transportable LIBS system, “*” marks the connection points of the fibres.

Since in the context of iVAMOS! the system was going to be used in uncertain operational conditions, design options were taken to ensure both versatility and safety at all times. To ensure the protection of the users and the integrity of the instrumentation, the system was sealed all around except for a few specific openings. These include the bottom opening of the tubular casing, which was the delivery point of the laser to the sample and includes a compressed air delivery point for cleaning the sampling point. Also, an aperture at the back provides a support for a fan located behind the laser cooler enabling efficient system ventilation. A valve was positioned at the back to connect and control a compressed air source. Additionally, there was an entrance for the cable that connects the laser to its external remote-control box, used to operate the laser. Both entrances were sealed with brush feedthroughs. The UPS is connected externally via a female power plug, allowing the system to connect to an external power source. Three external switches are available to control the UPS and turn the system on and off. The support housing of the system stands on four adjustable/removable legs, with handles

and sample holder. With this configuration it was possible to transport, instal and operate the system in an operational scenario at Lee Moor, during the field trials of ¡VAMOS!.

With the successful conclusion of the project the system was set to be adapted for a laboratory setting, configuring an all-purpose analysis system, designed to explore the potential of the LIBS technology in the context of the research activity at INESC TEC. A strong focus of the activity remained on geological samples, supported by a fruitful collaboration with the geology department of the Faculty of Science of University of Porto (FCUP in Portuguese). In this context, the system suffered a set of optimisation steps, focusing on automation, repeatability, and positioning precision which were implemented as needed over time. The system installed at INESC TEC laboratory can be seen in Figure 3.3.

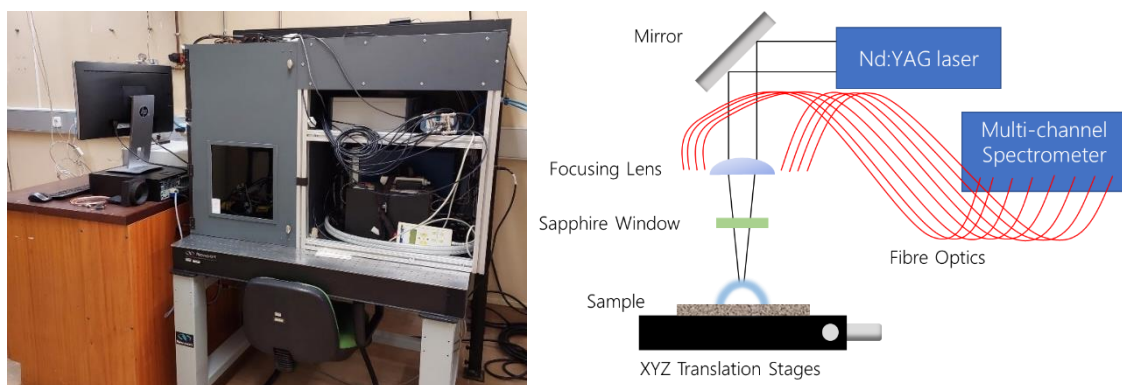


Figure 3.3 – (Left) Readapted LIBS system for laboratory operation and (Right) scheme of the LIBS setup.

In the following subsections, some aspects of the system configuration and operation are described in more detail.

3.2.1. Laser source and focusing system

The laser chosen for this system was a CFR 200 from Lumibird (formerly Quantel). This lamp pumped Nd:YAG laser features active Q-switching and was selected for its ability to withstand strong vibrations and operate in harsh environments. Despite having a cooling system it is fairly compact[309]. To accommodate a larger sample handling space, the inner arrangement of the instrumentation was adjusted. The laser head and the optical system now occupy the first level, while the spectrometer was moved to the second level. This rearrangement frees up space to include precision stages for sample positioning.

This laser operates at its fundamental wavelength, 1064 nm and is classified as a class IV laser. Its pulses can reach a maximum of 211 mJ with a pulse width of 8 ns (full width

half maximum, FWHM). The laser has a near-field beam diameter of 4.74 mm and a quality factor, M^2 , of 5.32 and can operate at a maximum of 20 Hz.

The laser can be manually controlled using its remote box, which also contains the emergency stop button. The remote allows users to change parameters such as the Q-switch delay and the repetition rate of the flashlamp, turn the flashlamp on and off, fire the laser and display its internal operation parameters, such as the temperature at critical points. While manual operation is convenient, automation is mandatory for handling large samples or perform a large number of repetitive operations as it also improves system repeatability. For this purpose, the laser can use a Recommended Standard 232 (RS-232) for serial communication with a computer, enabling the same functions as the remote box to be performed automatically with computer control. To achieve this, a Python script was developed to control the laser and monitor its status through the computer.

The pulses emitted by the laser are reflected by a 45-degree mirror, allowing for a vertical configuration, and are then focused by a 200 mm lens through a sapphire window. Both the lens and the window have anti-reflection coatings at 1064 nm (Figure 3.3 Right). With this arrangement, the beam waist, w_0 , and Raileigh distance, z_R , can be calculated using equations 2.5 and 2.6, resulting in values of 152 μm and 12.8 mm, respectively, which means that the spot size is 304 μm . The decision to employ a single mirror arrangement was made to simplify and condense the original setup and decrease the degrees of freedom that could be affected by small misalignments that might occurs during transportation. The long focal length was selected to manage the uncertainty in the positioning of the samples in in-situ experiments by providing a larger focal depth. This also allows for the inclusion of a sapphire window in the optical path, placed closer to the sample, serving as the first defence of the optical system against possible damage, dust and splashing resulting from samples in various conditions that could arise in an in-situ operation. Since these features were still convenient, they were retained in the lab setting.

In this type of laser, the energy of the pulses cannot be directly controlled. Instead, it can be adjusted by setting the time difference between the flashlamp pulse and the Q-switch trigger, referred to as the Q-switch delay. The longer the delay between the onset of fluorescence in the cavity and the Q-switch trigger, the lower the energy output of the laser. To understand this relationship, a study was conducted using an energy sensor (PE25BF-DIF-C) and an energy meter (Centauri Dual Channel) from Ophir, with the focusing lens removed. The energy-Q-switch delay dependency can be observed in

Figure 3.4. A maximum output is obtained for the minimum delay of 180 μs and it decrease steadily, in and approximately linear fashion to minimum values for delays above 385 μs .

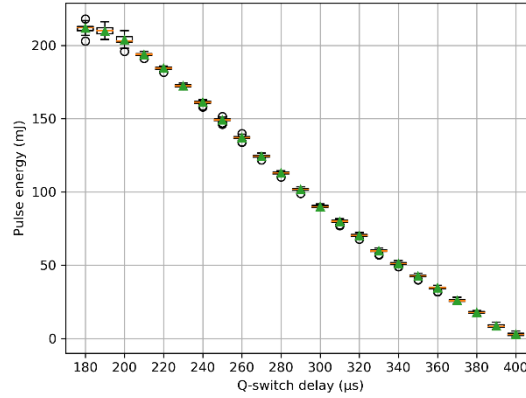


Figure 3.4 – Energy dependency on Q-switch delay.

Using the Q-switch delay to control the laser energy output can alter the dynamics in the laser cavity, resulting in pulses with different temporal profiles. To study these changes, the temporal shapes of the pulses were recorded as a function of the Q-switch delay using a custom photodetector with diffused reflections to prevent permanent damage. The results can be observed in Figure 3.5.

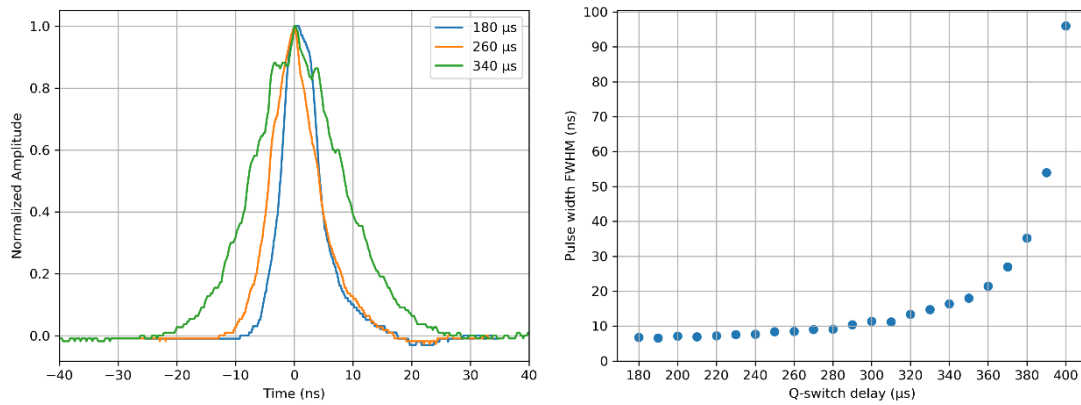


Figure 3.5 – (Left) Normalised pulse shape and (Right) FWHM variation with Q-switch delay.

As seen from the graphs, the energy of the pulses does not change in isolation. Within the analysed range, the FWHM increases exponentially, growing more than tenfold from the initial 8 ns. This is not ideal, as it causes the intensity of the laser pulse to vary non-linearly with the energy, potentially leading to different plasma dynamics at different delays as the energy will be absorbed by the samples at different rates.

Ideally, the system energy control should be implemented by attenuation using polarisation control[310]. However, due to experimental constraints this strategy could not be implemented during the duration of the experimental tests described here. Nevertheless, in most experiments performed, following an initial adjustment of the ideal energy for a specific purpose, the energy variability was kept within a small interval. This ensured that the temporal dynamics of a particular set of experiments remained approximately constant.

3.2.2. Collection system and spectrometer

The system for spectra acquisition was set up in an off-axis or non-colinear configuration due to its increased versatility, reduced collection of laser backscatter, and improved collection of the full plasma spectral range. This system comprised the detector, an 8-channel spectrometer, and the collection system setup with 8 separate fibres and collimators, all aligned to the plasm spot.

For this LIBS system, a multi-channel spectrometer AVS-RACKMOUNT-USB2 from Avantes was selected to allow simultaneously a large spectral range and a high resolution. With 8 channels, spectra with a wide wavelength range can be obtained without sacrificing too much resolution thus allowing the detection of elemental emission lines from as many elements as possible. While most relevant elements have their main lines in the UV range, some important elements in the context of mining have relevant information in the near IR (NIR) as well (eg. sulphur). Table 3.1 presents the specifications for each channel.

Table 3.1 – Specifications of each of the channels within the multichannel spectrometer.

Channel	1	2	3	4	5	6	7	8
Wavelength range (nm)	177.84-254.59	250.50-315.62	309.95-363.91	359.78-402.42	400.42-493.65	493.21-625.79	619.67-727.33	725.36-926.62
Resolution (nm)	0.06	0.06	0.05	0.05	0.08-0.11	0.10-0.16	0.10-1.16	0.18-0.22
Grating	UF-3600 lines/mm	UF-3600 lines/mm	UF-3600 lines/mm	UF-3600 lines/mm	VE-2400 lines/mm	VD-1800 lines/mm	VD-1800 lines/mm	NC-1200 lines/mm

This spectrometer covers a range between 177.84 and 926.62 nm with each channel containing a CCD detector with 2048 pixels. Each channel slightly overlaps with the neighbouring channels, ensuring that there are no gaps in between. The resolution varies between channels, generally decreasing as the wavelength moves further into the NIR. Each channel has its own individual grating selected based on the most suited for the wavelength region.

In Figure 3.6, the efficiency curves of these gratings are presented showing that efficiency varies widely across the spectrum. Notably, the efficiency of the grating for channel one (UV) significantly drops below 300 nm. This region also coincides with the minimum responsivity of silicon (Si) photodetectors, and higher absorption in the fibres. Therefore, no signal can be detected below 200 nm. In practice, when using fibre to detect the signals, channel one can effectively operate between 220 nm and 254 nm. While this shows that the response to intensity changes widely across the spectrum, since the overall response remains stable in time, it is still possible to evaluate, compare and calibrate the response for each spectral line. However, when comparison of results obtained in different instruments is at stake, a proper correction of the spectral response will be required.

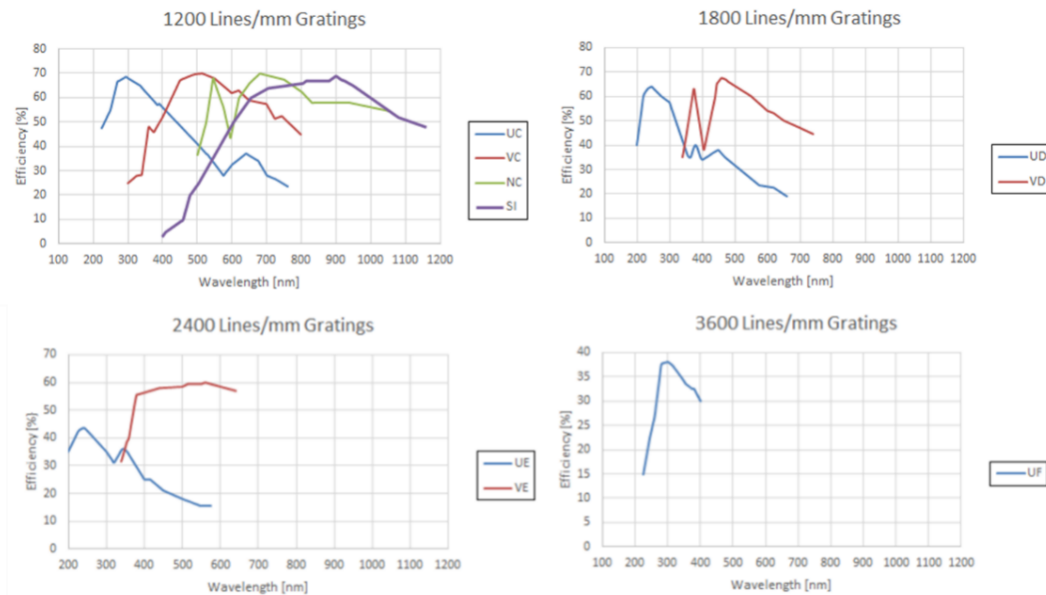


Figure 3.6 – Efficiency curves of Avantes gratings, including the ones present in the multi-channel spectrometer. Image adapted from graphs in [311].

All channels share common time parameters, namely the time delay and the integration time. For the time delay, while the minimum value can be set to 0 μ s, there is always an intrinsic delay of 1.3 μ s due to the triggering process. The integration time has a minimum value of 1.05 ms, which is extremely high for LIBS, as plasmas typically last only a few microseconds. To control the spectrometer, the AvaSoft software from Avantes was originally used. However, for the sake of automation and to achieve a more independent control of the spectrometer, a Python script was developed instead. This script utilises the AvaSpec dynamic-link library (DLL), which contains pre-built functions and manages the connections with each channel of the spectrometer.

To collect and guide the light from the plasma to the spectrometer, an attempt was made to use a 1-to-8 fibre coupler. However, since the single ferrule side had 8 cores arranged in a linear layout (two lines of four fibres each), the coupling was always uneven among the different cores. Furthermore, when adding a fibre collimator for better light collection, chromatic dispersion would worsen difference in coupling efficiency for different cores. As a result, eight individual optical fibres were used instead, each with its own fibre collimator, for maximum coupling efficiency. Channels 2 to 8 used optical fibres with stainless steel protection tubing from Sarspec (OF-UV-200-200-SS) featuring a 200 μm core diameter and a length of 200 cm. For the first channel a solarisation resistant optical fibre from Avantes (FC-UV200-1.5-SR) with improved UV transmission was used, having a 200 μm core diameter, and a length of 150 cm.

To accommodate all the fibres in a fixed, aligned position, a custom-made support was designed using SketchUp software from Trimble Inc. Multiple iterations were tested using 3D printing before the final version was machined in aluminium (Figure 3.7). The support features eight threaded circular holes that connect to the threads on the lens side of the fibre collimators, ensuring that the fibres are aimed at the same point, matching the focal point of the laser. The custom support was designed to fit around the focusing system optical axis and near the focusing lens. To align both, the lens was placed inside a tube that allowed for vertical adjustment. The support fixed each fibre in an almost vertical position, approximately 9.2° from the vertical optical axis, ensuring safe acquisition at a distance of approximately 22 cm from the plasma spot, and through the sapphire window.

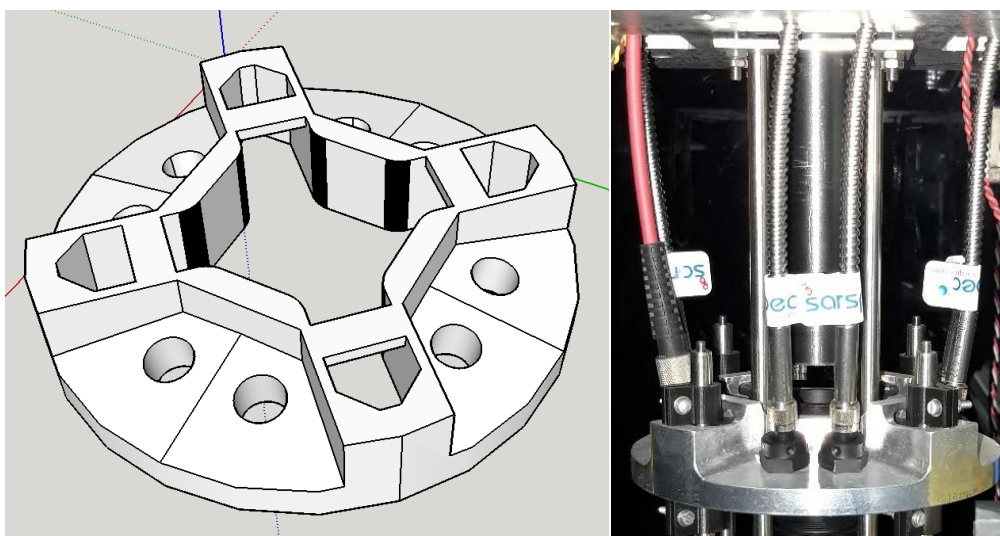


Figure 3.7 – (Left) 3D drawing of the part designed to hold and aim the fibre collimators and (Right) its final machined version installed in the LIBS system.

Finally, the collimators were aligned and adjusted for optimal response at each spectral region using light-emitting diodes (LEDs) at visible wavelengths that matched each spectrometer spectral region. For UV and NIR channels, the closest visible LED was used.

3.2.3. Other changes and upgrades

The layout of the LIBS system was modified to integrate it into an optical table. Legs and handles, no longer necessary, were removed. Some protective panels were also taken off to improve access to the equipment without compromising laser safety. One of the most substantial upgrades, was the replacement of the external casing with a larger safety housing equipped with a laser safety window. The window, with an optical density (OD) of 7+ at 1064 nm, allows for the safe observation of the plasma process from the outside, and shown in Figure 3.3. This modification not only improved access to the optical system for adjustments and modifications but also allowed for safe observation of the experiments, thereby eliminating the need for safety goggles. Figure 3.8 shows the interior of the safety housing, which now contains several essential components: the optical system, a tube for compressed air delivery, an exhaust tube for particle extraction and translation stages, for precise sample positioning.

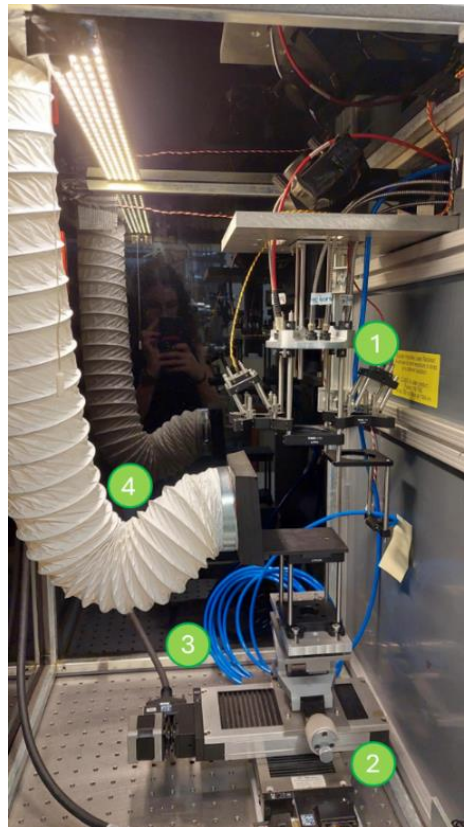


Figure 3.8 – Interior of the safety housing which contains the (1) optical system, (2) the translation stages, (3) the compressed air delivery tube and (4) the exhaustion tube.

3.2.3.1. Sample positioning system

As just mentioned, an important addition to the LIBS system was a set of precision translation stages. This set consists of two driver-controlled horizontal translation stages and one manual vertical translation stage, deployed as shown in Figure 3.8.

The horizontal translation stages, UTM100CC1HL and M-UTM100PP1HL, from Newport, are mid-range travel stages controlled by a universal motion controller (ESP7000). These stages use a direct current motor and a mini-step motor, respectively, and offer a 100 mm travel range with a 1 μm resolution and a maximum speed of 20 mm/s. The inclusion of these stages has greatly improved the system's performance. They facilitate precise positioning of the samples and expand the system's applications, introducing capabilities such as LIBS imaging, which will be discussed later in this chapter. They also give the users the ability to program coordinates for more complex analysis patterns. Their drivers have a RS-232 for serial communication, enabling computer control. A Python script was created to communicate and control the translation stages, thus automating their operation.

The vertical translation stage can only be adjusted manually and lacks a scale. However, it was combined with a set of laser pointers, that cross at the excitation laser focal plane, allowing the user to easily position the sample's surface at the focal points of the laser pulses.

3.2.3.2. System timing and triggering

Originally, the synchronisation of the LIBS system was achieved by directly triggering the spectrometer from the laser (which provided an output trigger synched with the Q-switch signal), while the laser was fired through commands sent via a Python script. This setup was sufficient for analysing individual samples but proved inefficient for larger tasks requiring higher throughput. When a study required analysing numerous spots at specific coordinates, the lack of synchronisation between the computer and the laser and the need for feedback at each operation caused delays. Moreover, without a way to trigger the spectrometer before the laser, there was no guarantee that no information would be lost.

To improve its synchronisation capabilities a DDG from AtomTrace was added to the LIBS system. This device has four outputs, named A, B, C and D, which can operate independently or dependently of each other, with each channel having its own mode of operation, pulse delay, pulse width, wait count, and other parameters depending on the mode. Due to physical constraints, channels A and D were connected to the eight

channels of the spectrometer, each addressing four spectrometers, with the same parameters. Channels B and C were connected to the trigger inputs for the flashlamp and Q-switch, respectively, with different parameters depending on the experiment.

Using a universal serial bus (USB) cable, a serial communication with the DDG was established, allowing a new Python script to send commands from the computer. This improved synchronisation, enabling more efficient and accurate analyses of samples, particularly in studies with large numbers of analysis spots at specific coordinates.

3.2.3.3. Automation of the LIBS system

The modifications described above created the conditions necessary to automate the LIBS system, a crucial upgrade that enabled the exploration of LIBS technology in various applications explored in this thesis. Using the customised Python scripts previously developed, a single desktop or laptop can attain full control over the system. Figure 3.9 presents a block diagram of the main script used on the LIBS system.

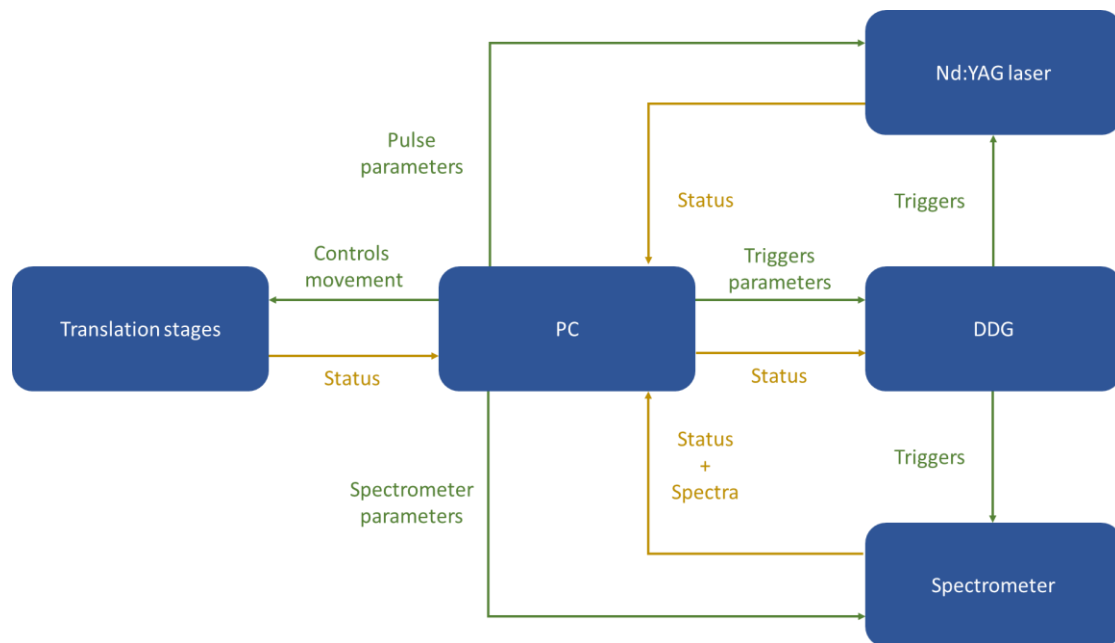


Figure 3.9 – Block diagram of the control software of the LIBS system.

The computer sends the trigger parameters to the DDG (frequency, number of triggers and delays), the pulse parameters to the laser (Q-switch delay and firing rate), prepares the spectrometer to react to external triggers for data acquisition with a set of parameters (integration time and number of spectra) and controls the movement of the horizontal translation stages. The DDG then sends the trigger signals to the laser and the spectrometer according to the parameters received from the computer. Lastly, the spectrometer sends the obtained spectra back to the computer.

This resulting script was developed to be adaptable for future LIBS systems. It only needs access to the scripts created for the new devices and, with minimal changes, can be quickly adapted to operate them. This flexibility ensures that the automation setup can be efficiently transferred to and utilised in various future LIBS applications.

3.3. Characterisation of system's performance

With a functional LIBS system, its operational performance needs to be evaluated to ensure optimised parametrisation for future experiments. Three noteworthy properties to examine are the range of useful energy for operation, where excess energy and plasma formation in air should be avoided, the determination of the effective plasma formation zone, which depends on both the depth of focus and the angle of acceptance of the collection system and the crater sizes.

3.3.1. Air breakdown

Since the laser can emit pulses with relatively high energy, one concern is breaching the breakdown threshold in air, which could compromise future experiments. To investigate this, the energy was adjusted by setting the Q-switch delays and assessing the threshold of plasma formation in air. This effect can be seen in Figure 3.10 and occurs consistently for Q-switch delays up to 230 μs , corresponding to an energy of 172.5 mJ or higher. Above this delay, plasma formation becomes more inconsistent but remains sensitive to the presence of airborne particles up until 300 μs , which corresponds to a 90 mJ output. Energies below this point could still achieve breakdown with airborne particles when operating at higher repetition rates over a sample. This limitation was mitigated by using compressed air to blow away the ablated particles from the plasma formation zone, leaving a range between 310 and 400 μs (corresponding to energies between 79.9 and 2.9 mJ) for regular operations, while higher energies were used only in special cases.



Figure 3.10 – Plasma formation in air.

3.3.2. Effective plasma formation zone

The range where effective plasma formation occurs along the vertical axis is a critical parameter that must be characterised. The positioning of the samples along this axis can vary between different experiments, and some samples may not be flat or may have a slight tilt. These variations lead to differences in ablation areas and can also misalign the plasma with the collection system, reducing the amount of light collected. In this context, understanding the optimal position and tolerance will enable more consistent analysis. For this characterisation, a 99.95% Fe sputtering target was selected (Figure 3.11), since iron presents a diversity of lines that populate all the channels of the spectrometer.

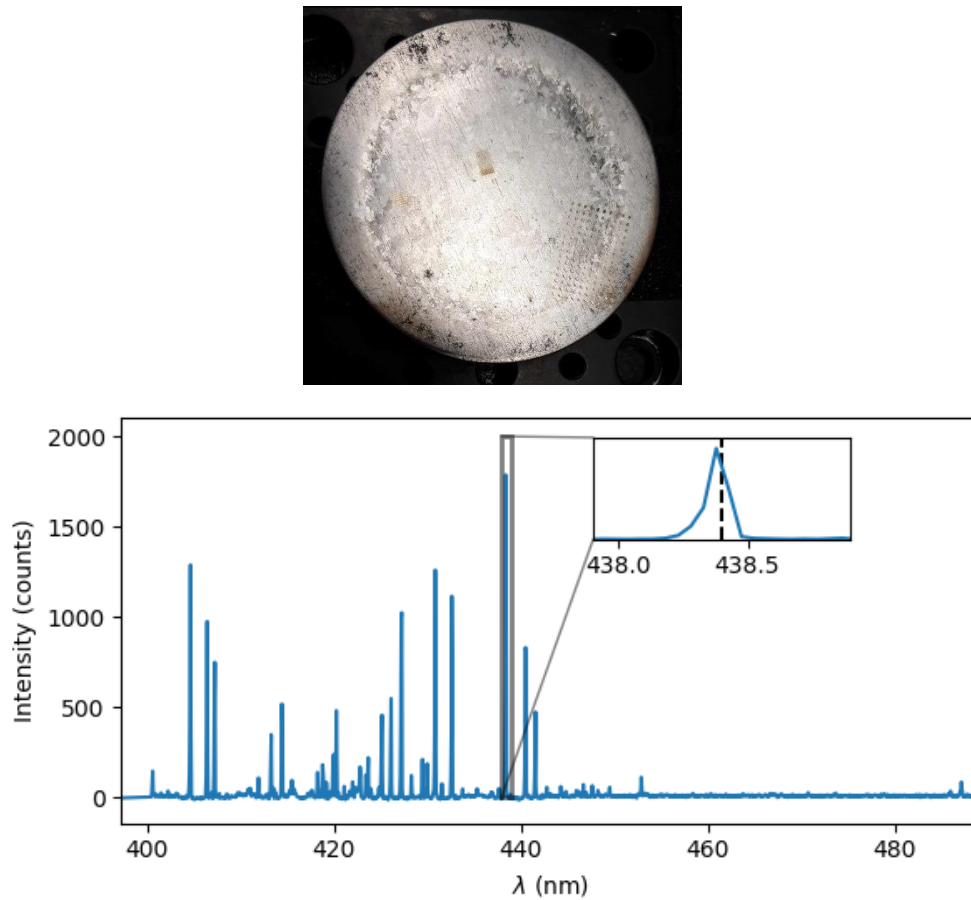


Figure 3.11 – 99.95% Fe sputtering target and spectrum at the fourth spectrometer with and inset of the analysed line at 438.35 nm.

The Q-switch delay was set to 340 μ s, corresponding to 51.1 mJ, to obtain intense spectra without reaching saturation. The positions analysed along the optical axis ranged roughly within the focus depth, which is two times the Rayleigh range, from -12 to 12 mm, relative to the focus. Measurements were taken in 2 mm steps, except near the focus where 1 mm steps were used. For each height, 10 spots were analysed to achieve an average signal. Each spectrum had its baseline removed using an asymmetric least

squares algorithm[312,313]. Figure 3.12 presents the results for the SNR for the most intense Fe line (438.35 nm) obtained near the focus.

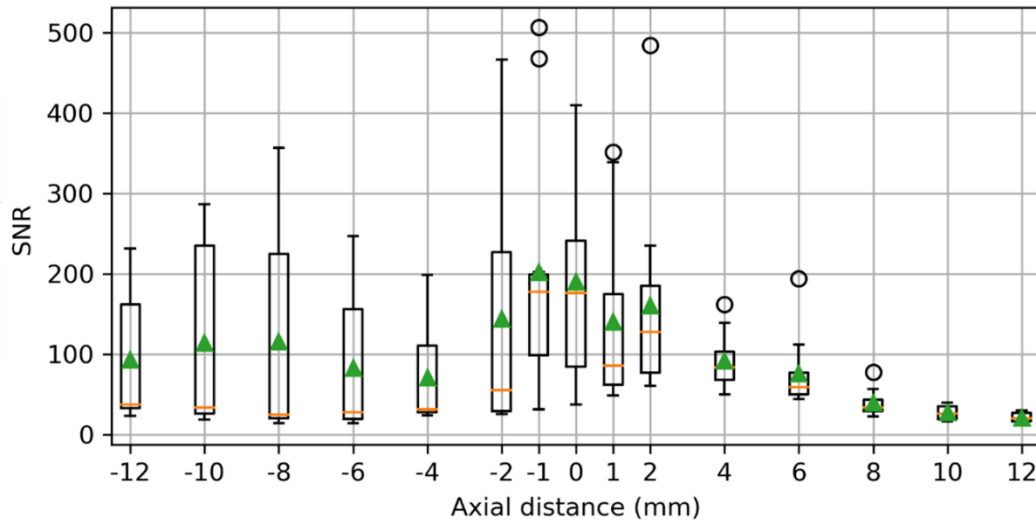


Figure 3.12 – Results obtained for the characterisation of plasma formed while the sample is positioned along the focus depth.

As expected, the most intense signal occurred near the focus. The fact that an exact match was not obtained might be due to positioning errors and significant shot-to-shot signal variability (approximately 10%[314]). Nevertheless, the focal region within ± 2 mm is clearly the hot spot in terms of signal intensity. Above the focus, the SNR drops faster than below, probably due to the three-dimensional asymmetry of the plasma plume, where some of its parts can exceed the acceptance angle of the collection system. In addition, when the sample is below the focal point, the most intense part of the beam hits the plasma formed above the sample. This may explain a longer zone with high SNR in this side of the focus. However, it can also account for higher variability, explaining the lower SNR obtained at 6 and 4 mm below the focal point. In the end, the working area could be delimited around 2 mm above and below the focal point, where the average SNR doesn't stray too far from the maximum value, accommodating small surface irregularities.

3.3.3. Crater size

The spatial resolution of a LIBS system is dependent on the size of the craters resulting from the laser ablation. The diameter of a crater is heavily dependent on the spot size of the focused beam, as most ablation will occur inside this region. As previously mentioned, the spot size of this LIBS system is 304 μm , which gives a rough estimation of the diameter of the craters. However, the dimensions of a crater depend on other factors such as the sample and the pulse energy, for which a variety of them were

attempted over time. Figure 3.13 presents a three-dimensional profilometry of two examples, the first one being quartz and second a section of a rock with montebrasite and turquoise.

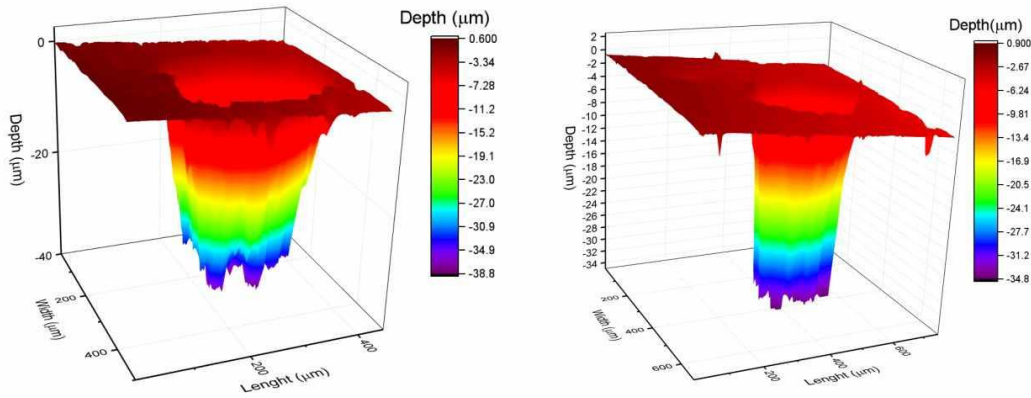


Figure 3.13 – 3D profilometry of a crater in (Left) quartz and (Right) montebrasite mixed with turquoise with a pulse with 21 mJ.

The results show that, for a pulse energy of 21 mJ, the craters have diameters of 310 μm for quartz and 250 μm for a section of a rock with montebrasite mixed with turquoise and depths of 35 μm for quartz and 29 μm for the mix of montebrasite and turquoise. In another case, an aluminium sample was shot with a 110 mJ pulse ending with 540 μm craters. This confirms that the size of the craters is a case-by-case scenario even if the spot size is a good estimation.

3.4. Applications of the LIBS system

Following the system reformulation, tests were conducted across a diversity of applications, each with distinct requirements and challenges. Overall, the applications examined in this study can be categorised in two types: qualitative and quantitative analysis.

3.4.1. Qualitative analysis

The primary application of LIBS is elemental identification, which involves matching spectral lines from a sample to the spectral features of known elements. This identification relies on databases like the one provided by the NIST[95]. These databases offer valuable information for matching spectral lines to specific elements. However, even identification is not always straightforward. NIST lines are derived from theoretical models. In practice, not all lines are observable, and when they are, their relative intensity will depend on the instrumentation, plasma temperature, and on the sample conditions, with matrix effects often playing a significant role in the relative line intensities.

Furthermore, the limited spectral resolution of instruments frequently results in lines from different elements overlapping, making identification very difficult, if not impossible. As a rule of thumb, a minimum of three lines from a given element must be identified to confirm its presence. A striking example of the discrepancies between database information and real experiments can be observed in Figure 3.14 which depicts a comparison between the signal obtained from a Fe sputtering target using the described LIBS system and the NIST information on the Fe spectral lines. The lines that match the NIST reference lines confirm the presence of Fe, while other lines reveal impurities or atmospheric elements. Notably, the relative line intensity can be strikingly different and plays a smaller role in the identification process, as it depends on factors such as the transmission efficiency of the collection system and the grating's wavelength dependence.

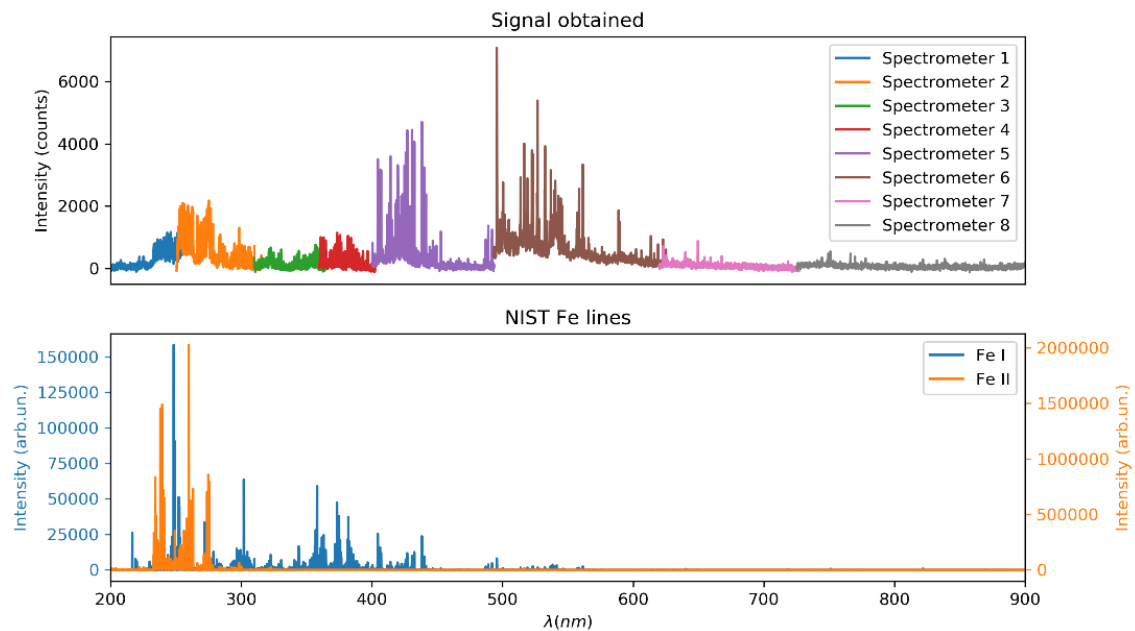


Figure 3.14 – (Top) Raw spectrum obtained from a Fe sputtering target and (Bottom) spectral lines for Fe I and Fe II from the NIST database[95].

Combining the elemental identification of LIBS with the scanning ability introduced by the two horizontal translation stages, it is possible to perform elemental imaging of the sample surface by defining a grid of analysis points. This is a very attractive feature across a diversity of application areas, and of particular importance in geology and mining where mineral identification is often challenging requiring substantial human expertise. In this context and considering an ongoing collaboration with the geology department at FCUP, several case studies of interest were conducted.

Figure 3.15 illustrates the basic concepts of the mapping process with a lepidolite case study. A sample characterised by having two distinctive areas of lepidolite with distinct

Li content was prepared for analysis. An 8x8 grid of points with a 1 mm step was programmed to analyse the transition zone, which in this case study could be easily identified by visual inspection. After preliminary tests to determine a suitable operation energy, a Q-switch delay of 340 μ s, corresponding to 51.1 mJ, was selected. With system parameters inserted into the control program, the system automatically performed the scanning of the samples, storing for each coordinate, the corresponding spectra.

A hypercube of data is then obtained where, for each coordinate point, the information regarding the over 16000 pixels for each spectrum is available. Therefore, once a given element line is selected, a map of its distribution on the surface can easily be obtained. In addition to the Python control routines, signal processing algorithms were developed that perform signal pre-processing, like baseline removal and/or normalisation, and map representation of a chosen line in a straightforward fashion. In this case study, the lithium content was the distinctive feature of the two mineral areas. The results in Figure 3.15 clearly show a match between the two different lepidolites (distinguishable by naked eye in the photo on the left) and the content of Li mapped on the plot on the right. In the picture, the purple region on the left side has high Li content while the yellowish grey area on the right side is poor on lithium. The map on the colour plot on the right-hand side of Figure 3.15 was obtained by plotting the intensity of the Li spectral line at 812 nm. The figure shows clear differentiation between lepidolite regions with high and low lithium content based on the intensity of the 812 nm line. Consequently, at the transition area between the two minerals, an intermediate value of Li content is displayed which is likely a transition zone, containing a mix of both regions.

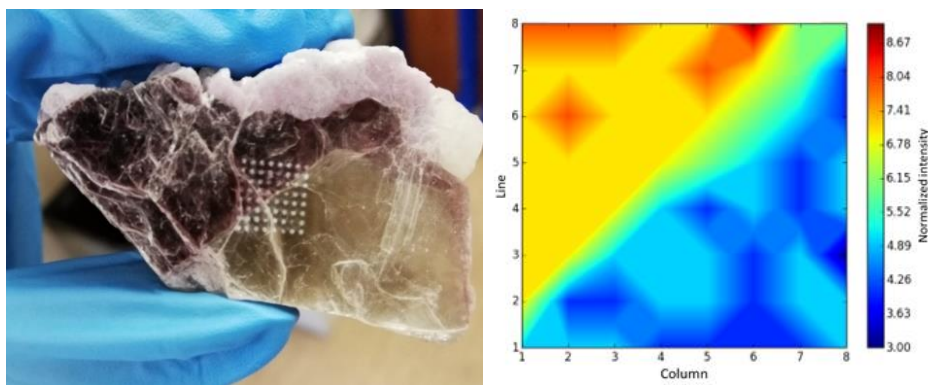


Figure 3.15 – (Left) Lepidolite sample with high (purple) and low (grey) Li content after analyses, showing the square shot grid in the transition area resulting from the laser shot induced damage. (Right) Normalised intensity map of 812 nm Li emission line.

While in this case distinction by visual inspection was straight forward, this is seldom the case in mineral analysis. Nevertheless, this simple case study allowed to identify the

system capabilities and limitations. Throughout this thesis, systematic improvements were established every time a specific challenge was posed by particularly difficult samples as will be shown in the remaining document. In the reaming of this chapter more challenging samples will be analysed.

3.4.1.1. Geological samples

In the context of the ongoing activity at INESC TEC in collaboration with the Geology Department at FCUP, one key application of this LIBS system is analysing geological samples to identify elements and the minerals they form. This is invaluable for the mining industry and geologists, as samples can have complex mineral structures. In this section, a diversity of samples of various degrees of complexity, analysed during ongoing projects are presented. The case studies are presented in chronological order, allowing to see the evolution of the system performance as the different hardware and software subsystems were gradually upgraded.

Silvermines Barite

A representative example of a complex mineral, where the boundaries between areas of distinct mineralogy are not clear, was investigated in earliest tests of project ¡VAMOS!. This sample is a barite extracted from Silvermines, Ireland, and can be observed in detail in the picture in Figure 3.16.

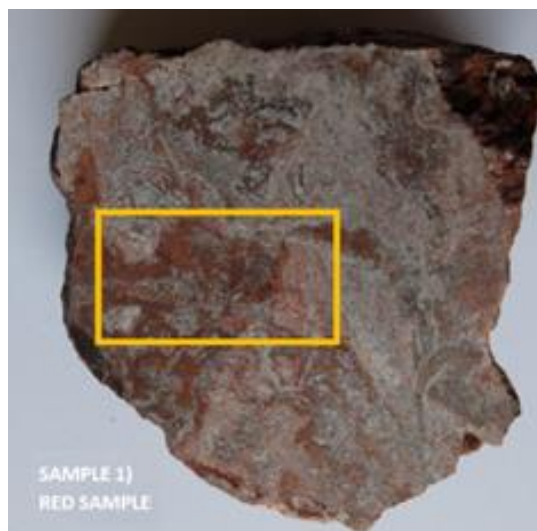


Figure 3.16 – Barite sample from Silvermines, with a rectangular section depicting the analysed region.

Using the imaging process, an elemental map within the rectangular region analysed can be obtained. Analysis was carried out with an energy of 17.7 mJ, a 14x8 grid with 2 mm steps, and 10 shots per point. Elemental maps for Ba (493.29 nm), Fe

(259.92 nm), Si (288.13 nm), S (921.23 nm), Ca (396.78 nm) and Sr (421.51 nm) were created from the average intensity of the 10 shots of each point. The resulting maps are presented in Figure 3.17

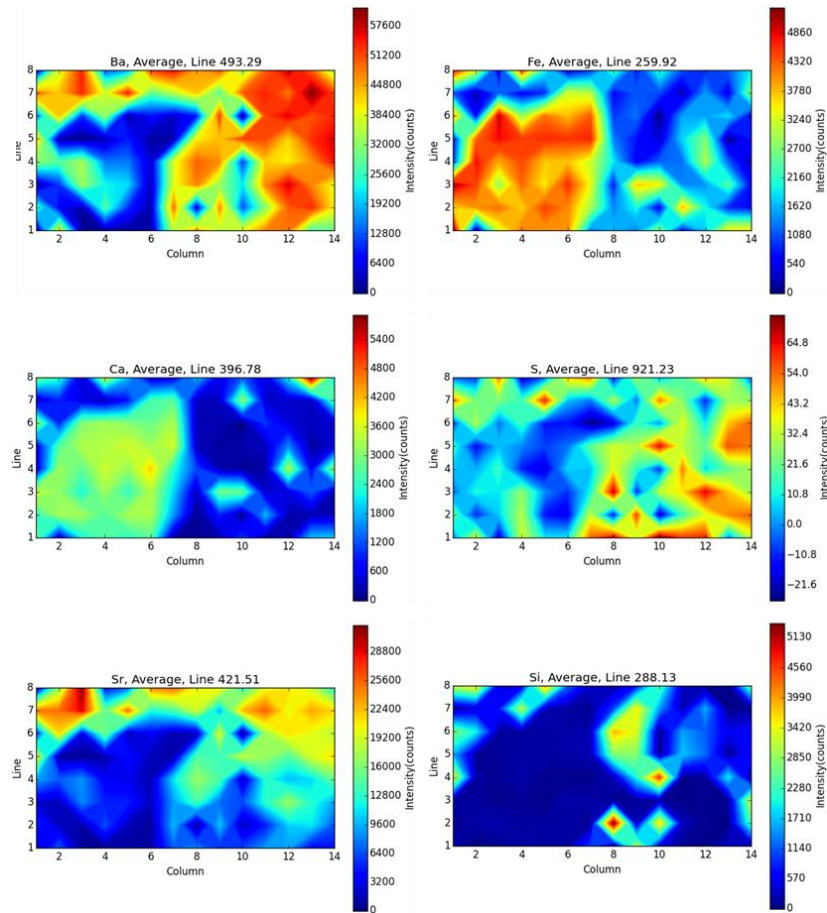


Figure 3.17 – Intensity maps for selected lines of Ba, Si, Sr, Ca, S and Fe obtained for the Barite sample.

Despite the limited spatial resolution and number of points selected in these early tests, the system was able to produce promising results. Considering the relative size of the mineral features, it produced interpretable results that were useful for discriminating the different mineralogy of various areas. The system revealed distinct elemental distributions, with minerals containing Ba lacking Fe and Ca. Ba co-occurred with S and Sr, indicating the presence of barite, but not with Si, suggesting potential quartz presence.

Turquoise from Argemela

LIBS is often a complementary technique to standards like XRF, which struggle to detect lighter elements such as Li. To assess the potential of LIBS and XRF complementarity, a series of tests were conducted in a sample of a quartz–montebrasite

hydrothermal vein from Argemela Tin Mine (Figure 3.18)[26]. The sample presents an intricate distribution of montebrasite, quartz and turquoise. Montebrasite, which contains Li, is not adequately characterised by XRF analysis alone. Therefore, both techniques were used to analyse the samples in different regions of interest.

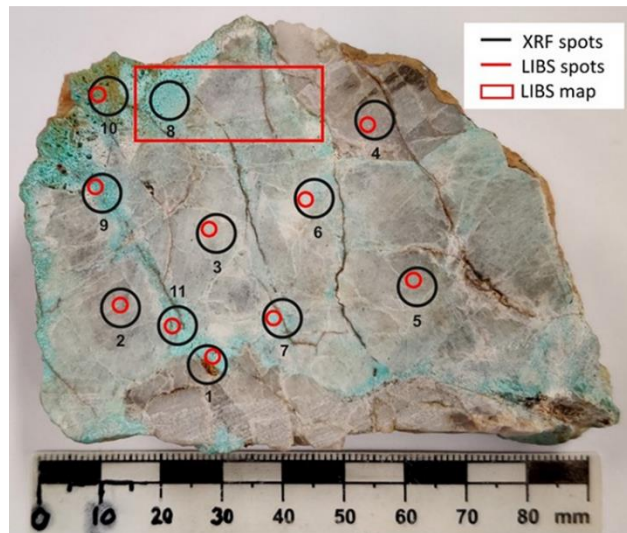


Figure 3.18 – Sample from Argemela Tin Mine, composed of montebrasite, quartz and turquoise. 11 different spots were measured by XRF and LIBS, one of them being mapped by LIBS instead.

The sample was analysed at 11 different spots using both XRF and LIBS (sampling point distribution depicted in Figure 3.18). Spot number eight was contained in the rectangular area that was mapped in more detail using LIBS. For XRF analysis, the study was performed by the geology department using a portable XRF system (S1 Titan from Bruker), which had a spot size of 5 mm. It concluded that spot 4 contained solely quartz as it contained a high percentage of SiO_2 , while spot 1 contained a mix of quartz, montebrasite and turquoise as it showed the presence of P and Cu besides SiO_2 . Results from spots 2, 3 and 5 suggested that only montebrasite was present, while spot 10 likely contained only turquoise, having a high Cu concentration opposed to the other 3 spots. The remaining spots, (6, 7, 8, 9 and 11), indicated a mix of montebrasite and turquoise since they had an intermediate concentration of Cu.

In the case of LIBS, with a much smaller spot size of 304 μm , a slightly different approach was taken. Aside from spot 8, three points inside the spots previously examined by XRF were analysed by LIBS, all contained in smaller areas delimited by the red circles in Figure 3.18. For each point, six shots were performed, where the first one was a lower-energy cleaning shot of 6.9 mJ followed by five others with an energy of 121.9 mJ, resulting in a total of 15 effective shots for each XRF spot.

From each region of analysis, the intensity of the 812.62 nm line, corresponding to Li, was taken from the 15 spectra and averaged. Figure 3.19 presents the average intensity, normalised to the highest average, for each region along with their respective error bars.

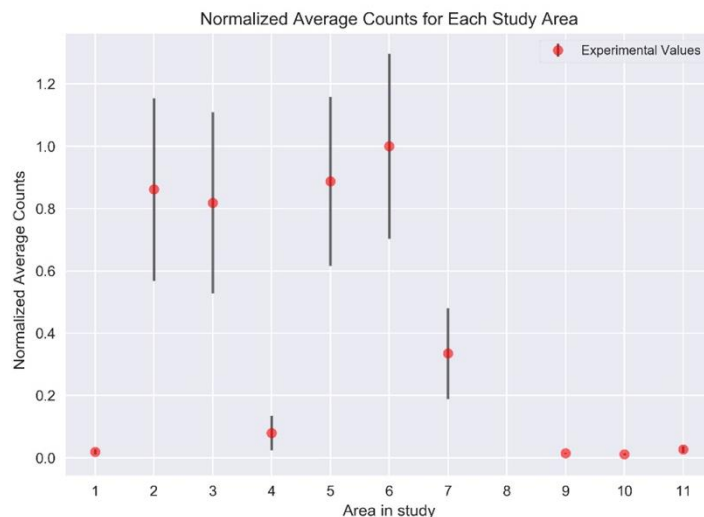


Figure 3.19 – Average intensity of the 812.62 nm Li line normalised to the maximum value of each area of study.

From these results, LIBS indicates that spots 1, 4, 9, 10 and 11 have little to no Li content, hence no montebrasite content. Spots 2, 3, 5 and 6, having the highest intensities, should be rich in Li and contain mostly montebrasite. Finally, spot 7 shows an intermediate value, suggesting a mix of montebrasite and another mineral.

When comparing to the XRF results: spots 2, 3 and 5 show the expected high Li intensity, as montebrasite was the only mineral present; spots 4 and 10 exhibit a residual Li intensity as no montebrasite was expected; spot 7's intermediate intensity matched XRF's conclusion of a mix of montebrasite and turquoise. However, spots 1, 6, 9 and 11 deviate from the XRF results. This can be explained by the difference in spot sizes between the techniques. As shown in Figure 3.18, the red circles for these spots target very specific parts: in spots 1, 9 and 11, LIBS aimed at the blue mineral, turquoise; in spot 6 LIBS aimed at the white mineral, montebrasite.

In spot 8, instead of analysing only within the XRF-analysed region, LIBS was used to map a wider area that included the spot, defined by the red rectangle in Figure 3.18. Using the same energy parameters and number of shots per point, a mapping scan with a grid of 26x11 points and a 1 mm step size was performed. Figure 3.20 presents the resulting elemental maps alongside a close-up of the analysed region with its minerals identified.

The Li map clearly shows that the presence of this element is restricted to the montebrasite boundaries. However, the Cu map implies that some turquoise is mixed in with some of the montebrasite areas. P and Al signals, being present in both montebrasite and turquoise, appear in both minerals. Lastly, none of these elements appear in the quartz region, although not being part of its standard composition.

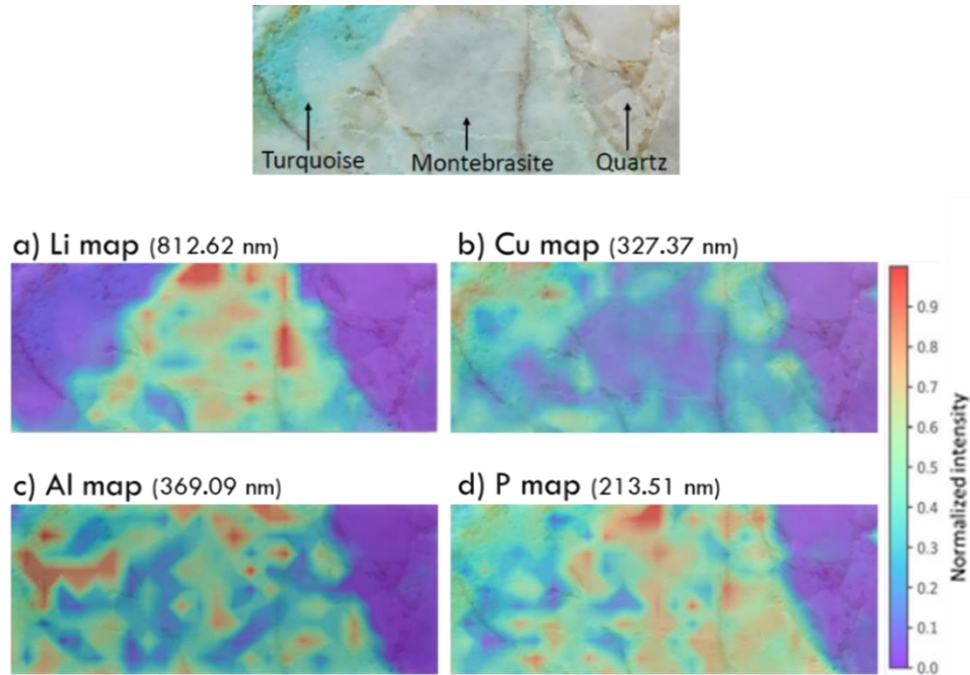


Figure 3.20 – (Top) Optical image of region mapped by LIBS. (Bottom) Elemental maps of a) Li (812.62 nm), b) Cu (327.37 nm), c) Al (369.09 nm) and d) P (213.51 nm).

Using the other half of the previous sample, another application was tested. LIBS was utilised to analyse a thin section, prepared from this half (Figure 3.21). This approach aimed to complement the petrography, a traditional technique used for mineralogic identification. The resulting thin section had a thickness of approximately 30 μm and was placed on a glass substrate.



Figure 3.21 – Thin section from the hydrothermal vein sample.

Due to the sample's thin nature and its resulting fragility, adjustments to the previously used experimental parameters were necessary. To avoid breaking the sample, the energy was reduced to 21 mJ, and the number of shots was reduced to one, without any clean shot, to prevent penetrating beyond the thin section. The results of this experiment can be seen in Figure 3.22 which also shows the thin section under cross-polarised light.

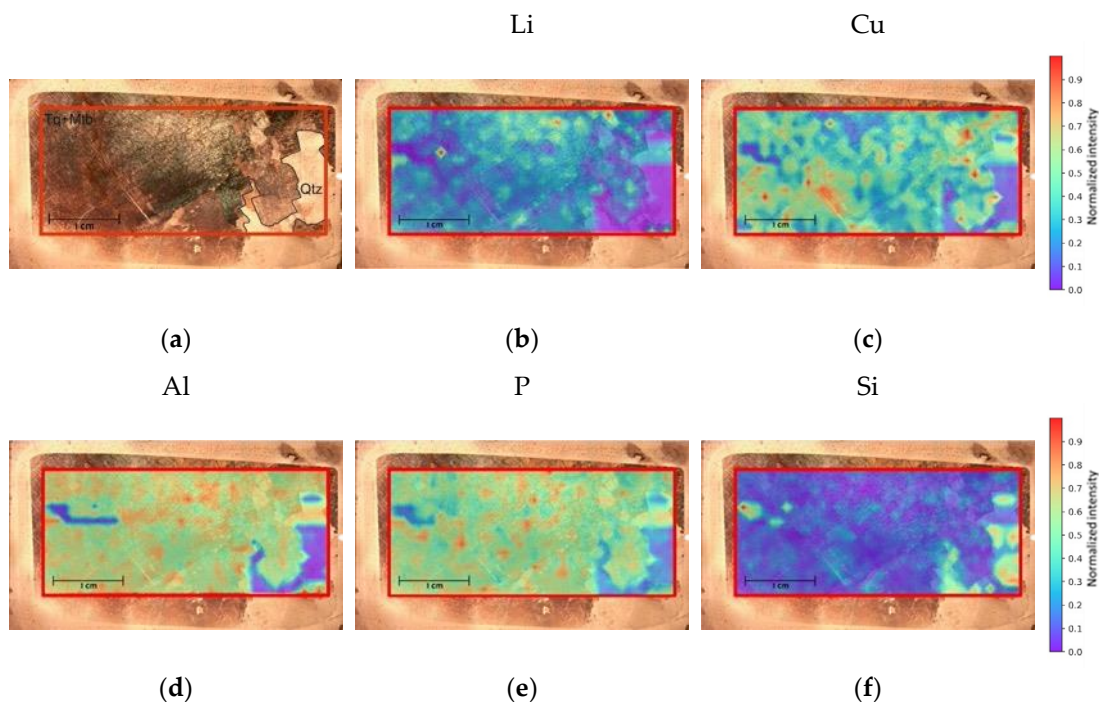


Figure 3.22 – (a) Thin section under cross-polarised light and (b) overlays of normalised intensity maps for Li (812.62 nm), (c) Cu (327.37 nm), (d) Al (369.09 nm), (e) P (213.51 nm) and (f) Si (288.13 nm).

From Figure 3.22 (a), only the quartz is situated in a well-defined area, while montebrasite and turquoise are significantly mixed across the rest of the thin section. The Al, P and Si LIBS maps, clearly differentiate these two regions. However, the Li and Cu maps provide additional information, enabling better identification of the areas containing montebrasite and turquoise.

While LIBS ablation is often negligible, this particular case features a thin section with a thickness of the same magnitude as LIBS craters' dimensions. Therefore, there is a possibility that the laser shots ablated past the thin section. To assess the dimensions of the craters, a two-dimensional profilometry analysis was performed along six analysed spots using a BRUKER Dektak XT Mechanical Profilometer. The system parameters were set to a 0.14916 μm scan resolution, a 17.9 mm scan length and a 3 mg stylus force, resulting in depth profile presented in Figure 3.23. The profilometry showed that the craters ranged between 35 and 41 μm in depth and between 250 to 310 μm in diameter.

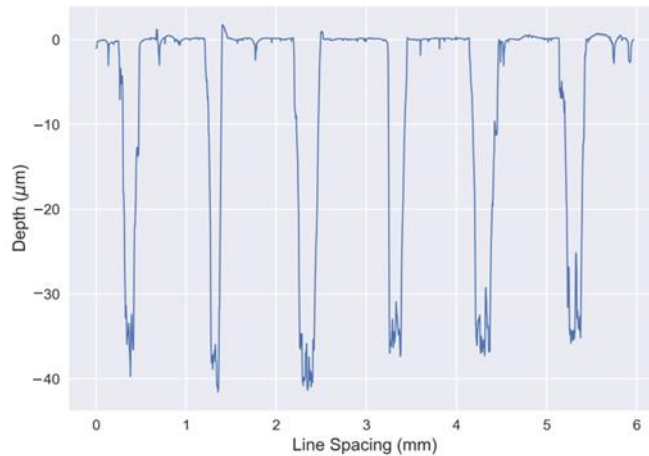


Figure 3.23 – Profilometry along six craters.

This was the first reported use of LIBS in a thin section, demonstrating the technique's strong potential for automated discrimination of distinct minerals. However, several improvements are necessary to enhance the quality of the analysis. Key areas for improvement include increasing the spatial resolution and limiting the penetration depth to avoid contamination from the substrate.

Large scale maps of Li-bearing samples

The introduction of the automatic positioning systems has made it possible to scan large areas of 10 cm by 10 cm. With the laser operating at 20 Hz, in synchrony with the spectrometer, it is feasible to scan these large areas within a reasonable operation time ranging from min to hours, depending on the total area being scanned, and the sampling pitch (from 400 μm to a few mm). The newly installed capabilities are a very attractive tool for geologists to study complex mineral samples, providing valuable data to understand the mineral formation process. In this context, the new tool was explored in collaboration with the Geology Department of FCUP. In particular, addressing the mineralogy of lithium-bearing minerals, which is a hot topic nowadays, as mineral deposits in Portugal are being addressed by various national and international companies. A tool that can identify the type of lithium mineral and assess its distribution in the rock can become invaluable not only for studying complex mineralogy but also for mineral prospecting and exploration. Several lithium minerals from exploration sites within the national territory were analysed using the upgraded LIBS system.

A representative example can be observed in the optical image of the mineral sample shown in Figure 3.24. This sample was obtained from the Gonalo pegmatite mine near the city of Guarda in central Portugal, a location of particular interest for its significant

lithium resources. The sample is representative of the local mineralogy, displaying three distinctive main minerals areas: zinnwaldite (brown), albite (white) and lepidolite (purple), from left to right.



Figure 3.24 – Sample from the Gonçalo pegmatite mine near Guarda, showing three main minerals: zinnwaldite (brown), albite (white) and lepidolite (purple).

The sample was analysed within a grid of 160x60 points with a 0.5 mm step size using single 51 mJ pulses. Working in fully automated mode, the laser operated at 20 Hz, achieving the system's maximum analysis rate. With this setting, the total duration of the analysis was approximately 28 min.

Considering the expected mineralogy and corresponding elemental composition, the intensities for Si, Li, K, Na, Al, and Fe were mapped. The corresponding surface distribution maps can be observed in Figure 3.25.

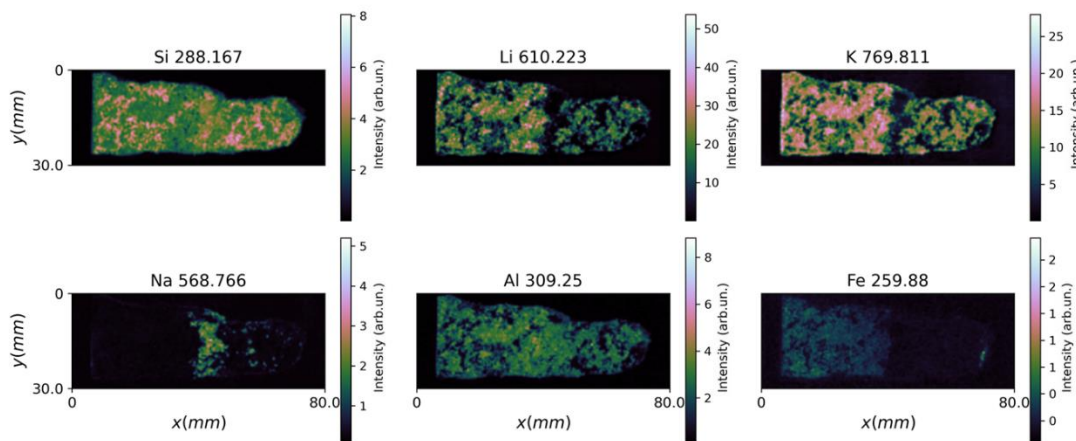


Figure 3.25 – LIBS elemental maps of Si, Li, K, Na, Al and Fe.

The results obtained clearly show the opportunities and challenges of LIBS-based mineral analysis. In this sample, both zinnwaldite and lepidolite are Li-bearing minerals, with lepidolite having a higher Li grade. Therefore, it would be expected that the Li maps

alone would allow discrimination between the three minerals. However, upon examining the Li distribution, it is evident that Li is present in both lepidolite and zinnwaldite, while it is absent from the albite area, as anticipated.

Contrary to their chemical composition, the intensity of Li spectral lines is higher in zinnwaldite than in lepidolite. This discrepancy may be due to matrix effects, where the presence of surrounding elements affects the spectral intensities. This phenomenon indicates that Li maps alone are not a reliable indicator of mineralogy.

Fortunately, in this particular case, the presence of exclusive elements allows for straightforward identification. Albite is marked by the presence of Na, while K discriminates zinnwaldite from lepidolite. This highlights the importance of considering multiple elements in LIBS analysis for accurate mineral identification. These results show both the potential and the fragility of LIBS analysis. More challenging cases, of economical relevance include the discrimination of spodumene and petalite, which by sharing the exact same elements in their composition, make their discrimination particularly challenging.

These results show both the potential and the fragility of LIBS analysis. More challenging cases include the discrimination of spodumene and petalite, which share the exact same elements in their composition, making their discrimination particularly difficult. Due to the strategic importance of accurately identifying these economically significant minerals, additional effort was placed in the development of more sophisticated algorithms for automatic mineral identification.

Automatic mineral identification

To address these challenges, machine learning strategies were used to classify the minerals. The idea relies on training and developing an interpretable model from data obtained by performing LIBS imaging on a known sample or set of samples, with known mineral distribution, so it can classify mineral in new unknown samples. A case study was set up, for developing an automatic identification pipeline with a lepidolite sample[200]. The area of the samples analysed can be seen in optical image in Figure 3.26, showing the different mineral areas, previously labelled by an expert geologist. This training sample was analysed with pulses of 47.5 mJ in a 40x40 mm² grid of points with a step size of 0.5 mm to acquire spectra for developing the mineral identification model. The data processing pipeline implemented is schematically represented in Figure 3.27.

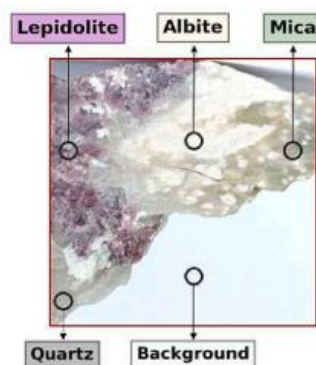


Figure 3.26 – Training sample composed of albite (beige), lepidolite (purple), mica (green), quartz (grey) and background (white).

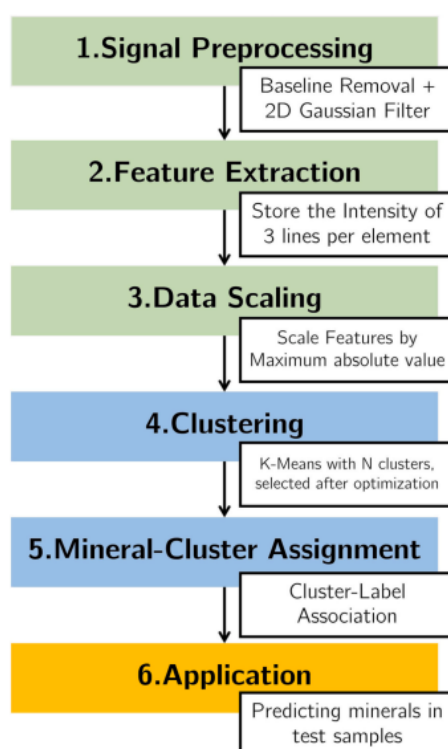


Figure 3.27 – Pipeline for mineral identification.

Following a pre-processing stage (steps 1 to 3), where the baseline is removed and the spectra are filtered and the intensity of the 3 chosen lines are extracted and scaled to the maximum absolute value, at step 4, the algorithm uses K-means clustering to identify clusters based on features of the spectral maps. The number of clusters is predefined according to the expected number of mineral types. The clusters resulting from the LIBS analysis of the training sample can be visualised (Figure 3.28) and were subsequently labelled according to their corresponding minerals (Figure 3.26) before applying the classification model to other samples.

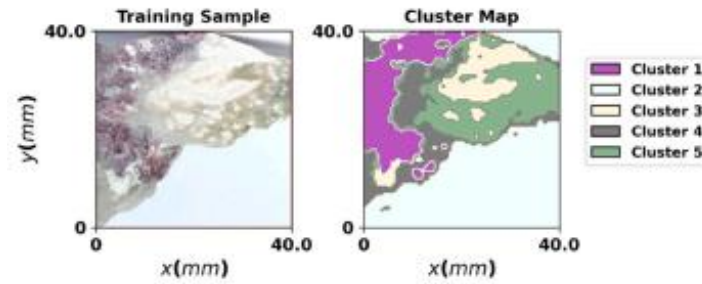


Figure 3.28 – (Left) Training sample and (Right) Clusters obtained from the clustering procedure using the optimal number of clusters using the unsupervised K-means algorithm.

New samples can then be analysed by LIBS using the same step size and pulse energy parameters to produce the test data. The trained model can be then applied to analyse the new data and automatically produce the mineral maps. The optical images (left) and corresponding mineral map (right) for four additional test samples can be observed in Figure 3.29. In these cases, the mineral regions can be discriminated visually. By comparison, it is possible to establish a strong correlation between the real mineral distribution and the classification model, demonstrating that the LIBS system can be applied to implement an automatic mineral identification system.

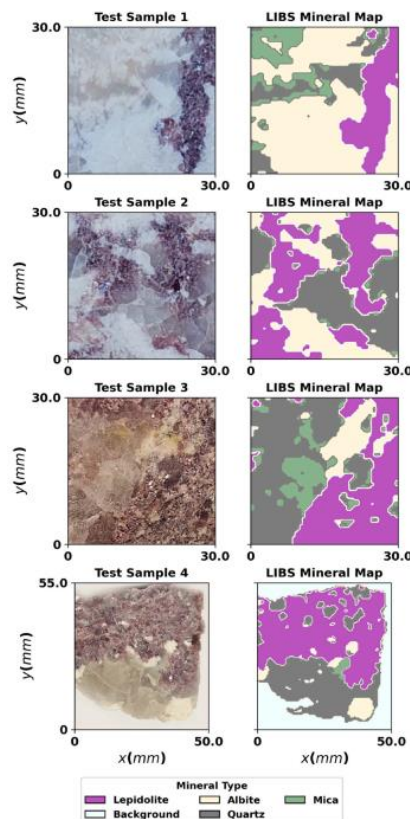


Figure 3.29 – (Left) Photographs of the test samples and (Right) mineral classification results. All these samples have similar mineralogy to the training samples.

These results demonstrate the successful implementation of automatic mineral classification using LIBS. The consistency in mineralogy between the training samples and the test samples explains the high quality of the results. In real-world scenarios, more complex situations may arise that could challenge the algorithm's capabilities. However, automatic sampling can facilitate training the system with a greater number and diversity of samples, thereby enhancing its classification abilities. Overall, these findings pave the way for more robust industrial tools based on LIBS technology.

3.4.1.2. Exploring new applications

Despite being designed primarily for analysing geological samples, the system was also explored in other areas to find new applications.

Biological samples

Understanding the elemental composition of biological tissues can provide insights into nutrient distribution, potential contamination, and overall health of the plant. This information can be valuable for agricultural research, food safety, and nutritional studies.

To evaluate the system's capabilities and assess the challenges of this type of samples, a carrot was tested. A transversal cut was performed on a carrot, leaving a profile that provided access to a region from its skin to its core (Figure 3.30).



Figure 3.30 – Profile cut of a carrot.

To analyse the sample, a 54x54 points grid with a step size of 0.5 mm was used to perform LIBS imaging, using pulses with 48.5 mJ. Figure 3.31 presents the resulting elemental maps. It is immediately clear that some elements are more prevalent in the outer region of the carrot, but in the case of Mg the core also displays a higher intensity than in the intermediate region. Fe also displays an interesting distribution that could warrant further studies. On the other hand, the very low signal of Ca may indicate methodological difficulties in detecting certain elements with LIBS in biological samples. While the results show that LIBS can be a valuable tool for visualising element

distribution in biological samples, further investigation is required to better understand the optimal operational parameters to improve analytical performance. This highlights both the potential opportunities and challenges of using LIBS for this type of analysis.

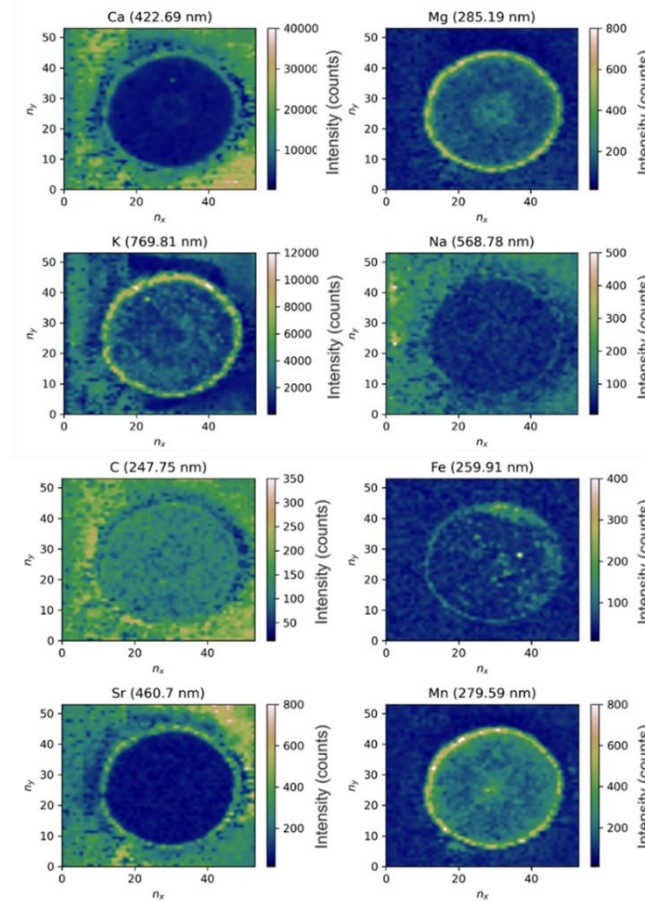


Figure 3.31 – Maps of Ca, Mg, K, Na, C, Fe, Sr and Mn of the carrot's profile cut.

Mapping Electrodes of Li batteries

Moving to electronics, another possible application that was investigated was the detection of the presence of Li in electrodes. Mapping the distribution of Li in lithium-ion battery electrodes is crucial because the Li coating of the electrodes occurs during the first charge. Understanding how Li is distributed can help optimise the battery fabrication process and improve the overall performance and efficiency of the batteries. Moreover, it can be used as a forensic tool to correlate battery performance with elemental distribution, providing insights into failure mechanisms and areas for improvement.

To evaluate the capability of the LIBS system to address this challenge, some tests were performed by conducting a forensic analysis on Li-ion battery electrodes produced by the research group MaTER from the Faculty of Engineering of the University of Porto.

In this case, a negative electrode was mapped using LIBS using a 59x59 point grid and a 0.5 mm step size. The results can be observed in Figure 3.32. While the results show the Li presence along the surface of the electrode, they miss the details of the fine distribution due to the relatively low spatial resolution. For this particular application, higher spatial resolution is required. Therefore, this case study was further investigated with another LIBS system with higher spatial resolution, which is described in Chapter 4.

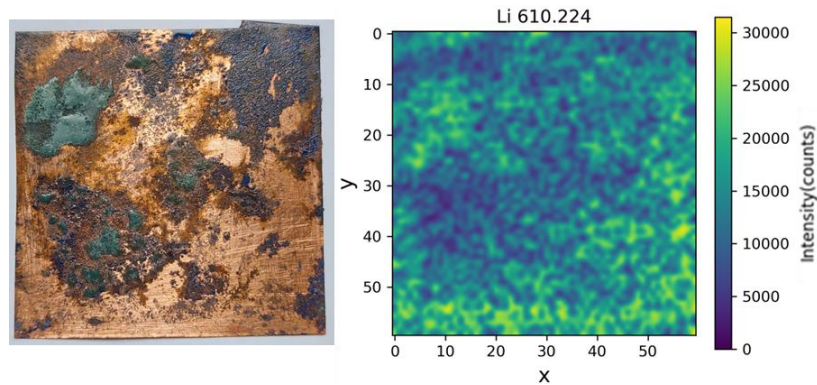


Figure 3.32 – Negative electrode and resulting Li map.

Heritage – Portuguese tiles

The analysis of heritage objects, such as historical tiles, is crucial for understanding and preserving cultural artifacts, providing insights into their materials, techniques, and historical significance. LIBS is a valuable tool in this field due to its ability to perform micro-destructive elemental analysis with high spatial resolution.

In this context, the system was also tested for applications in the field of heritage. Using a shard of a Portuguese tile, also known as *azulejo* (Figure 3.33), the potential of the LIBS system for analysing the composition of the pigments and varnish was examined. For that purpose, the sample was mapped using a 100x72 points grid with a step size of 0.5 mm with a pulse energy of 51 mJ.



Figure 3.33 – A piece of a Portuguese tile, also known as *azulejo*.

Before building the elemental maps from the resulting spectra, the average spectrum from all the analysed points was examined (Figure 3.34) to identify potential elemental lines that could potentially be related to the pigment used. This step was crucial to determine which elements were present in significant amounts and could provide meaningful information about the composition of the pigments on the tile. Two sets of lines revealed important information: those related to lead (Pb) and cobalt (Co). Pb was present throughout the entire sample, likely due to its historical use in glazes and varnishes, and could not be used to accurately map the painted regions. However, its presence confirms the analysis of unknown samples should always be made following standard protection measure such as using a particle extraction system, gloves and mask. On the other hand, Co lines, often associated with blue pigments used in traditional Portuguese tiles, provided valuable insights into the distribution of the paint[315].

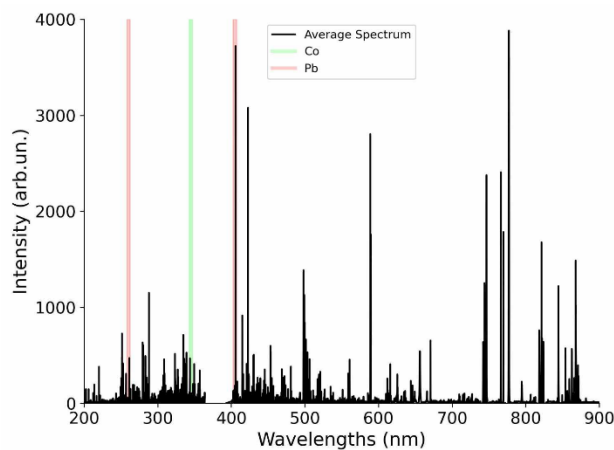


Figure 3.34 – Average spectrum of the azulejo.

The mapped distribution of the Co line, 345.32 nm, can be observed in Figure 3.35 clearly matching the blue painted areas of the azulejo.

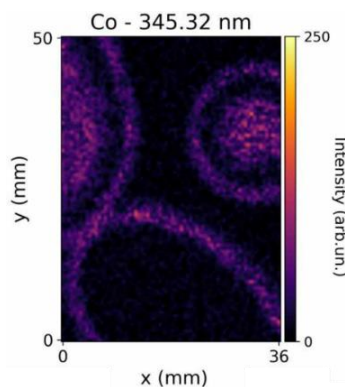


Figure 3.35 – Co intensity map of a section of the azulejo.

These results highlight the potential of LIBS for studying and mapping the composition of historical materials. LIBS can identify and map elements such as lead and cobalt, making it a valuable tool in heritage science. This technique provides detailed insights into pigments, varnishes, and other components used in historical artifacts, aiding conservation efforts and ensuring safe handling. Overall, LIBS offers a powerful method for analysing and preserving cultural heritage objects.

An industrial application

Lastly, a company named EGITRON sought a technique for analysing surface treatments applied to cork stoppers. This system was used to validate the applicability of LIBS to this challenge through preliminary exploratory work, as detailed in Annex I. The positive results led to the development of a dedicated LIBS system and further studies, which will be described in Chapter 6.

3.4.2. Quantitative analysis

Quantifying elements in mining sites presents a significant challenge distinct from the qualitative analysis performed in this chapter. While LIBS appears well-suited for elemental quantification at first glance, the technique's variability and matrix effects can hinder its effectiveness. Chapter 4 will provide a more detailed exploration of this application, highlighting the complexities and methodologies involved in achieving accurate quantitative analysis.

3.5. Concluding remarks and future work

This chapter has detailed the development, adaptation, and performance characterisation of a robust laser-induced breakdown spectroscopy system for geological sample analysis. Initially designed for in-situ operations, the system was repurposed for laboratory use and upgraded in terms of safety and automation. Its high pulse energies enable effective elemental identification and LIBS imaging of geological samples. Moreover, the system's versatility extends beyond geological applications, making it suitable for analysing samples from other fields, such as biological samples.

The LIBS system has significantly contributed to the spectroscopy field at INESC TEC, serving educational purposes, supporting multiple master theses[314,316], and inspiring the construction of two additional LIBS systems, described in later chapters, which further expanded the laboratory capabilities and variety of applications,.

Despite its successes, the system has limitations, particularly regarding the water-cooling mechanism of the laser, which demands regular maintenance, including partial

disassembly and realignment, and increases system size. Also, the laser intrinsic beam quality (relatively large M^2) combined with the long focal length selected for the original in-situ applications resulted into large beam waist at the focus limiting the resolution in LIBS imaging applications. This combined with the laser's relatively low repetition rate (20 Hz), results in large operation times. These limitations promoted further research that led to the implementation of more capable systems that will be discussed in later chapters.

Future improvements for the LIBS system are planned to address these issues. One critical enhancement involves developing a new method for controlling the laser pulse energy, potentially through polarisation rotation and a polarising beam-splitter. Additionally, integrating a new mirror will improve beam path control through the focusing lens. Upgrading the translation stages to include automated vertical movement could enable autofocus capabilities, further enhancing experimental automation. These advancements will not only improve the current system's performance but also pave the way for more sophisticated and efficient applications in various fields.

In summary, the LIBS system has demonstrated remarkable versatility and effectiveness in analysing geological samples and beyond. Continued development and optimisation will further expand its potential, ensuring it remains a pivotal tool for future research and industrial applications.

Chapter 4

Assessing lithium concentrations in mining samples using LIBS

4.1. Introduction

Nowadays, lithium is an increasingly sought-after material for the development of batteries[1]. Consequently, this growing demand from the battery industry has intensified the pressure for lithium mining, with brine and hard-rock deposits being its two primary sources[317].

LIBS, as a technique that yields almost instant information about the elemental composition of samples, requires no sample preparation and is effective with light elements such as lithium[2]. These features make it a viable alternative to X-ray fluorescence and the more expensive ICP-MS. In the mining industry, LIBS has been utilised for identification, quantification and spatial mapping of elements, crucial tasks to the field[10,115]. Furthermore, the application of LIBS has reached new heights by operating in underwater[307] and extra-terrestrial environments[89,90,143,308].

However, the performance of LIBS at the quantitative level remains rather inadequate, being plagued by two major issues. On one side, the technique itself, the experimental setup and the external environmental conditions all contribute to a relatively large variability in the data. This variability can be mitigated by acquiring several spectra per sample, averaging the results, and/or normalising the signal to references such as the total area or an internal standard[318,319]. On the other side, the issue lies in the difficulty of creating an adequate model using numerical algorithms. The performance of commonly used linear models such as univariate and multivariate calibration curves is greatly tied to the training set. Often, a matrix-matching calibration is employed, which fails to capture the high complexity of samples' composition typical present in real mining scenarios. Additionally, matrix effects influence the ablation process and, consequently, the plasma emission in a non-linear fashion, which exceeds the capabilities of linear models. To combat this, models based on high-dimensional methods like partial least squares[320] and non-linear methods such as artificial neural networks[224] are being explored. Another alternative is the use of calibration-free LIBS, which, despite showing promise in other fields, still struggles when analysing highly complex samples[201].

In this chapter, the performance of models created from a set of numerical algorithms is compared using 124 geological samples from a real mining site for the quantification of lithium across a wide range of concentrations. The chapter begins with the experimental procedure, followed by a brief description of each numerical method alongside their respective results, which focus on the mean absolute percentage error (MAPE) obtained from a leave-one-out cross-validation. A comparison of all the models reveals varied levels of performance, with the best results coming from the high-dimensional and non-linear models. These models demonstrate superior ability to estimate lithium concentrations by effectively addressing issues such as saturation and matrix effects. The chapter concludes with some remarks on how these results might support further research or applications in the context of geological samples.

4.2. Experimental procedure

Between the two main mining sources of lithium, brine deposits are the predominant source of the world's lithium production. However, hard-rock mining generally has lower operational costs, which makes it economically appealing[321].

The samples analysed in this study were obtained through reverse circulation (RC) drilling from 129 m prospecting hole at an undisclosed mining location. The extracted material was divided into 1 m sections, from which the first 5 m were discarded, resulting in a total of 124 sections. The predominant content in these samples was a mix of schist, quartz and pegmatite, the latter being the rock containing the lithium-bearing mineral, spodumene. Each 1 m section was further split into two representative subsamples. One subsample from each section was sent for ICP-MS analysis to serve as the ground truth for calibration, while the other was used for LIBS analysis, resulting in 124 samples in total. Figure 4.1 illustrates the distribution of lithium concentration along the depth of the hole and its statistical distribution across the samples.

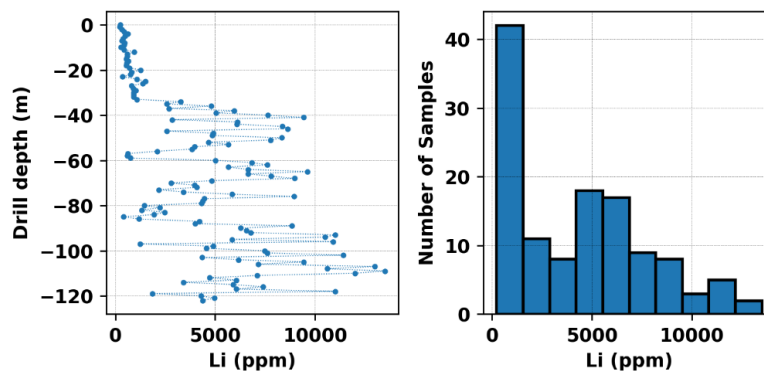


Figure 4.1 – (Left) Concentration of lithium along the depth of the drilled hole measured by ICP-MS and (Right) histogram of the concentrations of lithium.

It is important to note that the set of samples does not exhibit a uniform distribution of lithium concentrations. Given the nature of real mining cases, this variability is expected and the most likely scenario, offering a wide array of samples, predominantly with low lithium concentrations, that may have completely different compositions that must be considered ensure accurate calibration.

Since RC drilling is a destructive process, the final set of samples for LIBS analysis was in the form of powder. To optimise the conditions for LIBS analysis, each powder sample was moulded into a pellet, a process that involved several steps. First, the samples were completely dried in a Memmert GmbH + Co.KG Model 400 oven for 24 to 48 hours at 50°C. The dried samples were then further pulverised down to a grain size below 125 µm using either a vibratory quartz ring mill (Fritsch Pulverisette 9) or a mortar grinder (Mortar Grinder RM 200) followed by sieving. Using an electronic analytical balance (Kern model ABT 320-4M), approximately 0.75 g of each sample were collected to turn into a pellet. Lastly, the pellets for the LIBS analysis were formed by applying 10 tons of pressure for about 30 seconds using a Specac Atlas Manual Hydraulic Press, resulting in pellets with 13 mm of diameter. To prevent cross-contamination, all devices were cleaned after processing each sample.

From this set of samples, three spectral datasets were created using two different LIBS systems. One of the datasets was obtained with a portable LIBS system (SciAps Z-300), which acquires spectra by analysing 12 spots for each sample. Each spot includes a cleaning shot followed by four laser shots (1064 nm) with energies between 5 and 6 mJ, all conducted in an Ar atmosphere. The remaining two datasets were produced using the laboratory LIBS system described in Chapter 3, each obtained with a distinct pulse energy, 28 and 48.3 mJ, respectively. In both cases, 30 spots were analysed on each sample, with each analysis consisting of a single shot which was preceded by a cleaning shot.

4.3. Numerical methods and results

Before testing any numerical methods, several preprocessing steps were applied to the data. For starters, the spectra for each sample were averaged. For the laboratory LIBS, an average of 30 shots was taken for each energy, while for the portable LIBS, the output already included an averaged spectrum with saturation correction. All resulting spectra had their baseline removed using an asymmetric least squares algorithm[312,313]. Lastly, the spectra were normalised to the total area, while also keeping the non-normalised spectra for further performance evaluation. Along with the

implementation of the numerical methods, all the preprocessing was performed using the Python libraries, numpy[322] and scikit-learn[323,324].

In the field of LIBS, developing a calibration curve mathematically involves obtaining a function f such that the concentration C of specific element can be determined as follows:

$$C = f(I), \quad (4.1)$$

where I represents, in the case of this study, the vector containing the averaged spectrum obtained for each sample. The type of function resulting from the calibration methods categorises them as either linear or non-linear.

Prior to testing the performance of the models, an optimisation process was conducted for each model. A random 6-fold cross-validation was performed in order to fine-tune the parameters to those that minimise the MAPE. With the optimised parameters in place, the models were tested using a leave-one-out cross-validation, chosen to offset the small size of the dataset and to facilitate visual interpretation of the results. The performance was evaluated in terms of MAPE and mean absolute error (MAE), which are computed as follows:

$$MAPE = \frac{1}{n} \sum_i \left| \frac{c_{ICP-MS}^{(i)} - c_{LIBS}^{(i)}}{c_{ICP-MS}^{(i)}} \right| 100\% \quad (4.2)$$

$$MAE = \frac{1}{n} \sum_i |c_{ICP-MS}^{(i)} - c_{LIBS}^{(i)}|. \quad (4.3)$$

Here n represents the number of samples, $c_{ICP-MS}^{(i)}$ are the concentrations obtained using ICP-MS, which are assumed to be the true values, and $c_{LIBS}^{(i)}$ are the predicted concentrations obtained from the LIBS data.

4.3.1. Linear quantification methods

Methodologies that explore the linear relation of the intensity vector and lithium concentration can be described as linear methods. The function that describes this relationship can be expressed as:

$$f(I) = \overline{M}I + B. \quad (4.4)$$

The most common linear methods include univariate and multivariate calibration curves (UCC and MCC)[325], Ridge regression[326] and PLS regression[187], which were the ones implemented in this study.

4.3.1.1. Univariate calibration curves

The simplest method for creating a quantification model in LIBS is the UCC. This approach explores the relationship between the concentration of the element of interest and one of its emission lines, as predicted by the Saha-Boltzmann equation[327]. For the signal intensity I_λ , specific to the wavelength λ and obtained either from the peak intensity or by numerically integrating the area under the peak curve, the UCC performs a linear regression to establish its relationship with the concentration C in the form:

$$C = mI_\lambda + b, \quad (4.5)$$

where m is the slope and b is the y-intercept of the linear equation. Both parameters are crucial as they relate to the limit of detection and sensitivity of the method[328,329].

In machine learning terms, selecting the correct emission wavelength for the linear regression model in LIBS can be considered as hyperparameter tuning. To optimise this parameter, a peak search was performed across all spectra focusing on their respective peak areas. The optimal peak was selected using a 6-fold cross-validation for the UCC, aiming to minimise the MAPE. As depicted in Figure 4.2, the emission lines for Li at 610, 670 and 812 nm demonstrate the lowest regression errors. Interestingly, these are closely followed by emission lines for aluminium at 309 and 396 nm. This observation can be attributed to the composition of the spodumene mineral, $\text{LiAl}(\text{SiO}_3)_2$, which is prevalent in the pegmatites.

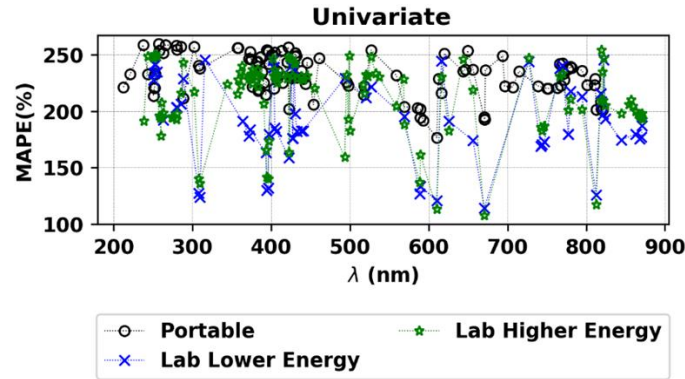


Figure 4.2 – Results of wavelength fine tuning for UCC using a 6-fold cross-validation.

With the peak area intensities of the peak with the minimum MAPE at 670 nm, the performance of the UCC method was evaluated using a leave-one-out cross-validation (Figure 4.3). It is immediately evident that the laboratory LIBS system outperforms the portable one. The laboratory system not only features a spectrometer with higher resolution, but also avoids the saturation issues prevalent in spectra from the portable LIBS. Nonetheless, the results generally indicate that linear regression does not provide

a good model across all regions of the data. In fact, the model struggles significantly with samples with lower concentrations of lithium, likely due to the presence of different types of minerals, which relates to matrix effects. At higher lithium concentrations, the model also struggles with saturation, failing to accurately estimate values in its presence.

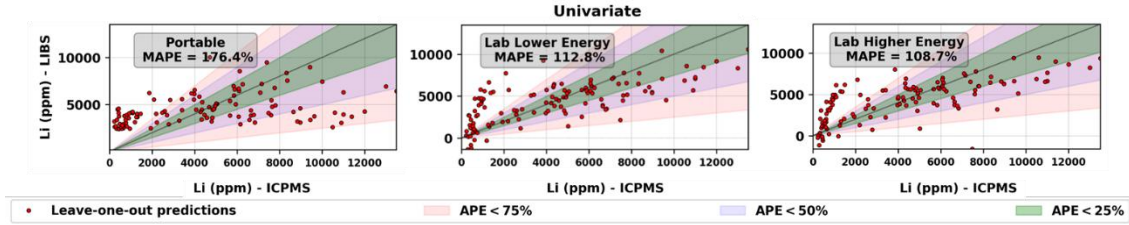


Figure 4.3 – Comparison of the predicted concentrations of lithium with a UCC of the LIBS signal against the measurements obtained with the ICP-MS technique.

4.3.1.2. Multivariate calibration curves

The natural progression from UCC is the implementation of multiple variables. In LIBS, this translates into using a vector I that contains the intensities of multiple emission lines, thus providing more data to the model to potentially overcome phenomena such as self-absorption and matrix effects. In this context, the calibration function is defined as:

$$C = M \cdot I, \quad (4.6)$$

where M is now a calibration matrix that is determined using numerical methods such as the Moore-Penrose pseudo-inverse[330] applied to the calibration set.

For this method, the parameter chosen for optimisation was the number of emission lines used in the calibration, which are selected from best to worst performance in the 6-fold cross-validation of the UCC. As it can be seen in Figure 4.4, increasing the number of lines for the calibration decreases the MAPE, but only to a certain point, as using an excessive number of lines is ultimately shown to be detrimental to the effectiveness of the calibration.

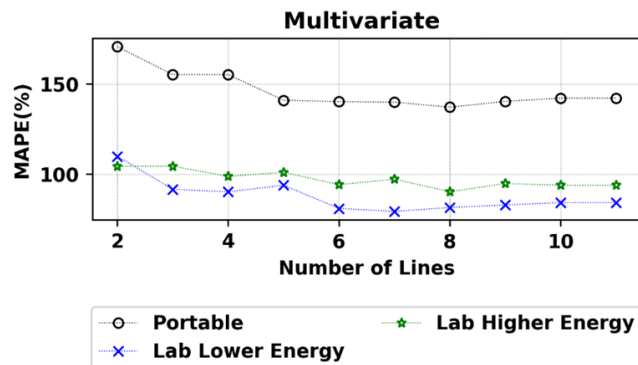


Figure 4.4 – Results of fine-tuning the number of emission lines in MCC using a 6-fold cross-validation.

Utilising the best results from the 6-fold cross-validation, a leave-one-out cross-validation was subsequently performed, leading to the outcomes depicted in Figure 4.5. Although there is a noticeable improvement compared to the UCC case, the performance remains suboptimal, particularly at lower concentrations where it continues to underperform.

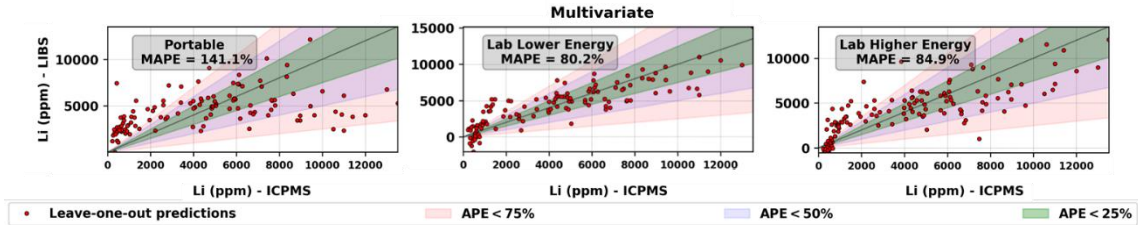


Figure 4.5 – Comparison of predicted concentrations of lithium with a MCC of the LIBS signal against the measurements obtained with the ICP-MS technique.

4.3.1.3. Ridge regression

Ridge regression can be viewed as an enhancement to standard multivariate calibration methodologies. By incorporating a regularisation parameter α into the loss function, it addresses multicollinearity and helps prevent overfitting. The modified loss function is given by:

$$L = \sum_i (c^{(i)} - MI^{(i)})^2 + \alpha M^T M, \quad (4.7)$$

where $c^{(i)}$ is the concentration of the i -th sample, $I^{(i)}$ is the spectrum of the i -th sample and M is the calibration matrix. Figure 4.6 illustrates the fine-tuning of the parameter α .

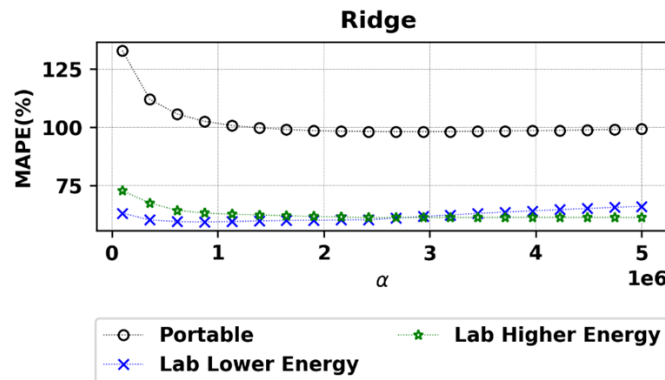


Figure 4.6 – Results of fine-tuning the regularisation parameter α in ridge regression using a 6-fold cross-validation.

Turning to the performance results depicted in Figure 4.7, it is evident that incorporating the regularisation parameter, α , improves the performance for the lower concentrations range of lithium, reducing the MAPEs in the laboratory datasets closer to 50%. Although these error rates are too high for a reliable quantitative analysis, the

results are sufficiently accurate for a qualitative one and can be useful for decision-making, particularly with the datasets obtained with the laboratory system.

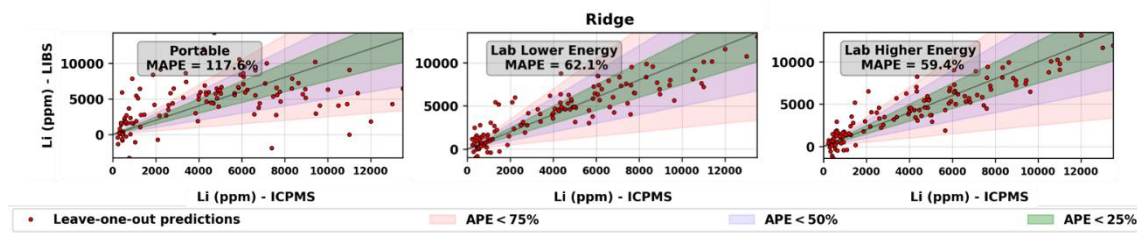


Figure 4.7 – Comparison of the predicted concentrations of lithium with a ridge regression of the LIBS signal against the measurements obtained with the ICP-MS technique.

4.3.1.4. Partial least squares regression

Two of the key challenges in multivariate calibration curves are the complexity introduced by matrix effects and the collinearity of information among different spectral regions[327]. PLS presents itself as a possible solution for these issues, as it aims to reduce the dimensionality of the spectrum I . This reduction is achieved through a projection into a basis of the feature space, known as components or latent variables[187]. Importantly, these components are chosen based on the directions that maximise the correlation between the spectra and the lithium concentrations in the targets, thus enhancing the predictive power of the model.

For PLS, optimisation involves fine-tuning the number of components to balance complexity and performance. Figure 4.8 presents the MAPE results from the 6-fold cross-validations conducted to determine the optimal number of components.

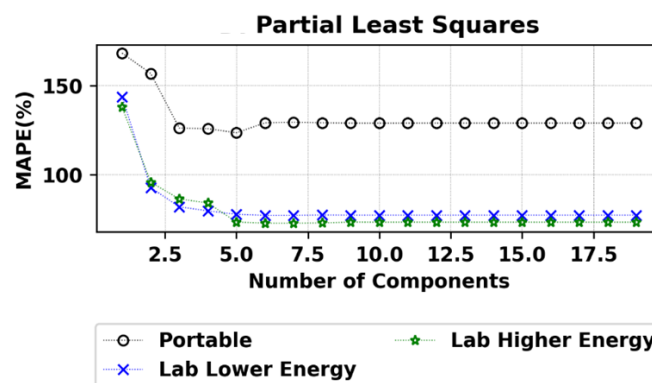


Figure 4.8 – Results of fine-tuning the number of components in PLS regression using a 6-fold cross-validation.

Typically, the optimal number of components is determined based on achieving the minimum MAPE. However, selecting a high number of components can make the model overly sensitive to noise. Consequently, to maintain a balance between accuracy and

robustness, 3 components were chosen for the leave-one-out cross-validations of the portable dataset, and 6 components were selected for the laboratory dataset (Figure 4.9).

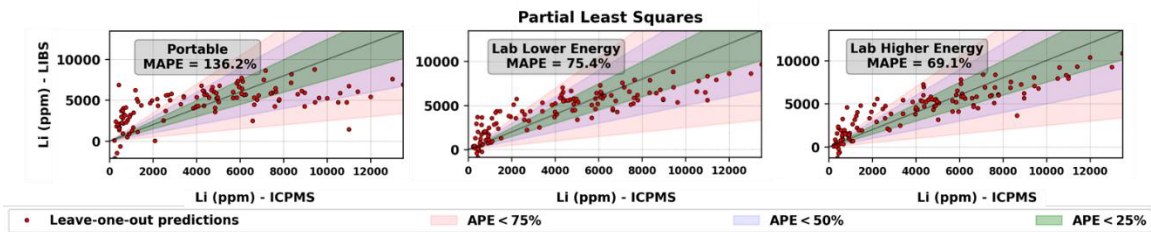


Figure 4.9 – Comparison of the predicted concentrations of lithium with a PLS regression of the LIBS signal against the measurements obtained with the ICP-MS technique.

Comparing these results with those from previous linear methods, it is apparent that PLS fares better than UCC and MCC performance-wise, yet it is surpassed by ridge regression. The PLS model still struggles with matrix effects at lower concentrations and tends to also underestimate higher concentrations, likely due to saturation. This highlights the limitations of linear models when dealing with a broad range of lithium concentrations. Nonetheless, for the laboratory dataset with the higher energy, PLS may still be capable of at least provide a valuable qualitative analysis despite these challenges.

4.3.2. Non-linear quantification methods

As demonstrated, linear methods struggle with matrix and saturation effects, which are prevalent in mining contexts and when dealing with a wide range of element concentrations. The issues caused by the first mentioned effects can be partially mitigated, whether by using regularisation parameters or dimensionality reduction techniques, but the latter effects require non-linear approaches. These include a variety of machine learning techniques, including K-nearest neighbours regression[190], Support Vector Machines regression[193] and Artificial Neural Networks regression[198] which will be explored in this study.

4.3.2.1. K-nearest neighbours regression

K-nearest Neighbours regression operates on the principle that similar samples are likely to be found in close proximity. In the context of this study, the method predicts the lithium concentration of a target by calculating a weighted average concentration of lithium from a k of the nearest neighbours in the training set. The weights are determined by the inverse of their distances to the target's spectrum[190].

For this work, the KNN regression algorithm was implemented using the Euclidean distance as a metric. The parameter tuning of this method involved optimising the number of neighbours used to calculate the weighted averages, as illustrated in Figure 4.10.

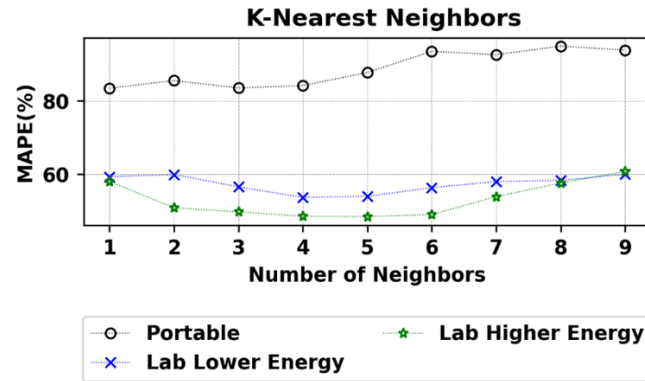


Figure 4.10 – Results of fine-tuning the number of neighbours in KNN regression using a 6-fold cross-validation.

Using the optimal values determined from each dataset's 6-fold cross-validations, the performance results depicted in Figure 4.11 were obtained. The algorithm shows its strongest performance at low concentrations, with MAPE values nearing 50% for the laboratory datasets, which contrasts with the performance of the linear methods. Overall, this non-linear methodology significantly outperformed all linear methods, and its reliance on a similarity measure, helps maintain the interpretability of the results. This makes K-nearest neighbours regression a compelling alternative for straightforward field applications in the mining industry.

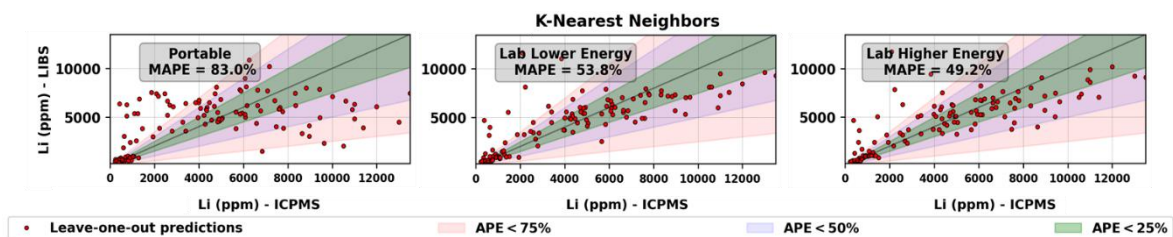


Figure 4.11 – Comparison of the predicted concentrations of lithium with a KNN regression of the LIBS signal against the measurements obtained with the ICP-MS technique.

4.3.2.2. Support vector machine regression

Known as support vector regression, this technique employs the popular SVM framework to establish a hyperplane or a set of hyperplanes functions in a high-dimensional space that best captures the relationship between the training data and continuous target values. As an extension of SVM, the computation of this method is

performed using only a subset of the data – referred to as support vectors – while ignoring training data that is close to the model's prediction[193]. One significant advantage of SVR is its ability to handle non-linear tasks by using a selected kernel function, such as the Radial Basis Function, to project the data into a higher-dimensional feature space where linear regression can be more effectively applied. However, being a black-box method is a major drawback, as no relation can be found between its parameters and the predictions.

Using the Radial Basis Function kernel, the parameter selected for fine tuning for this method was the regularisation parameter C (Figure 4.12) which prevents the model from overfitting[193], like the α parameter in Ridge regression.

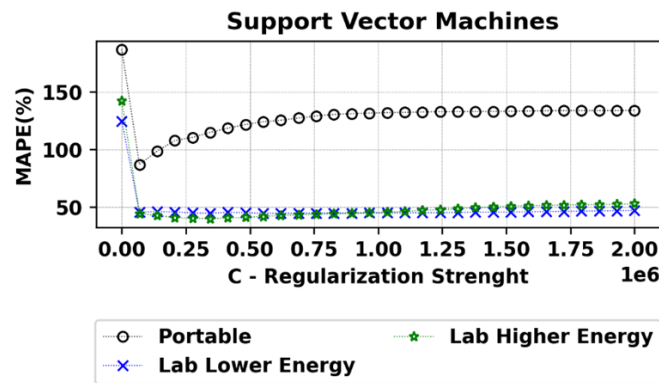


Figure 4.12 – Results of fine-tuning the regularisation strength in SVM regression using a 6-fold cross-validation.

With the parameter optimised to minimise the MAPE, the performances of the method across each dataset are presented in Figure 4.13. The results are very similar to the ones obtained using KNN regression, showing particularly strong performance in the dataset corresponding to the lower energy pulses using the laboratory LIBS system, where the MAPE falls below 50%. This level of accuracy suggests that the method could be effectively used for semi-quantitative analysis.

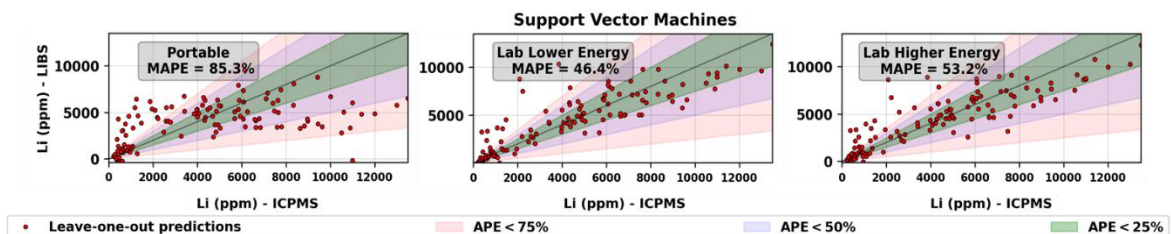


Figure 4.13 – Comparison of the predicted concentrations of lithium using SVM regression of the LIBS signal against the measurements obtained with the ICP-MS technique.

4.3.2.3. Artificial neural networks regression

Over the past two decades, advancements in hardware and software have made Artificial Neural Networks Regression one of the most prominent and efficient algorithms for complex computational tasks. Deep learning algorithms, which are essentially ANN with multiple hidden layers, have gained significant attention in scientific applications. They are particularly noted for their efficacy in handling non-linear features and high-dimensionality data, like in the case of LIBS[220,331]. However, similar to SVM, the major drawback of ANN is its “black box” nature, which obscures the relationships between the parameters of the model and the predictors.

Due to the high number of parameters involved, this study did not perform a detailed parameter tuning for ANN. Instead, a coarser analysis was conducted to assess its performance. Remarkably, even without any optimisation, this method achieves a MAPE near 50% with the dataset from the portable LIBS device (Figure 4.14). This suggests that with further optimisation, ANN could be used for semi-quantitative evaluations regardless of the LIBS setup employed.

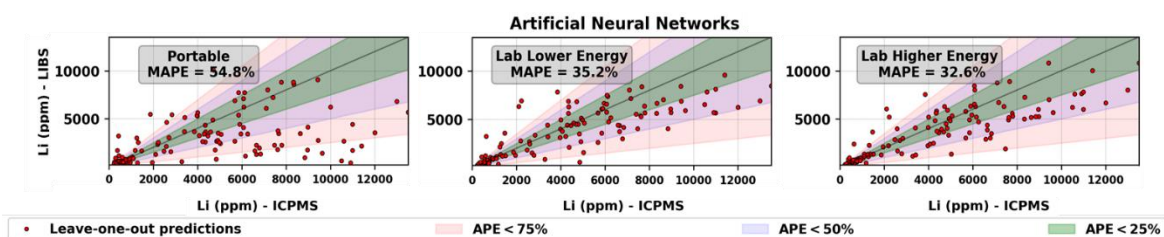


Figure 4.14 – Comparison of the predicted concentrations of lithium using ANN regression of the LIBS signal against the measurements obtained with the ICP-MS technique.

4.4. Comparison of results and discussion

To facilitate the evaluation of each model's capability to provide a trustworthy estimate of the concentration of Li, four regions were defined based on the MAPE metrics. The first region, defined by a MAPE below 25%, indicates that a model can offer a reliable estimate suitable for quantitative analysis. The second region, with a MAPE between 25% and 50% suggests that the model can provide reasonable but less reliable semi-quantitative predictions. The third region, spanning MAPEs from 50 to 75%, implies that models are only suitable qualitative evaluations. Models falling outside these three regions are deemed inappropriate for predicting lithium concentrations. With these classifications, the results attained up to this point in the chapter are summarised in Figure 4.15 and Table 4.1.

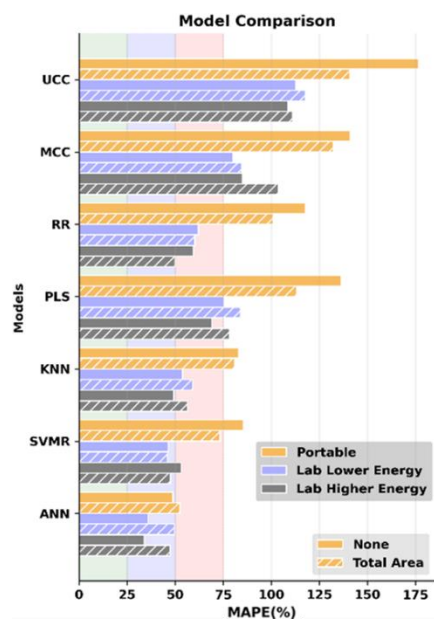


Figure 4.15 – Comparison of model performance for all methods explored, with and without normalisation to the total area of each spectrum.

Table 4.1 – Comparison of the MAPE and MAE for all the methods explored, with and without normalisation to the total area of each spectrum.

Method	Dataset	Without normalisation		Normalisation to the total area	
		MAPE (%)	MAE (ppm)	MAPE (%)	MAE (ppm)
Univariate calibration curve	Portable	176.4	2444.1	140.9	2380.7
	Lab. Lower Energy	112.8	1811.4	117.8	1961.7
	Lab. Higher Energy	108.68	1818.21	111.1	1957.7
Multivariate calibration curve	Portable	141.1	2337.0	132.13	2438.13
	Lab. Lower Energy	80.2	1327.5	84.58	1424.99
	Lab. Higher Energy	84.9	1678.1	103.78	1383.54
Ridge	Portable	117.62	2484.04	100.92	1943.24
	Lab. Lower Energy	62.08	1119.55	60.22	1137.88
	Lab. Higher Energy	59.36	1092.28	49.93	987.17
Partial Least Squares	Portable	136.2	2094.4	113.3	2008.9
	Lab. Lower Energy	75.4	1421.3	84.0	1433.2
	Lab. Higher Energy	69.1	1276.8	78.1	1323.8
K-Nearest Neighbours	Portable	83.0	2144.7	80.8	1944.8
	Lab. Lower Energy	53.8	1268.7	59.1	1365.4
	Lab. Higher Energy	49.2	1224.6	56.3	1303.7
Support Vector Machines	Portable	85.3	2134.8	73.3	2064.0
	Lab. Lower Energy	46.4	1132.0	45.9	1257.5
	Lab. Higher Energy	53.2	1176.6	47.6	1160.4
Artificial Neural Networks	Portable	48.8	2174.5	52.46	2194.91
	Lab. Lower Energy	35.95	1373.46	49.64	2232.64
	Lab. Higher Energy	34.01	1338.81	47.31	2115.8

As expected, the laboratory settings with both high and low energy pulses demonstrated better performance of the methods compared to the portable version. This improvement is due to the fewer operational constraints in the laboratory system, where

it is possible to use laser pulses of higher energy and spectrometers with better resolution and sensitivity. These enhancements allow for the acquisition of spectra that are richer in information and free from issues such as saturation. In contrast, the portable system was limited by its need for close proximity to the samples, which was problematic given the brittleness of the pellets and often lead to inconsistent positioning between the system and the samples. Despite these issues, the difference in performance between the laboratory and portable settings decreased when transitioning from linear to non-linear methods, suggesting that the essential spectral characteristics related to the concentration of Li are still present in the data collected by the portable system.

Reviewing the results from Figure 4.15, it is visible that normalising the signal does not consistently resolve the issues across different methodologies and datasets. Ridge regression, for instance, benefited the most from normalisation, showing improved predictions primarily for the portable system, while often degrading the results for the laboratory ones. This discrepancy could be attributed to the use of multiple spectrometers in the laboratory system, where the normalisation is based on the total area of the spectrum, which was divided among eight spectrometers, each requiring individual calibration.

Regarding the methods themselves, the results show that non-linear methods consistently outperform linear ones. The relationship between lithium concentration and the intensity of the related peaks is influenced by matrix effects and saturation, which turn an otherwise linear behaviour into a non-linear one. This complicated the effectiveness of linear methods, while non-linear methods manage to navigate these issues, albeit at the cost of some interpretability. Given their robust performance, non-linear methods are the preferable choice for deployment in lithium mining applications.

Nevertheless, it is important to note that the best results failed to achieve a MAPE lower than 30% when attempting to replicate the ICP-MS results, which at first glance might seem to limit the applicability of LIBS. However, the complexity of the samples and its potential effects to the reliability of the reference technique warrants a re-evaluation from a different perspective. Revisiting the sampling process, each sample originated from a 1 m section of the drill core, which was homogenised and then split it in two parts. The reference measurements were conducted on one part, while the LIBS analysis was performed on the other. This means that the efficiency of this process relies on assuming that the original 1 m sample was effectively homogenised before splitting, ensuring both share similar compositions. Nevertheless, inconsistencies between the parts used for reference measurement and those analysed by LIBS could occur due to the complex

nature of the samples, in terms of composition and granularity. Such discrepancies would introduce significant measurement errors, potentially exceeding the expected intrinsic error of ICP-MS, thereby adversely affecting the performance of the methodologies tested. Therefore, improving the synchronisation between the reference and LIBS samples can potentially improve the performance of all the methods by providing a more accurate training set.

On a different approach, the analysis of the mineral distribution within the drill core reveals sections with varying mineralogy. For instance, schist regions, which contain smaller concentrations of lithium, may yield comparable emission intensities to pegmatite regions that are lithium-rich but also contain a significant amount of quartz. This occurs because plasma formation is more efficient in schist than in quartz, resulting in stronger emission lines for lithium, even when its concentration is lower. To address this specific matrix effect, one strategy could be to develop separate calibration curves for each distinct mineralogy. Another approach could be the addition of information through other techniques, such as UV-VIS reflectance. This would allow to better distinguish the different matrices and thus allow for more effective models to be obtained, resulting in a better performance by minimising false positives in the low lithium concentration regions. Finally, improving signal acquisition techniques, such as incorporating filters to prevent saturation of lithium emission lines and conducting outlier searches to identify underrepresented samples, could significantly enhance the overall performance of the methods tested.

4.5. Concluding remarks

In this chapter, a comprehensive comparison between linear and non-linear regression methodologies was conducted to evaluate their predictive performances using three datasets: one from a portable LIBS device and two from the system described in Chapter 3, comprising 124 samples from a real mining site. These samples were divided for ICP-MS analysis, which served as representative reference measurements, and for LIBS analysis, to test the methodologies. The findings clearly demonstrate that non-linear methods outperform linear methods by achieving a semi-quantitative level of prediction, albeit at the cost of reduced interpretability. The results also indicate that normalisation, while not a universal solution, can be beneficial for datasets with inherent limitations.

The insights gained in this chapter are intended to support future applications in mining and have already been used as a stepping stone in the search for more robust calibration models[332]. This subsequent work involves unsupervised clustering using Uniform Manifold Approximation and Projection to reduce the dimensionality of the dataset. This

approach has been paired with linear methods to test their performance using the same set of samples as in this chapter and later apply the training in new drilling holes. Notably, these efforts have enhanced quantitative performance at lower lithium concentrations, facilitating more robust calibration across a wide range of Li concentrations.

Looking ahead, future research should focus on moving beyond pellet production, which is not only time-consuming but also limits the potential of LIBS. It is essential to test the methodologies in a real mining environment using raw samples to fully leverage the capabilities of LIBS. Additionally, it is crucial to test the results presented in this chapter against new target data, as was done in the follow-up study, to assess the possibility of generalising the results. By evaluating datasets from additional drilling holes, both from the same and different mining sites, the validity of the results obtained in this work can be further verified.

Part III

LIBS for High-resolution Elemental Imaging

Chapter 5

Implementation of fibre laser-based LIBS

5.1. Introduction

The Nd:YAG laser system, reported in Chapter 3, proved to be a highly versatile and robust tool for various applications, making it an essential asset for experimental investigations. However, despite its strengths, the system showed some limitations, particularly in the pulse repetition rate, the beam quality and the reliance on a water-cooling system, which became evident when exploring LIBS imaging and during the iVAMOS! project. These constraints motivated the development of a new LIBS system based on a fibre laser.

Fibre lasers operate using an optical fibre as an active gain medium[333], typically doped with rare earth materials such as erbium (Er), ytterbium (Yt) and neodymium (Nd). These dopants determine the emission wavelength of the laser, with erbium emitting at 1540 nm, ytterbium at 1064 nm and neodymium at 900 nm. Fiber lasers are known for their long operational lifetimes, low maintenance requirements and high efficiency. Additionally, they can be air-cooled, making them more compact and lighter than traditional laser systems. Their output pulses are close to Gaussian ($M^2 < 2$) and, in pulsed versions, they can operate from single shots up to hundreds of kHz, with the flexibility to adjust the pulse width.

These features make fibre lasers particularly attractive for LIBS applications. In fact, they were first introduced to LIBS in the late 2000s[334,335], with subsequent performance evaluations in the early 2010s[27,28]. Since then, fibre lasers have been tested on a wide variety of materials, including metals[113,336,337], minerals[112,337], biological tissues[336] and even explosives[338]. The growing interest in this type of laser highlights its potential across diverse sample types and experimental conditions.

In this chapter, the assembly of a newly constructed LIBS system, based on a fibre laser, will be presented. After a brief overview of the system, each component will be described, beginning with a thorough look at the laser and its features, namely its default and custom-design pulses, exploring how these pulses are affected by various laser parameters. Following this, the optical systems, the spectrometers, the positioning stages and the DDG will be described, concluding with the system's automation. The system will be tested with custom pulses to examine the effects of pulse duration on the LIBS signal, followed by a characterisation along the focus depth using the highest

energy pulse. Lastly, the primary application of the laser in high-resolution, high-speed elemental imaging will be presented, followed by concluding remarks.

5.2. Fibre laser-based LIBS system

To evaluate the capabilities of a newly acquired fibre laser, a new LIBS system was built from scratch (Figure 5.1). The system is housed in a protective, box-like structure with safety windows (OD7+), designed to shield users while allowing safe observation of the experiments. The structure includes doors for easy access to the system's components. Inside, the laser head, the optical systems, the focusing and the collection optics and sample positioning stages are housed. External to the enclosure are the remaining components, including the laser command box, the spectrometers, the DDG and an UPS, added to protect the system against power outages and voltage spikes.

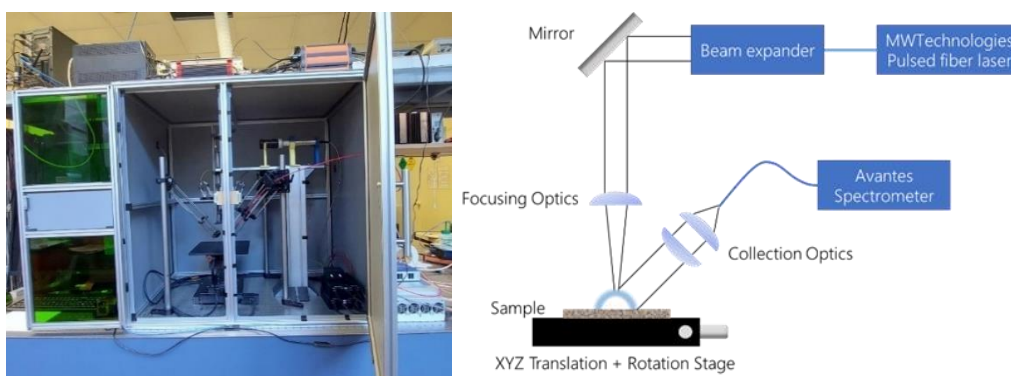


Figure 5.1 – (Left) Photograph and (Right) schematic of the fibre laser-based LIBS system.

5.2.1. Characteristics of the fibre laser

The LIBS system is based on a pulsed ytterbium fibre laser (model PFL-1064-FL-10kW) developed by the company formerly known as MWTechnologies, now Amplitude Portugal. This laser operates at a wavelength of 1064.8 nm using a master oscillator power amplifier (MOPA) configuration (Figure 5.2).

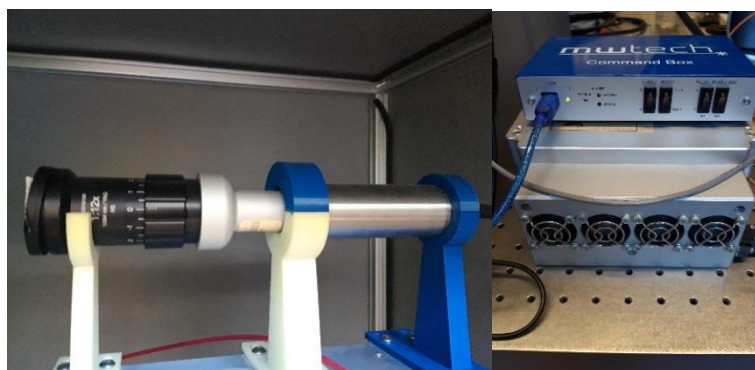


Figure 5.2 – (Left) Laser head, beam expander, (Right) laser and command box.

The laser system can be divided into three main parts: the laser itself, the laser head, and the command box. The laser includes the optical fibre containing the gain medium, and the laser box which houses the electronics, fans and pump diodes. The laser head is equipped with a magneto-optical isolator to protect the system from returning reflections. The command box allows the user to control the laser. It contains a physical switch to initiate emission, trigger ports for firing laser shots, a pump inhibit feature and switches to directly control laser parameters. Additionally, it has a USB port for computer control, either through the manufacturer's software or via serial communication. To enhance user control, a custom Python script was developed to track and manage the laser's operation.

The fibre laser outputs a near perfect Gaussian beam with a M^2 of 1.4 and a beam diameter of 0.51 mm and it can operate from single pulse to 250 kHz, including burst and continuous operation. The laser's maximum energy output is influenced by several factors, such as pulse shape, repetition rate and the selected energy mode (regular or high). The system offers default pulses provided by the manufacturer and allows the user to introduce custom-designed pulses, with pulse durations ranging from 5 to 320 ns.

When the laser is ready to fire, a continuous emission related to amplified spontaneous emission (ASE) from the pump is present. Using an Ophir power sensor (L50A-SH), this continuous emission was measured, showing average powers of 0.42 W in regular mode and 2.1 W in high energy mode. The ASE can be disabled using the pump inhibit port located in the command box, a feature that will be discussed further into this subsection.

5.2.1.1. Default pulses options

This fibre laser offers eight different default pulse configurations (Table 5.1) with only one operating in high-energy mode (Gaussian 100 ns, 1 mJ), a restriction imposed by the manufacturer. The efficiency of each pulse depends on the repetition rate, with each having an optimal value. The pulses exhibit, in principle, two distinct operational regions, separated by their transition frequency, f_T , where the energy of the pulses and the average power reach their maxima. Below this frequency, pulse energy remains nearly constant, while above it, the average power is approximately constant.

To characterise these pulses, their average power was first measured at their respective f_T , as specified by the manufacturer, using an Ophir power sensor (L50A-SH). The pulse energy was then roughly estimated (Table 5.1). Simultaneously, the temporal shapes of the default pulses were recorded using a custom high-speed photodetector and a triggered oscilloscope (Figure 5.3). It's worth noting that the pulse

names do not always reflect their final shape of the pulse but rather the input design to the amplifier, which can saturate depending on the input and repetition rate. Also, for the “Gaussian 10 ns” pulse, the actual f_T is unknown, as its value exceeds the laser’s maximum repetition rate; therefore, its average power and shape were obtained at 250 kHz.

Table 5.1 – Default laser pulses

Pulse name	f_T (kHz)	$P_{average}$ (W)	E_{pulse} (mJ)
Square (1x10 ns)	158	11.07	0.070
Square (1x100 ns)	37	11.04	0.298
Square (1x200 ns)	29	11.08	0.382
Gaussian 10 ns	>250	10.45	0.042
Gaussian 20 ns	108	11.14	0.103
Gaussian 50 ns	57	11.2	0.196
Gaussian 100 ns	33	11.16	0.338
Gaussian 100 ns, 1 mJ	20	11.05	0.553

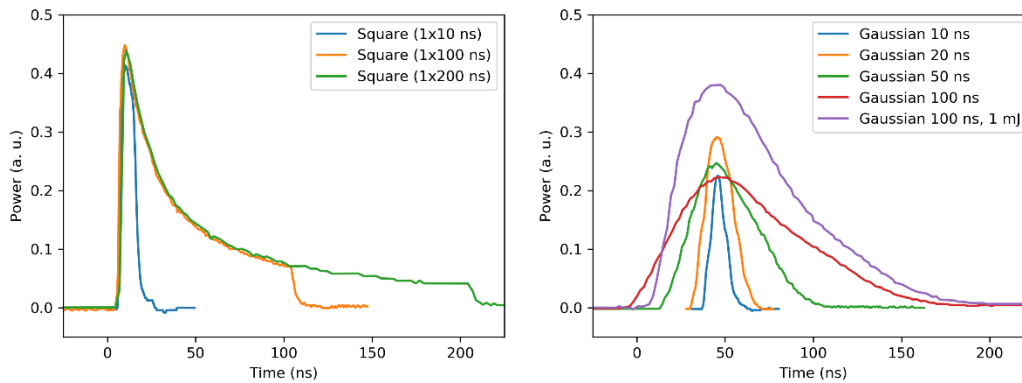


Figure 5.3 – Time traces of the default pulses, acquired with a high-speed photodetector and triggered oscilloscope, of (Left) the “Square” and (Right) “Gaussian” pulses at their respective f_T .

One noteworthy observation can be disclosed for the “Gaussian 100 ns, 1 mJ” pulse. Although this pulse is designed for high energy mode, it delivers less energy than expected, around half of the intended 1 mJ, despite surpassing the energy of the regular “Gaussian 100 ns” pulse. This discrepancy was later confirmed to be a calibration error by the manufacturer.

As the repetition rate changes, so does the behaviour of these pulses. While the general trends were anticipated, the average power was characterised for each type of pulse (Figure 5.4), offering deeper insight into the two operational regions separated by the transition frequency. Indeed, the transition frequencies roughly match the ones given

by the manufacturer, with the one from the “Gaussian 10 ns” pulse operating outside the laser’s repetition rate limits.

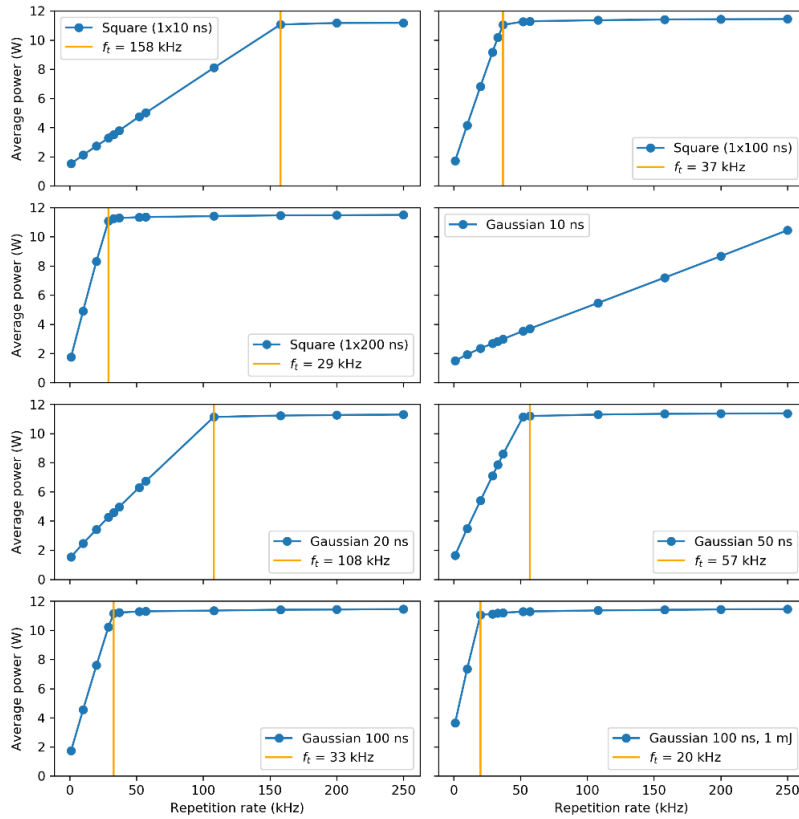


Figure 5.4 – Plots of the average power of each default pulse as a function of the repetition rate showing the transition frequency provided by the manufacturer.

When operating above the transition frequency, it was confirmed that the average power is nearly constant. This implies that the energy of the pulses diminishes as the repetition rate increases, which could affect the pulse shape. This phenomenon is demonstrated in Figure 5.5, which compares the “Square (1x100 ns)” pulse at 10 and 108 kHz, showing significant differences at distinct repetition rates.

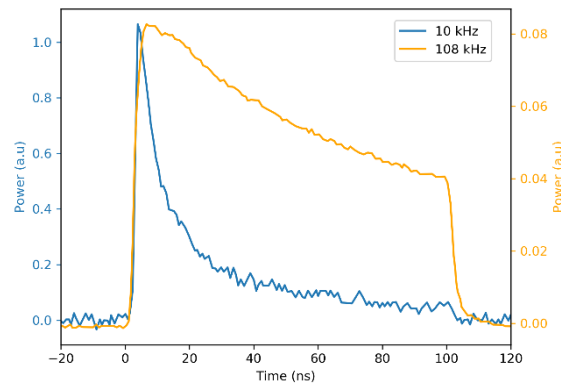


Figure 5.5 – Time traces of the “Square (1x100 ns)” pulse at 10 and 108 kHz.

At higher frequencies, the laser's amplifier is unable to overcome the saturation caused by preceding pulses, which leads to shape distortion. However, logically, the first pulse in a burst is the exception and should remain unaffected, thus differing from the following pulses. This difference is clearly visible in Figure 5.6, where the first pulse in a burst of “Gaussian 100 ns” pulses at 200 kHz, above the pulse's transition frequency, exhibits a much higher peak power than the subsequent pulses whose shape eventually stabilises.

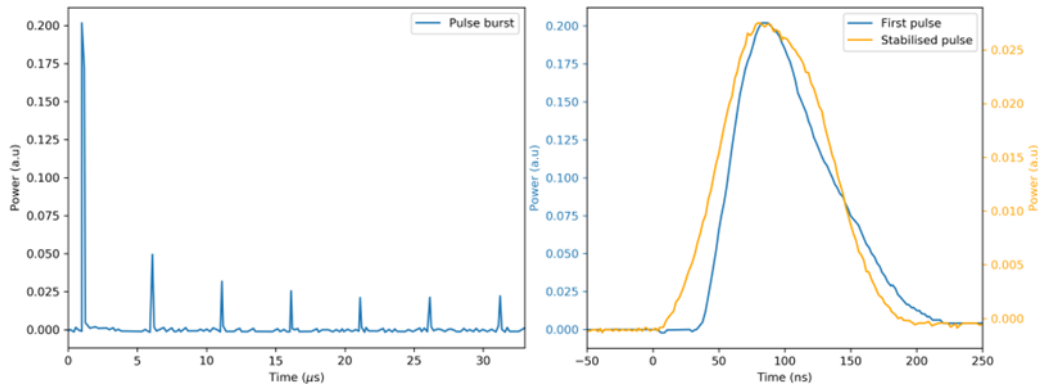


Figure 5.6 – Time traces of (Top) the start of a burst of “Gaussian 100 ns” pulses at 200 kHz, with close-ups of the (Bottom left) first pulse and of (Bottom right) a stabilised pulse.

These results emphasise the need for caution when operating above the transition frequency, as bursts may contain a variety of pulse shapes and energies rather than a uniform array of identical pulses. Furthermore, the first pulse in a sequence or single pulses, must be considered carefully.

To better understand this behaviour, a new set of measurements was conducted for single pulses of each default configuration, allowing for comparison with pulses measured at their transition frequencies.

Table 5.2 presents the energy of a single pulse measured using an energy sensor (PE50-DIF-C) and an energy meter (Centauri Dual Channel) from Ophir for each pulse, while Figure 5.7 displays the temporal profiles obtained using a custom high-speed photodetector and an oscilloscope. The major difference between this case and the pulses at their transition frequency appears to be in the pulse energy. The temporal profiles appear very similar, but the single pulses have comparable or higher energy than a stabilised pulse at its transition frequency, meaning that results obtained at a single pulse regime cannot be extrapolated to the average pulse when operating in burst mode at the transition frequency.

Table 5.2 – Default laser pulses energy in the single pulse operation mode.

Pulse name	E_{pulse} (mJ)
Square (1x10 ns)	0.080
Square (1x100 ns)	0.295
Square (1x200 ns)	0.373
Gaussian 10 ns	0.080
Gaussian 20 ns	0.132
Gaussian 50 ns	0.219
Gaussian 100 ns	0.296
Gaussian 100 ns, 1 mJ	0.566

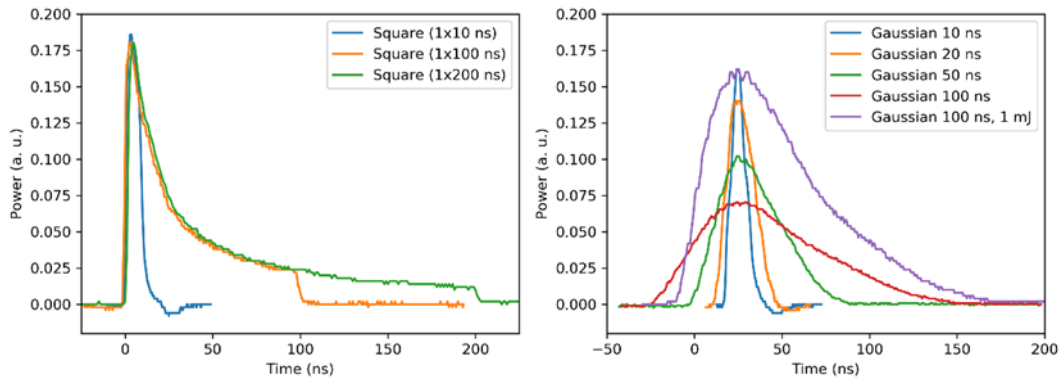


Figure 5.7 – Temporal shapes of (Left) the “Square” and (Right) the “Gaussian” pulses in single pulse operation.

5.2.1.2. Pulse design capabilities

A key feature of this fibre laser is its ability to generate custom-designed pulses in the temporal domain. The system allows users to design pulses up to 320 ns in duration by assigning intensity values in 5 ns increments across 64 steps. However, limitations in the amplifier can lead to efficiency drops if the input leads to saturation, resulting in distorted pulse shapes, as illustrated in Figure 5.8. This is the same effect that causes default “square” pulses to deviate from an ideal square shape.

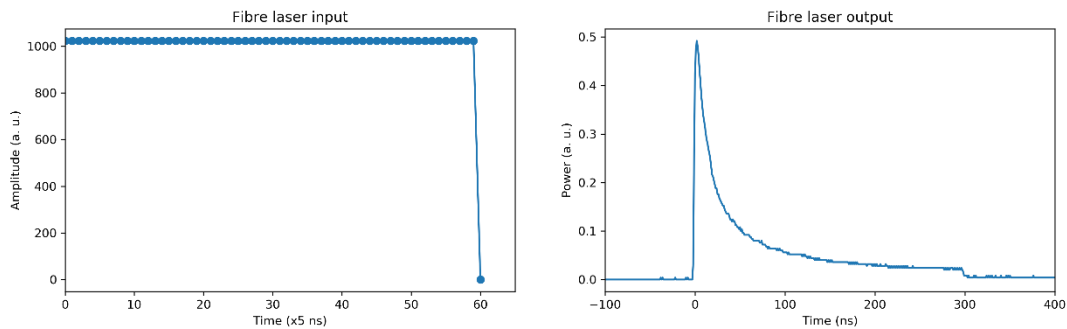


Figure 5.8 – (Left) Input pulse design and (Right) its respective output pulse shape.

To fully leverage the laser's capabilities, a pulse-shaping prediction tool was developed (discussed in Annex II). This tool, implemented via a Python script, predicts the necessary input to achieve the desired output pulse shape for single-pulse operation. It enables the creation of pulse shapes resembling square functions, Gaussians, ramps, and more, all within the system limitations of range and resolution.

One particular interest is the creation of pulse shapes of varying durations with similar energies. Figure 5.9 shows a set of custom square pulses designed with lengths of 10, 20, 50, 75 and 100 ns. While not perfect, they are a reasonable approximation to square functions. Due to the laser's 5 ns resolution, slight deviations from the intended pulse durations are expected.

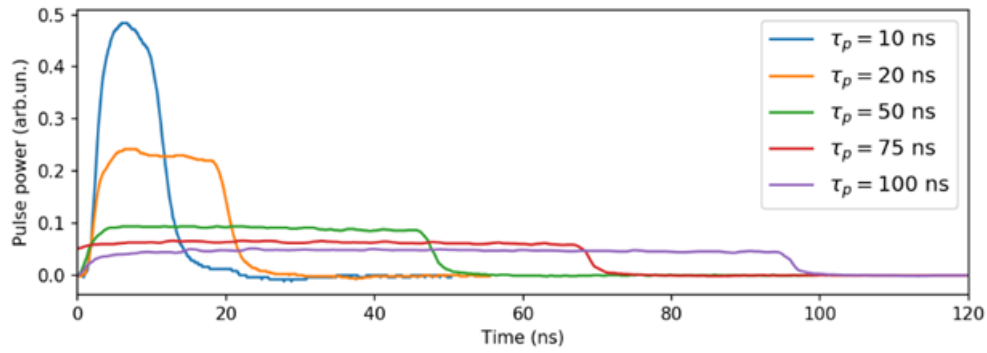


Figure 5.9 – Customised square pulses of different durations with similar energy.

Also, to confirm that the energies are similar within a small deviation, the energy of each pulse was measured using an energy sensor (PE50-DIF-C) and an energy meter (Centauri Dual Channel) from Ophir. Table 5.3 shows the measured FWHM and total pulse energy for each custom pulse (average of 10 measurements) showing minimal energy variation across different pulse lengths.

Table 5.3 – Characteristics of the custom square pulses.

Square Pulse	<i>FWHM</i> (ns)	<i>E_{pulse}</i> (μJ)
10 ns	8.9	92.87
20 ns	18,0	89.74
50 ns	46.4	89.66
75 ns	70.4	93.88
100 ns	94.4	93.00

Although the custom pulses are slightly shorter than their intended lengths (up to a maximum of 11%), the deviation decreases with longer pulses. In terms of energy, the

differences between pulses are minimal, with difference being within a 4.22 μJ across all pulse lengths, around an average pulse energy of 91.83 μJ .

While longer pulses are technically feasible, the pulse shaping prediction tool requires further refinements when handling low-intensity inputs, making pulses longer than 100 ns impractical without compromising shape quality.

5.2.1.3. Laser pump control: safety and system implications

If left unchecked, the continuous emission from ASE caused by the pump being on can significantly heat up samples before any LIBS analysis is performed. To mitigate this issue, the pump inhibit feature can be used to disable the pump until its needed. However, to fire laser pulses without impacting efficiency, the pump must be activated a certain amount of time before firing. This aspect of the pump inhibit feature and its impact on the practical operation of the laser needs to be characterised. Using the “Square (1x100 ns)” pulse, its temporal shape was acquired for varying time delays between pump inhibit deactivation and laser triggering, ranging from 0 to 40 ms, in 1 ms increments (Figure 5.10). The manufacturer’s recommendation was a delay of 35 ms.

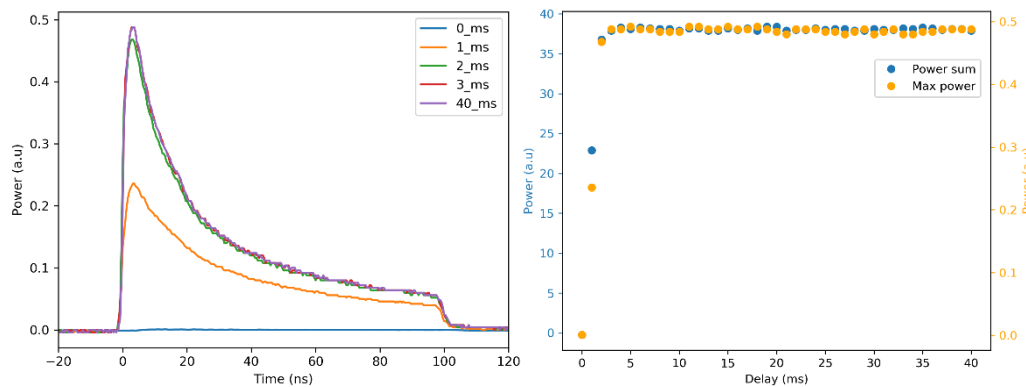


Figure 5.10 – Pulse dependence with the delay between the pump inhibit deactivation and the laser trigger, for the “Square (1x100 ns)”: (Left) impact on temporal profile, (Right) impact on power sum and peak power.

From the temporal profiles, it is possible to extract the peak power and calculate the sum of the power to estimate the optimal delay to reach maximum pulse efficiency. Contrary to the manufacturer’s information, these parameters converge at 3 ms, making this the optimal delay value.

5.2.2. Optical configuration and spectrometer system

Since the laser outputs pulses with relatively low energies and a small beam diameter, a 12x beam expander was incorporated at the laser head (Figure 5.2 Left), increasing the diameter to 6.12 mm, to improve the efficiency of the focusing lens (Equation 2.5) and thereby increase the pulse intensity at the focal point. The pulses are then reflected

by a mirror and then focused using a 100 mm focusing lens with an anti-reflection coating, resulting in a beam waist, w_0 , of 15.5 μm and a Raileigh range, z_R , of 0.5 mm. Other focusing systems were tested, such as a 10x microscope objective, which broke due to the proximity of the plasma, and a reflective microscope objective, which was inefficient due to its design, causing significant energy loss at the focus. To protect the optics, a sapphire window, with anti-reflection coatings on each face, was placed between the focusing lens and the sample.

For plasma emission measurements, a similar setup to the previous system was used. However, this system employs four independent AvaSpec-ULS2048CL-EVO spectrometers from Avantes. Each spectrometer covers a different spectral range and can be used individually or in combination to achieve a wider wavelength range while maintaining a reasonable resolution. Table 5.4 details the specifications of each spectrometer.

Table 5.4 – Specifications of each of the four spectrometers.

Spectrometer	1	2	3	4
Wavelength range (nm)	217.50-339.67	330.98-488.76	479.46-613.83	607.34-826.83
Resolution (nm)	0.05-0.07	0.06-0.09	0.05-0.08	0.09-0.13
Grating	UE - 2400 lines/mm	UD-1800 lines/mm	VD-1800 lines/mm	VC-1200 lines/mm

Each spectrometer is equipped with a CMOS detector with 2048 pixel. When used together, the spectrometers provide a continuous spectral range from 217.50 to 826.83 nm, with slight overlaps between adjacent spectral ranges. The resolution varies slightly within each spectrometer, with the one operating in the IR having the highest values. Each spectrometer has a grating optimised for its respective spectral region, as depicted in Figure 3.6.

All four spectrometers share certain parameters. Their intrinsic time delay is 0.9 μs , and their minimum integration time is 30 μs . Although this integration time is slightly longer than the plasma lifetime, it is still a significant improvement over the previous system, reducing background noise and improving signal quality.

To operate the spectrometers, the Python script developed for the previous system can be reused without modification, as both systems utilise the same functions present in the AvaSpec DLL functions.

Regarding the collection system, a few configurations were tested. Initially, a setup similar to Figure 5.1 was used, where plasma emission was focused into an optical fibre using 2 lenses. However, this setup proved too bulky to use with four spectrometers. The current setup uses an optical fibre coupled with a more compact fibre collimator aimed at the focal point, allowing for multiple collection fibres to be installed in closer proximity to the sample, minimising light loss due to spherical propagation.

5.2.3. Sample positioning and manipulation stages

Akin to the previous LIBS system, this setup includes three motorised stages with a controller from Standa (Figure 5.11) for sample positioning. Two are translation stages that handle 3D positioning and the third is a rotation stage for rotating along the vertical axis.

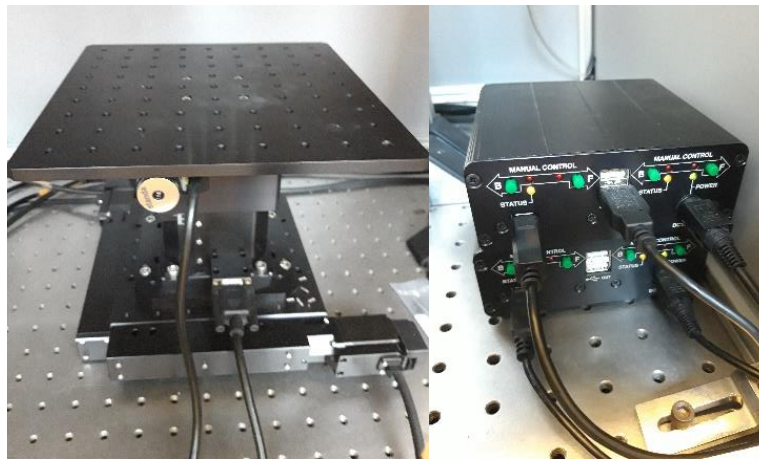


Figure 5.11 – (Left) Translation and rotation stages and (Right) their controller.

The horizontal translations are managed by a motorised XY scanning stage (8MTF-102LS05), which uses two stepper motors to move in perpendicular directions. This stage offers a travel range of 102 mm and a resolution of $0.31\ \mu\text{m}$, with a maximum speed of 10 mm/s for each direction.

Given the system's small Rayleigh range, a high-resolution vertical stage is essential for precise alignment of the samples at the focal plane. A motorised vertical stage (8MVT100-25-1) was selected, providing a 26 mm travel range and a $0.625\ \mu\text{m}$ resolution at a maximum speed of 20 mm/s. It provides the necessary precision and versatility to handle a convenient range of sample sizes.

Additionally, a motorised rotation stage (8MR190-2-28) was included for increased versatility, enabling handling samples with circular symmetry. This stage uses a stepper

motor, allowing continuous rotation past the 360°, with a resolution of 0.01° and a maximum angular speed of 8 turns/min.

All stages are controlled by a four-axis controller (8SMC5-USB-B9-B9) which allows users to manually control each motor in jog mode, via Standa's software or through USB serial communication. Utilising the provided DLL and examples, a Python script was developed to automate the movement of the stages.

The system is completed with a 240x240 mm² breadboard at the top that serves as the base for samples placement. Custom sample holders can be mounted on the breadboard to prevent slipping or to force samples into specific orientations.

5.2.4. Timing control with digital delay generator

As in any LIBS system, synchronisation of the laser pulses and the spectrometers acquisition is critical. However, the fibre laser introduces the additional complexity of synchronising its pump inhibit feature, which must operate for at least 3 ms before the laser operation to ensure optimal performance, minimising continuous emission.

To handle this timing requirement, a new DDG from Lightigo, a SyncRay, was acquired. The SyncRay has one input/output (I/O) port, which can be changed digitally, through its software or through commands, and four output ports (A, B, C and D), which can be configured independently or dependently of each other, each with its own settings, such as polarity mode or relative delay. The SyncRay connects to a computer via USB, allowing to send control commands through serial communication. A new Python script was developed to manage these functions.

In the configuration implemented, ports A and B control the spectrometers, each being able to trigger 2 spectrometers, while ports C and D control the laser shots and the pump inhibit feature, respectively. The polarity of the port D is inverted, so that it remains high, except when sending a pulse to disable the pump. Figure 5.12 shows a visual representation of the trigger operation for two analyses. The signal in port D starts high and the pump is inhibited. It is then inverted enabling the pump preparing for analysis. Roughly 3 ms later, ports A and B trigger the spectrometers, while port C triggers the laser in burst mode, all 3 synchronised with predetermined delays so the acquisition starts as the plasma emission begins. Once the acquisition is complete, the pump inhibit is reactivated, and the process repeats for the next analysis. The I/O port is currently unused, but it is planned for future integration with the translation and rotation stage drivers for improved device synchronisation.

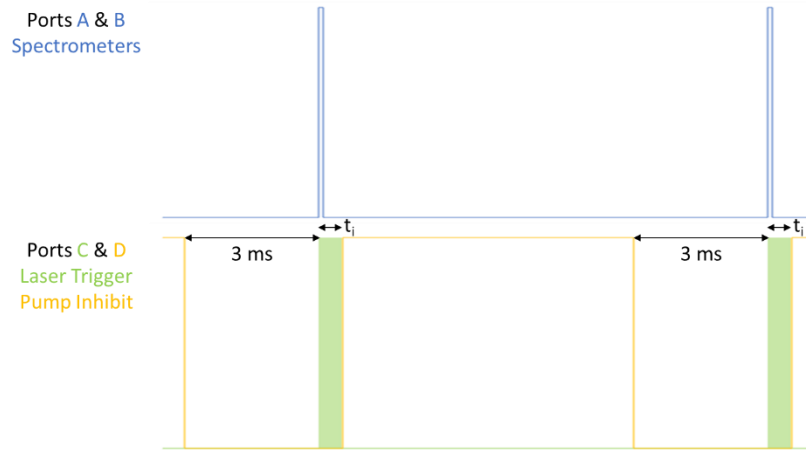


Figure 5.12 – Visual representation of trigger timings for two analyses, the pump inhibit is first disabled for 3 ms before sending a trigger to the spectrometers and burst of triggers to the laser (contained within the integration time t_i), reactivating the pump inhibit at the end and repeating for the second spot. The laser triggers appear like a filled rectangle due to the high frequency of the triggers.

5.2.5. Automation and integration of the system

By leveraging the Python script discussed in subsection 3.2.3.3, the fibre laser-based LIBS system has been successfully automated (Figure 5.13). Similar to the previous system, the computer sends trigger parameters to the SyncRay (such as frequency, number of triggers, delays, widths, etc.), pulse parameters to the fibre laser (pulse type and power), and prepares the spectrometers to acquire data upon receiving external triggers with a set of parameters (integration time and number of spectra) and controls all stage movements.

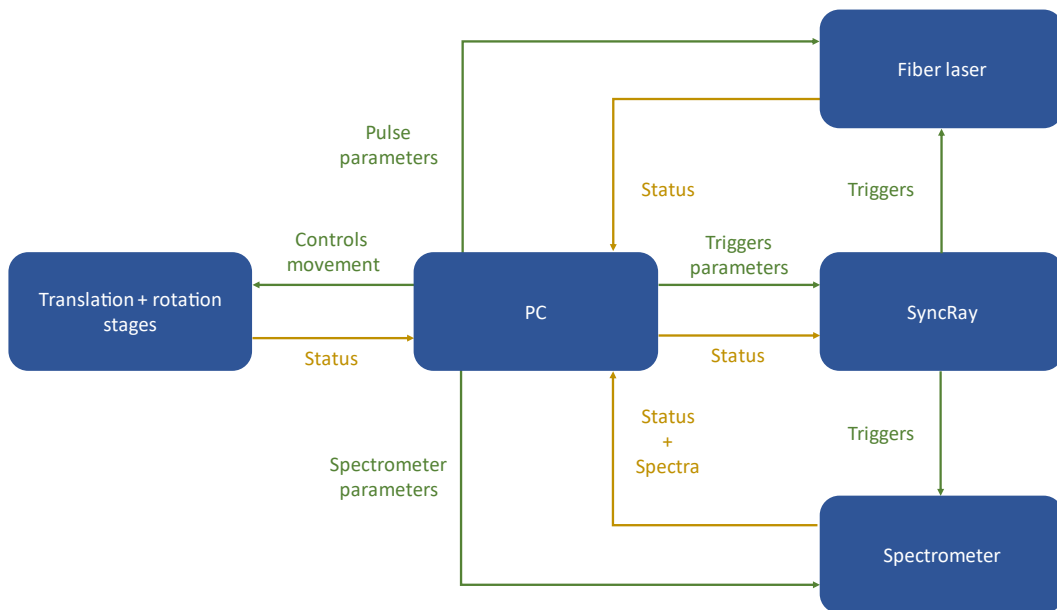


Figure 5.13 – Block diagram of the control software of the fibre laser-based LIBS system.

The SyncRay sends trigger signals to the fibre laser (for pulse generation and pump inhibit control) and to the spectrometers, all synchronised based on the parameters received from the computer. The spectrometers then send the acquired spectra to the computer. Currently, laser emission can only be initiated manually via physical button.

The resemblance of this block diagram with that of Figure 3.9 highlights the success of the original script, which was easily adapted to this new system with minimal modifications.

5.3. Characterisation of the LIBS performance

Two critical aspects in characterising the performance of this LIBS system are: first, evaluating the effects of different pulse lengths on optimising the signal quality, and second, analysing the signal response along the z-axis to understand the system's limitations when dealing with samples that have uneven or variable surface topography.

5.3.1. Effects of pulse length

The interaction between the laser pulse and the sample is significantly influenced by the pulse characteristics. The total energy, shape and temporal length of a laser pulse dictate the ablation, ionisation and emission transpire. The influence of pulse length on LIBS performance has been the subject of several studies, many focusing on pulses at different time scales[339–341], with a few specifically examining the ns range[342,343].

Given the laser's pulse design capability, a set of five custom square-shaped pulses (as shown in Figure 5.9 and detailed in Table 5.3) were previously created with different pulse lengths but nearly identical energies, averaging 91.83 mJ. To assess their performance in this LIBS system, the effect of pulse shape in the plasma efficiency was characterised and compared in terms of SNR of specific emission lines.

For this study, a high purity Cu sputtering target (99.999%, ref. C8-9000-D70) was chosen for analysis (Figure 5.14). For each pulse, 10 single shots were fired onto different spots on the sample, maintaining a 1 mm distance between spots. The integration time was set to the minimum of 30 μ s, sufficient to encompass the entire plasma lifetime. Prior to analysis, the data underwent pre-processing, including averaging each set of 10 spectra and applying baseline removal using an asymmetric least squares method[312,313].

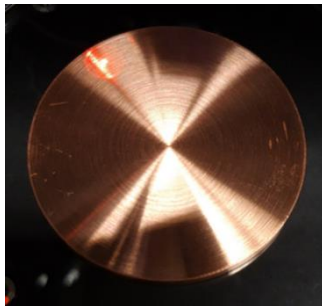


Figure 5.14 – Cu sputtering target with 99.999% purity.

Three of the resulting averaged spectra are shown in Figure 5.15. A basic inspection reveals that the intensity of the Cu emission lines increases with the pulse length. A more detailed analysis, focused on the Cu emission line at 578.2 nm, yields the results in Figure 5.16, where the intensity for the longest pulse is shown to be 150% higher compared to the shortest pulse.

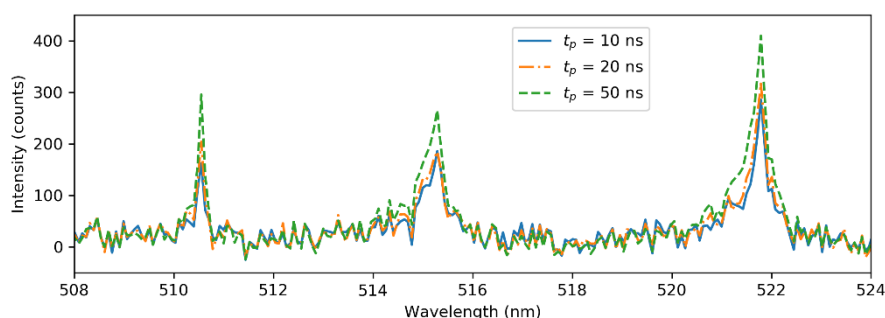


Figure 5.15 – Close-up of three Cu lines from the averaged spectra of 10 shots, collected for three different custom pulse lengths.

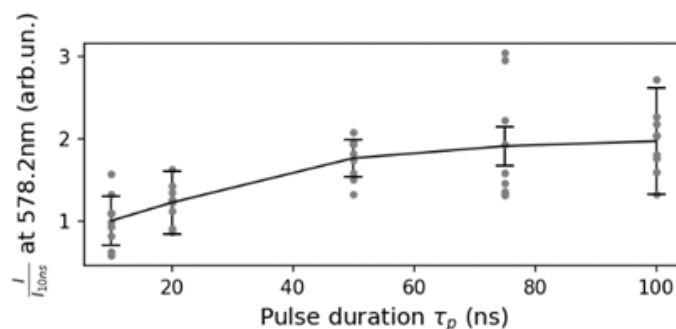


Figure 5.16 – Variation in intensity of the Cu 578.2 nm emission line, normalised to the intensity obtained for the 10 ns pulse, as a function of pulse length.

These observations can be explained using the Boltzmann theory, which is valid under the assumption of LTE. According to this theory, the intensity of a given emission line, resulting from a transition between an upper energy level E_i and a lower energy level E_j ,

follows equation 2.2. Additionally, the atom density in a particular ionisation state, denoted as $N(T_p)$, can be calculated using the Saha ionisation equation (equation 2.4):

By analysing equation 2.2, two possible mechanisms could account for the observed intensity increase: an increase in plasma temperature and an increase in the ratio $R(T_p) = N(T_p)/Z(T_p)$, with $Z(T_p)$ being the partition function. Both possibilities can be estimated by taking the logarithm of equation 2.2, constructing a Boltzmann plot (see Figure 5.17). From the slope of this plot, the plasma temperature can be determined, while the y-intercept provides an estimate of the ratio $R(T_p)$.

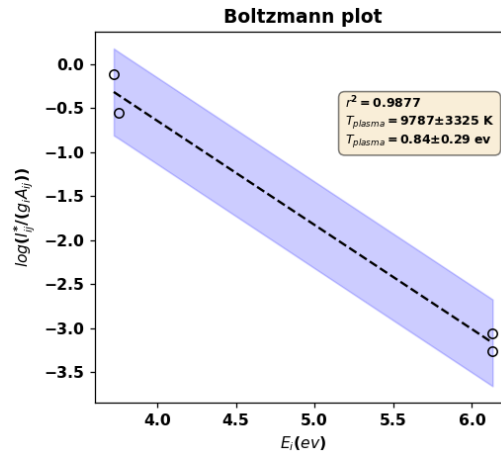


Figure 5.17 – Boltzmann plot obtained for the 50 ns pulse.

Figure 5.18 presents the estimates for plasma temperature and the ratio $R(T_p)$ for each pulse length. The results show that while the plasma temperature decreases as the pulse length increases, the ratio $R(T_p)$ rises by a factor of approximately 1.5. This suggests that the increase in SNR for longer pulses is primarily due to increase in $R(T_p)$, rather than plasma temperature.

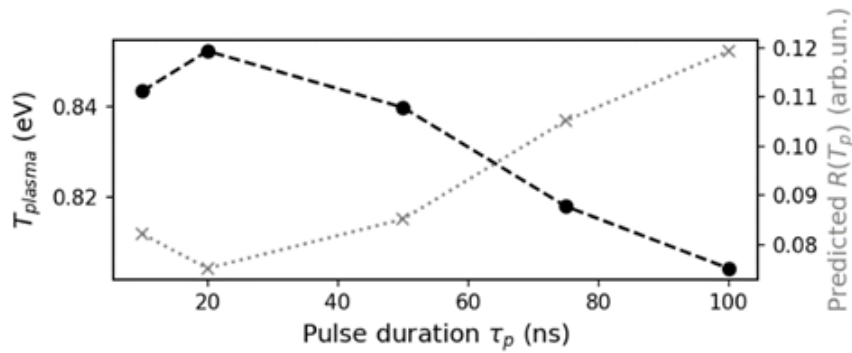


Figure 5.18 – Variation of the plasma temperature and the ratio R (defined in the text) as a function of pulse length.

Ultimately, these results suggest that, at least for the nanosecond scale, longer pulse can enhance the SNR of the emission lines when compared to shorter pulses. This implies that, as long as the longest pulses exceed the plasma threshold of a sample, they may be the optimal choice for analysis.

5.3.2. Effective plasma formation zone

As with the previous LIBS system, it is essential to understand the extent of the working area of this fibre laser-based LIBS system. Due to the low energy of the pulses and the small Raileigh distance, plasma formation is bound to occur only within a very short range around the focal point.

For this characterisation, a 99.95% Fe sputtering target (as shown in Figure 3.11) was used. Given the relatively low energy of the laser pulses, the highest energy pulse, “Gaussian 100 ns, 1 mJ”, was selected to achieve the best possible SNR. With a Raileigh distance of less than 1 mm, the positions selected for analysis ranged from 1 mm below the focal point to 1 mm above it, in 0.25 mm steps. At each height, 10 spots were analysed using single shots, and the average spectrum for each height was obtained. Baseline correction was applied using an asymmetric least squares algorithm[312,313].

Figure 5.19 displays the results of the characterisation, focusing on the 273.96 nm Fe line, the most intense line with minimal interference from other spectral lines. As expected, the highest SNR is observed at the focal point. Furthermore, the signal rapidly decreases as the distance from the focal point is increased, which aligns with the small Raileigh distance of the system. Compared to the previous LIBS system, this setup requires much more precise alignment to operate optimally, and it performs best with samples that have flat surfaces, either naturally or through pre-preparation. The effective working area is roughly confined to 0.25 mm around the focal point, as any misalignment or surface irregularity beyond this range results in a significant drop in SNR.

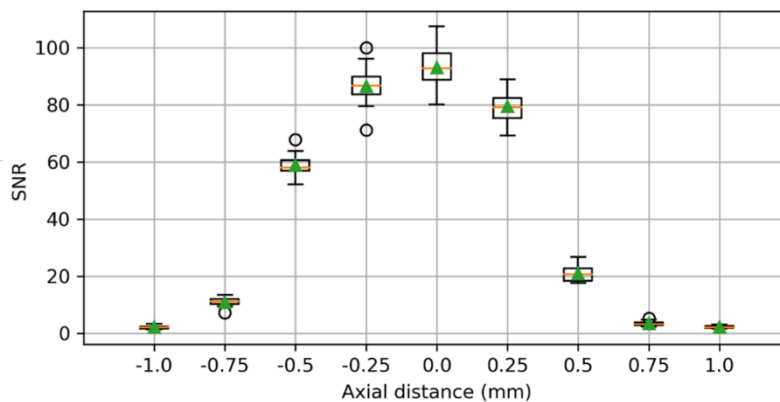


Figure 5.19 – Results from the characterisation of the working area of the fibre laser-based LIBS system.

5.4. High-resolution imaging applications

The primary application identified for this fibre laser-based LIBS system is high resolution elemental imaging. While the previous system from Chapter 3 produced promising imaging results, its resolution was limited by a beam waist of approximately 150 μm , preventing finer details from being captured. However, with the new fibre laser system, the beam waist is reduced to around 15 μm , approximately 10 times smaller, enabling much higher resolution mapping of samples.

To take advantage of the laser's high repetition rate capability, the system was automated to fire continuously without pausing the translation stages, significantly reducing analysis time compared to point-by-point movement. By knowing the speed and acceleration of the stages, the laser triggers could be precisely timed to achieve the desired step size.

One of the first challenges encountered was that, even with the highest energy pulse, the resulting spectra had low intensity, leading to poor contrast in the generated maps. To address this, the system was configured to fire multiple pulses at each analysed spot, accumulating more plasma emissions in a single measurement (as illustrated in Figure 5.12 for two analysed spots). While this increased the size of the craters, careful control was implemented to limit the increase in crater size to no more than 50%, using a maximum speed of 10 mm/s and a repetition rate of 20 kHz.

Another issue arose from the large number of data points, as each spot generated a separate .txt file. This caused maps to consume several gigabytes of storage, increasing storage requirements and significantly slowing down data analysis. To resolve this, the Python code was modified to save data in Hierarchical Data Format (HDF), more specifically HDF5, using the *h5py* library[344]. Additionally, a more powerful computer was acquired to improve data processing times.

The system was tested on a variety of samples, similar to the previous setup, with the most challenges encountered in biological samples (no plasma formation or burning). However, it found success with geological and metallic samples.

5.4.1. Mapping of Geological samples

Following the steps of the previous system, one of the first applications of this new system was imaging geological samples. A particularly interesting sample was a rock composed of montebrazite, quartz, and turquoise, similar to the one shown in Chapter 3 (Figure 3.18), which can be seen in Figure 5.20.



Figure 5.20 – Rock composed of montebrazite, quartz and turquoise, positioned horizontally using a sample holder.

Initial mapping was performed on smaller sections, such as the one in Figure 5.21. A 100x100 grid of points with a 50 μm step size was used to analyse the sample, with 10-shot bursts fired at 20 kHz per point to improve signal intensity. Since Li was a key element of interest, the spectrometer covering the 607.34-826.83 nm range, which includes three of the most intense Li lines, was used with a 500 μs integration time. The intensity of the 670.22 nm Li line was used to create the map shown in Figure 5.21 (Right).

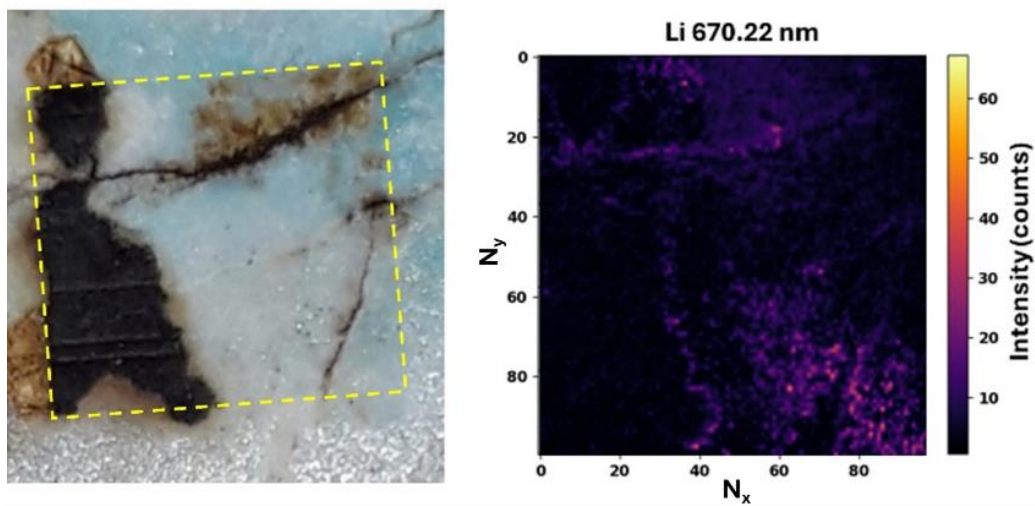


Figure 5.21 – (Left) Mapping area and (Right) resulting Li map.

Although a section of the sample burned in the process, the Li signal remained relatively weak, with minimal contrast. This suggested that increasing the number of shots was necessary for improved imaging.

The imaging process was then repeated with different parameters, to capture more of the sample's surface. In this case, a 200x200 grid of points with a 400 μm step size was used, and each point was analysed with 40-shots bursts at 20 kHz. The integration time was increased to 2 ms, and the resulting map is shown in Figure 5.22. While the intensity map still had low contrast due to some spots having high intensity compared to others, applying the logarithm of the intensity significantly improved the clarity of the image.

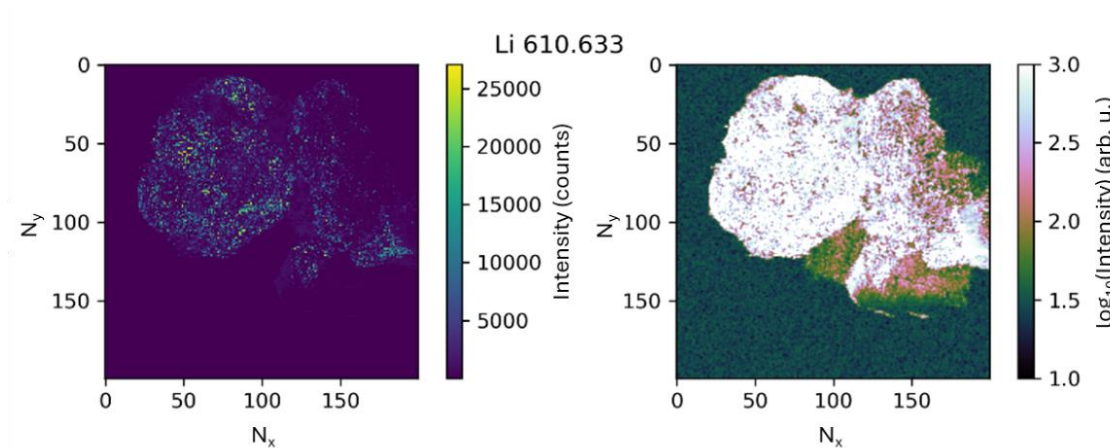


Figure 5.22 – Maps of Li using the 610.63 nm line's (Left) intensity and (Right) its logarithm.

This method can be extended to other elements. For instance, in the case of the sample shown in Figure 5.23, two spectrometers were used to capture maps of additional elements.



Figure 5.23 – Rock slab containing petalite; the red area indicates the area analysed.

This sample, which contains Li-bearing minerals such as petalite and spodumene, was analysed using a 250x250 grid of points with a 100 μm step size. Each point was analysed using a 40-shot burst and a 2 ms integration time, resulting in the maps in Figure 5.24.

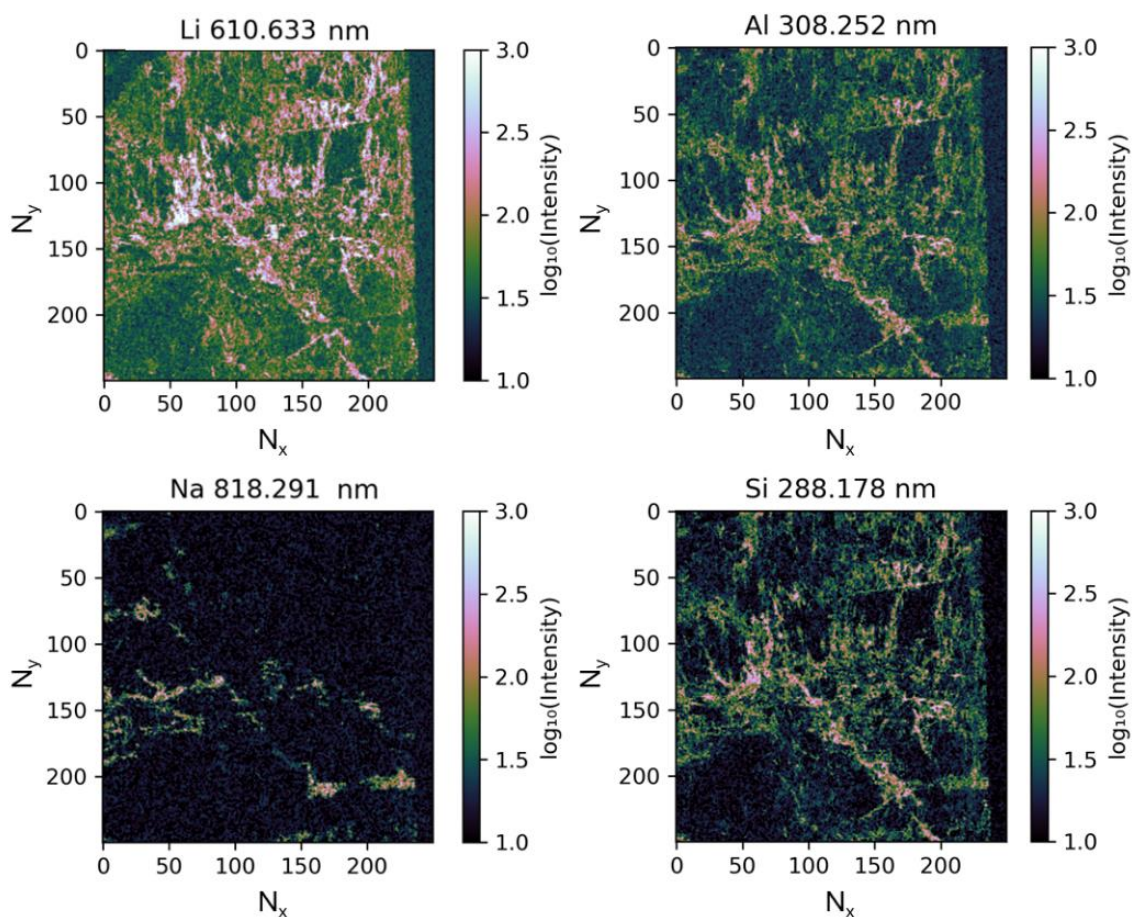


Figure 5.24 – Li, Al, Na and Si maps of the area marked by the red square in the slab sample.

As expected, the Li, Al and Si maps overlap significantly, as these elements are components of petalite and spodumene, while Na exhibits a different distribution.

High-resolution imaging can also be combined with wide-area analysis. One proof of concept is shown in Figure 5.25, where a sample with montebrasite, a Li-bearing mineral, was analysed with a grid of 900x500 points, creating a 0.45 MP image with a 100 μm step size. Each spot was analysed with a 40-shots burst, and the Li map (Figure 5.25 Bottom) was obtained using a 2 ms integration time.

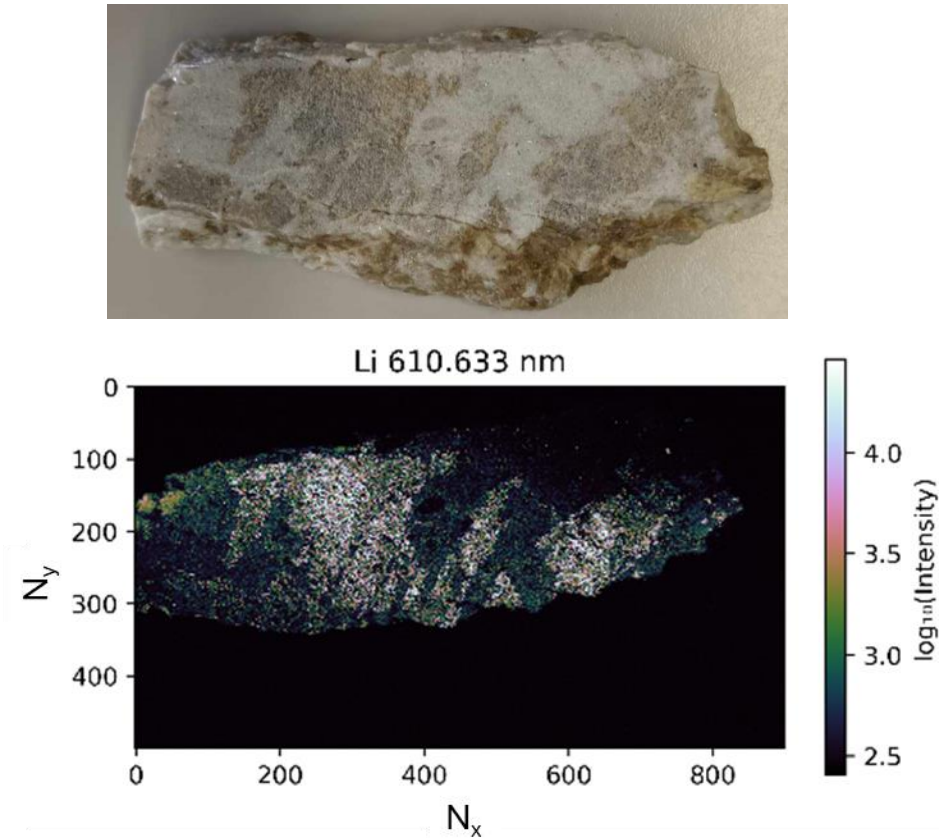


Figure 5.25 – (Top) Sample with montebrasite and (Bottom) corresponding 900x500 points Li map.

While this approach produces highly detailed maps, it is time-consuming. This example in Figure 5.25 took over 3 hours to complete, and the data processing and the subsequent analysis added significant time. Despite the time investment, it is an important achievement and it represent the most detailed map produced by any system in this thesis.

Despite obtaining good results, a limitation became apparent as more samples were analysed. For minerals with some degree of transparency, such as quartz, the plasma formation was inconsistent, leaving gaps in the data where these minerals were present. This transparency raised the plasma threshold, further reducing the already limited working area. Rugosity or tilt in the sample could also prevent plasma formation. An extreme case is shown in Figure 5.26 where a rock composed mainly lepidolite, albite and quartz, was analysed using a 180x120 grid of points with 500 μm step size and 40-pulse burst per point, with a 2 ms integration time.

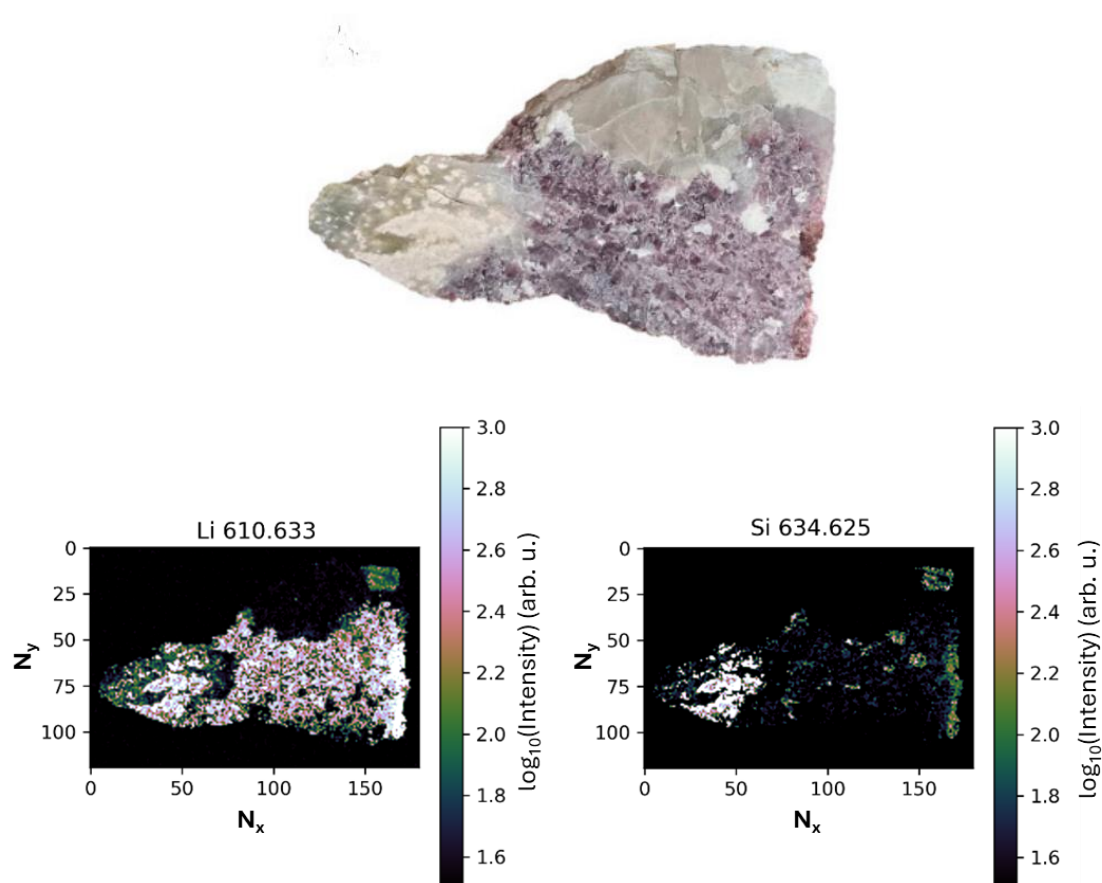


Figure 5.26 – (Top) Photo of the rock mapped with LIBS, primarily containing lepidolite (purple), albite (white) and quartz (grey) and (Bottom left) Li and (Bottom right) Si maps, showing no signal in the quartz regions.

These results suggest that, while the system performs well on geological samples, careful sample preparation, ensuring a clean cut, or a polished surface, is essential for best results. Moreover, samples need to be precisely positioned at the focal point, with minimal tilt, to avoid signal inconsistencies.

5.4.2. Mapping of Li battery electrodes

As the system was improved, other types of samples were tested, including metal alloys. These samples typically have lower plasma thresholds than rocks, allowing plasma formation at greater distances from the focal point. One metal alloy that was tested for imaging was an oxidised iron plate (Figure 5.27). The mapping was performed on a 100x100 spots grid with a 50 μm step size, with each spot receiving a burst of 10 shots at 20 kHz. The goal was to distinguish iron from rust, so the spectrometer covering the 607.34-826.83 nm range was selected (this was an early stage of the setup with only one optical fibre for collection) to capture Fe and O lines. An integration time of 500 μs was used, and the Fe II line at 770.49 nm was successfully used to create a map, distinguishing the rust from the iron.

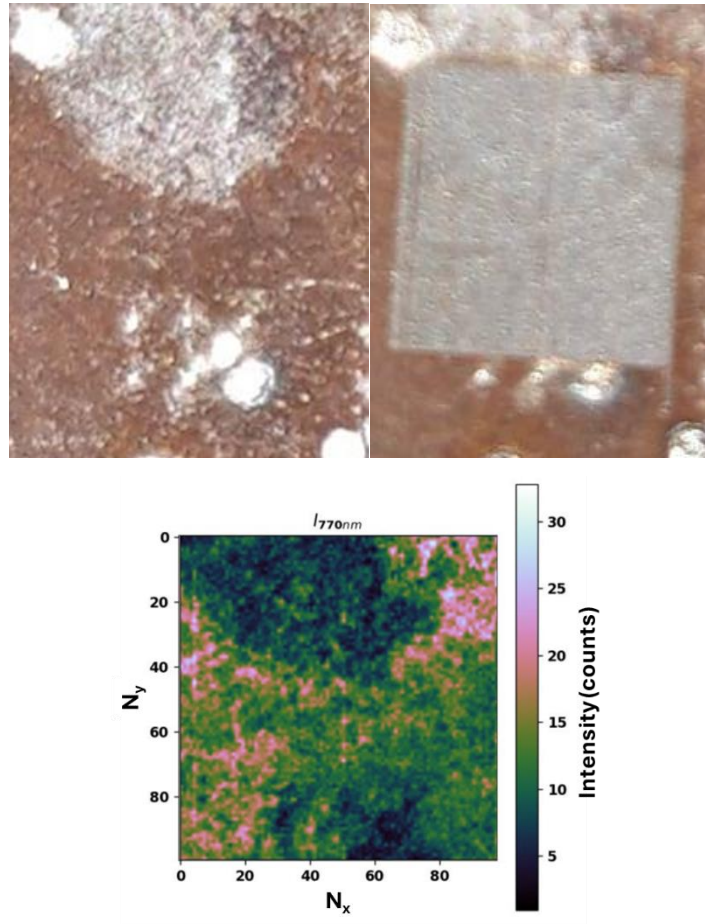


Figure 5.27 – (Top left) Oxidised iron plate before and (Top right) after mapping and (Bottom) the resulting map using the Fe II line at 770.49 nm.

As rust's molecular bonds are ionic, during ablation and plasma formation, breaking these bonds should result in a higher presence of Fe ions compared to unoxidized iron. With more ions present, the rusted regions show higher intensity in lines associated with ionic species like Fe II.

This result demonstrated the LIBS system's potential for analysing metallic samples, particularly for distinguishing between different oxidation states at high resolution. With this success, attention shifted to a new application: battery electrodes.

As mentioned in Chapter 3, previous attempts to map Li in two battery electrodes produced lacklustre results, primarily due to low resolution. The fibre laser LIBS system, however, resolved this issue. For each of the two electrodes, a 400x400 spots grid with a 100 μm step size was used to map the surface. At each point, a burst of 40 shots was fired to accumulate emissions within a 2 ms integration time. Figure 5.28 presents the resulting Li maps for both the positive and negative electrodes.

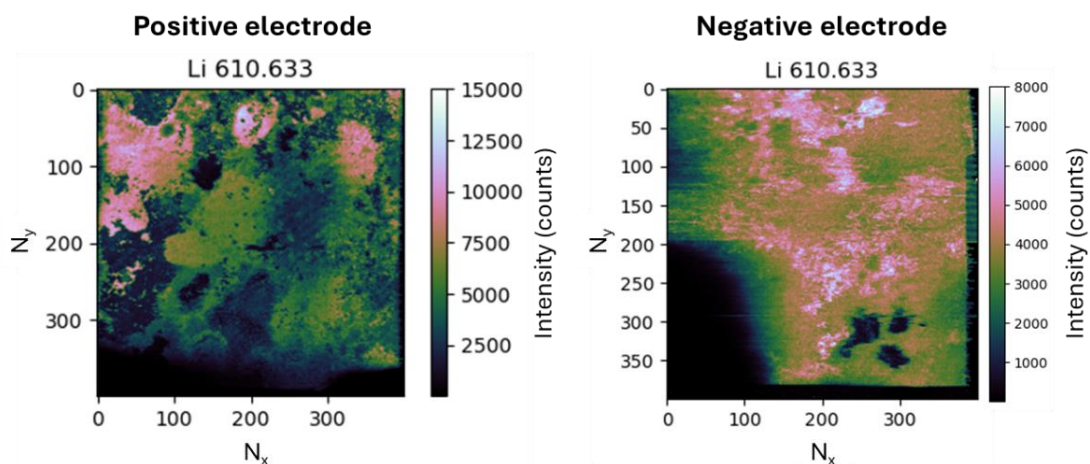


Figure 5.28 – Li maps for (Left) the positive and (Right) the negative electrodes.

Unfortunately, during analysis, the heat generated by the laser pulses caused the electrodes to bend, placing some sections out of focus. These out-of-focus regions appear as black regions in the maps.

To address this issue, clamps were used to hold the electrodes flat during analysis (Figure 5.29). After the adjustment, a new negative electrode was analysed using a 320x320 grid of points, with a 100 μm step size, and a 40-shots burst per point and a 2 ms integration time. The resulting map is shown in Figure 5.30, where the black regions on the left are shadows cast by one of the clamps blocking the plasma emission from reaching the spectrometer.

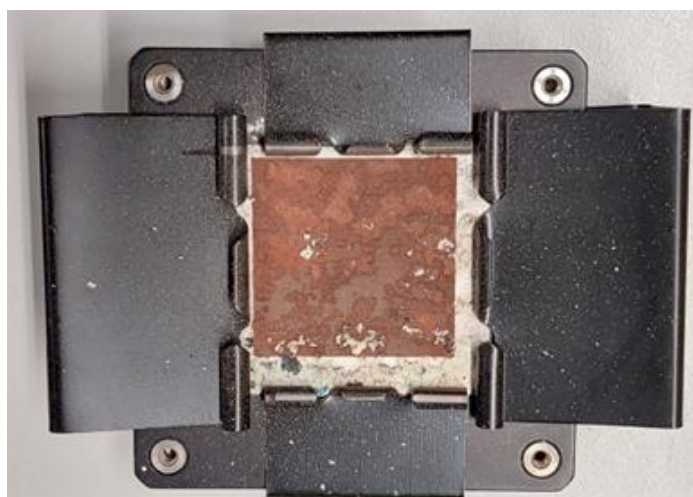


Figure 5.29 – Negative electrode held by four clamps, photo obtained after the analysis.

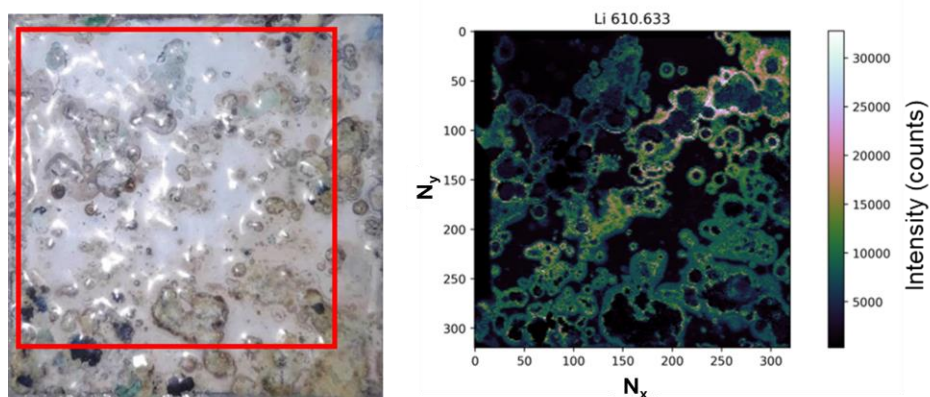


Figure 5.30 – (Left) Negative electrode with the analysed area marked in red and (Right) the resulting Li map.

Following this successful trial, new samples were obtained for further analysis. These samples included one negative and one positive electrode from a disassembled anode-less battery cell. Both electrodes are 99.9% copper sheets, with the negative electrode having been in contact with a cellulose separator containing a solid electrolyte ($\text{Li}_{2.99}\text{Ba}_{0.005}\text{ClO}$), while the positive one had been in contact with a LiFePO_4 cathode. The goal was to use LIBS to detect Li and correlate its presence with other elements present on the electrode surfaces.

For the LIBS analysis, each sample was mapped using a grid with a 100 μm step size in the x direction and 200 μm in the y direction, with a 40-shot burst per spot. Three spectrometers covering the 217.50-488.76 and the 607.34-826.83 nm ranges were used, all with a 2 ms integration time. The resulting spectra were baseline-corrected and elemental maps were created using the peak areas of Li (610.38 nm), Cl (808.21 nm) and Fe (382.56 nm), as shown in Figure 5.31.

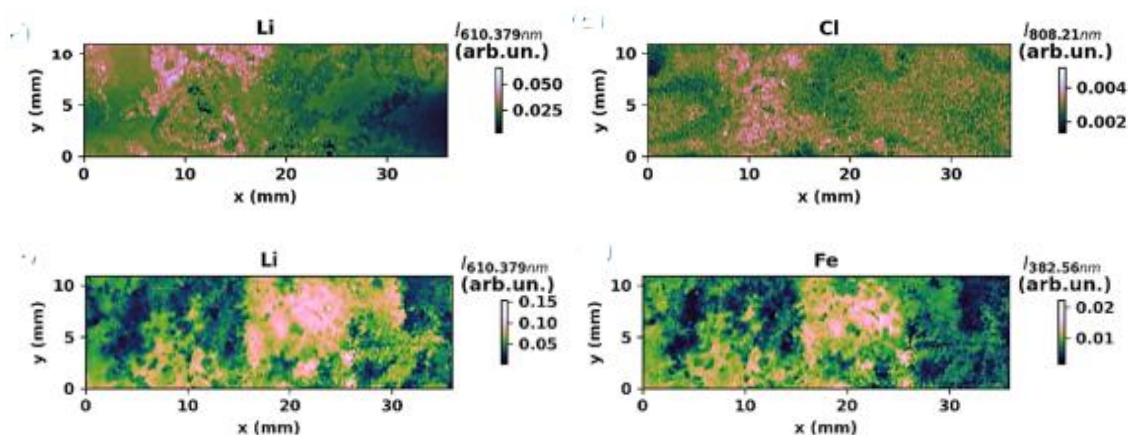


Figure 5.31 – (Top) LIBS maps of Li and Cl for the negative electrode and (Bottom) LIBS maps of Li and Fe for the positive electrode.

The presence of non-copper elements in the electrodes indicates that the elements have migrated from the surfaces in contact. Li and Cl migrated from the electrolyte to the negative electrode, while Li and Fe migrated from the cathode to the positive electrode. In the negative electrode, Li and Cl show inhomogeneous distributions, with a mismatch between the two elements, suggesting that lithium may have results from nucleation with the electrode rather than simply being transferred by contact. A similar scenario occurred in the positive electrode, with Li and Fe showing inhomogeneous distributions, despite their apparent similarity at first glance. This suggests that plated lithium may be present in certain regions.

These results demonstrate the fibre laser LIBS system's viability for electrode analysis. Cross-verification with other techniques, such as x-ray photoelectron spectroscopy, confirmed the system's high performance, establishing it as a reliable tool for LIBS analysis of electrode samples[345].

5.5. Concluding remarks

In this chapter, a LIBS system based on a fibre laser, designed primarily for high-resolution mapping, was described. The system was built from the ground up and it is fully automated. To ensure safety, a protective chamber was constructed around the setup, adhering to laser safety standards to minimise disruptions for coworkers while maintaining a safe environment. The system is capable of successfully imaging geological samples but excels particularly in metallic samples, achieving spatial resolutions as fine as 50 μm due to the high beam quality.

With a current record of mapping a 900x500 grid of points, totalling 450000 points, this system not only surpasses the resolution of the LIBS system described in Chapter 3 but also allows for larger map sizes. Furthermore, it has proven useful for electrode analysis, thus expanding the scope of LIBS applications to complement the previous system in a new field. The efficiency gained by automating the mapping process (firing the laser without pausing the translation stages) also led to the decision to add a DDG to the previous system, significantly improving its mapping speed, even if limited to 20 Hz. While this system did not directly influence the LIBS design in the next chapter, it contributed to decisions on laser selection, demonstrating that a balanced approach in pulse energy and beam quality is ideal.

Despite its strengths, the system has a notable limitation: its low pulse energy renders some samples impossible to analyse, as it cannot generate plasma. However, this limitation can be addressed in future improvements. The manufacturers have indicated

that an increase in pulse energy is possible. Additionally, reducing the focal distance can decrease the beam waist, thus increasing the intensity at the focal point. Furthermore, acquiring spectrometer with higher sensitivity could help boost the overall signal quality.

While the system is operational, it is not yet complete. The installation of a fourth collection system, which would allow the four spectrometers to work simultaneously, remains pending. Additionally, plans to install a second mirror to enhance the optical path from the laser to the focusing lens are underway. The system also lacks an extraction system or airflow to remove particles during analysis, which would improve imaging quality, prevent particles from contaminating the chamber and allow the use of a focusing system with a smaller focal distance by reducing the risk of dirtying or damaging the lens. Lastly, although the system is automated, further improvements could include using the translation and rotation stages' drivers to trigger the SyncRay.

Looking ahead, new experimental applications are still to be explored. With a similar fibre laser from the same manufacturer, underwater plasma on a limestone was successfully achieved using pulse bursts, indicating potential for this system in underwater analysis. Additionally, expanding upon the rust imaging results with samples from real-life settings or more challenging oxidation states could provide further insights.

Part IV

LIBS Application in the Cork Industry

Chapter 6

Industrial LIBS prototype for cork stoppers analysis

6.1. Introduction

One of the most important products produced by the cork industry is the cork stopper, a ubiquitous item used as a sealing solution for various containers, most notably wine bottles. Derived from the bark of the cork tree (*Quercus suber L.*), cork is a natural and renewable product with exceptional properties such as impermeability to liquids and gases and high compressibility and flexibility. These characteristics make it an ideal material for manufacturing bottle stoppers[346].

To enhance their sealing capabilities, manufacturers often apply surface treatments to cork stoppers. These treatments result in a coating, usually paraffin and/or silicon-based, with a thickness around 50 μm [347]. This coating forms a continuous hydrophobic seal on the cork stoppers' surface, improving their impermeability and lubricating the surface to reduce friction, allowing for an adjustment of the strength necessary to insert and remove a cork stopper from a bottleneck[347,348]. These enhancements add value to the final product, making it more appealing to clients, which underlines the importance of ensuring the quality of the coatings.

At the surface treatment stage, cork stoppers are processed in batches, which can lead to uneven coating quality. Current quality control methodologies include attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy[349,350], chemical extraction using organic solvents, and measurements of insertion and extraction forces[351]. These methodologies, however, have significant drawbacks such as slow analysis times, sample damage, lack of batch representativity and reliance on indirect methods. These limitations hinder the study and optimisation of treatment processes, often resulting in late detection of defective batches, which can lead to the disposal of days' worth of products or even recalls. More critically, defective products can go undetected, causing economic losses, reputational damage, and even lawsuits[352].

As mentioned in Chapter 1, EGITRON was searching for a method to analyse the uniformity of coatings along the curved surfaces of cork stoppers, for which LIBS was proposed. LIBS can perform real-time elemental analysis without requiring sample preparation[327], making it suitable for the non-planar topography of a cork stopper in

industrial operations. Additionally, the micro-destructive nature of LIBS, allows for depth analysis using consecutive shots at the same spot[29,30] without compromising the samples. Following positive preliminary results using the LIBS system described in Chapter 3, it was decided to pursue the implementation of a dedicated system, optimised for analysing cork stoppers. This led to a collaboration between INESC TEC, EGITRON, Azevedos Indústrias and CTCOR within the framework of CorkSurf project (reference NORTE-01-0247-FEDER-047040), where the industrialisation of the technology was addressed.

In this chapter, a novel application of LIBS will be presented along with a new prototype designed for the analysis of coatings on cork stoppers in an industrial setting. The initial validation results of this new application will be discussed. The chapter begins with a detailed walkthrough of the various subsystems, focusing on the critical components of the LIBS setup: the laser, optical systems, spectrometers, sample positioning system, and digital delay generator. The architecture of these components and the system's automation will also be explained. Subsequently, the effective plasma formation zone of the system will be assessed. The chapter will then discuss the initial analysis of cork stoppers, reproducing preliminary results obtained with the previous system (Chapter 3, Annex I). The same samples were analysed using the new system. In these tests, corks that were partially masked during treatment were examined to image the treated and untreated areas, checking the system's ability to assess treatment uniformity. Finally, the chapter will conclude with some remarks.

6.2. Industrial LIBS system prototype

In cooperation with the companies EGITRON and Azevedos Indústrias, a new LIBS system was developed from the initial concept to a functional prototype. One of the key aspects to be considered in creating a marketable product was cost, along with compactness and low maintenance. The system, shown in Figure 6.1, is the first prototype, and it is composed of several subsystems: the LIBS setup, sample holder, vision system, distribution board, and a computer. Figure 6.2 presents (a) a schematic, and (b) an image showing the LIBS setup and vision system, and (c) a detail of the sample holder. The system utilises a straightforward LIBS setup' with off-axis detection and attenuation-based energy control. It also features a specially designed sample holder and a positioning system, that will be discussed in more detail later in the chapter. The vision system, programmed by EGITRON, is composed of a Line-scan camera (Linea Color CL 4k Color) accompanied by a white light source for illumination. The goal of this subsystem is to acquire a full 2D image of the cylindrical face of the cork stoppers

to be analysed, allowing the detection of natural defects and the estimation of the best coordinates for the LIBS analysis.



Figure 6.1 – CorkSurf analyser industrial prototype.

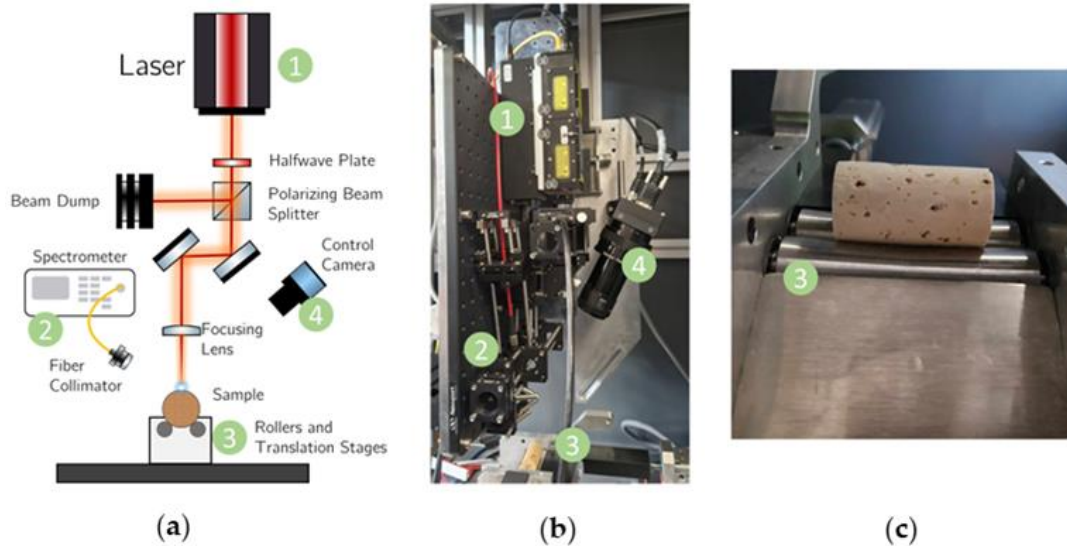


Figure 6.2 – (a) Scheme of the LIBS setup, including the vision system. (b) Photo of the LIBS setup and (c). Photo highlighting a cork stopper placed on top of the custom-made rollers. 1 - Laser source (VIRON laser); 2 - Spectrometer (AvaSpec-ULS2048CL-EVO); 3 - custom-made rotation system; 4 - Line-scan camera (Linea Color CL 4k Color).

To power the full system, a distribution board connects to an external power source and ensures that all the system components receive the necessary electrical power. The integration of a Power Line Communication (PLC) module, from Beckhoff, within the distribution board facilitates the seamless integration of hardware and software, allowing for efficient communication and control of the system components.

In the following lines a more detailed description of the most important subsystems will be given.

6.2.1. Laser and focusing system

Considering the preliminary studies and the requirements for a compact system with low maintenance, the candidate for laser source did not require such high energies as the ones from the CFR-200 laser and it should be air-cooled, since they are more compact and require lower maintenance than water-cooled lasers. With these points in mind, the VIRON laser from LUMIBIRD was selected (Figure 6.2 (b) 1). This air-cooled, diode-pumped Nd:YAG laser with active Q-switching emits 7.3 ns pulses at 1064 nm, with a near field beam diameter of 3.89 mm and an M^2 value of 3.04. It has a maximum energy output of 50 mJ and can operate at a maximum repetition rate of 22 Hz. It is a very compact system with a footprint of 117.3x90.1x213.8 mm³ (with fan shroud) and its laser parameters comfortably meet the system's operational requirements. It is also accompanied by its trigger box, where the trigger and interlock connections can be assembled, and the laser can be turned on/off with its key.

To operate the laser, an ethernet connection is required. Initially, for the preliminary tests, the host computer was set up to control the laser using software like PuTTY or a similar Telnet software to send commands. Later, to achieve system automation, a Python script was developed to facilitate communication between the user and the laser. This script was eventually translated into the industrial program in TwinCAT 3 (Beckhoff) for a more advanced control.

One of the means to control the laser pulse energy is by adjusting the current of the pumping diodes, where the energy increases with the current. To analyse how this adjustment affects the beam's parameters, a custom photodetector was used to assess its temporal shape as the control current was varied. The results obtained can be observed in the plots of Figure 6.3, where the pulsed width is represented for driving currents going from 140 A to the maximum value of 217 A.

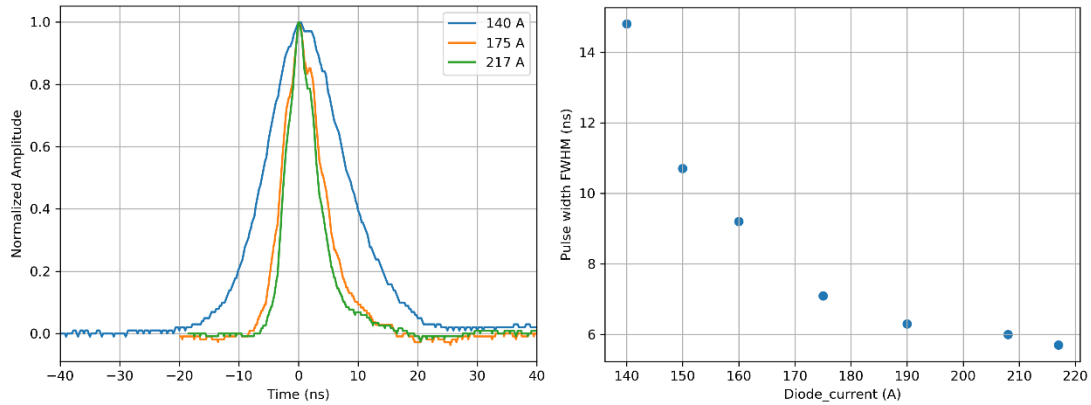


Figure 6.3 – (Left) Normalised shape of the laser pulses and (Right) temporal pulse width variation with diode current.

A clear dependence of the pulse shape on the diode current can be observed, with the pulse width increasing around 2.5 times from the highest energy of 50.8 mJ (217 A) to the lowest in the analysed range, 9.5 mJ (140 A). Like mentioned previously, this is not ideal, as the intensity of the laser pulses will vary non-linearly with the pulse energy, leading to different plasma dynamics.

In the context of an industrial application, ensuring consistent performance for LIBS analysis requires operating at a fixed pulse profile while being able to adjust the energy. To achieve this, a polarisation-based attenuation system was set up to control the energy delivered to the sample. This system includes a half-wave plate, a polarising beam-splitter, and a beam dump (Figure 6.2 (a)). By rotating the half-wave plate, the polarisation of the beam is also rotated, allowing the polarising beam-splitter to divide the beam into two perpendicular polarisations. One polarisation is directed to the beam dump, while the other is directed to the sample, thus adjusting the energy used for analysis. To simplify the energy control, the half-wave plate was mounted in a motorised rotation stage from Thorlabs, controlled by their Kinesis software. With this setup, the energy of the pulses was first measured against the angle of the step motor containing the half-wave plate using an energy sensor (PE25BF-DIF-C) and an energy meter (Centauri Dual Channel) from Ophir. The diode current was set to 208 A, value at which the manufacturers obtained the beam parameters as per the datasheet. The results depicted in Figure 6.4 show that the energy can be adjusted from its maximum value (42.5 mJ) down to zero by simply adjusting the waveplate angle. During this process, measurements were also made of the pulses' shape and width. These results, shown in Figure 6.5, indicate that the pulse shape remained consistent across all energy values, with a width rounding 6 ns, likely due to the laser's natural fluctuations.

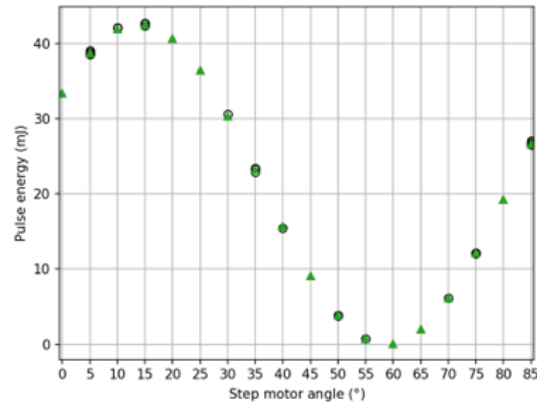


Figure 6.4 – Pulse energy as a function of the rotation of the step motor that holds the half-wave plate, ranging from 0 to 42.5 mJ.

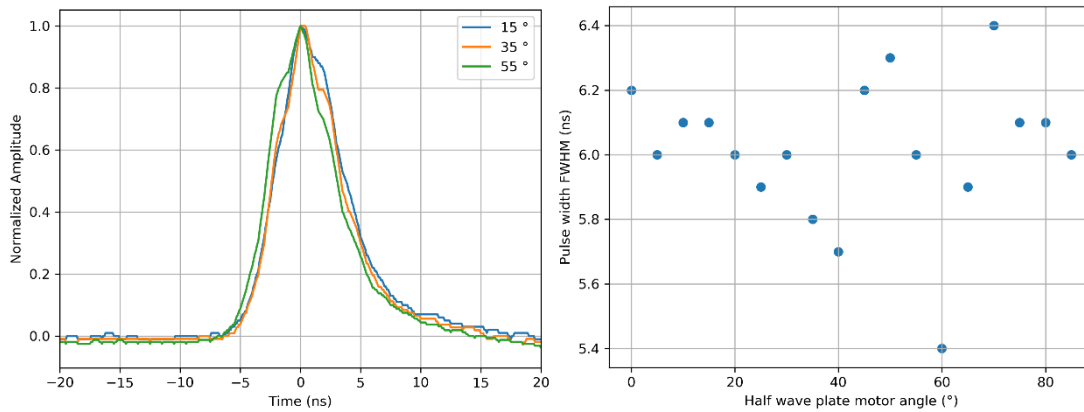


Figure 6.5 – (Left) Normalised shape of the laser pulses and (Right) temporal pulse width variation with the motorised rotation mount that contains the half-wave plate. Now the pulse shape and width are similar within the laser's own fluctuations, the latter rounding 6 ns.

After passing through the beamsplitter, the pulses are redirected to the focusing lens using two laser line mirrors, which ensure that the beam hits the centre of the lens aligned with the optical axis. The beam is then focused onto the sample by the plano-convex lens with a focal length of 150 mm. This focal length was chosen to provide space for other subsystems, such as the vision system. Using equations 2.5 and 2.6, the beam waist, w_0 , and Raileigh distance, z_R , were estimated to be $81.3 \mu\text{m}$ and 6.4 mm, respectively, resulting in a spot size of $162.6 \mu\text{m}$. With this setup, a stable, high-quality pulse with adjustable energy can be delivered to the sample, enabling more consistent LIBS performance.

6.2.2. Collection system and spectrometer

The detection system was set up in an off-axis configuration to enable higher versatility and improved signal collection across a large spectral range. The collection system was

based in a single optical fibre and collimator, to avoid increasing costs, installed as near as possible to the focal spot, in a nearly vertical alignment not to interfere with the vision system line of sight (Figure 6.6).

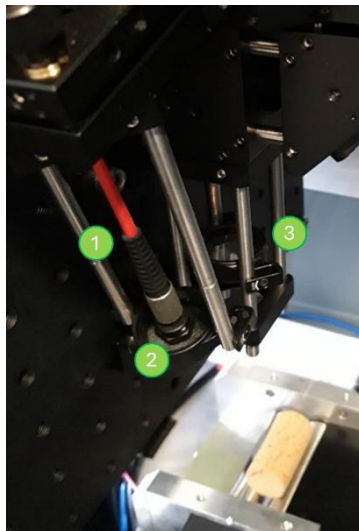


Figure 6.6 – Collection system, consisting of an (1) optical fibre and a (2) fibre collimator, next to the (3) focusing lens.

To determine the best spectral range for analysing the cork stoppers, four spectrometers from Avantes (AvaSpec-ULS2048CL-EVO) covering the full UV to NIR range were used in the preliminary experiments (Table 5.4). Once the most effective spectral range is determined, a single spectrometer for the specified range will be used to keep the system as compact as possible and at a lower cost.

6.2.3. Sample positioning and manipulation

To hold and manipulate the cork stoppers and address their cylindrical surfaces, a more sophisticated handling system was required. It was necessary to rotate the samples and move them longitudinally to access the entirety of the surfaces and raise/lower them to align with the focal plane. To meet these requirements, one custom rotation system, along with horizontal and vertical translation stages, were integrated into the main system.

The rotation system had to rotate the samples while avoiding cross-contamination from the surface coatings. To prevent the handling parts from contaminating different corks with residue from previous samples, a custom-made rotation system was created by Azevedos Indústrias. This system consists of several key components. One such component consists of the rollers that are in direct contact with the samples (Figure 6.2 (c)). As shown in the technical drawing (Figure 6.7), these rollers are designed with a radius that increases from the centre to the extremities, allowing the cork stoppers to

stand on the rollers with minimum contact and achieve repeatable positioning with minimal effort.

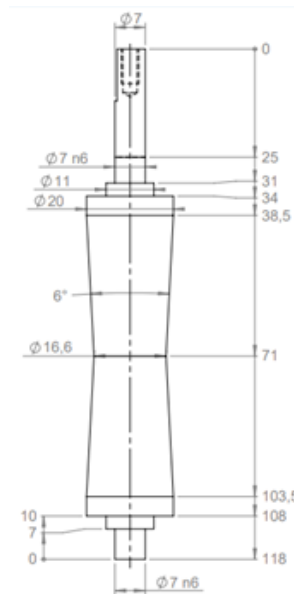


Figure 6.7 – Technical drawing of one roller made by Azevedos Indústrias.

The two rollers are connected to a servomotor through a belt (Figure 6.8). This servomotor is controlled by a servo drive embedded in the PLC, enabling seamless communication. The system was easily integrated into EGITRON's overall control system, which uses a program created using TwinCAT to manage the entire operation.

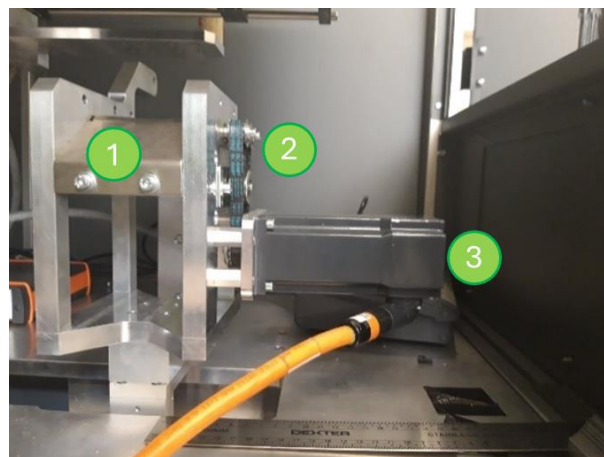


Figure 6.8 – Rotation system. (1) Rollers, (2) belt and (3) servomotor.

For horizontal and vertical positioning, two translation stages with step motors from FESTO were acquired. The horizontal stage allows the LIBS system to analyse along the longitudinal direction of a cork stopper, while the rotation system handles the analysis

in the transverse direction. The horizontal stage has a 100 mm travel range, sufficient to analyse cork stoppers of various lengths. The vertical stage has a 50 mm travel range, enabling easy positioning of the samples' surface at the laser focal plane, accommodating a wide range of diameters. The two motors are controlled by CMMO-ST-C5-1-LKP motor controllers, which allowed communication through a ModBus TCP/IP protocol. This setup allowed EGITRON's program to control the two stages seamlessly.

6.2.4. Synchronisation of laser and spectrometer triggers

Like the systems described in other chapters, a means to synchronise the triggers for the laser shots and the spectrometer's acquisition was necessary. The original plan was to utilise the PLC itself to adjust the delay between the laser and the spectrometer, but it could not provide a stable solution with the necessary requirements (jitter below hundreds of nanoseconds).

Akin to the other systems, a pulse delay generator (PDG) from Amplitude Portugal (formerly MWTechnologies) was used to properly handle synchronisation. This device has one input channel for external triggers, allowing it to be triggered by the PLC, and three output channels, named "1", "2" and "gating", with the first two used to trigger the laser and the spectrometer, respectively. The two output channels can be adjusted in terms of pulse width (t_p) and delay (t_d) from the external (or internal, if used) trigger with 5 ns resolution and is triggered by both rising and falling edges (Figure 6.9). With an USB connection, it is also possible to use a serial communication to control the PDG, for which a new Python script was developed to send commands to the device from the computer.

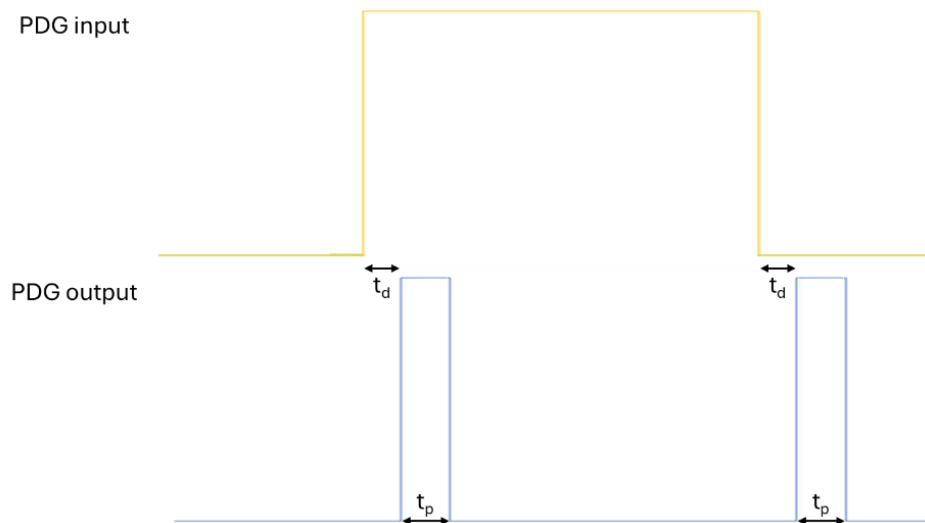


Figure 6.9 – Visual representation of the PDG output in relation to an input for pulses with a pulse width and delay of t_p and t_d , respectively.

6.2.5. Automation of the system

The ultimate plan is to fully automate the entire LIBS system using a single program built with TwinCAT by EGITRON. For the final product, all automation processes should be controlled by this unified program. However, during the development process, experiments had to be run, and several devices could not be accessed by EGITRON's control software team. As previously mentioned, communications with devices were performed using either Python or TwinCAT, depending on the device, except for the motorised rotation mount, which used Thorlabs's Kinesis software as it was a temporary solution for energy control. Figure 6.10 presents a block diagram of the first instance of automation used in the LIBS system.

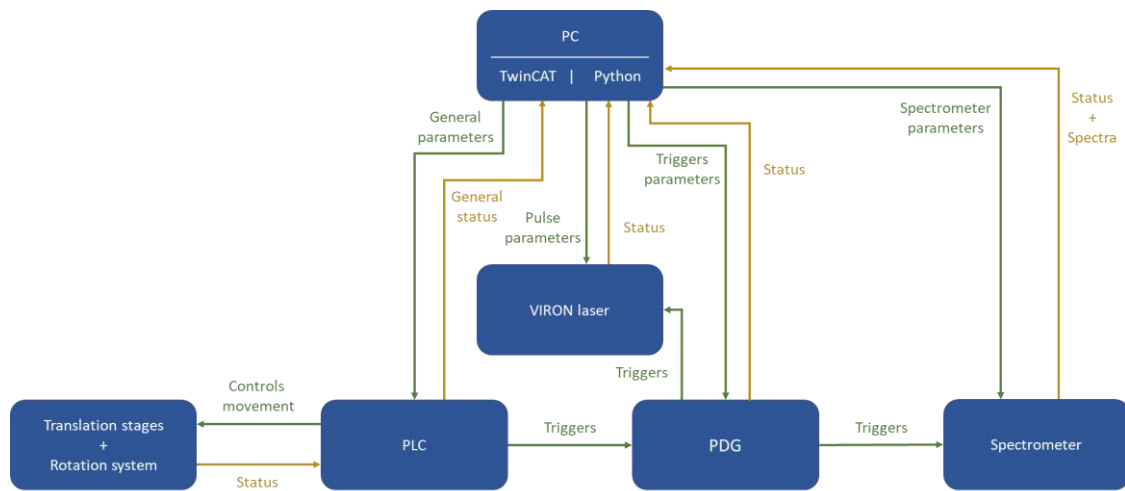


Figure 6.10 – Block diagram of the first instance of automation for running experiments.

Since both programs run independently, the Python script runs first to ready all its devices before prompting the user to start the TwinCAT program. At this time of development, the vision system was not yet fully operational, so it was not incorporated in the automation routine.

To start, the computer uses the Python script to send trigger parameters (delays and widths) to the PDG. It then sends operation mode parameters to the laser and begins its warm-up process, waiting for it to be finish before setting it ready to fire when triggered. The computer also prepares the spectrometer to acquire data with the specified parameters (integration time and number of spectra) in response to external triggers.

When prompted by the Python scripts, the user can set the parameters for the experiment (cork stopper dimensions, number of lines, number of points per line, number of shots per point, shot frequency and rotation between lines) in the TwinCAT program's

graphical interface (Figure 6.11). The PLC will then control the translation stages and the rotation system to position the sample at each calculated point, avoiding 5 mm on each end, two regions that have the highest potential of suffering from cross-contamination or damage. It sends the appropriate number of triggers to the PDG at each coordinate. The PDG will then synchronise the laser and the spectrometer by sending new triggers with the specified delays. Lastly, the Python script resumes upon user input and retrieves the spectra from the spectrometer.

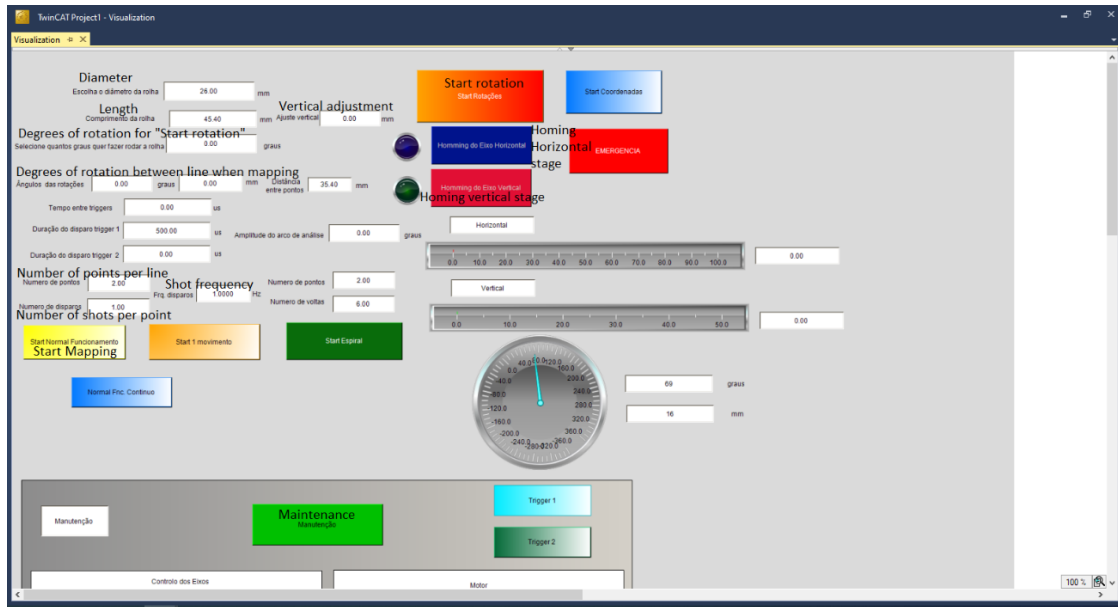


Figure 6.11 – Preliminary graphical interface of the TwinCAT program, with English translations for key elements.

6.3. Characterisation of the effective plasma formation zone

While the positioning of samples is fully automated and accounts for their specified dimensions, it is not feasible in an industrial setting to measure every single cork stopper. Instead, cork stoppers have standard dimensions with slight fluctuations for each individual cork. Therefore, as in the previous two systems, it is important to characterise the effective plasma formation zone of this new system. For this characterisation, cork stopper sample with standard dimensions was utilised, with a length of 45 mm and a diameter of 24 mm.

When assessing the effective plasma formation zone, the goal is to identify the range of coordinates around the focus where a plasma of sufficient quality for consistent analysis is obtained. Specifically, it is important to ensure that the tolerance in the dimensions of the cork stoppers (± 0.1 mm) is compatible with the tolerance for the plasma formation zone. This compatibility is crucial for maintaining the accuracy and reliability of the analysis despite the slight dimensional variations in the cork stoppers.

Following some preliminary tests, the laser energy was set to 46 mJ, achieving intense spectra devoid of saturation. The distances along the optical axis, from the focal plane were chosen within the depth of focus of the focal system, ranging from -4 to 4 mm, relative to the focal plane. Plasma measurements were taken at various vertical distances from the focal plane: at 1 mm intervals far from the focus, and at 0.5 mm intervals near the focus. For each distance, 10 spots were analysed to determine the average signal. The baseline of each spectrum was removed using an asymmetric least squares algorithm. Figure 6.12 presents the results of the characterisation using the most intense Si line that had minimal interference from other lines, at 288.2 nm.

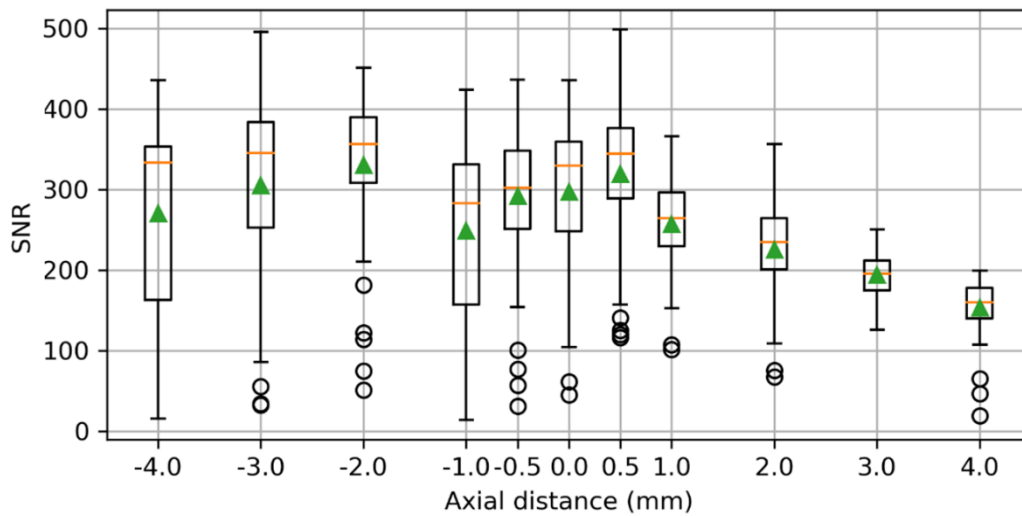


Figure 6.12 – Results from the working area characterisation in a cork stopper with a silicone coating.

As is the case of cork, the surface is irregular, containing many small holes and natural craters, resulting in a high rate of outliers. Therefore, the signal is best tracked using the median instead of the average. The maximum median appears near the focus, which aligns with the expectations. Considering the medians around the focus, an effective plasma formation zone can be established to be approximately 0.5 mm above and below it, as the variation of the signal with height is negligible compared to the overall variability of the signal at each position. Most importantly, the results show that the standard tolerance of cork stoppers (± 0.1 mm) is compatible with the higher tolerance of the effective plasma formation zone.

6.4. Replicating preliminary results

Project CorkSurf was initiated following a preliminary validation of the viability of the LIBS technique for evaluating silicone-based coatings on cork. This initial validation used the Nd:YAG system described in Chapter 3. During these preliminary tests, several

reference samples of cork stoppers with standard silicone and paraffin-based coatings were produced. These samples were masked before the coating process, resulting in samples with both treated and untreated areas. This setup allowed to perform blind tests to evaluate the viability of LIBS to assess the uniformity of the coating by identifying the shape of the untreated areas (Annex I). For the initial test of the CorkSurf system, using the Viron laser, similar tests were conducted on the samples available from the previous experiments.

6.4.1. Cork stoppers, coatings and methodology

The cork stoppers tested had standard dimensions, with a length of 45 mm and a diameter of 24 mm. To evaluate the viability of LIBS imaging for analysing coatings on the curved surface of the cork stoppers, samples were prepared by applying masks with different geometric shapes before both surface treatments of paraffin and silicone (Figure 6.13). After the treatments, the masks were removed, resulting in samples with both coated and uncoated zones. The goal was to determine if LIBS could distinguish these areas and assess the uniformity of the coatings. These essays were originally performed as blind tests to avoid unintentional bias, allowing for a comparison of the spectra obtained from the coated and uncoated zones. This comparison aimed to identify features that could discriminate between the surface treatment and the cork itself. The initial focus was set on the emission lines of silicon, present in the silicone treatments.

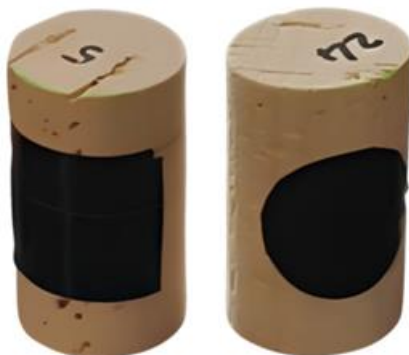


Figure 6.13 – Two of the analysed cork stoppers, submitted to surface treatments of both paraffin and silicone, before the mask removal.

It is important to note that at the time of these new tests, the samples were four years old and had been kept sealed in a dry, dark place. Therefore, there is a possibility that diffusion of the coating or cross-contamination may have occurred. Nevertheless, if the LIBS analysis can detect these changes, it also serves as a validation for the technique.

For simplicity, a single spectrometer was used, covering the UV spectral range of 220-336 nm, which typically carries a higher density of information and includes the most important silicon and carbon emission lines, the latter related to paraffin. The integration time was set to the minimum, 30 μ s, as it is already larger than a plasma lifetime. Using a half-wave plate and a polarising beam-splitter, the pulse energy was set to 33 mJ, providing high-intensity spectra without saturation. To avoid creating secondary plasmas on suspended particles released from prior shots, the repetition rate was set to 10 Hz. Finally, the laser and spectrometer were synchronised to ensure there was no delay between the laser pulse and the start of the signal acquisition.

Figure 6.14 illustrates different aspects of the analysis procedure. The cylindrical face of the cork stopper was analysed point by point, automatically avoiding the top 5 mm at each end to prevent contamination or alteration from the manipulation process. For each point, several consecutive shots were performed, a procedure known to provide depth information about the samples[29,30]. The number of shots per point and the size of the sampled area were balanced, considering the maximum number of spectra that the spectrometer's random-access memory (RAM) can store.

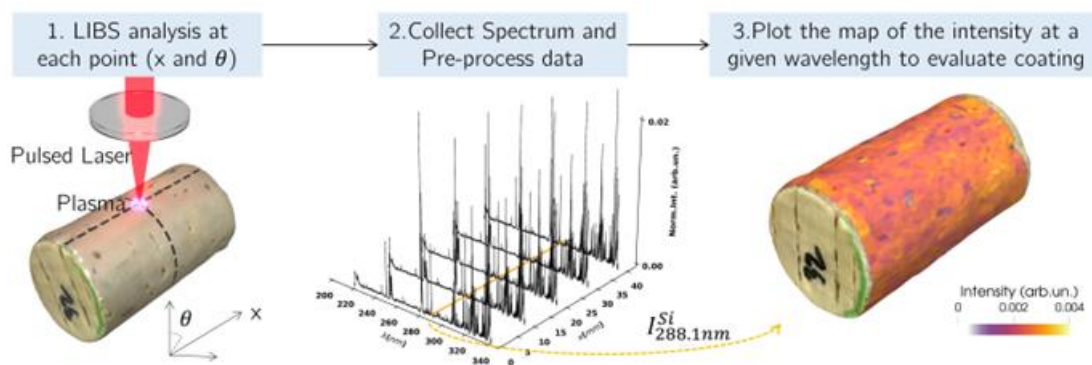


Figure 6.14 – Illustration of LIBS imaging applied to the analysis of a coating deposited on a cork stopper.

Before extracting any data from the elemental lines, signal pre-processing was performed on each acquired spectrum. First, the baselines were removed using an asymmetrical least squares algorithm[312,313], extracting the continuous background components of the plasma. Each spectrum was then normalised to the sum of all its intensities, a known methodology to lessen the impact of the matrix effects. This approach was used as an alternative to an internal standard since no lines that could be held as standard were present[318,319]. Figure 6.15 presents three close-ups of the main emission lines from an average spectrum of a sample.

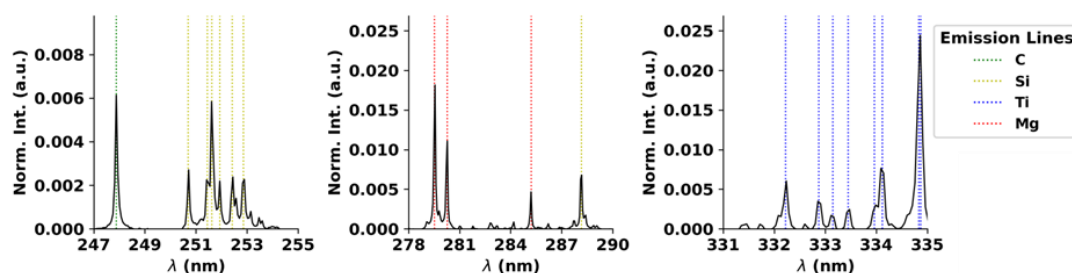


Figure 6.15 – Close ups of an average spectrum obtained from the first shots.

As highlighted, the spectrum contains several emission lines corresponding to carbon, silicon, magnesium (Mg) and titanium (Ti). C and Mg are elements naturally found in cork[353], while silicon indicates the presence of silicone coating. Titanium could originate from a bleaching treatment often applied to cork stoppers. All elements have spectral lines with a decent SNR (above 3) proving the good quality of the spectrum.

6.4.2. Surface maps

The goal of the analysis was to obtain maps of elemental distribution on the cork surface to assess the treatment uniformity and identify the coated and uncoated areas. For imaging paraffin and silicone-based coatings, the best approach is to focus on the elemental lines that may be exclusive to these coatings and not present in cork[354]. Intensity maps were created using selected lines. The intensity of each line was calculated by considering the peak area within a span of 0.2 nm around the peak wavelength. Using these calculated intensities, surface maps were created with the matplotlib Python library[355].

6.4.2.1. Imaging of silicone coatings

To map the silicone-based coatings, focusing on the Si lines is effective, as this element is exclusive to the coating in this setting. Given that the chosen spectrometer operates in the UV range, it can detect several specific Si lines, with the two strongest being 251.6 nm and 288.2 nm.

The results for one of the samples with a square-shaped mask, can be seen in Figure 6.16. This figure shows: a) a 3D photo (obtained by photogrammetry) of the original cork with the square mask, b) a similar 3D photo with the Si distribution map overlaid, and c) and d) the maps obtained in a planar representation for two different Si lines. These results were obtained using a grid of 90×40 points with a step size of 0.85 mm. The sample was analysed around its entire 360° circumference, with four shots per point. The maps were reconstructed by processing the distribution of the Si lines over the surface.

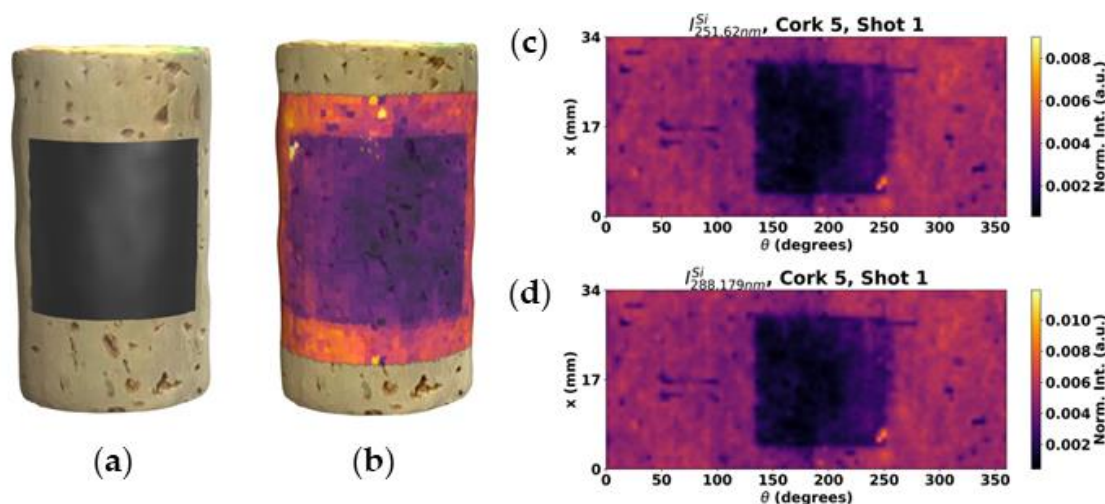


Figure 6.16 – (a) 3D models illustrating the cork stopper 5, with the tape mask and (b) with the resulting intensity map of the 288.2 nm emission line from Si overlaid. (c) Normalised intensity maps of the Si emission lines at 251.6 and (d) 288.2 nm.

The resulting maps obtained from the two Si lines are very similar, differing slightly in intensity, and both correctly identify the untreated square region. The maps show that Si has a relatively uniform distribution in the unmasked regions, as anticipated. In the masked regions, darker areas indicate little to no Si presence. Despite this, some Si signal is visible in the untreated area, hinting some Si contamination. Both maps reveal a gradient of Si on the right side, encroaching into the masked regions. This gradient could be due to contamination during storage or leakage of the treatment under the edges of the mask.

To assess the degree of contamination, maps for the second shot were produced. Since material is ablated by the laser with each shot, the map from the second shot looks deeper into the coating. Therefore, any superficial contamination should become fainter or disappear. Examining the map obtained from the second shot, at each analysed spot (Figure 6.17), some of these suspicions can be confirmed. While the overall Si content decrease, as expected, in the unmasked region the contaminated area became much darker, approaching the appearance of the uncoated region. This indicates the removal of part of the superficial contamination. Additionally, a very bright spot corresponding to high Si content, in the bottom right corner remains in the second shot map. This point is most likely a surface deformation or natural crater, which, being located at the extremities of the mask, probably accumulated a thick layer of coating, causing the signal to drop more slowly than on the rest of the cork stopper.

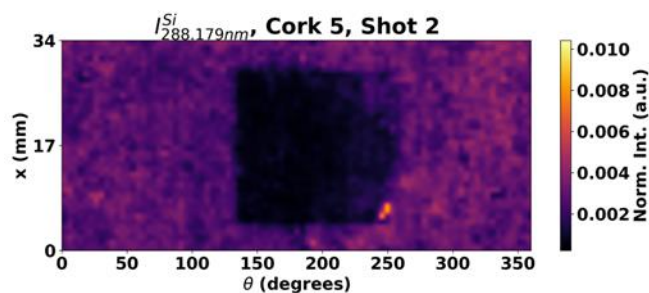


Figure 6.17 – Cork stopper 5's map of Si for the second shot on each spatial point.

The results of this essay were very satisfactory, indicating the capability of LIBS to assess the uniformity of the coating over the surface and even qualitatively evaluate its thickness.

However, in other instances, the results were not as conclusive. One such cases can be seen in Figure 6.18, where the sample was analysed using 45×40 spots with the same step as the previous case, covering 180° of the circumference that included the untreated area. In this instance, the circular shape of the mask was less distinguishable in both the first and second shots. Along with Sample 51 (Figure A.2), a section of the treated area displays a far weaker signal than the rest, resembling the untreated area. This suggests either poor deposition or damage inflicted on the silicone coating. The uneven drop in the Si signal in the treated regions observed in the second shot map may indicate fluctuations in the thickness of the coating. These variations highlight the influence of the coating technique and underline the need for further optimisation and validation of the LIBS method to ensure consistent and reliable results across different samples and conditions.

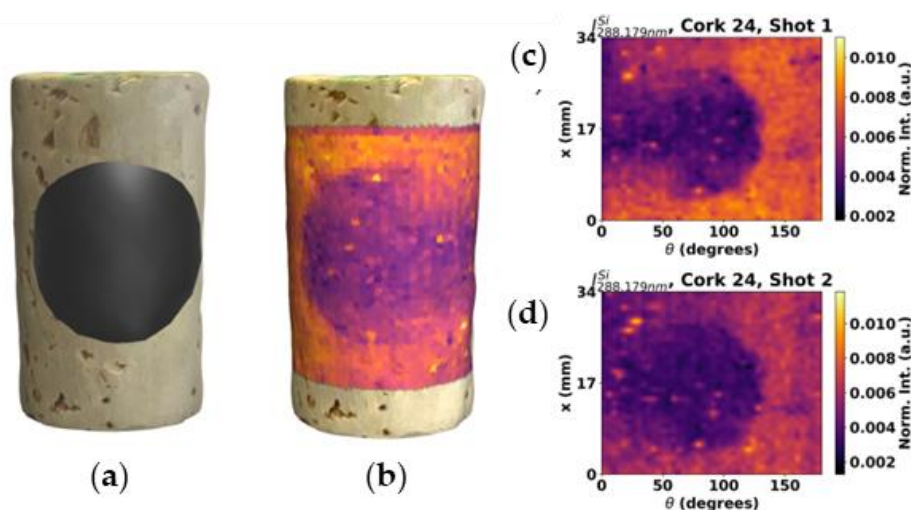


Figure 6.18 – 3D models illustrating the cork stopper 24, with the tape mask and (b) with the resulting intensity map of the 288.2 nm emission line from Si overlaid. (c) Normalised intensity maps of the 288.2 nm Si emission line for the first and (d) second shots.

Overall, considering both the results from the new system and the preliminary study, a total of 10 out of 12 cork stoppers were successfully mapped by analysing Si lines (Table 6.1).

Table 6.1 – Success rate of the LIBS technique for each sample and its respective masks.

Sample	Geometrical shape	Correctly identified (Y/N)
1	Square	Y
5	Square	Y
16	Triangle	Y
17	Triangle	Y
22	Circle	Y
24	Circle	N
25	Circle	Y
37	Parallelogram	Y
46	Irregular heptagon	Y
51	Cross	N
52	Cross	Y
53	Cross	Y

The results from both the new system and the preliminary study were very satisfactory, demonstrating the capability of LIBS to assess the uniformity of silicone-based coatings on cork stoppers. LIBS was able to qualitatively evaluate the thickness of the coatings, providing high spatial resolution and sensitivity that allowed for precise mapping of both coated and uncoated regions, as well as the detection of potential contamination or heterogeneities. The ability to discern variations in the Si distribution and identify surface deformations or natural craters further validates LIBS as a reliable method for analysing coating integrity.

Even though there were instances where the identification was unsuccessful, these cases could be attributed to issues with the coating techniques rather than the LIBS method itself. This highlights the potential for further optimisation of the system. Overall, LIBS proves to be a suitable technique for detecting silicon-based surface treatments, capable of distinguishing treated from untreated regions, and its success rate is expected to improve with system enhancements.

6.4.2.2. Imaging of paraffin coatings

Even though both surface treatments were affected by the same masks, it is important to see if paraffin can be detected by itself. In this case, however, the analysis is more challenging as the paraffin lacks exclusive elements. Paraffin shares the same elements as cork, although the molecular composition is different. In this scenario, it may be possible to investigate the presence of paraffin by examining the differences in emission intensities between the cork and the coating. These differences arise from the distinct molecular compositions and matrices of the cork stopper and paraffin coating.

Impurities apart, paraffin is composed of molecules with carbon and hydrogen, both of which are also present in organic materials such as cork. In the wavelength range of the selected spectrometer, there are no H lines, thus the best course of action is to analyse the only C line in the range, 247.9 nm. Figure 6.19 presents the imaging for cork stoppers 5 and 24, showing that it is still possible to distinguish between the treated and untreated regions despite the contrast being lower than in the silicone case. While this result is positive, it indicates that further analysis to the coating, such as its thickness and uniformity, may struggle with lack of resolution.

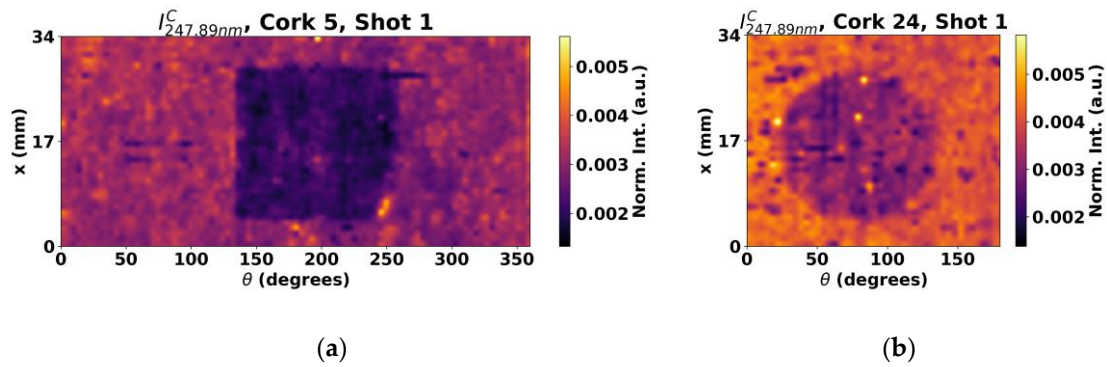


Figure 6.19 – (a) Normalised intensity maps of C of the first shot on the cork stoppers 5 and (b) 24 using the 247.8 nm line.

6.4.2.3. Analysing other elements

Apart from the Si and C, two other elements found on the spectra may have relevant information about the coatings or the cork stoppers. One of these elements is Ti, which is present in an optional bleaching treatment composed of titanium oxide, used to alter the pigmentation of cork stoppers before applying functional coatings. It appears in the spectra as several Ti^+ lines, with the most intense being 334.9 nm. Figure 6.20 presents the Ti maps for samples 5 and 24.

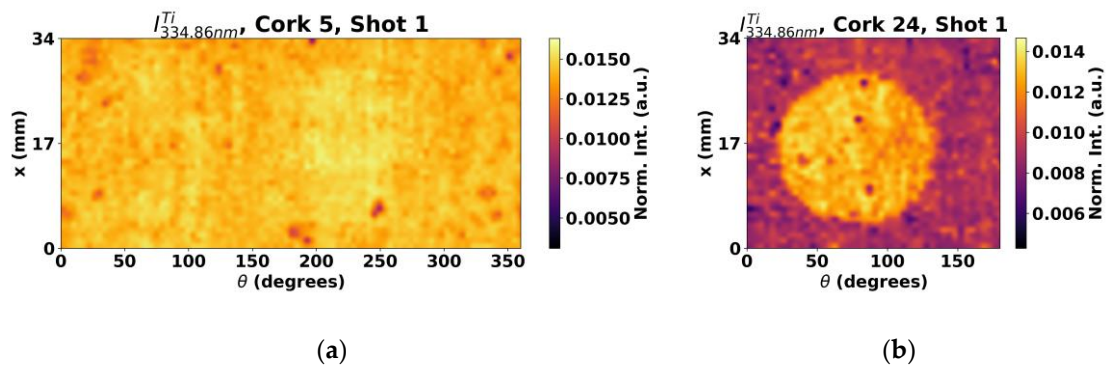


Figure 6.20 – Ti maps using the normalised intensity of the 334.9 nm Ti^+ line of (a) cork stopper 5 and (b) 24.

In this new analysis, two different results were obtained. In most samples, like sample 24, the untreated area can be easily identified as seen in Figure 6.20 (b). Interestingly, the Ti^+ intensities in the untreated region are higher than in the treated region. This behaviour may be related to the order of the various surface treatments, as the bleaching process with titanium oxide precedes the surface treatments related to the functional coatings. This leads to latter treatments to reduce the Ti^+ intensities compared to the masked areas where the Ti^+ signals are more intense. In the other outcome, seen in Figure 6.20 (a) while a semblance of the untreated area can be observed, it is impossible to determine the shape of the mask. An analysis of the previously shown maps of Si and C for both the cork stoppers 5 (Figure 6.16 (c) and Figure 6.19 (a)) and 24 (Figure 6.18 (c) and Figure 6.19 (b)), suggests that since their intensity is smaller in the former sample, it may have a very thin coating, thus having a near non-existent effect on the Ti signal.

Another element found in the spectra is Mg which is naturally present in cork as one of the most common elements in mineral form. From a few Mg-related lines present in the spectra, the 279.6 nm line from a Mg^+ emission was chosen for imaging, resulting in the maps in Figure 6.21. Unlike titanium, however, the untreated areas display a lower intensity of the Mg^+ line than the treated ones. This suggests that the surface treatment products may also contain magnesium in some capacity and in a much higher concentration than cork stoppers.

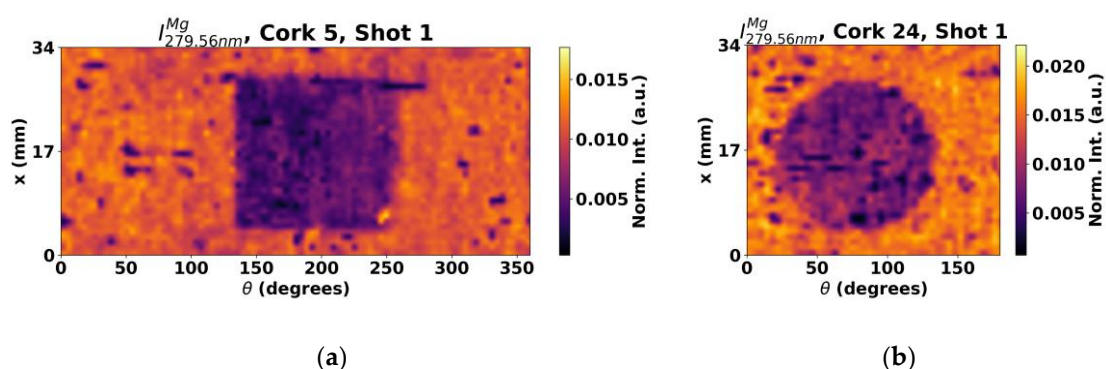


Figure 6.21 – Mg maps using the normalised intensity of the 279.6 nm line of (a) cork stopper 5 and (b) 24.

6.4.3. Depth analysis

To this point, the new LIBS system was tested as an imaging solution to evaluate the coatings' presence in a very extreme case of coating defects in order to not only revalidate the application of the technique but also to validate the system itself.

Indeed, for a real industrial application, the goal is to assess the overall quality of the surface treatment. This implies measuring both the thickness of the resulting coating and its uniformity, as an effective coating should evenly cover the entire cork stopper. Therefore, LIBS effectiveness for this application depends on its ability to perform depth analysis using its micro destructive nature by firing several shots per spot[29,30].

The strategy to assess thickness relies on the fact that successive laser shots will gradually ablate the surface, providing an in-depth profile of the coating distribution. As the shots progress, they approach the base cork, reducing the contribution from the coating elements and causing the intensity of the coating signals to fade. In Figure 6.22, this hypothesis is confirmed by the data obtained from cork stopper 24. The normalised intensity of the 288.2 nm Si line in the treated region decreases with consecutive shots, eventually nearing the values obtained in the untreated region, indicating that coating was penetrated. A similar effect is observed in the Ti case (Figure 6.22(b)).

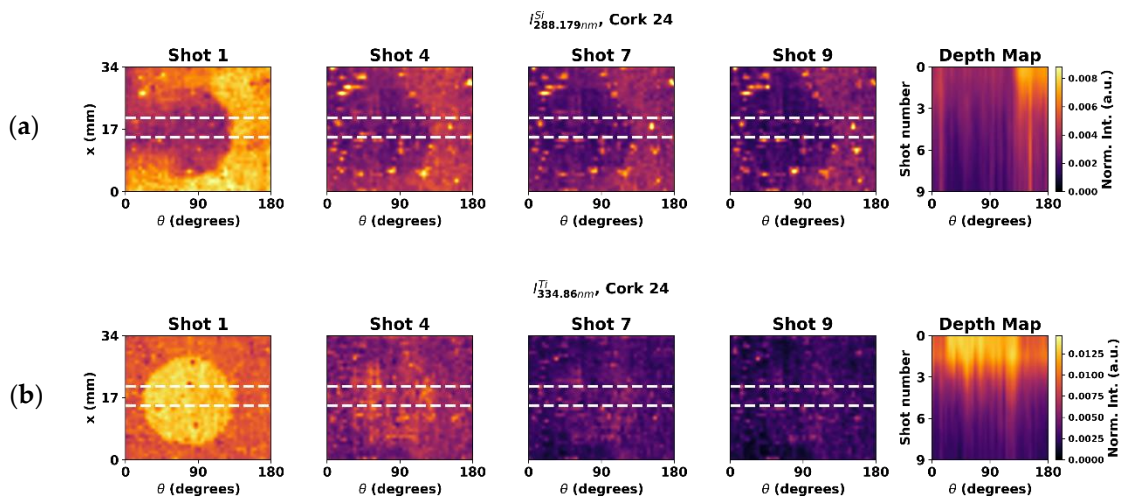


Figure 6.22 – (a) Si and (b) Ti normalised intensity maps of the cork stopper 24 using the 288.2 and 334.9 nm lines, respectively, for a few shot numbers, corresponding to different depths, and depth map at the rightmost column using the average intensity calculated for the area demarked by the dashed lines.

6.4.4. Discussion

Replicating the results from the preliminary tests reinforces the position that LIBS is a good candidate for evaluating the quality of surface treatments in cork stoppers. The success of these tests validates the initial assessment of the system's performance and highlights its potential for broader applications.

As anticipated, Si lines proved useful for imaging the silicone-based coatings, confirming their role as reliable indicators. Exploring new grounds with the system, an attempt to analyse the paraffin coating yielded positive results. Using the available C

line, it was possible to image the paraffin coating. However, these results indicate that a more complex analysis might be necessary. The presence of C in both the cork stoppers and the paraffin contributes to lower contrast and sensitivity, suggesting that additional methods or calibration may be required to enhance accuracy.

Alternatively, indirect methodologies using other elements showed potential for evaluating surface treatments. For instance, Ti emission was more intense in untreated regions. While tracking Ti emission lines may not be the most reliable method to infer the quality of the surface treatments or identify them, it presents a promising avenue for further research due to its apparently immunity to cross contamination and thin coatings. Similarly, Mg analysis could serve as a secondary option if the surface treatment contains this element, providing another means of identifying the coating.

With the new and automated system, a fairer comparison in terms of operational time can be made against the current methods, in which LIBS outperforms significantly. Depending on the methodology and coating, current times range from 2 to 24 hours per sample. In contrast, the LIBS system managed to analyse the largest map grid (Sample 5) in around 2 hours. This grid was an overdetailed analysis; in an industrial setting, the number of analysed spots is expected to be fewer than 100, which would drastically reduce the already superior time compared to current methods.

The depth analysis was replicated, demonstrating that the Si signal decays with the number of shots that progressively penetrate through the coatings. This indicates the potential of LIBS for analysing coating thickness and uniformity. This promising result warrants further study with fresh samples with a fully optimised system, as discussed in the next chapter.

6.5. Concluding remarks

This chapter presented a LIBS system prototype designed for the novel application of analysing functional coatings on cork stoppers through surface treatments. The system, developed in cooperation with EGITRON and Azevedos Indústrias, was automated for efficient analysis using the LIBS technique.

Despite being under development during its initial experiments, the system not only replicated previous results but also expanded upon them. It successfully imaged the silicone coating using Si and the paraffin coating using the distinctive C proportions of cork and paraffin. Multiple shots per spot also established the potential for depth analysis, demonstrating the system's viability for comprehensive coating analysis.

Following these validation results, the system optimisation towards a truly functional industrial prototype will be address in the next chapter. The system parameters will be optimised with fresh samples. A complete real case study of surface treatment will be conducted. Using the concept of the depth analysis, a methodology with adequate metrics will be developed to provide practical measures that can potentially represent the coatings' characteristics, namely their thickness and uniformity.

Chapter 7

System optimisation and development of metrics for coating analysis

7.1. Introductory remarks

The previous chapter detailed the development of a new LIBS system specifically designed for analysing coatings deposited on cork stoppers, demonstrating promising results through the mapping of coated and uncoated areas on the cork surfaces. This system showcased the potential for imaging silicone and paraffin-based coatings using their characteristic elements, providing a strong foundation for further analysis.

While these initial results were encouraging, the test samples were specifically altered with significant variations in the amount of treatment to highlight contrasts. In real industrial applications, the goal is to achieve a perfectly uniform coating. Thus, it is essential to assess the uniformity and, if possible, the thickness or overall intensity of the coating across the entire surface. The positive findings from the previous work underscore the feasibility of conducting such detailed analyses.

This chapter focus on the ongoing development of metrics to assess the thickness and uniformity of coatings. It begins with a description of the optimisation process, using new samples with various surface treatments to identify the best operational parameters and improve the system performance. The chapter then progresses to the development of metrics for estimating the thickness and uniformity, using new samples with silicone coatings subjected to different treatment parameters. Finally, an update on the current state of CorkSurf project is provided, including recent results, and concluding with remarks on future work.

7.2. System optimisation

To ensure the system's effectiveness for analysing cork stoppers, several parameters were thoroughly tested and optimised. These parameters included the energy of the laser pulses, repetition rate, spectral range, and spectrometer delay relative to the laser pulse. The optimisation process was conducted using a case study representative of industrial samples provided by CTCOR. These samples were prepared according to best practices but varied in treatment parameters to reflect different coating qualities, as

detailed in Table 7.1. These samples were subsequently used both for optimising the system and for establishing metrics to assess coating quality.

Table 7.1 – Treatment parameters for samples used in optimisation and quality assessment.

Type of treatment	Treatment	Code
Treatment A	Paraffin	A + sample number
Treatment B	Silicone	B + sample number
Treatment C	Paraffin + Silicone	C + sample number
No treatment	Cork stopper only	N + sample number

These treatments were applied to standard cork stoppers with the following characteristics:

- Stoppers with natural cork with a visual quality dubbed *Superior/Extra*;
- 45 and 24 mm of length and diameter, respectively;
- Volumetric mass of $175 \pm 20 \text{ kg/m}^3$;
- 5 to 7% of humidity;
- Hydrogen peroxide washing, light whitening (Sunrise type);
- Uncoated;
- Unmarked.

7.2.1. Optimisation of spectrometer selection and integration delay for coating analysis

Selecting the optimal energy for operation begins with identifying the spectral region that contains the elemental lines of the elements in the samples with the best SNR. Following this, the spectrometer integration delay in relation with the laser pulse must be optimised. The key elements to monitor in the samples are silicon and carbon, although hydrogen may be considered if it proves more useful than carbon.

Utilising the NIST database[95], the spectral ranges of interest for the target elements were determined and then checked against the coverage provided by the four spectrometers described in Table 5.4. Each type of sample was analysed under each available spectrometer using sequence of 50 single shots, taken along a line, at a fixed energy of approximately 10 mJ. The spectrometer delays ranged from 0 to 2 μs in 200 ns increments. Integration times were set to 30 μs , the minimum value, which exceed the plasma lifetime. The spectra obtained for each line sampled were averaged, and their baselines were corrected using an asymmetrical least squares algorithm[312,313].

As a criterion for establishing the suitability of a given line to be used for analysis, the presence of a peak and its SNR were considered. A peak with an SNR < 3 was considered not detectable. The first spectrometer, previously used with satisfactory results, covers the spectral range from 220 to 336 nm. This range includes several elemental lines for Si and C but none for H. For Si, significant lines at 251.6 and 288.2 nm, the two most intense according to the database, were easily identifiable when analysing cork stoppers with silicone or both paraffin and silicone, as illustrated in the average spectra in Figure 7.1 and Figure A.5. For C, the most intense line is at 247.9 nm, which is present in the average spectra of all sample types, as shown in Figure 7.2.

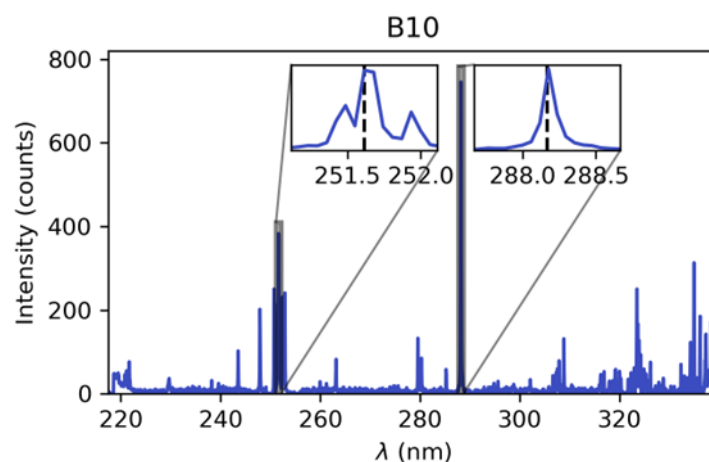


Figure 7.1 – Average spectra obtained with the first spectrometer for a cork stopper with a silicone coating, with zoom-ins on the 251.6 and 288.2 nm Si lines.

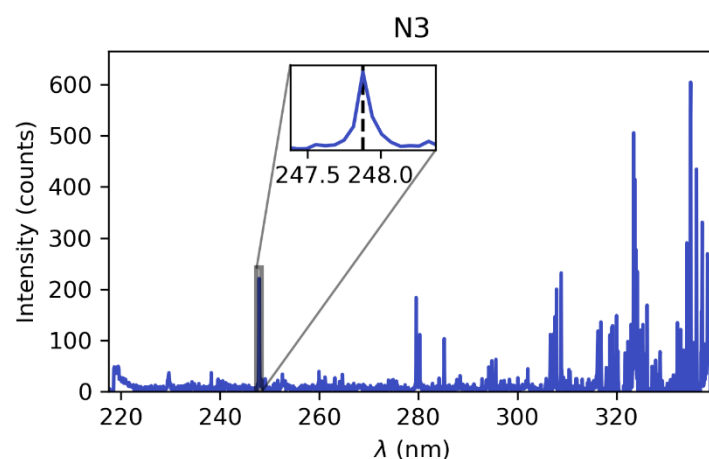


Figure 7.2 – Average spectra obtained with the first spectrometer for a cork stopper without functional coatings, with a zoom-in on the 247.9 nm C line.

With the second spectrometer, which has a range of 330 to 490 nm, additional elemental lines for Si, C and H were investigated. For Si, the strongest line appears at 390.6 nm, with other significant lines from Si⁺, including one at 385.6 nm. In an average

spectrum of a sample with a silicone coating (Figure 7.3), the 390.6 nm Si line is clearly detectable, while the 385.6 nm line is significantly interfered by a CN molecular band (multiple peaks around 385 nm, resulting from emissions from CN molecules formed during the plasma cooldown). For C, the most relevant lines are at 426.9 and 477.2 nm. These lines were not detectable in any samples; however, as stated before, the CN molecular band was detectable, and could potentially be used for analysis (Figure 7.4, left inset graph). Lastly, for H, the two most intense lines are at 434.0 and 486.1 nm. However, as with C, the H lines were not detectable in any sample (example in Figure 7.5).

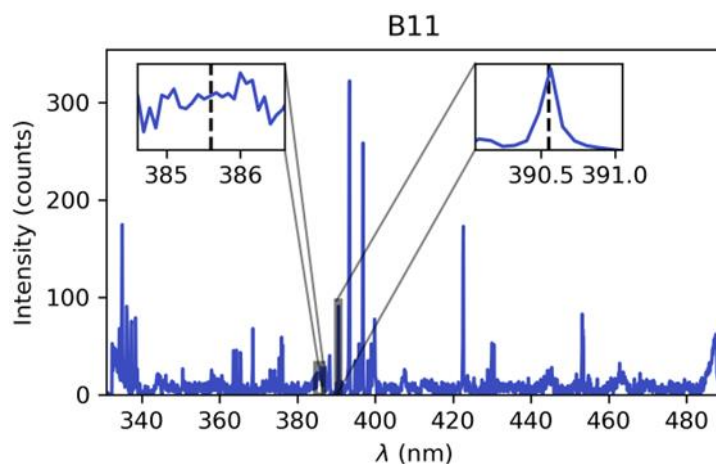


Figure 7.3 – Average spectra obtained with the second spectrometer for a cork stopper with a silicone coating, with zoom-ins on the 385.6 (not detected) and 390.6 nm Si lines.

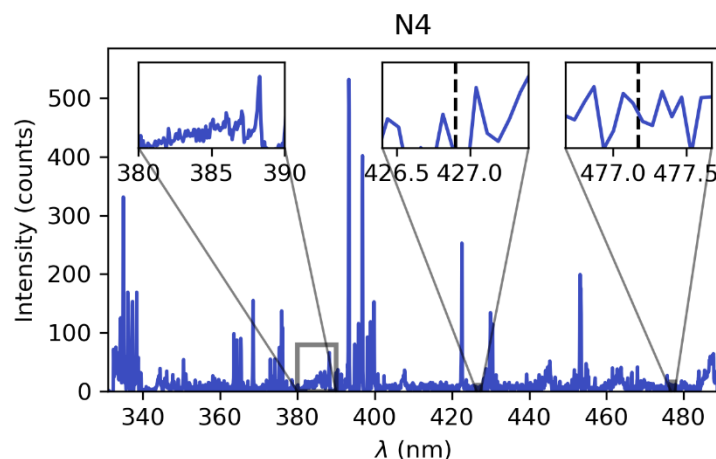


Figure 7.4 – Average spectra obtained with the second spectrometer for a cork stopper without functional coatings, with zoom-ins on the CN band around 385 nm and on the 426.9 and 477.2 nm C lines (both not detected).

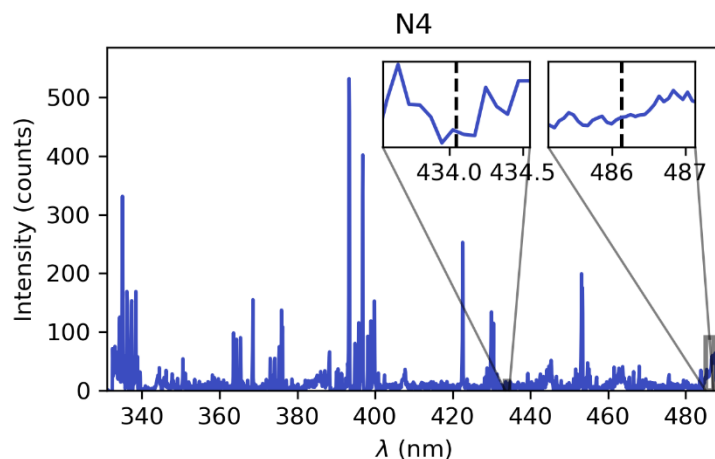


Figure 7.5 – Average spectra obtained with the second spectrometer for a cork stopper without functional coatings, with zoom-ins on the 434.0 and 486.1 nm H lines (both not detected).

In the third spectrometer, with a range of 480 to 615 nm, despite containing elemental lines for Si, C and H, no meaningful signal for Si lines could be detected in any of the samples (example in Figure 7.6), rendering this spectrometer unsuitable for this work.

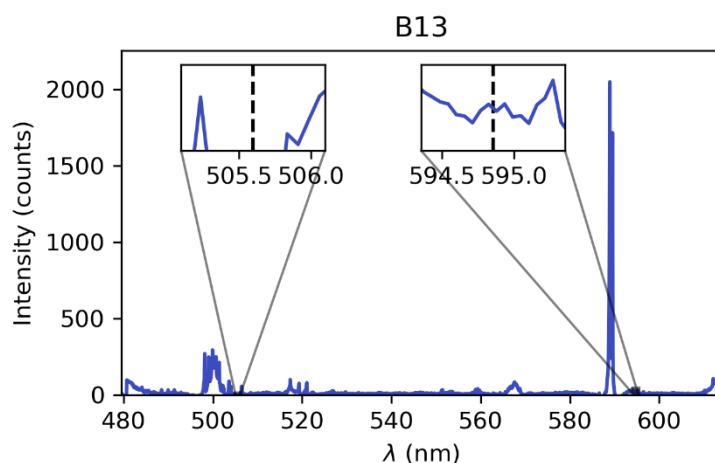


Figure 7.6 – Average spectra obtained with the third spectrometer for a cork stopper with a silicone coating, with two zoom-ins on the 505.6 and 594.9 nm Si lines (both not detected).

Lastly, the fourth spectrometer has a range of approximately 610 to 825 nm. In this range, Si, C and H have relevant emission lines. For Si, while the most intense lines are from Si^+ emissions, the strongest at 634.7 nm is the only one detectable in samples with a silicone coating (Figure 7.7), albeit at a very low SNR. For C, two lines have a significant intensity, 658.8 and 711.3 nm; however, no signal from either of these lines could be found in any type of sample (example in Figure 7.8). As for H, only one line is present in the range, at 656.3 nm, which can be easily spotted in every type of sample due to its large broadening (Figure 7.9).

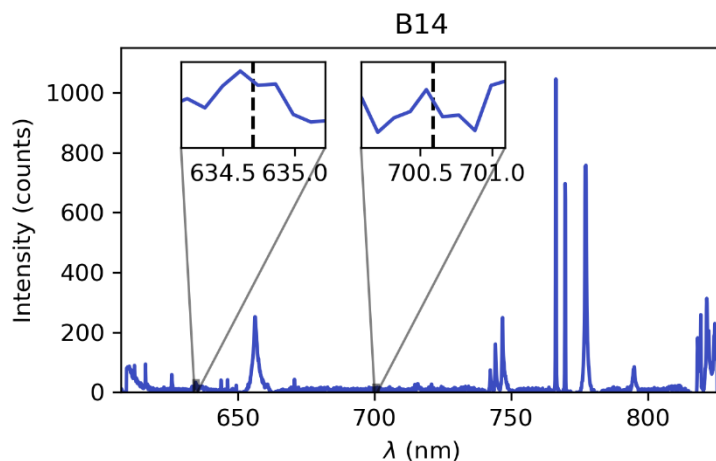


Figure 7.7 – Average spectra obtained with the fourth spectrometer for a cork stopper with a silicone coating, with zoom-ins on the 634.7 (detected) and 700.6 nm (not detected) Si lines.

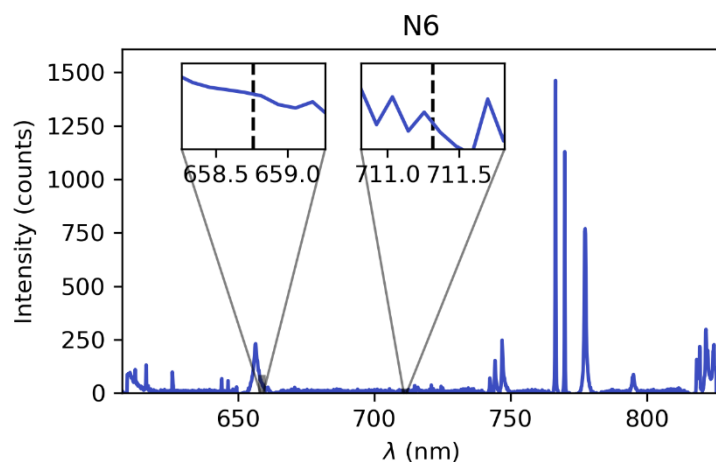


Figure 7.8 – Average spectra obtained with the fourth spectrometer for a cork stopper without functional coatings, with zoom-ins on the 658.8 and 711.3 nm C lines (both not detected).

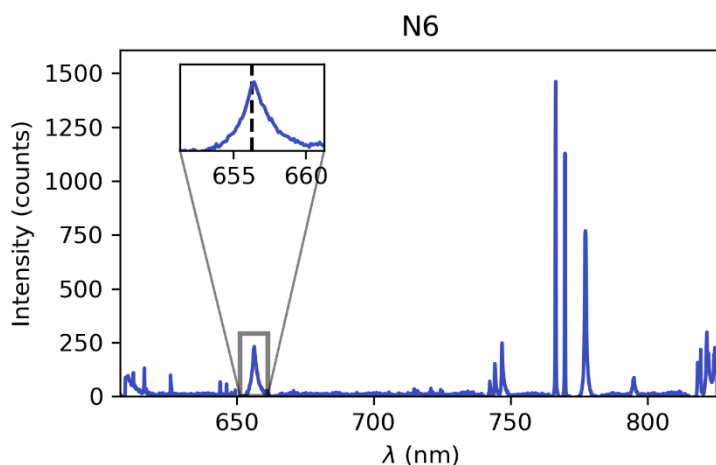


Figure 7.9 – Average spectra obtained with the fourth spectrometer for a cork stopper without functional coatings, with a zoom-in on the 656.3 nm H line.

Table 7.2 summarises the information discussed, facilitating the investigation of which of the spectrometers is the best choice for analysing the coatings deposited on cork stoppers. Out of the four available spectrometers, only three were viable for the intended purpose, but it is possible to conclude that the best option is the first one, which covers the spectral range from 220 to 336 nm. While it does not detect any H lines, it is not an eliminating factor as it can detect one C line and, in terms of SNR, it outperforms the remaining spectrometers for Si and C by a large margin, making it the best choice to add to the system. Plus, it is also worth noting that the Si lines on this spectral range are also detected on the paraffin coated cork stopper, making track these lines an alternative to the C line in case the latter fails to provide metrics to assess the coatings' quality.

Table 7.2 – SNR of the analysed lines related to Si, C and H across four spectrometers. * These potential lines have no visible peaks, SNR is caused by the presence of nearby peaks.

Spectrometers	Analysed lines	Median SNR			
		Treatment A	Treatment B	Treatment C	Treatment N
Spectrometer 1 220-336 nm	Si _{251.6 nm}	8.27	66.11	46.60	3.90
	Si _{288.2 nm}	13.21	128.09	75.59	3.75
	C _{247.9 nm}	32.48	34.56	30.25	36.32
Spectrometer 2 330-490 nm	Si _{385.6 nm}	4.93*	3.96*	4.19*	3.52*
	Si _{390.6 nm}	1.71	14.48	5.44	5.86
	C _{426.9 nm}	1.19	1.12	1.47	0.93
	C _{477.2 nm}	1.98	2.12	1.82	2.06
	CN _{388.29 nm}	11.65	6.32	7.92	10.62
	H _{426.9 nm}	2.13	1.89	2.03	1.55
	H _{426.9 nm}	5.89*	5.43*	5.90*	5.71*
Spectrometer 3 480-615 nm	Si _{505.6 nm}	0.87	0.33	1.28	0.27
	Si _{594.9 nm}	3.74*	3.99*	3.91*	4.09*
Spectrometer 4 610 to 825 nm	Si _{634.7 nm}	2.33	5.17	4.26	1.62
	Si _{700.6 nm}	2.49	2.43	2.33	2.18
	C _{658.8 nm}	9.82*	9.09*	8.81*	8.13*
	C _{711.3 nm}	1.85	1.83	2.13	1.31
	H _{656.3 nm}	40.34	38.49	34.66	33.81

Having chosen the spectrometer, a closer examination of the integration delay can now be conducted. By analysing the average spectra for different delays, it can be determined if there is any advantage to removing early plasma emission. Larger delays can help reduce the intense continuum emission, improving SNR, it can minimise Stark

broadening and improve the detection of low concentration elements. In this case, only the impact in SNR was investigated. Therefore, the SNR of each line was evaluated as a function of the integration delay time.

Some representative examples of the results obtained are shown in the Figure 7.10, where the SNR variations as a function of the integration delay are given for the 251.6 and 288.2 nm Si lines for a cork stopper with a silicone coating. Results for the 247.9 nm C line across all samples and for the Si lines in another sample, showing similar behaviour, are given in the Attachments, Figure A.31 and Figure A.32.

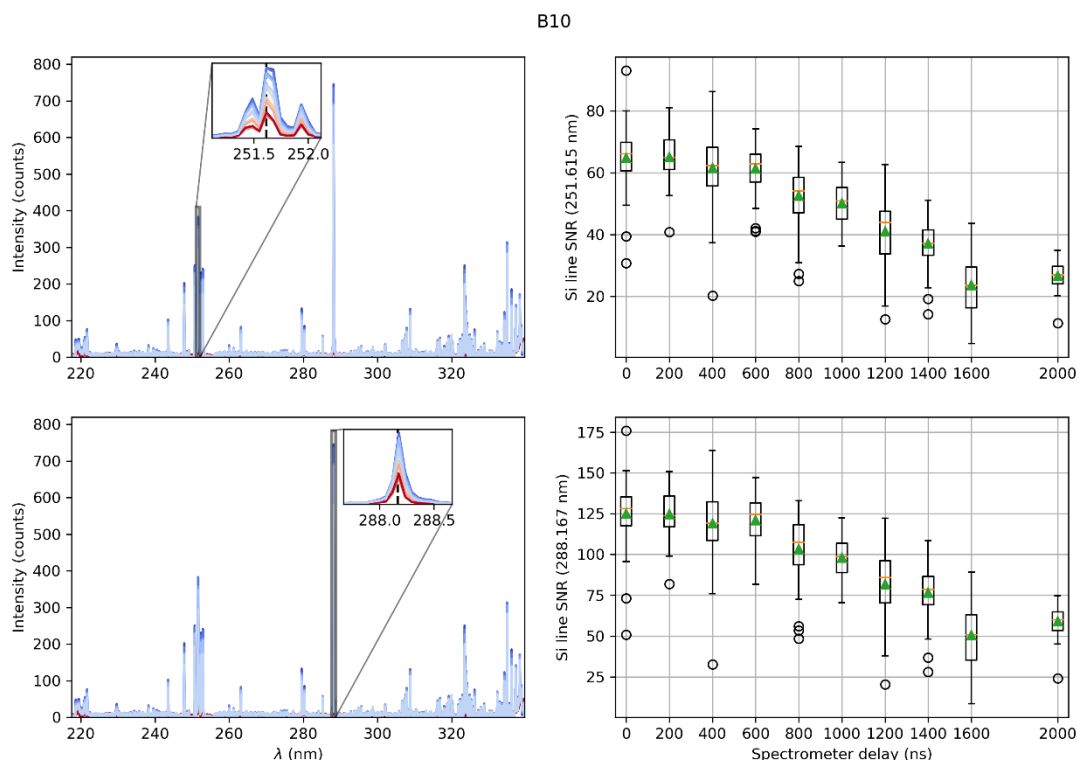


Figure 7.10 – Variation of the SNR of the Si lines, 251.6 and 288.2 nm, with the spectrometer delay for a sample with silicone coating.

The results show, in almost all cases, that the maximum SNR occurs at 0 or 200 ns of delay time, both with similar median SNR, decreasing very slowly for the first microsecond and then more rapidly. From the results in these studies, having no delay between the laser and spectrometer appears to be the optimal parameter as no discernible advantage in terms of SNR or signal variability can be attained by setting any delay. The advantage that could occur from setting a delay would normally be removing the continuous emission from the spectra, but that was solved by removing the baseline. Future refinement work may explore further the effects of the delayed integration, where a more detailed analysis can assess how different lines evolve with distinct lifetimes,

eventually identifying optimal parameters for specific target line. For the present work, zero delay time will be applied.

Considering the emission line selection for corks treated with silicone, the evaluation showed that both Si lines (288.2 nm and 251.6 nm) performed similarly. However, the 288.2 nm line was superior as it not only outperformed the 251.6 nm line in terms of detection capabilities but also avoided overlaps with other emission lines, which the 251.6 nm line presented. Therefore, based on the comprehensive assessment, the 288.2 nm line was selected as the optimal choice for tracking Si in corks treated with silicone.

7.2.2. Optimisation of pulse energy and repetition rate for enhanced SNR

To establish the optimal pulse energy, the primary criterion was the maximisation of the SNR. However, while using higher energy for analysis will, in principle, improve the SNR, exceeding a certain limit can lead to undesirable effects such as saturation or excessive surface damage, which would negatively impact the SNR and any future analysis. Additionally, since the thickness is being evaluated through partial ablation, SNR should not be the only criterion, as a high depth resolution is important for precise thickness measurements. Finally, when working at high repetition rates, limitations may arise due to secondary plasmas formed from previous pulses. Therefore, a study was conducted for the different samples to evaluate the best pulse energy that balances high SNR and repetition rate.

To begin this study, a preliminary assessment was conducted using silicone-coated cork stoppers previously used for exploratory work to identify any unforeseen setbacks. Four different pulse energies—9, 19, 30, and 40 mJ—were chosen for this purpose as they cover most of the energy range available. Each energy level was tested by analysing a line of 50 single shots.

Results obtained for selected Si and C lines can be observed in Figure 7.11 and, at a first glance, 40 mJ may seem the best option, as the SNR of both Si lines are the highest when using it. However, on closer inspection, some issues of using higher energies surface, one of them being the high variability of the signal and the other being the non-linear growth of the SNR with the pulse energy, which suggest that weaker energies may be more adequate for future analysis.

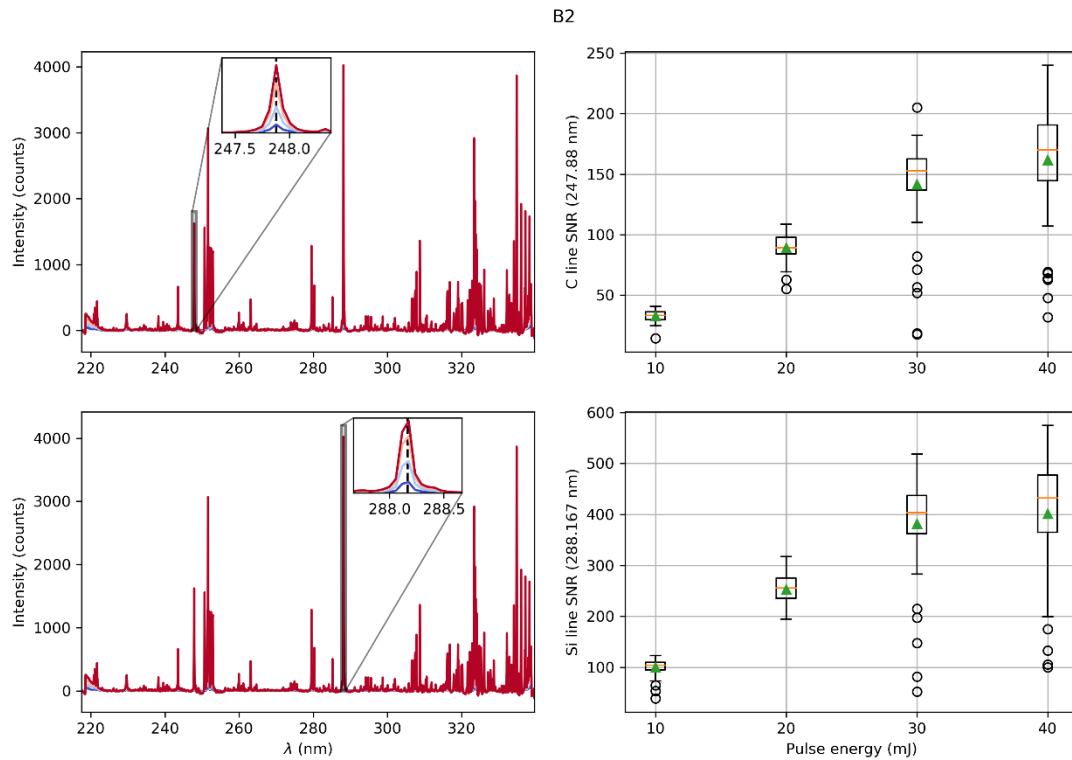


Figure 7.11 – Variation of the SNR of the 247.88 nm C and 288.2 nm Si lines with pulse energy, for a sample with a silicone coating.

Another issue with using higher energies is that they lead to larger craters and thus less depth resolution, so they should be avoided. Besides, and perhaps more crucial at this point, the speed of the analysis can also be limited by the excess of energy. Since time is very important in an industrial setting, optimally the repetition rate should be as high as possible. However, high energy combined with a high repetition rate can lead to plasmas forming on suspended particles (Figure 7.12). These secondary plasmas can produce spectra that do not accurately represent the layer and affect the ablated mass, leading to inconsistent analysis results. Therefore, considering the described effects, it is advisable to explore the use of lower energies, even if it means sacrificing some SNR.



Figure 7.12 – Secondary plasmas formed above the primary blast due to suspended particles.

Next, a more detailed analysis was performed for different repetition rates. Each energy was tested at different repetition rates, starting from 20 Hz, down to 1 Hz, in lines

of 50 spots, with 20 shots each. To ensure proper operation during the analysis, it was required to visually detect if plasmas were being formed in the air at any point. The results for the highest repetition rates for each energy level, for which no airborne plasma was detected, can be seen in Table 7.3.

Table 7.3 – Maximum repetition rate for each energy for cork stoppers with silicone coating.

Energy (mJ)	Maximum repetition rate (Hz)
9	7
19	2
30	<1
40	<1

For the experimented energies, the maximum repetition rate achieved with no secondary plasma formation was 7 Hz. This rate implies that completing 20 shots per spot would take almost 3 s, which is not deal when compared to the laser's maximum capability of 20 Hz. This limitation would significantly reduce the number of samples that could be analysed or the number of spots analysed per cork stopper, thereby compromising the reliability of the results for the sake of time-saving.

To improve the speed of operation, the addition of an airflow above the samples' surface was tested. This airflow could blow the ejected particles away from the laser's trajectory between shots, preventing secondary plasma formation at higher repetition rates. To test this hypothesis, the system was connected to a compressed air supply with a custom nozzle aimed over the samples (Figure 7.13). Developed by Azevedos Indústrias, this custom nozzle was designed to create a horizontal flow over the cork stoppers. To avoid a constant stream of compressed air, an air valve was installed halfway the nozzle and the compressed air supply. The valve can be controlled using electrical triggers to open and close and was connected to the PLC. This setup allowed for the compressed air to activate only when a burst of shots was made on a spot, a routine added to the automation protocol (Figure 7.14).

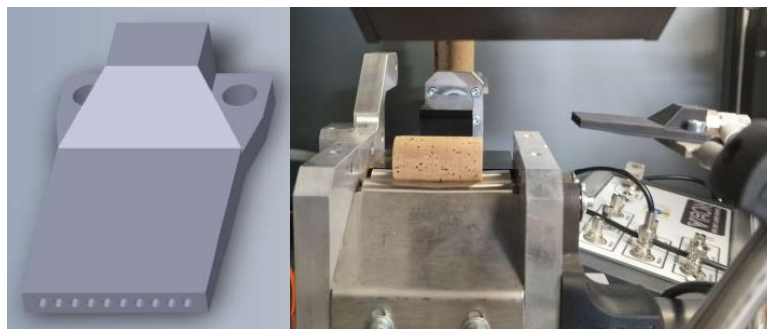


Figure 7.13 – (Left) 3D drawing of the custom nozzle and (Right) the custom nozzle aiming over a cork stopper.

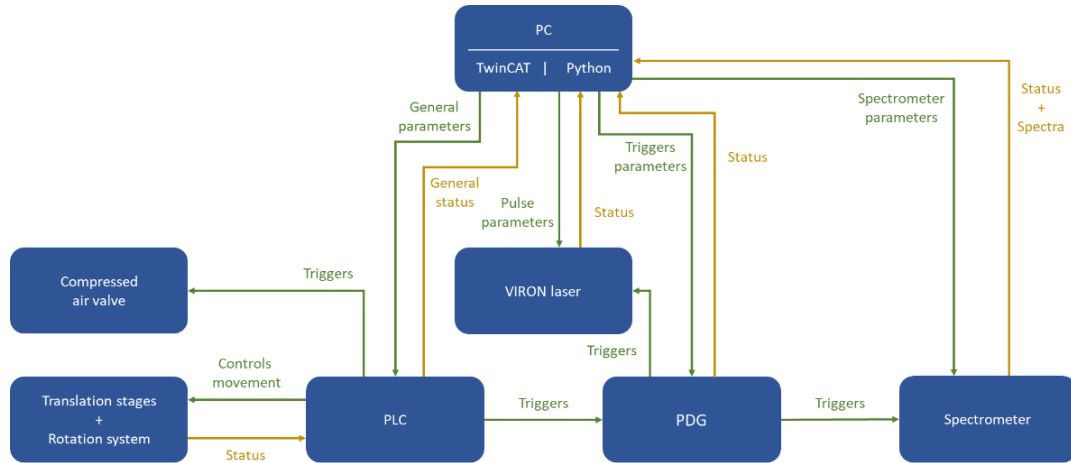


Figure 7.14 – Updated block diagram of automation, now with the compressed air valve.

With the introduction of the upgrade to the system, the energy optimisation process was restarted, now testing all sample types. The minimum energy level was reduced to 6 mJ to determine if it was possible to further increase the repetition rate. The results obtained for selected lines of C and Si were very similar in terms of the SNR values observed and their growth tendency with pulse energy (Figure 7.15, Figure 7.16 and Attachments). Similar to the previous attempt, a C and Si SNR growth tendency with pulse energy can be seen for all types of samples.

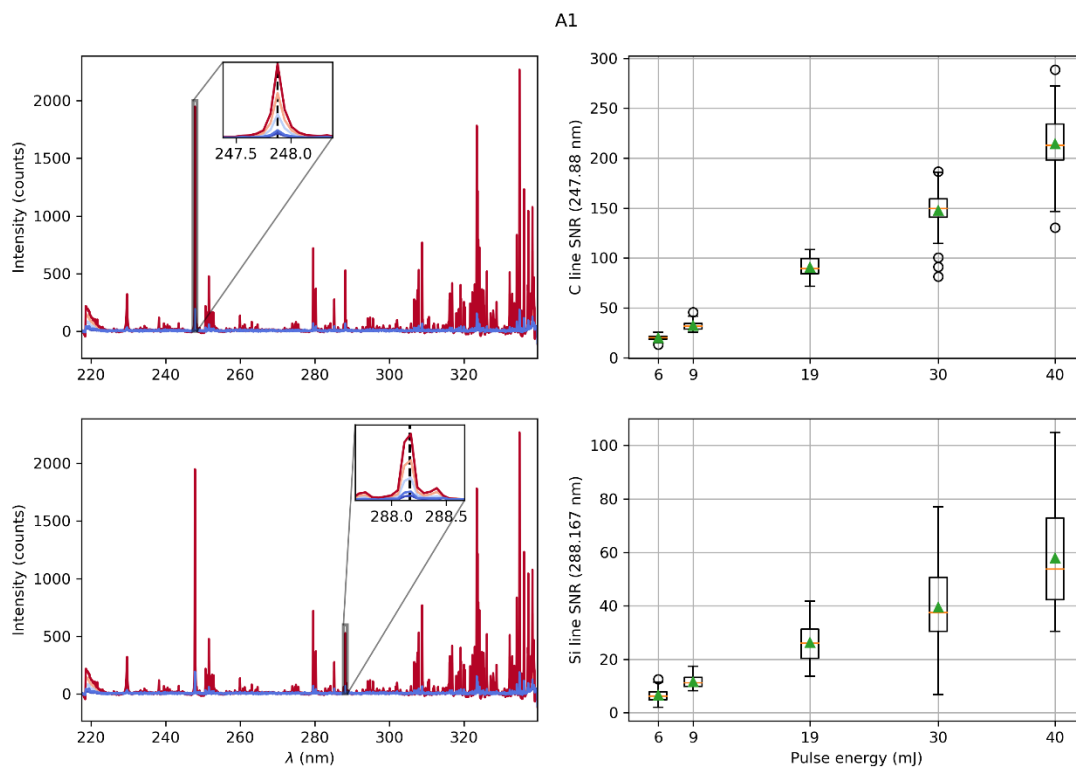


Figure 7.15 – Variation of the SNR of the 247.88 nm C and 288.2 nm Si lines with pulse energy, for a sample with a paraffin coating.

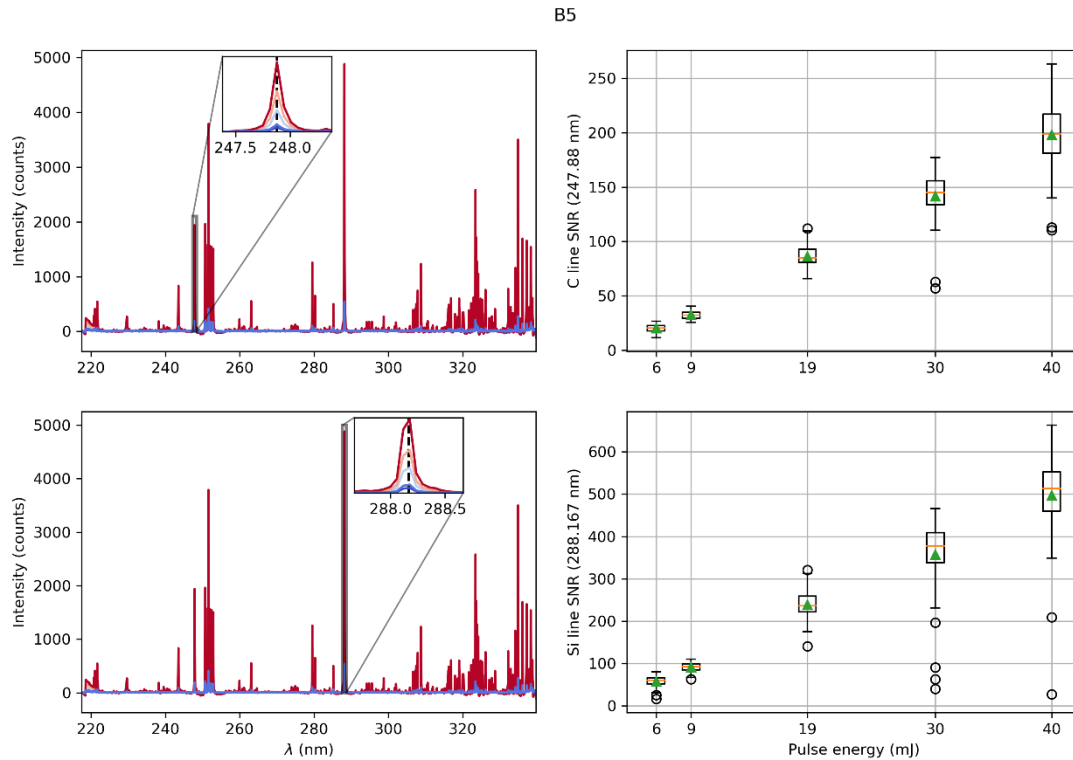


Figure 7.16 – Variation of the SNR of the 247.88 nm C and 288.2 nm Si lines with pulse energy, for another sample with a silicone coating.

With the new compressed air system, the tests of repetition rate as a function of energy were repeated (Table 7.4), to test its effectiveness.

Table 7.4 – Maximum repetition rate for each energy for each type of sample when using compressed air.

Energy (mJ)	Maximum repetition rate (Hz)			
	A	B	C	N
6	20	20	20	20
9	20	20	20	20
19	<1	1	1	4
30	<1	<1	<1	<1
40	<1	<1	<1	<1

Indeed, the repetition rate at 9 mJ and below could be increase to 20 Hz in all instances, putting the system at its maximum repetition rate.

Having achieved maximum repetition rate operation for 9 mJ and lower pulses, an attempt was made to analyse the craters and assess the depth resolution. Ten cork stoppers with a silicone coating were ablated with different numbers of shots and varying energy levels. However, due to difficulties in accurately analysing the craters, these tests were set aside and resumed later at CTCOR. Results related to the craters' dimensions

will be discussed later in the chapter. Therefore, 9 mJ was chosen as it delivered the highest SNR. Results related to the craters' dimensions will be discussed later in the chapter.

Having optimised the system parameters, the LIBS system was prepared to evaluate the coating thickness. The goal was to determine the system's capabilities and to develop a reliable metric for assessing coating uniformity. This involved systematically analysing the treated cork stoppers to measure variations in coating thickness and identify any patterns or inconsistencies related to the treatment process.

7.3. Assessing coating thickness and uniformity

When a cork stopper undergoes a surface treatment, the treatment product does not simply form a layer above its surface. Instead, the product infiltrates the surface and diffuses along the surface's cellular structures (Figure 7.17).

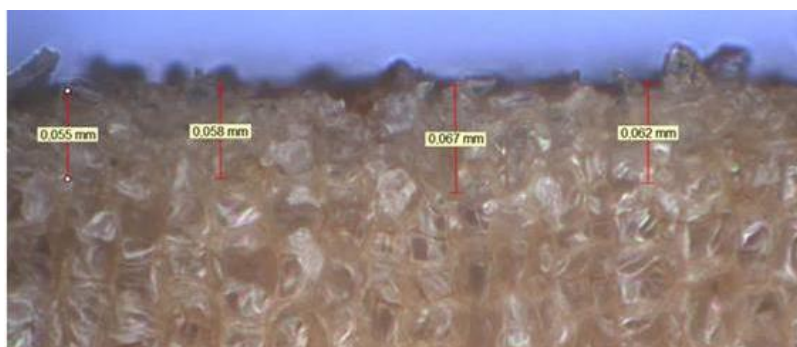


Figure 7.17 – Profile cut of a cork stopper that underwent a surface treatment, provided by CTCOR.

This layer of cork with the treatment product is what coats the rest of the cork stopper. Its thickness fluctuates along the surface depending on a variety of conditions and it is thus important to assess its uniformity. In each batch, the average thickness and the overall uniformity of all its coated cork stoppers are highly dependent on the treatment parameters.

Considering the results from Chapter 6, which showed poor contrast for paraffin-coated samples, and due to time restrictions, this study focused solely on cork stoppers with silicone-based surface treatments.

7.3.1. Treatment parameters and methodology

Two main treatment parameters are responsible for the characteristics of the resulting coatings, the mass of treatment product per cork stopper and the duration of the treatment process. To investigate if LIBS could assess the quality of each cork stopper

by extension of distinguishing between differently prepared corks, CTCOR prepared a set of samples with various silicone-based surface treatments. These samples had different treatment masses (5, 10 and 15 mg/cork stopper), and different durations of treatment (5, 10, 15 and 20 minutes) (Table 7.5). CTCOR also kept a share of samples of each type of treatment for standard analysis for comparison. In Table 7.4, the samples are labelled using a format where the first number represents the treatment mass and the second number corresponds to the treatment time. For example, in the label B5-10, '5' denotes the treatment mass, and '10' indicates the treatment time, allowing for straightforward identification and comparison of the different treatment conditions applied to each sample."

Table 7.5 – Types of silicone-based treatments and their codenames for the experiments.

Treatment duration (min) \ Treatment mass (mg/cork stopper)	5	10	15	20
5	B5-5	B5-10	B5-15	B5-20
10	B10-5	B10-10	B10-15	B10-20
15	B15-5	B15-10	B15-15	B15-20

Again, these treatments were applied to standard samples with the following characteristics:

- Stoppers with natural cork with a visual quality dubbed *Superior/Extra*;
- 45 and 24 mm of length and diameter, respectively;
- Volumetric mass of $175 \pm 20 \text{ kg/m}^3$;
- 5 to 7% of humidity;
- Hydrogen peroxide washing, light whitening (Sunrise type);
- Uncoated;
- Unmarked.

With the optimal system parameters defined, the analysis procedure involved analysing 10 samples of each type of treatment. Each sample was examined using a 10x6 grid of points on its cylindrical face, avoiding the 5 mm at each top of the cork stopper (Figure 7.18). 20 shots per point were selected to provide data for the depth study.

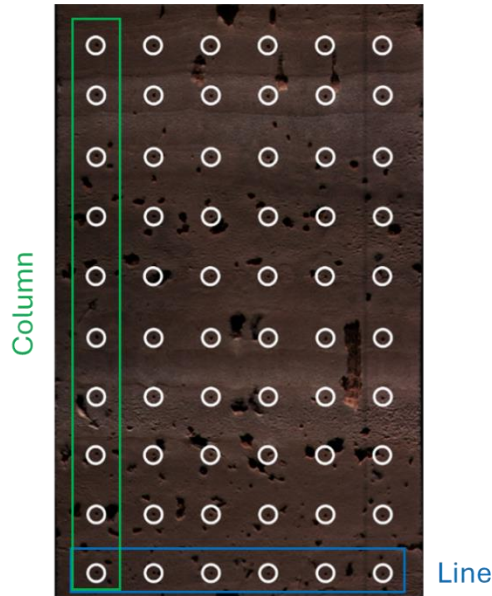


Figure 7.18 – Image obtained using the vision system of a typical cylindrical face after analysis. Circles mark the craters formed in a 10x6 sampling grid.

Lastly, all spectra were subject to a signal pre-processing. Starting with background removal, their baselines were removed using an asymmetrical least squares algorithm[312,313]. This was followed by a noise extraction from each spectrum to calculate the SNR for Si line (288.17 nm) and for the C line (247.89 nm) of each spectrum. The C line was used for control and to evaluate the potential for, the latter being used for control and possibly normalisation.

7.3.2. Creating metrics for assessing coating thickness and uniformity

Developing metrics for assessing the coating thickness and uniformity, requires establishing a link between the LIBS results and the treatment parameters. Similar to the approach used in Chapter 6 (Figure 6.22), a depth map for an individual line of points can be created. This involves i) obtaining the SNR of the 288.17 nm Si line from multiple shots that ablate the sample's surface. ii) using this SNR data to generate depth maps that show the distribution of the coating along the surface. By analysing these depth maps, the effect of treatment parameters on the coating's thickness and uniformity can be better understood. Figure 7.19 show the results obtained along line 5 of the analysis grid. On the left, it displays a map of the SNR as a function of depth and position along the line. This visual representation helps in assessing the distribution and consistency of the silicone coating.

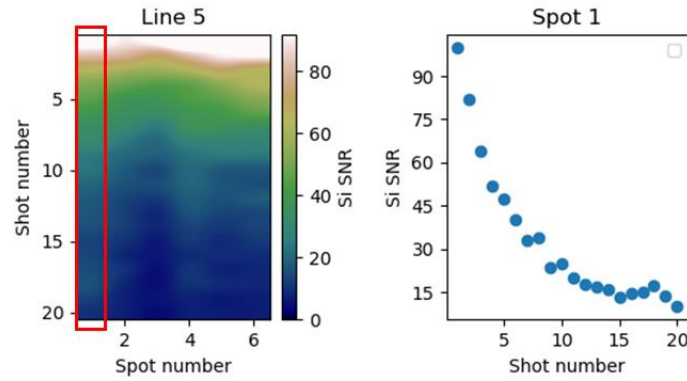


Figure 7.19 – (Left) Si SNR depth map for the fifth line of a B15-10 sample, smoothed for better visualisation, and (Right) Si SNR for each shot of the first spot of the fifth line, the region marked in red in the left figure.

It is clear that the SNR of the Si line decreases with the number of shots, with some slight variations between each spot, as demonstrated in Figure 7.19 (Right). This suggests that the multiple shots are progressively ablating the silicone coating. However, this decrease in SNR could also be due to the laser digging deeper into the material, thus reducing the SNR regardless of the presence of silicon. To investigate this further and rule out the latter hypothesis, the behaviour of the SNR of the C line was also tracked (Figure 7.20).

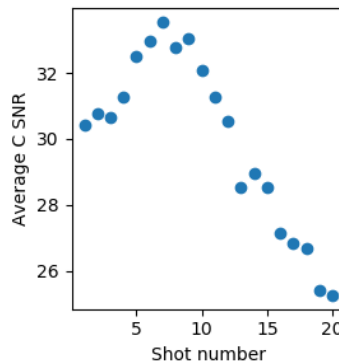


Figure 7.20 – Average SNR of the 247.89 nm C line for each shot for the same B15-10 sample as in Figure 7.19.

In every sample of each type, a drop in the average SNR of the C line was observed after a few shots. Unlike the Si line, the average SNR of the C line fluctuates and even increases during the first five shots before dropping. In contrast, the SNR of the Si line consistently decreases, likely following an exponential decay. This behaviour suggests that the two effects, progressive ablation of the silicone coating and the increasing depth of the hole, coexist. Therefore, normalisation using the C line could potentially correct for these effects and improve the results, although this method would not be viable for future tests on paraffin coatings, it can be applied to the silicone ones.

Through the visual analysis of the depth maps, some outliers were detected. Two main types are illustrated in Figure 7.21. The first type, shown at the top, involves weak detection of Si, where the signal curve starts at a very low SNR value or is sometimes non-existent. These cases are due to natural craters in the cork stoppers. Since a grid of points is used, it is probable that one of the analysed spots lands on a crater, leading to these outliers.

The second type, shown at the bottom, involves a persistently high Si SNR, where the SNR drops very slowly and sometimes does not reach values that would indicate crossing the silicone coating. These cases are harder to explain. In some instances, they occur at the edges of craters, suggesting that an accumulation of coating might cause these high SNR values, which could potentially be discarded from the analysis. Other instances have no discernible physical reason, indicating that they could be a sign of uneven deposition and should be considered in the analysis.

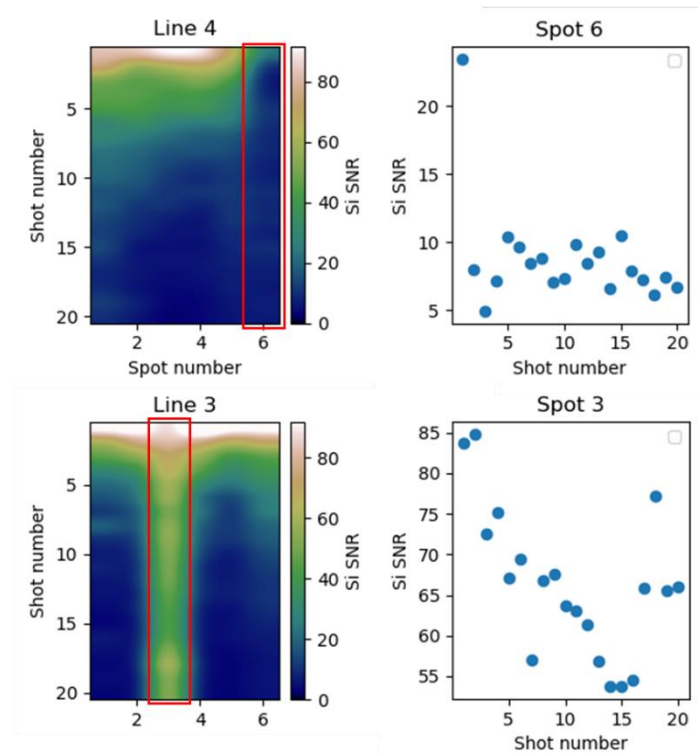


Figure 7.21 – Outliers related to (Top) a spot landing on a natural crater and (Bottom) an accumulation of silicone.

Taking all these observations into account, the study can proceed to search for a link between the depth curves and the treatment parameters. Overall, the results demonstrate a strong capability to reveal the depth distribution of the coating. This capability extends to detecting outliers that may be defects in the coating, whether

natural or otherwise. Thus, the next step is to extract metrics or merit parameters from this data to enable an easy assessment of the coating quality.

Aiming to distinguish between two different treatments, two samples with different treatment masses but the same treatment duration were analysed. Figure 7.22 shows the Si SNR at a given spot as a function of the shot number, for two types of samples (B5-20 and B15-20). It can be observed that their average decay curves behave differently, prompting the need to search for a metric that can easily distinguish between both cases.

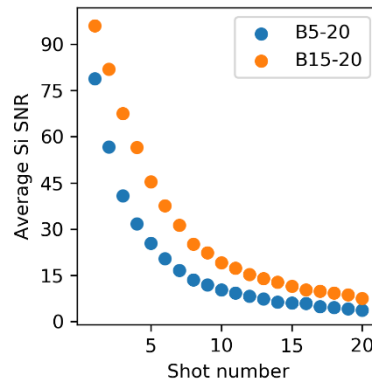


Figure 7.22 – Comparison between the average depth curve of a B5-20 and a B15-20 samples.

Since the intensity of the Si line drops at different rates for two different treatment masses, a threshold can be set to mark how many shots are necessary to reach it. This threshold can be used as a metric to distinguish treatment masses and, by extension, possibly thicknesses (Figure 7.23).

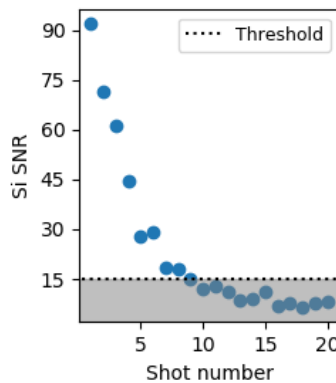


Figure 7.23 – Example of a decay curve marking the point at which the predetermined threshold is crossed, representing the limit of the treatment.

Preferably, the threshold would be determined through visual analysis of the progressively ablated crater. This involves recording the number of laser shots needed

to ablate past the coating and noting both the shot number and the corresponding SNR. However, as previously mentioned, physical inspection of the damage was not feasible at the time. Therefore, the threshold was set by identifying the base value of the decaying curve, which is the value to which the signal converges, and then adding a predefined margin to it. In practice, when using SNR as the metric, the threshold was defined as an SNR of 15. For the Si to C ratio, the threshold value was set at 0.5 for the normalised case.

With these metrics for SNR and Si/C established, the next step involved testing the samples and applying this evaluation to the results. Figure 7.24 shows the results obtained for a B15-5 sample, which represents a set of samples with a surface treatment of 5 minutes using 15 mg of silicone per cork stopper. Rather than obtaining a consistent measure of the thickness (indicated by the number of shot to threshold), a distribution of values was observed. This suggests that an individual spot measurement cannot accurately represent the mass of the treatment. Therefore, it is more meaningful to analyse the distribution, including its average, median, and width, rather than single values.

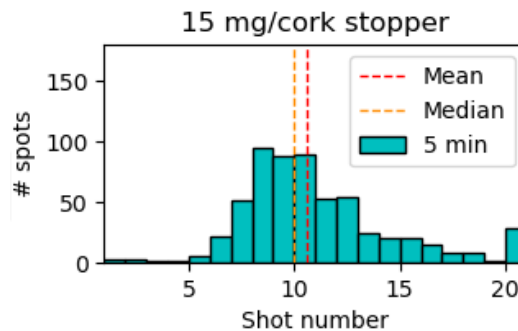


Figure 7.24 – Histogram showing the distribution of the number of laser shots required to reach the SNR threshold for the Si line, measured across the surface of cork stoppers treated with 15 mg of silicone for 5 minutes.

To find a relationship to the treatment mass, two metrics were considered: the mean and the median of the distributions. However, since only 20 shots were used per spot, spots where the threshold was not reached were set to 21 to indicate that the actual threshold was not crossed. The presence of these “artificial” values, along with several outliers, distorts the mean, making the median a more appropriate metric. Thus, the median number of shots to reach the threshold against the treatment mass was evaluated for all samples. In the plots of Figure 7.25, it can be seen that both the SNR (left) and the Si/C normalised parameter (right) show a clear dependence on the treatment mass, as measured by the median number of shots necessary to reach the

threshold. Higher treatment masses consistently result (with some minor exceptions) in an increase in the observed medians, indicating a coating with higher thickness.

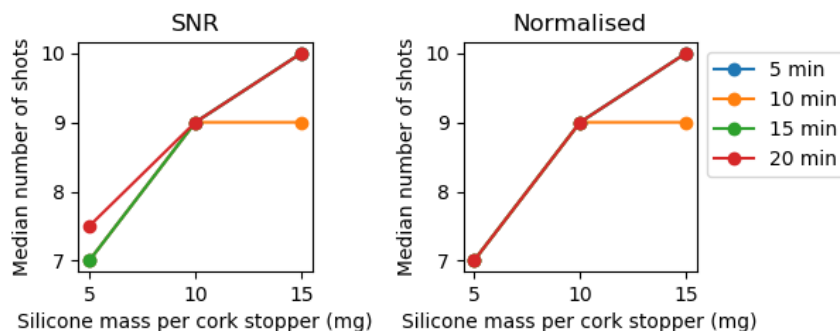


Figure 7.25 – Plots showing the median number of shots required to reach the threshold against the treatment mass for the SNR and normalised Si/C cases.

While not perfect, this method appears to be capable of distinguishing between distinct treatment masses. However, as seen from the plots, simply counting the shots is somewhat limiting for the median, as it deals with discrete values. In some cases, the threshold may lie closer to the value of the shot just before it is breached than to the value of the shot that actually breaches it. To address this, a linear interpolation between the two points is executed to estimate a more accurate shot number that intercepts the threshold, leading to the results in Figure 7.26.

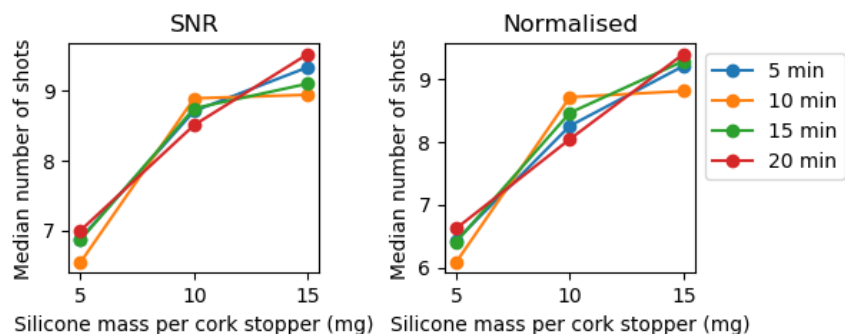


Figure 7.26 – Plots showing the median number of shots required to reach the threshold, using linear interpolation, against the treatment mass for the SNR and normalised Si/C cases.

The results indicate that the median number of shots is a viable metric for determining the treatment mass used on a cork stopper, with interpolation further enhancing this prediction. Given that the thickness of the coating is correlated with the treatment mass, it is reasonable to infer that the median number of shots can also serve as a metric for estimating coating thickness.

However, to robustly link this metric to actual coating thickness, it must be calibrated against direct measurements of thickness. While this was not possible within the current scope, this calibration is being addressed in the ongoing CorkSurf project and will be briefly mentioned later in this chapter.

A critical challenge remains in assessing the uniformity of the coating. Variations in thickness across the surface determine this uniformity. If the median number of shots to reach the threshold is indicative of thickness, its distribution could provide insights into uniformity. Therefore, analysing the distribution of shot numbers for each sample type is essential and can eventually provide a metric for uniformity. The threshold shot distribution for all samples tested, including all masses and all treatment times, can be seen in Figure 7.27.

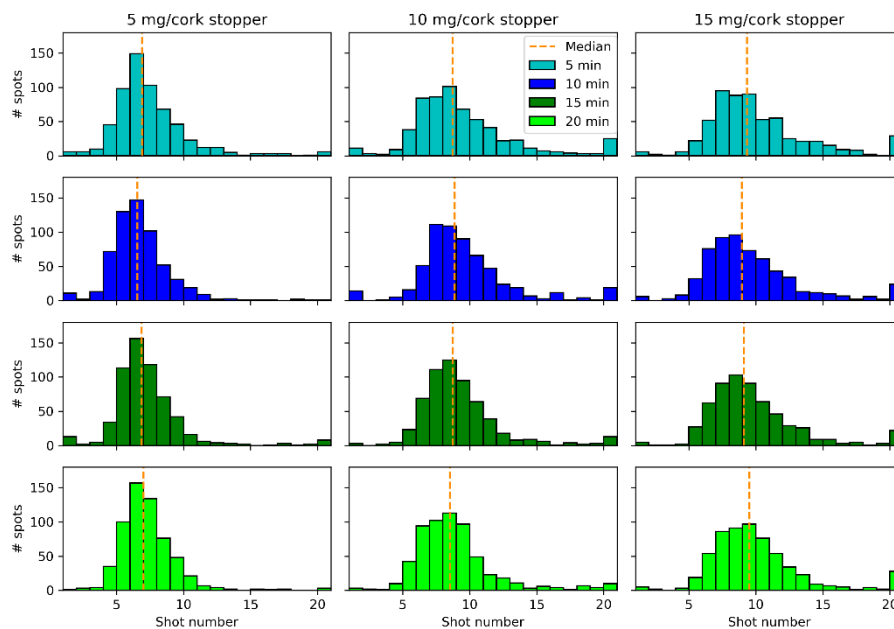


Figure 7.27 – Histograms showing the distribution of the number of laser shots required to reach the SNR threshold for the Si line, measured across the surface of various types of coated cork samples.

One expectation of a longer surface treatment duration is that it will lead to a more uniform coating. This is supported by the histograms, which show a narrower distribution of the number of shots as the treatment duration increases. Additionally, though less obvious, the mass of the treatment also affects the distribution, causing it to widen with increasing mass per cork stopper. Typically, the standard deviation is a good indicator of distribution width; however, it is not the best representation here for the same reasons as the mean before. Instead, since the median is being utilised, the interquartile range (IQR), the difference between the third and first quartiles of a distribution, can effectively represent the spread. The IQR is more robust to outliers, making it a suitable choice for

this analysis. The relationship between the IQR of the number of shots to reach the threshold and both the treatment time and treatment mass is depicted in Figure 7.28. Overall, the results indicate that the IQR is useful for extracting tendencies related to increasing mass or time.

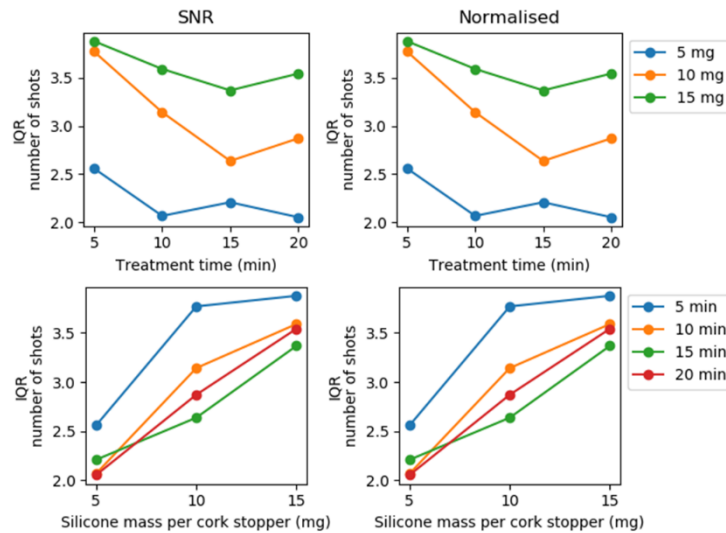


Figure 7.28 – Plots of the IQR of the number of shots to reach the threshold using linear interpolation against the treatment time and treatment mass for the SNR and normalised cases. The top plots show the relationship between treatment time and IQR, while the bottom plots display the relationship between treatment mass and IQR. Each pair of plots includes results for both the SNR (Signal-to-Noise Ratio) and normalised conditions, highlighting the relationship between these variables.

While the IQR generally shows a decreasing trend with increasing treatment time (indicating improvement in homogeneity with increasing time), an increase is observable at the 20-minute mark for the 10 mg and 15 mg cases. This can either be related to outliers or may indeed show that too much time or too much mass could be deleterious to uniformity. Confirming the observation made from Figure 7.27, the results also show that the distribution is dependent on the silicone mass per cork stopper as well, widening with the increasing mass. This suggests that more treatment time may be needed to achieve even coatings, or that increased mass leads to thicker but less homogeneous distributions.

Given the lack of information from standard methods, insights from LIBS are valuable and should be further investigated. However, these results should be approached with caution because there are a significant number of outliers. Removing these outliers can potentially improve the accuracy of the results.

One method to flag outliers is using Tukey's fences[356]. Tukey's fences set two limits, which are calculated as 1.5 times the IQR beyond the first quartile (Q1) and the third quartile (Q3). Any values that fall outside these limits are considered outliers. Applying

this method, extreme values that might skew the results can be identified and excluded. Figure 7.29 presents the histogram with the distributions obtained without these flagged outliers, offering a clearer view of the underlying trends.

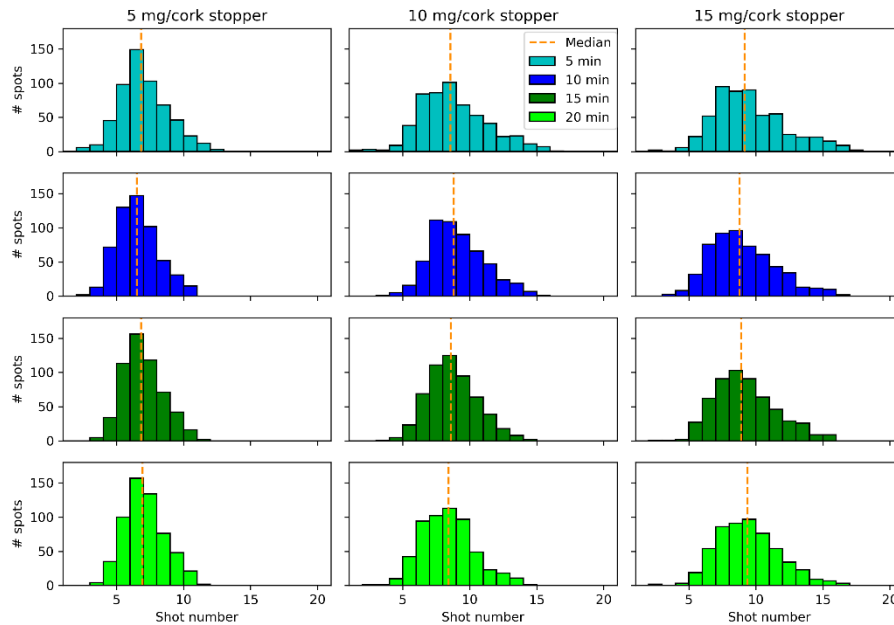


Figure 7.29 – Histogram showing the distribution of the number of laser shots required to reach the SNR threshold for the Si line, measured across the surface of various types of coated cork samples, without outliers.

With the removal of outliers, the distributions now resemble a Poisson distribution more closely. While it might be justifiable to use the mean and standard deviation given the absence of outliers, to maintain methodological consistency and allow for comparison with the previous analysis, the median and IQR will continue to be used.

Looking at the reprocessed data of SNR and Si/C normalisation, it is evident that the same tendencies persist in both cases with and without outliers: the median increases with the treatment mass (Figure 7.30).

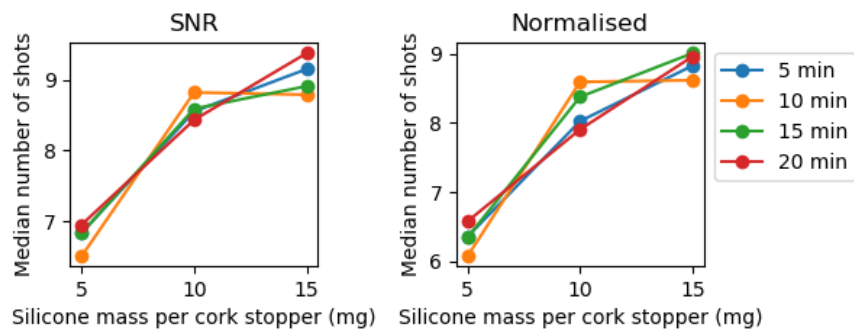


Figure 7.30 – Plots of the median number of shots to reach the threshold using a linear interpolation without outliers against the treatment mass for the SNR and normalised cases.

In the same manner, the distributions seem to behave similarly to the case with outliers, narrowing with the increasing duration of the treatment and increasing with the treatment mass (Figure 7.31).

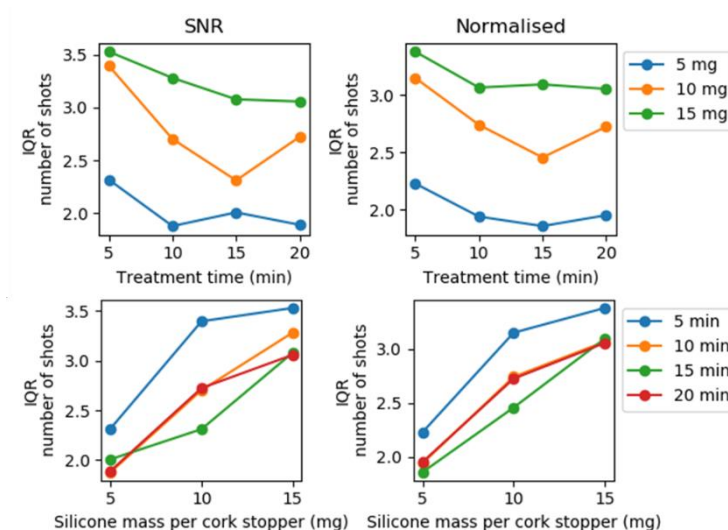


Figure 7.31 – Plots of the IQR of the number of shots to reach the threshold using linear interpolation against the treatment time and treatment mass for the SNR and normalised cases, without outliers. The top plots show the relationship between treatment time and IQR, while the bottom plots display the relationship between treatment mass and IQR.

7.3.3. Evaluation of metrics and sampling considerations

Although the expectation was that removing the outliers would improve the results, this did not occur. Instead, the results have slightly worsened in some cases, suggesting that certain outliers may indeed be crucial. This indicates both the inherent complexity and variability of the LIBS technique, as well as the intrinsic variability in the coating process, which LIBS is capable of detecting.

Despite some uncertainty, the results presented show a promising path for evaluating the characteristics of coatings using LIBS. The metrics identified, namely the median and IQR, appear to effectively distinguish between different silicone-based surface treatment parameters, despite significant overlap in data distribution.

Before delving into the metrics, it is worth noting that normalising the spectra to the intensity of the C line provides little to no improvement in the results. Given that other coatings of interest will also rely on the C line, it is safe to conclude that the normalisation step can be discarded.

Focusing on the metrics, the median has demonstrated the ability to differentiate between treatment masses, although it struggles with the 10-minute samples. This issue may be due to factors external to the LIBS analysis, such as inconsistencies in the

samples themselves. Moving to the IQR, while it successfully distinguishes between different durations of treatment, it is also affected by the treatment masses. Therefore, the median is necessary to accurately identify the correct duration of treatment. Overall, using both parameters provides a good estimate of sample quality.

It is important to note that these metrics depend on the sampling size. The number of samples and points per sample is critical. Since dealing with statistical metrics, a much more detailed study with a larger dataset is necessary. This will help determine the required minimum sampling size in an industrial setting to ensure reliable results without compromising operation time. Future analysis should focus on identifying the optimal sampling size to balance accuracy and efficiency in industrial applications.

To ensure the robustness and reliability of the LIBS results, it is essential to validate these findings against a known standard. Establishing a ground truth by comparing the results with a reference technique can provide insight into the origin of the variability and validate the LIBS results. Such analyses were made by CTCOR and are presented next.

7.3.4. Comparison with reference techniques to validate LIBS results

To validate the LIBS results, samples from the same lot were evaluated using industry-standard techniques, specifically ATR-FTIR and chemical extraction using organic solvents. These techniques are considered the gold standard in the industry for evaluating coatings on cork. The analyses were performed by CTCOR.

For the ATR-FTIR analyses, five samples from each type of treatment were examined, with three small fragments removed from each sample. The metrics in this case rely on the area of the 1260 cm^{-1} absorption band, corresponding to Si-O stretching vibrations and therefore ascribed to silicone. In this case, the averages and standard deviations (for the 5 items of each treatment) were considered, analogues to the median and IQR used for LIBS. The results for all samples can be observed in Figure 7.32. To facilitate comparison, the data is organised in a similar fashion to the LIBS data, showing the band area as a function of silicone mass for all treatment times (Left), the standard deviation of the band area as a function of treatment time for all masses (Centre), and the standard deviation of the band area as a function of silicone mass for all treatment times (Right).

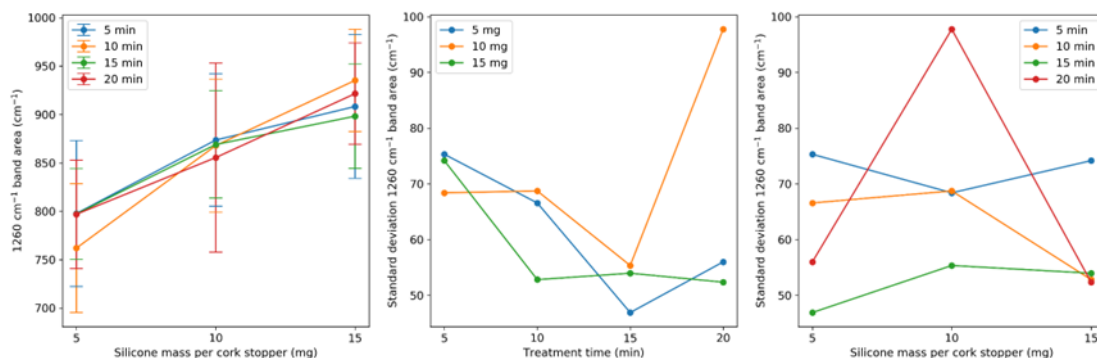


Figure 7.32 – Results from the ATR-FTIR analysis. (Left) 1260 cm⁻¹ band area variation with the silicone mass per cork stopper for all treatment times. (Centre) Standard deviation of the band area as a function of treatment time for all masses. (Right) Standard deviation of the band area as a function of silicone mass for all treatment times.

For the band area versus silicone mass per cork stopper (Figure 7.32 Left), the band area increases along with the treatment mass. This indicates a positive correlation between the amount of silicone applied and the measured band area, consistent with the expectations from the treatment process, and in good agreement with the LIBS results using the median metric.

For the standard deviation of the band area versus treatment time (Figure 7.32 Centre), the standard deviation decreases with increased treatment time. This suggests that longer treatment times lead to more uniform coatings. However, there is an outlier for the samples with the treatment parameters of 10 mg, 20 min, indicating that the batch related to that treatment may have been defective.

When comparing these results with LIBS, a similar overall trend can be observed. However, for the standard deviation of the band area versus treatment mass (Figure 7.32 Right), the results do not match the LIBS ones, behaviour-wise. Aside from the outlier, the results suggest that the treatment mass should not affect the standard deviation. This discrepancy indicates that the IQR variation with the silicone mass per cork stopper in the LIBS case may be inherent to the methodology used to obtain the metrics. Given that only five samples per treatment were tested in this case, the statistical strength is not robust. Therefore, it is challenging to determine whether the LIBS results or the ATR-FTIR results are more accurate, as the ATR-FTIR analysis covers only a small portion of the surface. This uncertainty highlights the need for more extensive sampling to confidently ascertain the reliability of either method.

To further investigate the mass of coating, CTCOR employed chemical extraction using organic solvents. The silicone coating was extracted from each type of sample and weighed, with three replicas each (Table 7.6). While this method reduces the number of

samples further from five to three, it analyses the entire surface of the cork, making it more representative of the overall surface quality. This comprehensive approach provides additional insights that may help clarify the differences observed between the LIBS and ATR-FTIR results.

Table 7.6 – Surface treatment quantification from chemical extraction using organic solvents, table readapted from the original made by CTCOR.

Sample	Silicone mass per cork stopper (mg)				Mass reference value	ΔM
	Replica 1	Replica 2	Replica 3	Mean		
B5-5	15	5	3	8	5	60%
B5-10	5	1	4	3		-40%
B5-15	4	4	4	4		-20%
B5-20	3	6	3	4		-20%
B10-5	8	9	7	8	10	-20%
B10-10	7	7	14	9		-10%
B10-15	12	8	8	9		-10%
B10-20	7	7	8	7		-30%
B15-5	13	8	9	10	15	-33%
B15-10	12	9	9	10		-33%
B15-15	12	8	9	10		-33%
B15-20	10	11	7	9		-40%

The chemical extraction results in Table 7.5 reveal that higher silicone treatments (10 mg and 15 mg) yield more consistent and uniform coatings, as indicated by smaller deviations and overlapping measurements between samples. Conversely, the 5 mg treatments exhibit significant variability, suggesting that this lower level of application may not be sufficient for achieving uniform coatings.

For each mass level, the deviation from the reference value becomes smaller with longer treatment times. This suggests that while the amount of silicone applied has a significant impact on coating uniformity, increasing the treatment duration also contributes to achieving more consistent coatings. Overall, the chemical extraction method emphasises that higher silicone treatments and longer treatment times provide more uniform and predictable coating results.

However, even for higher treatment levels, the percentage deviations are still quite high, indicating inherent variability in the coating process. This high dispersion can also help explain the variability observed in the LIBS measurements, suggesting that the coating application process itself may need further refinement to achieve truly uniform coatings across all samples. Indeed, this is precisely why the market is looking for a tool that can perform online and at a much higher rate than present methods.

The comparison with standard methods further reinforces the validity of the results obtained with LIBS, motivating the CorkSurf team to enhance the readiness level of the prototype. Following its development at INESC TEC, the system was shipped to Azevedos and EGITRON for further upgrades, and finally, it arrived at CTCOR. New tests were conducted to assess the system's performance consistency. The system is now prepared for a more systematic refinement with a significantly larger dataset provided by CTCOR. The details of the industrial upgrades can be seen in Annex III, and the validation in a relevant environment will be addressed in the following section.

7.3.5. Validation in a relevant environment

Following the successful validation of the LIBS analysis against standard techniques, the system underwent several industrial upgrades and was moved to CTCOR for validation in a relevant environment. The most significant enhancement was the incorporation of a vision system, enabling image-based analysis of the samples' surface to identify optimal spots for LIBS analysis. This system allows for the avoidance of problematic areas such as natural craters on the cork stoppers. The vision system provides coordinates that replace the previously used grid protocol. For user operation, a new graphical interface was developed using JavaScript, which communicates with the PLC. Under this setup, it is now possible to automatically establish an analysis grid on surface points with no defects. This improvement is expected to minimise outliers introduced by the inhomogeneity of the cork itself.

Since the system was modified and relocated, a full operation check was performed, including the re-alignment of the optical systems, setting of the laser energy to 9 mJ, and optimisation of signal collection. This was followed by a new calibration of the system, requiring the repetition of the tests with newly prepared samples. For this purpose, CTCOR prepared a new set of samples with treatment parameters varying only in mass per cork stopper, specifically 5, 10 and 15 mg, with a single treatment duration of 25 minutes. From the chemical extraction using organic solvents, the estimated masses per cork stoppers were 6, 10 and 15 mg, respectively.

For the LIBS analysis, 10 cork stoppers per treatment were analysed, with 20 spots selected per cork stopper. For these tests, the analysis spots were chosen using the vision system, targeting smooth regions of the cork as presented by the user interface of the CorkSurf system. Figure 7.33 shows the sampling points automatically selected by the vision system. Each spot was then analysed with between 20 to 30 shots, with the higher number used in some samples due to the presence of possible outliers. Following the established methodology, the metrics for each treatment was calculated from the

spectral data. The results obtained can be observed in Figure 7.34, alongside the results of the initial tests at INESC TEC.

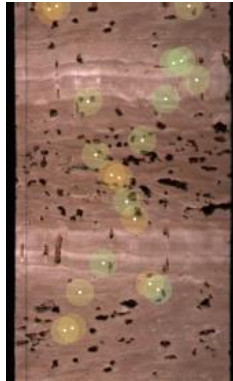


Figure 7.33 – Image of the cork surface with coordinates of analysis spots automatically selected by the vision system.

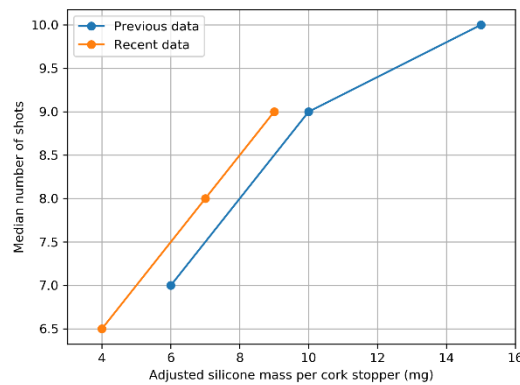


Figure 7.34 – Comparison of the results obtained in the initial tests at INESC TEC (orange curve, 20-minute treatments) and the new calibration performed at CTCOR (blue curve, 25-minute treatments). They show the median number of shots to reach the threshold against the treatment mass.

There is a reasonable agreement between the data from both tests. However, the comparison should consider several aspects. In the latest dataset, due to constraints in the industrial version, the spectra were not saved and only the calculated metrics were available. Consequently, it was not possible to perform the interpolation step. To ensure a fair comparison, no interpolation was used in both cases, which limited the resolution for determining the threshold. Additionally, the new calibration set was obtained with the aid of the vision system, reducing the number of outliers. Therefore, it was compared with the outlier-free dataset from the initial tests. For operational reasons, the number of samples and shots per sample was reduced in comparison with the first test, further limiting its statistical validity. Finally, the masses measured by the standard methods occupy slightly different ranges in both datasets; however, both overlap in the range of 6 to 10 mg. Despite these limitations, the two curves provide coherent results, demonstrating the robustness of the method. This consistency suggests that the LIBS

analysis, even with varying conditions and constraints, can reliably identify and quantify the treatment mass of cork stoppers. Considering the statistical nature of the metrics, the inherent uncertainties of LIBS, and the variability in the coating process, achieving more reliable performance will require much larger datasets. This task will be the responsibility of CTCOR in the next stages of development. By expanding the dataset, CTCOR aims to enhance the statistical reliability and overall accuracy of the method, paving the way for its effective industrial application.

Crater analysis

As mentioned priorly, a set of samples were prepared to assess the depth resolution of the laser ablation. In this set, different energies and different number of shots were employed to determine a relation between the number of shots and the depth penetration and confirm the optimal pulse energy in the process, but the opportunity to make this assessment was delayed.

The measurements were performed by CTCOR using an optical microscope (Leica Microsystems). The diameter and depth of the craters created by the laser pulses were measured using the microscope software. While diameter measurements required only a top view perspective, depth measurements involve sectioning the crater precisely through its midpoint to reveal its cross-sectional profile. For this task, a very sharp razor blade was used, minimising the risk of deforming the craters profile. However, due to the extremely small crater sizes, aiming for the cut was challenging and time-consuming. Consequently, due to time constraints, the analyses were limited to a single parametrisation: craters formed by 20 shots of 9 mJ.

For diameter measurements, 11 craters were assessed, yielding an average diameter of 440 μm with a standard deviation of 48.7 μm . For depth measurements, 10 craters were analysed, resulting in an average depth of 526 μm with a standard deviation of 57.2 μm . These measurements were deemed acceptable by CTCOR, suggesting that the samples could potentially be reused. However, there were concerns regarding the depth measurements, as aiming at the centre of a crater smaller than half a millimetre was prone to errors and possible deformations.

An alternative method to measure the depths was found using the Leica Microsystems microscope, which could estimate the distance between two specific focal planes. This method required only a small off-centre cut for illumination purposes (Figure 7.35). With this technique, three additional measurements were performed, yielding depths of 573, 516, and 573 μm , roughly confirming the validity of the initial measurements.

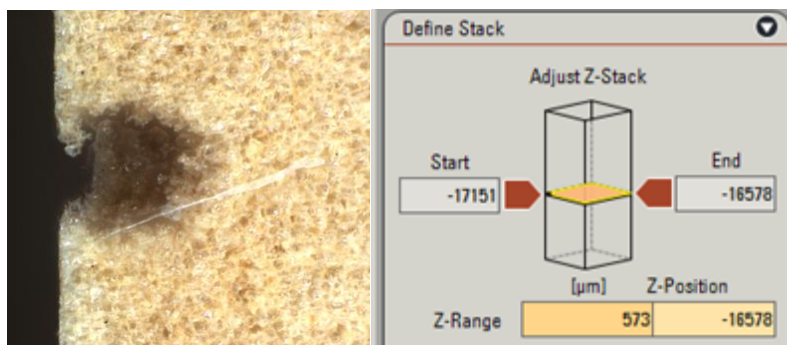


Figure 7.35 – (Left) Top view of the crater, with cut on the side for illumination purposes, and (Right) software display of the depth measurement.

While the craters did not pose an issue in terms of damage, depth resolution remained a concern. For a rough estimate, disregarding the assumption that ablation is not constant across multiple shots (with initial shots ablating more than later ones), 20 shots resulted in an average depth of 526 μm , suggesting an ablation rate of approximately 26.3 μm per shot. Given that some coatings are around 60 μm thick (Figure 7.17), the laser shots would penetrate through the coatings in 2 to 3 shots. This indicates that the chosen energy leads to poor depth resolution, likely explaining the broad distributions observed in the obtained metrics. To improve depth resolution, it will be necessary to reduce the pulse energy. This reduction may require enhancing the light collection capability to maintain or increase the SNR. While this might necessitate some modifications to the system, it offers a clear path for improvement, building on already promising results.

7.4. Conclusion and future work

Following the implementation and preliminary validation tests of the CorkSurf system, this chapter presented a detailed study aimed at establishing metrics extracted from the spectral data to evaluate the thickness and uniformity of the coatings. This was done by exploring the gradual ablation of the coating as the laser was shot successive times at the same spot.

The study primarily focused on coatings which are particularly relevant for the cork stopper industry: silicone, paraffin or a combination of both.

The methodology involved optimising the LIBS system using fresh samples and conducting depth analyses to gather spectral data from multiple laser shots at the same spot. Key metrics established included the median and interquartile range of the number of laser shots required to reach a pre-determined threshold. These metrics were found

to correlate reasonably well with the treatment mass and duration, suggesting their potential for evaluating coating thickness and uniformity.

Following the initial validation tests, the system underwent industrial upgrades and was presented to stakeholders at two commercial and scientific events. The upgraded system was then moved to CTCOR to perform validation in a relevant environment.

System tuning and repetition of the calibration tests compared very favourably with previous results, reinforcing the potential of LIBS analysis for this challenging task.

Despite the positive indications, several limitations and key points for improvement were identified. The statistical nature of the established metrics, combined with the inherent uncertainty of both LIBS and the coating process, implies that to improve the method's reliability and robustness, a much higher number of samples and analysis points must be acquired and validated with reference techniques.

A preliminary attempt to establish a methodology to assess the actual penetration depth of the LIBS analysis was successfully tested. The laser-induced craters were observed by optical microscopy, successfully measuring the extent of the laser penetration.

These findings indicate that the extent of the physical damage is negligible from the perspective of cork usability, establishing the method as non-destructive. This means it can potentially be applied to full batches of treated corks, providing a more solid metric, and allowing the same corks to be used in tests for extraction forces, potentially creating a cycle that enables process optimisation methodologies.

On the other hand, the results showed that lower energies, providing a higher in-depth resolution, are preferable for a more reliable analysis. This will eventually require some system readjustment to increase the collection capability and maintain or enhance the SNR. Although challenging it is perfectly manageable.

The system is presently at CTCOR, ready to start another round of systematic tests with significantly larger data sets, encompassing the wide variety of treatments utilised in the industry. This phase will provide a comprehensive validation of the LIBS system's capabilities across diverse conditions, ensuring its robustness and adaptability. This milestone marks the culmination of the initial stage of a successful development journey for a novel LIBS application. It also signs the beginning of a new industrialisation phase, where CTCOR, the technology centre of the cork sector, will rigorously validate this highly sought-after technology. The goal is to confirm its efficacy and reliability for real-

world industrial applications, thereby addressing a critical need in the market and paving the way for its widespread adoption.

Part V

Conclusion

Chapter 8

Retrospective analysis, impact and future prospects

8.1. Retrospective analysis

This chapter marks the conclusion of the thesis by reflecting on the work carried out, the knowledge acquired and the opportunities that emerged throughout the research. It also presents directions for future work.

The primary focus of this thesis was the development of LIBS systems for applications in a variety of industries. A total of three LIBS systems were developed, including a readaptation of an existing system for laboratory operation. Each system was thoroughly described, with detailed characterisation of their operation, applications and key findings.

As this document is centred on LIBS, Chapter 2 provides an overview of the technique enabling the reader to understand its fundamentals aspects, and the opportunities and challenges of its application in a variety of settings. This introduction provides the essential context to understand the development of the new LIBS systems and how they can be applied to novel applications.

The first LIBS system was originally designed as a transportable device for in-situ analysis of mineral samples at mining sites, in a research project that set the stage for the work developed in this thesis. The focus of Part II describes the system readaptation to laboratory operation, where several improvements were introduced, enhancing its performance, allowing for more complex analysis of geological samples and enabling new applications. The addition of translation stages facilitated the implementation of LIBS imaging, while adding a DDG improved the temporal control over the system enabling full automation. The system was characterised in terms of energy and plasma formation region to grasp its operational limits. With high energy pulses, the system managed to perform elemental analysis and LIBS imaging on geological samples. Additionally, it proved quite versatile to analyse other types of samples such as biological and heritage-related samples, making it suitable to test new applications and new types of samples.

To evaluate the performance of this system in real-world conditions, it was used alongside a commercial portable LIBS system to assess quantification models on lithium-rich samples from a mining site. A total of 124 samples, exhibiting a wide range of Li

concentration, were analysed. The laboratory LIBS system generated two datasets, using two different pulse energies, which were compared with the dataset from the portable system. Using a leave-one-out cross-validation in terms of MAPE, the results demonstrated that non-linear methods outperformed the linear ones, with the best performance obtained for the laboratory LIBS. Predictions of Li content at a semi-quantitative level were attained, suggesting that non-linear methods can work around saturation and matrix effects, but at the cost of interpretability.

In Part III, the focus shifted to a fibre laser-based LIBS system. The chapter that is composed of provided a detailed description of the system, with emphasis on the fibre laser's customisable pulses. It discussed how different laser parameters could influence pulse shapes and described other key components such as the optical system, the spectrometers, the translation and rotation stages and the SyncRay delay generator. The system's capabilities were tested for custom pulse lengths, revealing improved SNR for longer pulses. However, the system's performance suffered with rough-surfaced samples due to low pulse energy and very thin plasma formation zone. Despite these challenges, the system proved valuable in high-resolution imaging of battery electrodes, achieving resolutions down to 50 μm , providing valuable insights on the dynamics of Li ions and their migration to the electrodes.

Part IV introduced a novel application of LIBS in the cork industry. In collaboration with EGITRON, Azevedos Indústrias and CTCOR, a specialised LIBS system was developed for analysing coatings on cork stoppers. The system's key components were described, with special emphasis on the LIBS setup, which included the laser, optical systems, spectrometers, sample positioning system and a PDG, followed by an explanation of the automation process. A characterisation of the plasma formation zone allowed to demonstrate that the plasma formation range around the focal plane (± 0.5 mm) was larger than the specified industry tolerance for the cork stoppers dimensions, accommodating the typical surface irregularities without loss of performance. The initial results confirmed the system's capability to detect the presence of silicone and paraffin coatings by mapping the cylindrical surfaces of cork stoppers and identifying untreated areas with distinct shapes. This was done by tracking the distribution of the emission intensity of Si and C lines along the surface. Additional elements such as Mg and Ti were also found to have different distributions in treated and untreated areas, but without identifying the coating types.

These initial findings were followed by a more specialised analysis of the coating depth using fresh samples with different combinations of silicone, paraffin, and uncoated corks.

System parameters, such as the spectrometer's spectral range and delay, pulse energy and its repetition rate were optimised. This optimisation process led to the addition of a custom nozzle to introduce compressed air, to remove particles from the laser path avoiding the formation of airborne plasmas, when operating at faster repetition rates. Through a depth analysis using multiple shots, a methodology was found to attain metrics that could represent the thickness and uniformity of the coatings. The median and IQR of the number of shots required to reach a pre-determined SNR threshold showed a good correlation with the treatment mass and treatment time, parameters that are related with the coating's thickness and uniformity. Since then, the system has been upgraded and is currently stationed at CTCOR (Specialised Centre for certification of cork related technology). Further tests were conducted, indicating a performance consistent with the essays carried out at INESC TEC, showing that the system has a robust performance, even after being subjected to transport and relocation. Presently the new equipment is being tested and optimised for the stages of certification and productization, indicating the suitability of the approach developed for real world operation in an industrial sector of strategic national importance.

8.2. Impact, contributions and legacy

The value of the work presented in this PhD thesis extends beyond the new knowledge it contributes. It established foundational systems, methods, and findings within the research group that have significantly advanced the field. Notably, this work laid the groundwork for the establishment of a new research area at the Centre of Applied Photonics of INESC TEC, creating a strong basis for ongoing research and new technological developments.

From the seed work performed, a solid cooperation with the Geology Department of the Faculty of Sciences of the University of Porto was established, supported by new research projects and interactions with industry, particularly framing the challenges of extracting Li based materials. The newly established laboratory infrastructure, combined with the knowledge and methodologies developed, has paved the way for new research endeavours and academic contributions. This includes multiple Master's[314,316,357] and ongoing PhD theses that build on the advancements achieved in this thesis. Additionally, the LIBS systems have been integrated into educational programs, providing students with hands-on experience through coursework and research internships, and fostering active participation in ongoing projects.

The establishment of these new LIBS systems has not only expanded research capabilities but also created new opportunities for technology transfer and collaboration

with industry. Building on the advancements made in this thesis, the research group is now securing new projects with industrial partners, including initiatives focused on glass and wood recycling.

Publication-wise, the first two LIBS systems have enabled further studies beyond the original scope of this PhD thesis, resulting in multiple new publications. Representative examples include studies on improved calibration models using unsupervised clustered regression techniques[332], the analysis of acoustic waves to differentiate between different materials[358] and the integration of LIBS with hyperspectral imaging for mineral identification using their combined data or leveraging one technique to enhance the other[359].

Additionally, several analytical tools were developed from data gathered using these systems, also leading to further publications. These tools include intelligent grids for more efficient sample imaging[360], the identification of relevant elemental lines for imaging using Fourier space analysis[361], and the creation of interactive three-dimensional chemical maps through photogrammetry[362].

8.3. Future work and optimisations

The work presented in this thesis lays a strong foundation for further advancements to the LIBS systems and the exploration of new applications. The following improvements and studies are proposed for each system:

First LIBS System: Future improvements include implementing a new method for energy control, integrating a second mirror for better beam alignment through the focusing lens and adding an automated vertical stage. Follow-up studies should focus on comparing the performance of quantification models using raw samples instead of pellets. The findings should then be validated with new target data from different drilling holes within the same mine, as well as from different mines, to assess the generalisability of the results.

Fibre Laser LIBS System: Planned enhancements for this system involve adding a fourth collection channel to extend the spectral range using the combined capabilities of the four spectrometers. Other improvements include integrating a second mirror, similar to the first LIBS system, and an extraction system to eliminate particles. Automation-wise, utilising the driver from the translation and rotation stages to trigger the SyncRay could further refine the system's operation. If increasing the maximum pulse energy remains a challenge, altering the focal lens to one with a shorter focal distance could help reduce the beam waist and increase the intensity at the focal point. With these

optimisations in place, follow-up studies could explore the use of multi-pulse features for submerged sample analysis and oxidation imaging, potentially in combination with laser cleaning techniques.

CorkSurf LIBS System: Based on recent results, this system requires energy optimisation, followed by a reassessment of the metrics used to estimate the thickness and uniformity of silicone coatings. If successful, the process should be extended to analyse new samples with different coatings, such as paraffin or a mix of paraffin and silicone, as well as various types of cork stoppers, including champagne and agglomerate stoppers and cork stoppers with different dimensions.

In a broader perspective the group is now expanding its Spectral Imaging Area. Building on the established foundations of spectral imaging capabilities acquired during this thesis, there is a promising opportunity to adopt a multimodal approach by integrating complementary technologies such as Raman spectroscopy, hyperspectral imaging, and X-ray techniques. This combined approach offers substantial potential for solving complex technological problems by providing a more comprehensive understanding of materials. Such a multimodal strategy is already being explored within the research group, with efforts focused on combining these techniques to enhance material characterisation, defect detection, and analysis of complex systems. This approach aims to leverage the strengths of each modality, offering a deeper and more holistic analysis, and more robust performance in the context of industrial and scientific challenges.

8.4. Final thoughts

In conclusion, this PhD thesis successfully developed three LIBS systems to address challenges that emerged over the past few years. The first system, designed for mining applications, was repurposed for laboratory operation and provides elemental identification, mapping and even semi-quantitative analysis. Despite its main purpose, it is not bound to geological samples, being used to research other samples like biological samples, electrodes and heritage samples. The fibre laser-based system found its use in high-resolution mapping with its small spot size. Its low pulse energy proved to be an issue with some types of samples, but it did find some promising applications in metallic samples, mainly electrodes. The last system was built specifically for analysing cork stoppers, proving that not only it can image surface treatments applied on their surfaces, but also provide a depth analysis that can identify the treatment parameters. As a prototype it still has some areas to be improved, such as the pulse energy, but it has shown to be in a good path to become a viable product.

As most, if not all, PhD theses, setbacks were faced. Between being a new field at INESC TEC, a broken laser, COVID-19, among other issues, compromises and detours from the initial plans had to be made. But with teamwork and perseverance, LIBS has been established as research field within the group. The systems are now tools for internal and external cooperations in current and future projects and are sure to bring value to a variety of industries.

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Attachments

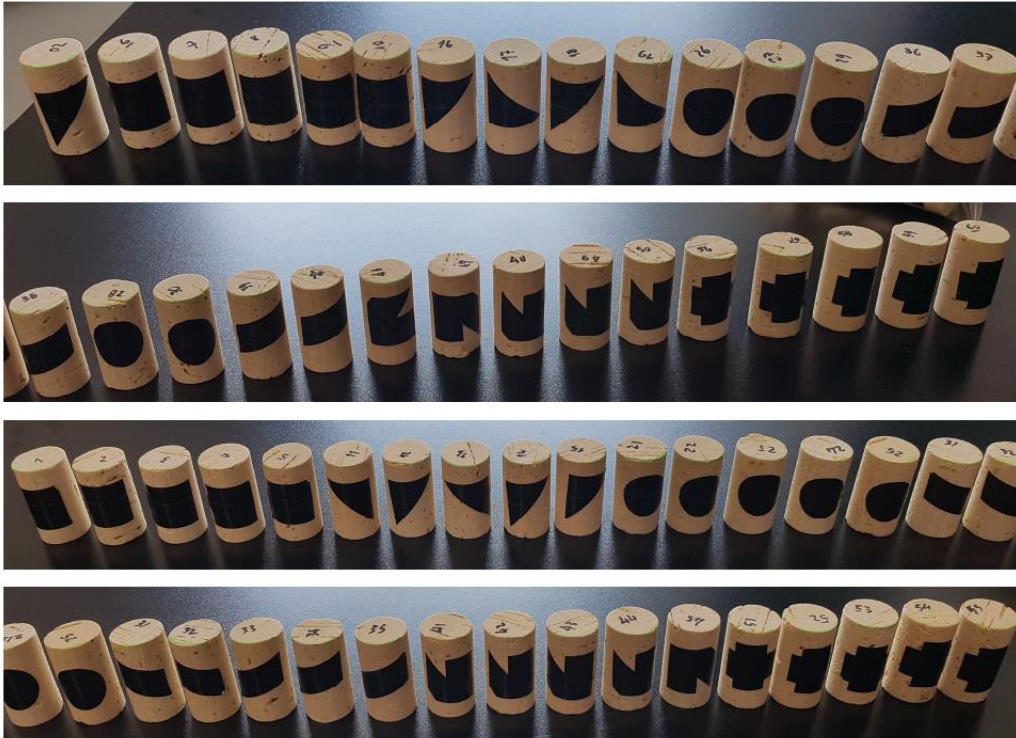


Figure A.1 – Cork stoppers with masks for treatment shielding prepared by EGITRON.

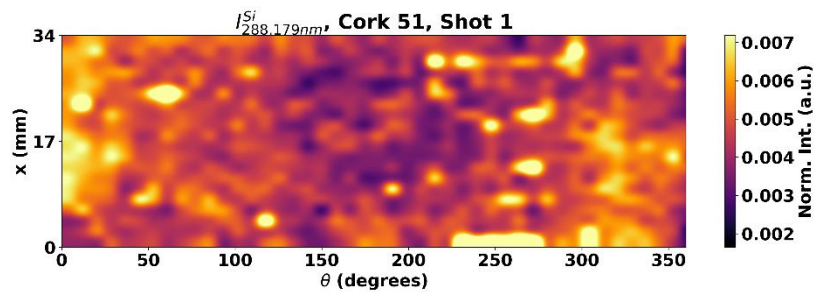


Figure A.2 – Normalised intensity map of the 288.2 nm Si emission line for the first shot on the cork stopper 51. Failed case.

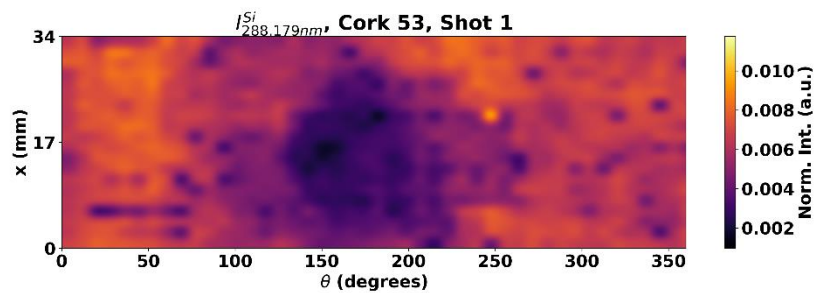


Figure A.3 – Normalised intensity map of the 288.2 nm Si emission line for the first shot on the cork stopper 53. Cross-shaped mask with some apparent damage and silicone diffusion.

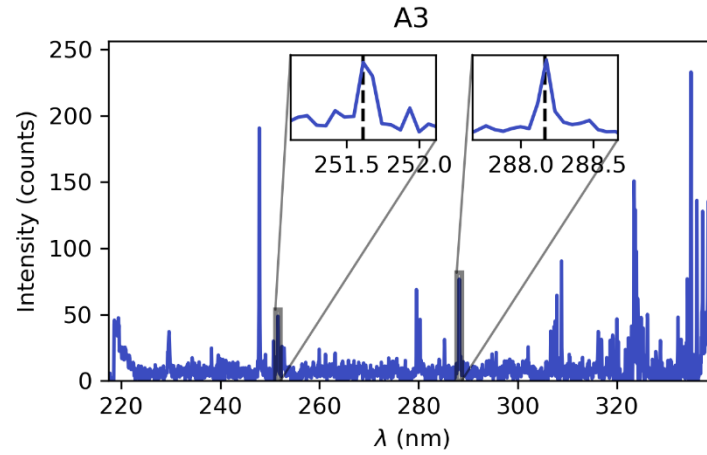


Figure A.4 – Average spectra obtained with the first spectrometer for a cork stopper with a paraffin coating, with zoom-ins on the 251.6 and 288.2 nm Si lines.

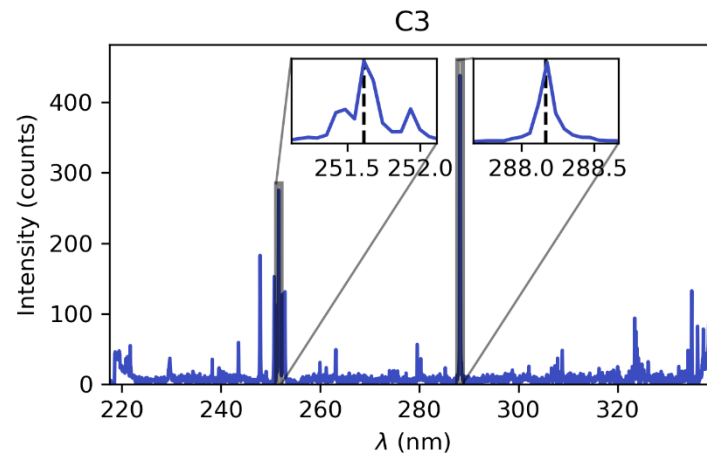


Figure A.5 – Average spectra obtained with the first spectrometer for a cork stopper with paraffin and silicone coatings, with zoom-ins on the 251.6 and 288.2 nm Si lines.

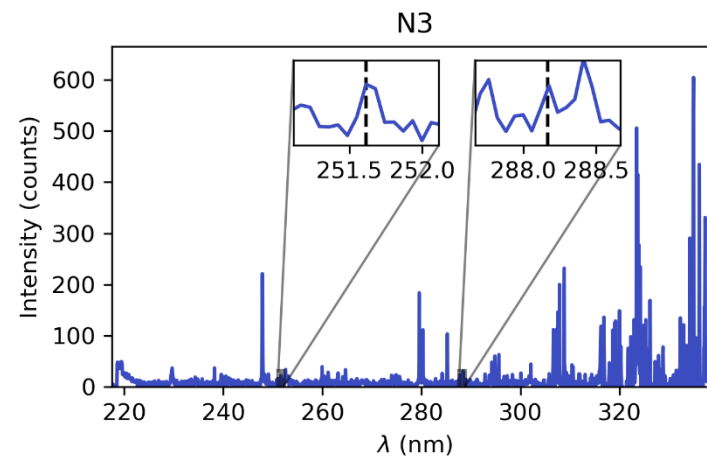


Figure A.6 – Average spectra obtained with the first spectrometer for a cork stopper without functional coatings, with zoom-ins on the 251.6 and 288.2 nm Si lines.

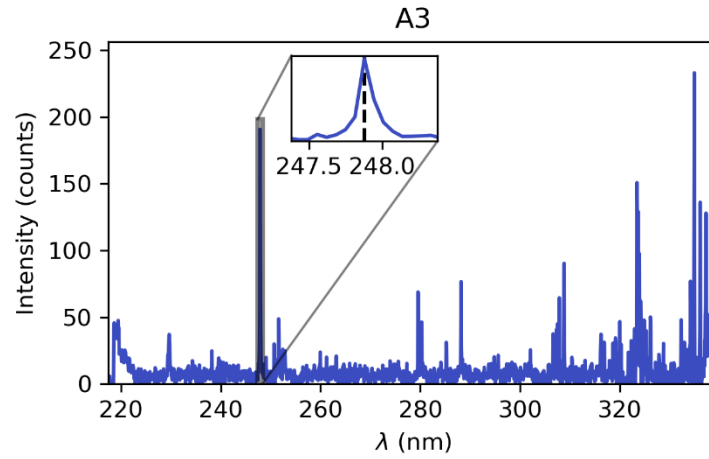


Figure A.7 – Average spectra obtained with the first spectrometer for a cork stopper with a paraffin coating, with a zoom-in on the 247.9 nm C line.

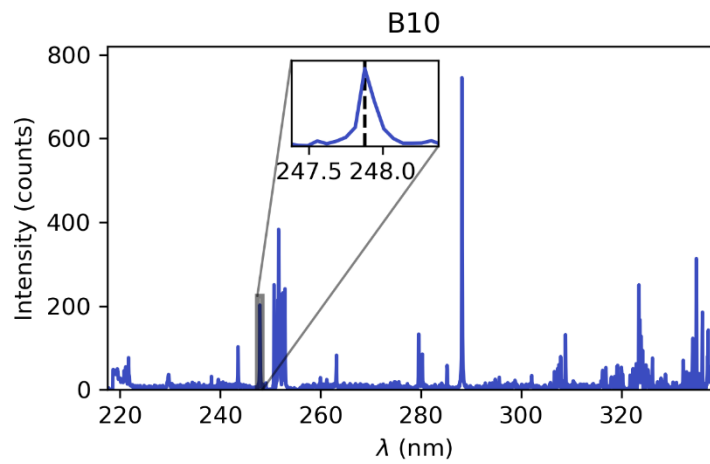


Figure A.8 – Average spectra obtained with the first spectrometer for a cork stopper with a silicone coating, with a zoom-in on the 247.9 nm C line.

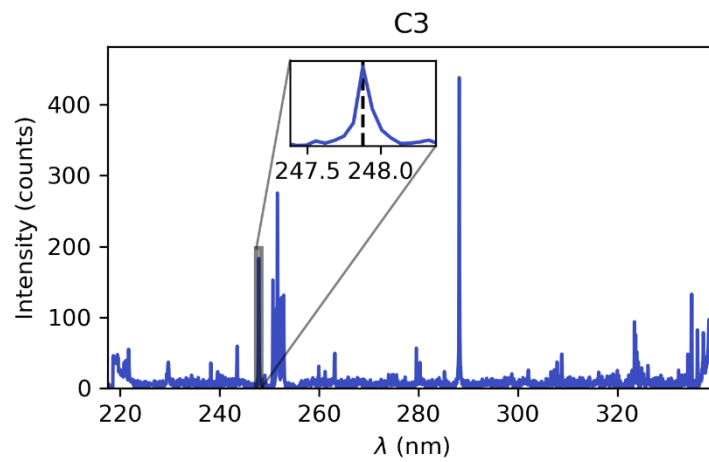


Figure A.9 – Average spectra obtained with the first spectrometer for a cork stopper with paraffin and silicone coatings, with a zoom-in on the 247.9 nm C line.

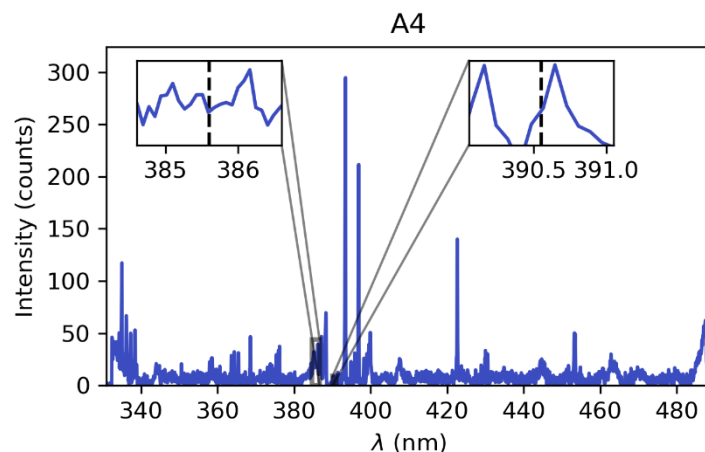


Figure A.10 – Average spectra obtained with the second spectrometer for a cork stopper with a paraffin coating, with zoom-ins on the 385.6 and 390.6 nm Si lines (both not detected).

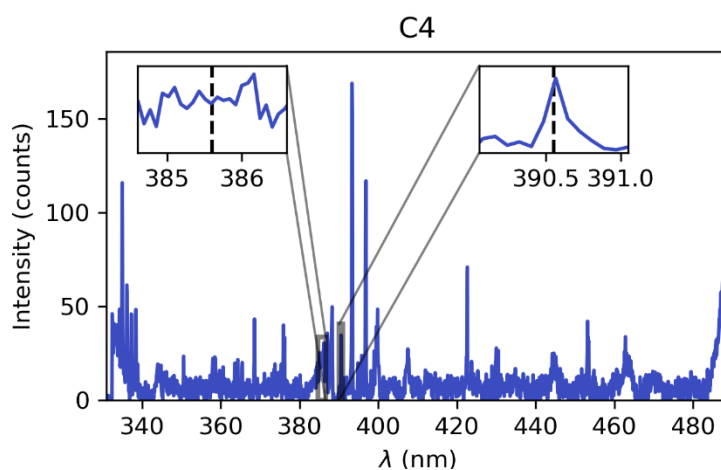


Figure A.11 – Average spectra obtained with the second spectrometer for a cork stopper with paraffin and silicone coatings, with zoom-ins on the 385.6 (not detected) and 390.6 nm Si lines.

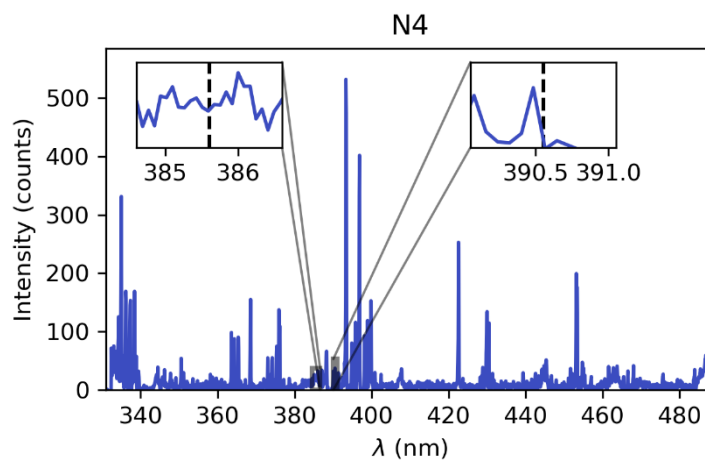


Figure A.12 – Average spectra obtained with the second spectrometer for a cork stopper without functional coatings, with zoom-ins on the 385.6 and 390.6 nm Si lines (both not detected).

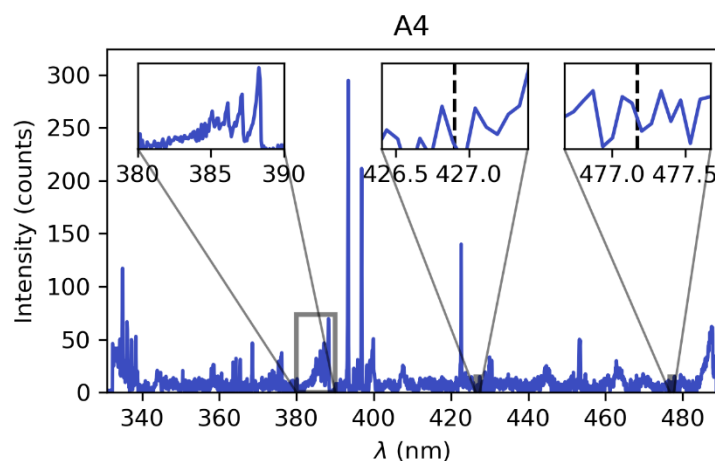


Figure A.13 – Average spectra obtained with the second spectrometer for a cork stopper with a paraffin coating, with zoom-ins on the CN band around 385 nm and on the 426.9 and 477.2 nm C lines (both not detected).

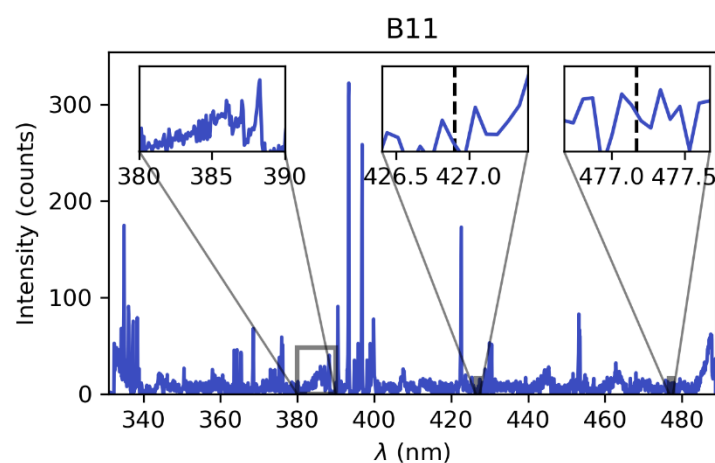


Figure A.14 – Average spectra obtained with the second spectrometer for a cork stopper with a silicone coating, with zoom-ins on the CN band around 385 nm and on the 426.9 and 477.2 nm C lines (both not detected).

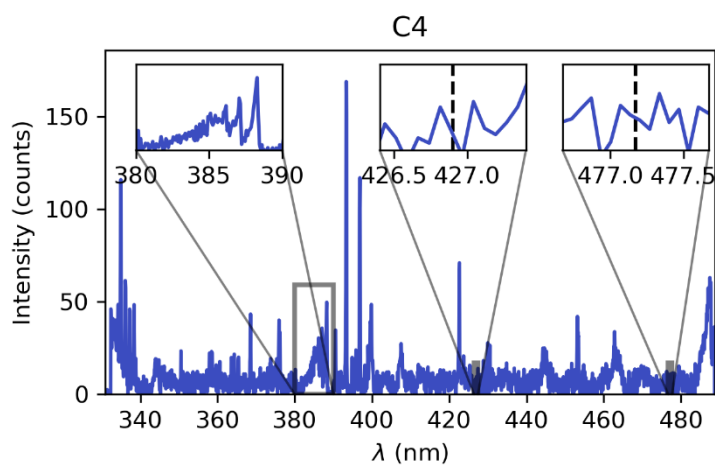


Figure A.15 – Average spectra obtained with the second spectrometer for a cork stopper with paraffin and silicone coatings, with zoom-ins on the CN band around 385 nm and on the 426.9 and 477.2 nm C lines (both not detected).

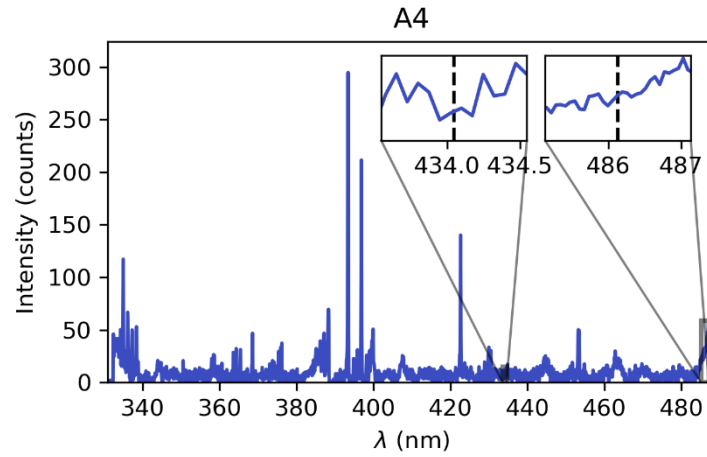


Figure A.16 – Average spectra obtained with the second spectrometer for a cork stopper with a paraffin coating, with zoom-ins on the 434.0 and 486.1 nm H lines (both not detected).

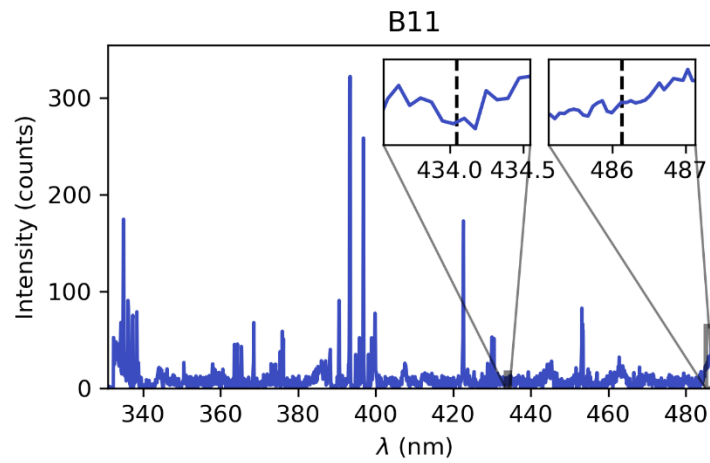


Figure A.17 – Average spectra obtained with the second spectrometer for a cork stopper with a silicone coating, with zoom-ins on the 434.0 and 486.1 nm H lines (both not detected).

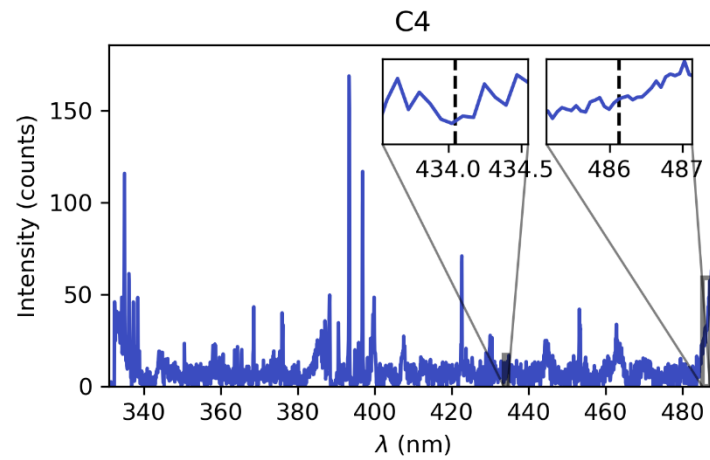


Figure A.18 – Average spectra obtained with the second spectrometer for a cork stopper with paraffin and silicone coatings, with zoom-ins on the 434.0 and 486.1 nm H lines (both not detected).

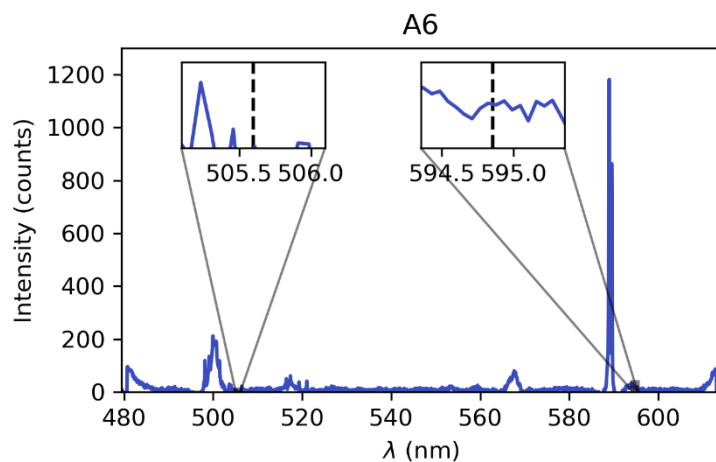


Figure A.19 – Average spectra obtained with the third spectrometer for a cork stopper with a paraffin coating, with two zoom-ins on the 505.6 and 594.9 nm Si lines (both not detected).

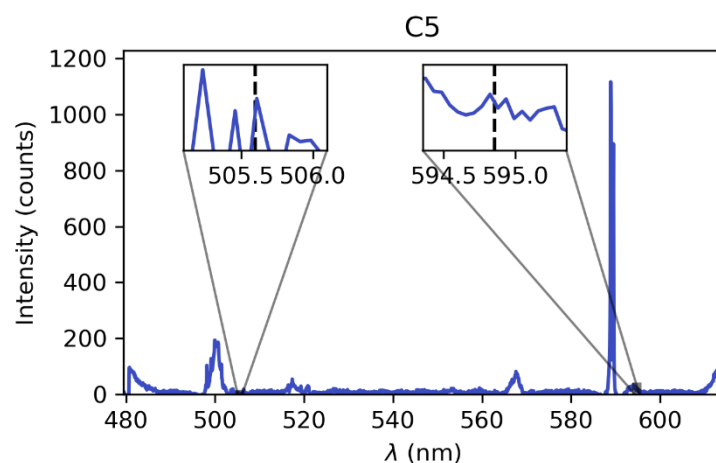


Figure A.20 – Average spectra obtained with the third spectrometer for a cork stopper with paraffin and silicone coatings, with two zoom-ins on the 505.6 and 594.9 nm Si lines (both not detected).

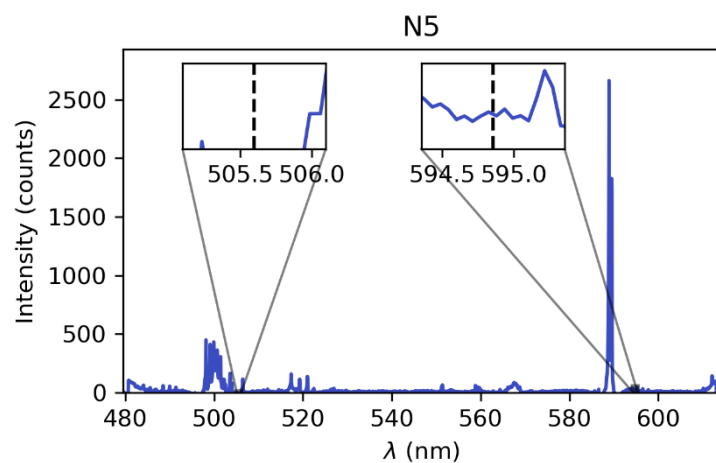


Figure A.21 – Average spectra obtained with the third spectrometer for a cork stopper without functional coatings, with two zoom-ins on the 505.6 and 594.9 nm Si lines (both not detected).

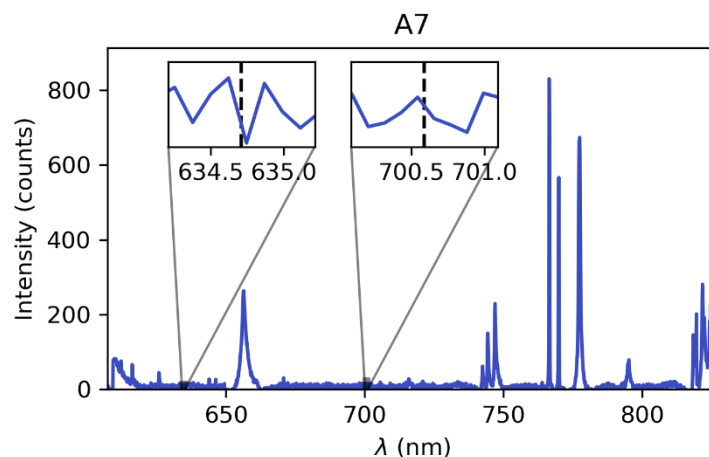


Figure A.22 – Average spectra obtained with the fourth spectrometer for a cork stopper with a paraffin coating, with zoom-ins on the 634.7 and 700.6 nm (both not detected) Si lines.

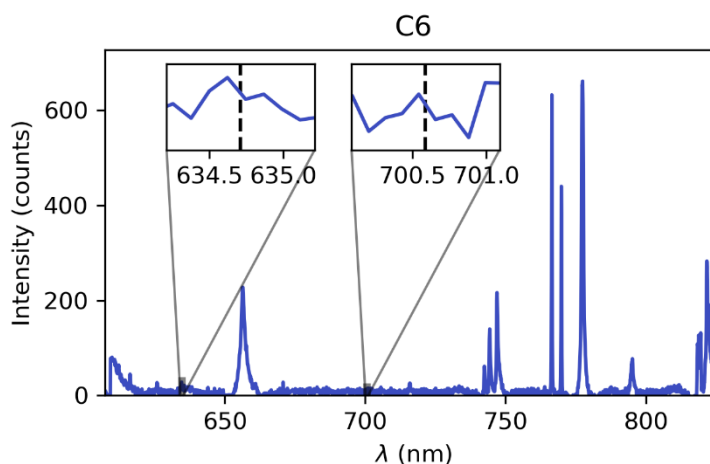


Figure A.23 – Average spectra obtained with the fourth spectrometer for a cork stopper with paraffin and silicone coatings, with zoom-ins on the 634.7 (detected) and 700.6 nm (not detected) Si lines.

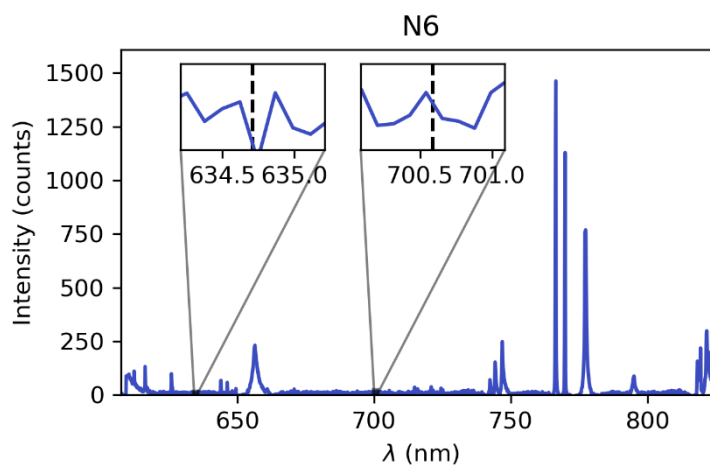


Figure A.24 – Average spectra obtained with the fourth spectrometer for a cork stopper without functional coatings, with zoom-ins on the 634.7 and 700.6 nm (both not detected) Si lines.

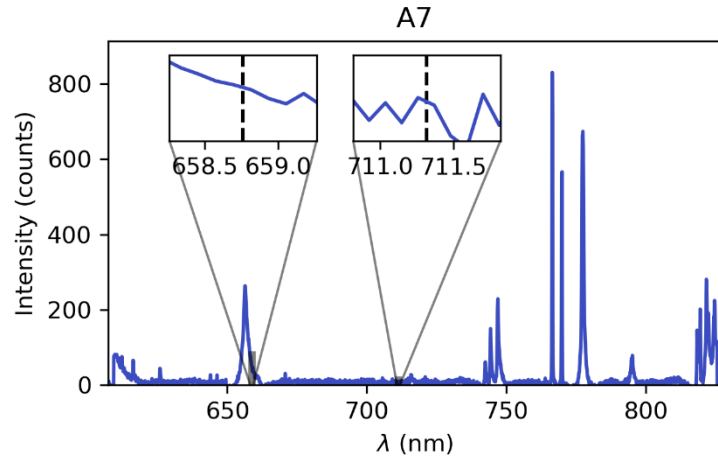


Figure A.25 – Average spectra obtained with the fourth spectrometer for a cork stopper with a paraffin coating, with zoom-ins on the 658.8 and 711.3 nm C lines (both not detected).

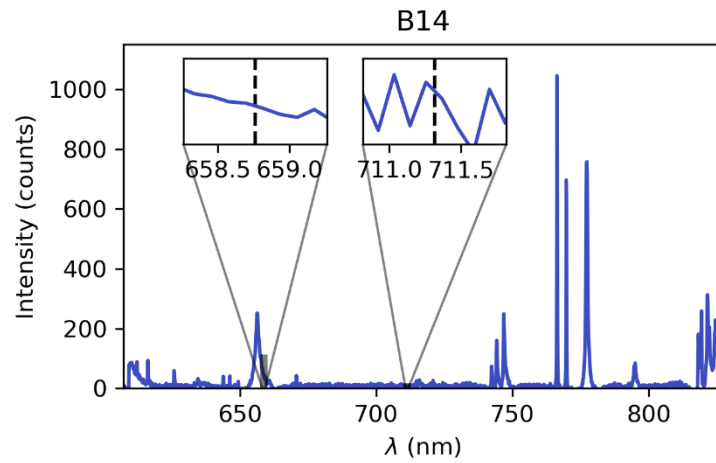


Figure A.26 – Average spectra obtained with the fourth spectrometer for a cork stopper with a silicone coating, with zoom-ins on the 658.8 and 711.3 nm C lines (both not detected).

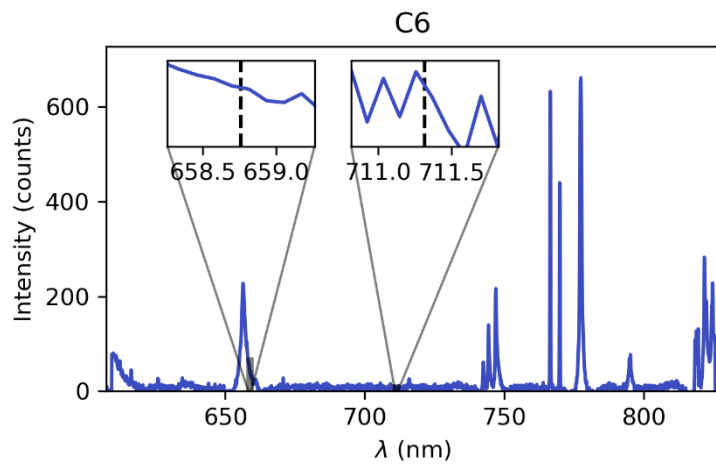


Figure A.27 – Average spectra obtained with the fourth spectrometer for a cork stopper with paraffin and silicone coatings, with zoom-ins on the 658.8 and 711.3 nm C lines (both not detected).

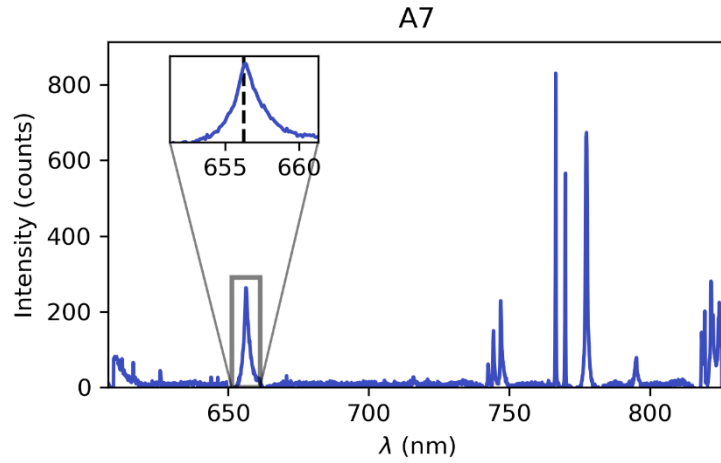


Figure A.28 – Average spectra obtained with the fourth spectrometer for a cork stopper with a paraffin coating, with a zoom-in on the 656.3 nm H line.

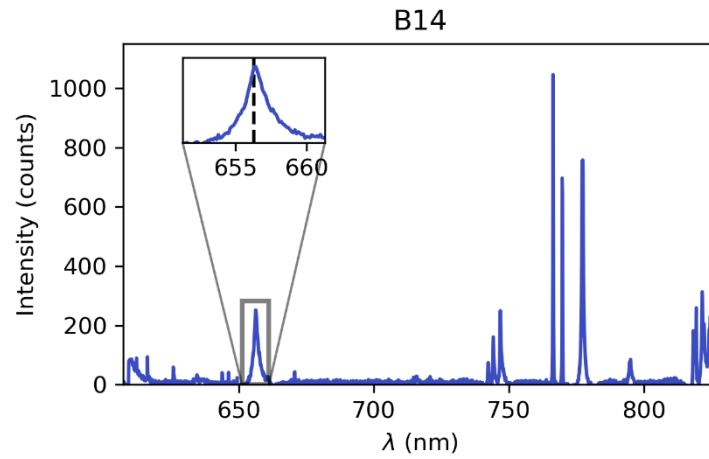


Figure A.29 – Average spectra obtained with the fourth spectrometer for a cork stopper with a silicone coating, with a zoom-in on the 656.3 nm H line.

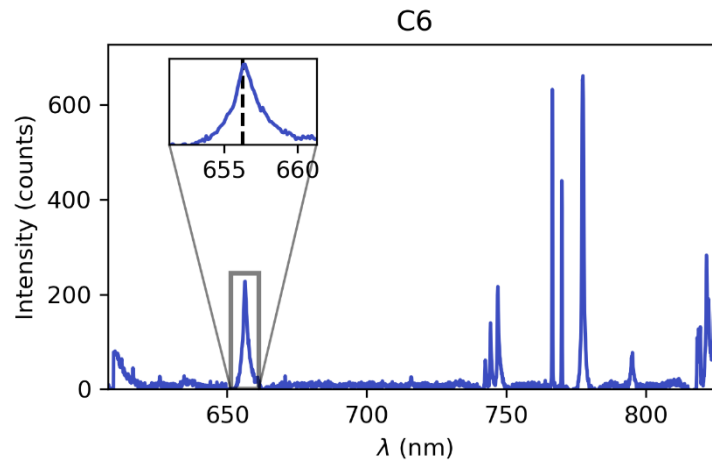


Figure A.30 – Average spectra obtained with the fourth spectrometer for a cork stopper with paraffin and silicone coatings, with a zoom-in on the 656.3 nm H line.

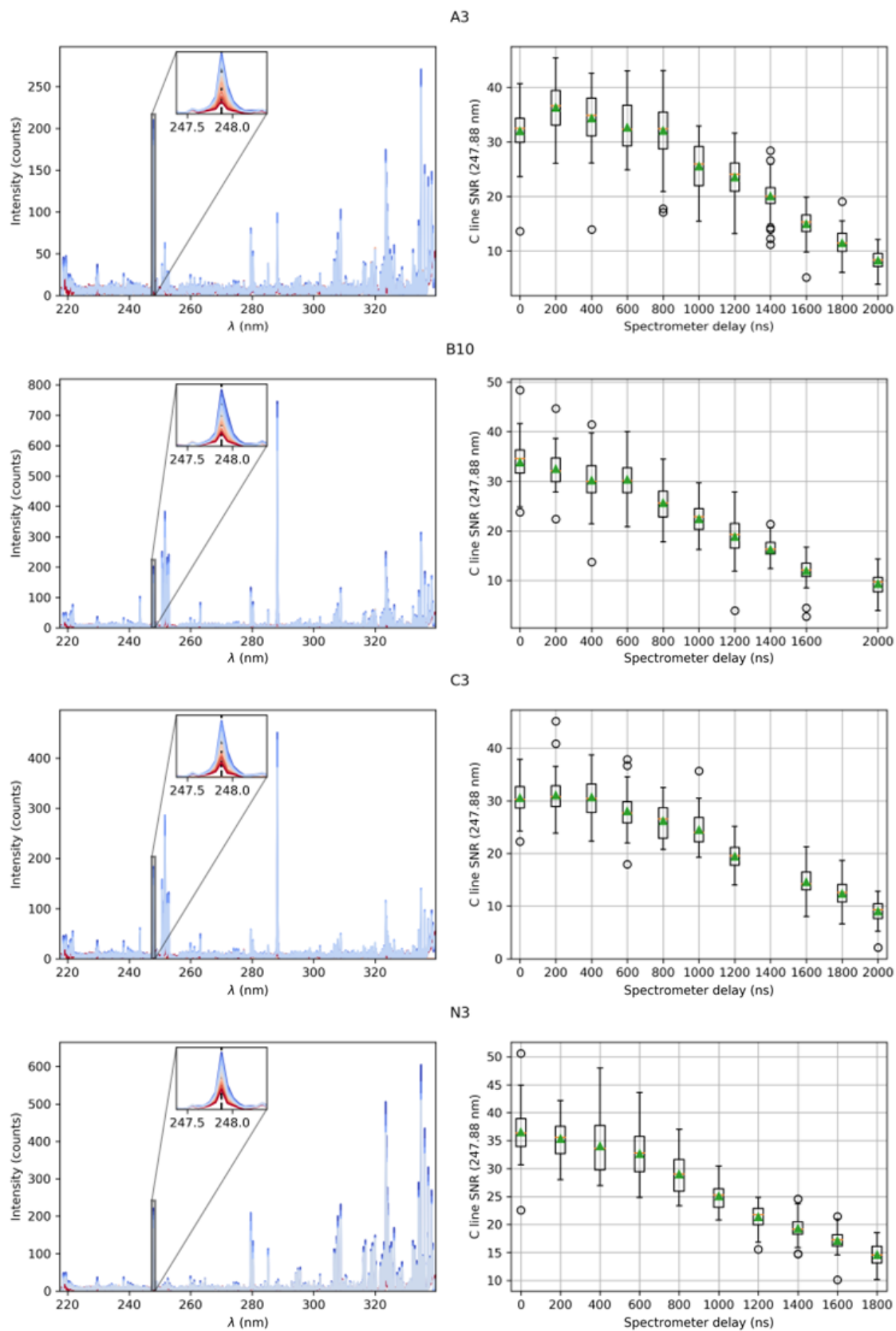


Figure A.31 – Variation of the SNR of the 247.9 nm C line with the spectrometer delay for all types of samples.

C3

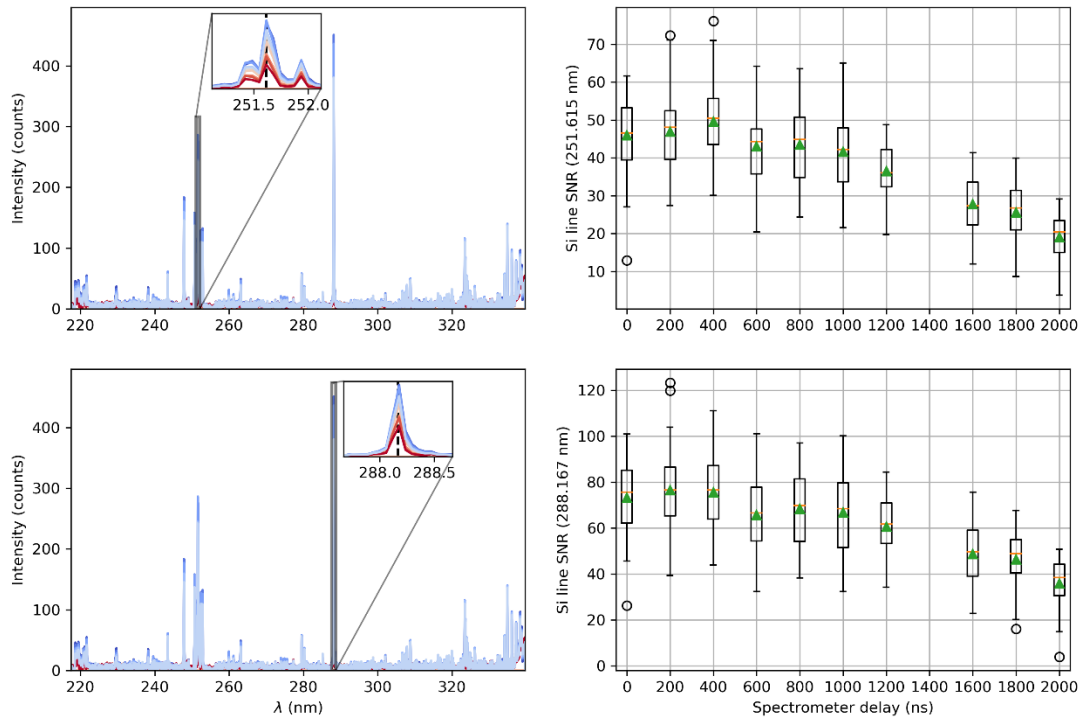


Figure A.32 – Variation of the SNR of the Si lines, 251.6 and 288.2 nm, with the spectrometer delay for a sample with paraffin and silicone coating.

C1

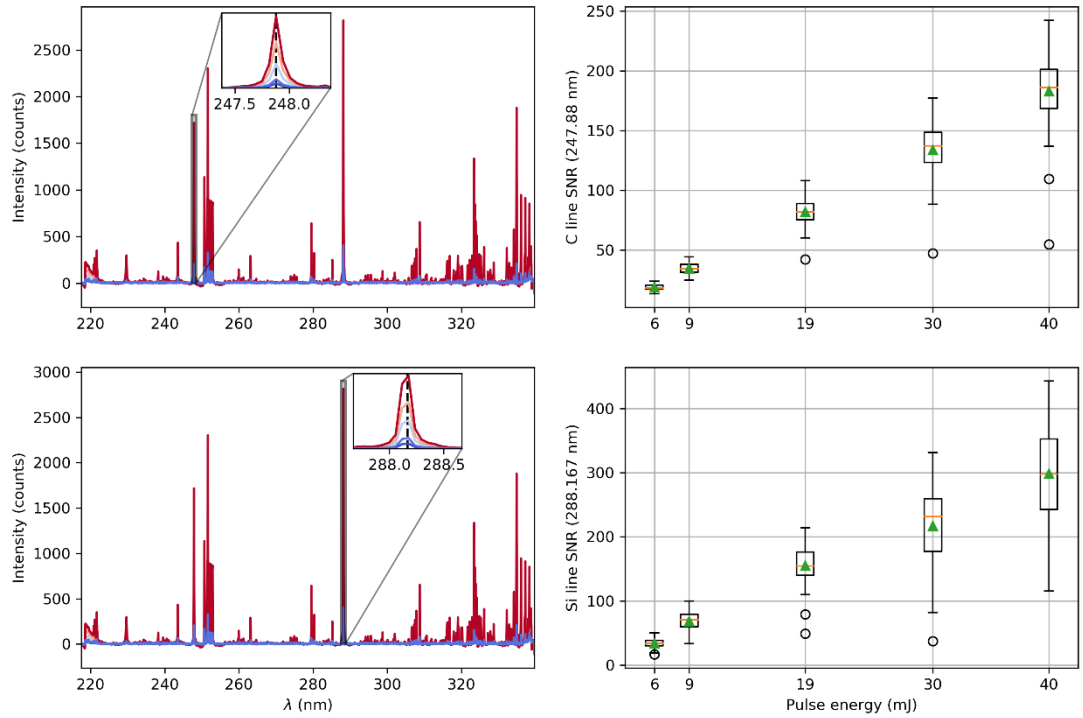


Figure A.33 – Variation of the SNR of the 247.88 nm C and 288.2 nm Si lines with pulse energy, for a sample with paraffin and silicone coating.

N1

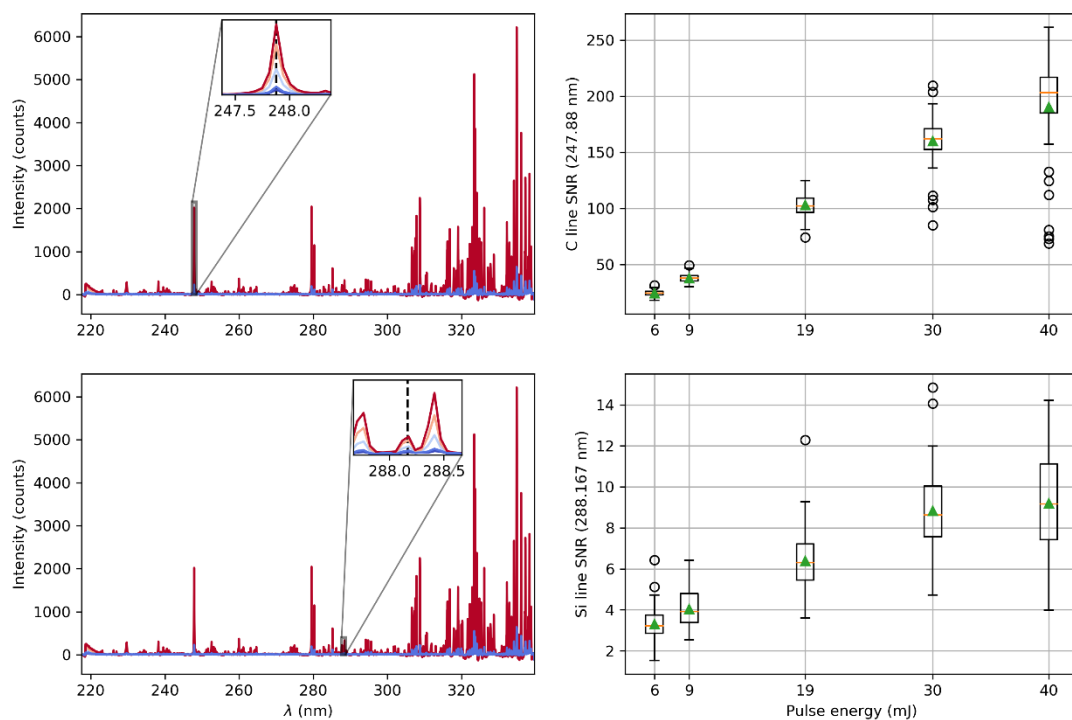


Figure A.34 – Variation of the SNR of the 247.88 nm C and 288.2 nm Si lines with pulse energy, for a cork stopper without functional coatings.

Annex I

Preliminary work of LIBS analysis of cork stoppers' surface treatment

I.1. Introduction

In this annex, it is presented the preliminary work done to test the viability of using LIBS to analyse the coatings that were formed on cork stoppers. To start, the LIBS system used is described, followed by preliminary evaluation of damage caused by LIBS. Then, with a wider array of samples, with different types of cork stoppers and different surface treatments, the signals are analysed to check if LIBS is capable of detecting the coatings. Lastly, the assessment of the viability of using LIBS as a solution with a blind test is described, where LIBS is used to image untreated areas, which were shielded from treatment using geometrically shaped masks, and, using multiple shots, visualise the coating disappearing with the increasing depth showing LIBS potential to assess the coating's thickness and distribution along the samples.

I.2. Experimental system

Before setting out to build a new system for the purpose of analysing cork stoppers, a few studies were conducted to infer the viability of the task. For these, an early version of the system described in Chapter 3 was used, which was not automated. In order for the system to be able to handle cylindric-like samples such as cork stoppers, a custom-made platform suitable to hold and rotate the samples was added (Figure I.1). This way, it was possible to analyse every region of the curved surface when paired with the translation stage that moves along the longitudinal direction of the cork stoppers.



Figure I.1 – Sample holder inserted in the early version of the Nd:YAG system to handle cork stoppers.

I.3. LIBS vs. cork stoppers and coatings

With the LIBS system ready to analyse cork stoppers, there are 2 main issues that require attention. Firstly, it is important to study the limitations that the physical characteristics of the samples may impose on LIBS and vice-versa. These may affect the performance of the technique or lead to far more damage than the desired one. Lastly, and key to this study, it is necessary to assess if the technique is able to distinguish the coatings deposited on the cork stoppers, by finding differences between the spectra, otherwise LIBS will be incapable of assessing the uniformity of the coatings.

I.3.1. Preliminary damage evaluation

While not vital to determine the viability, there was some interest in the possibility of reutilising analysed cork stoppers which would make LIBS a far more attractive technique. As it is a micro-destructive technique, the damage made in the process may be small, but it is still present and could potentially render the samples unusable.

In an optimal case, the damage would be studied for every kind of sample with their respective optimal pulse laser's energy, but it was not feasible for an early-stage examination of damage, so an extreme scenario was tested first. If the damage is acceptable while using an extremely high energy of operation, the damage for the optimal cases should be the as well.

With the Q-switch delay set to 280 μs , a line of 10 spots, with a 1 mm separation between them, was hit with a growing number of shots per spot, from 1 to 10 shots (Figure I.2). As expected, the damage increases with the number of shots, going from a nearly imperceptible crater to a diameter of around 700 μm .

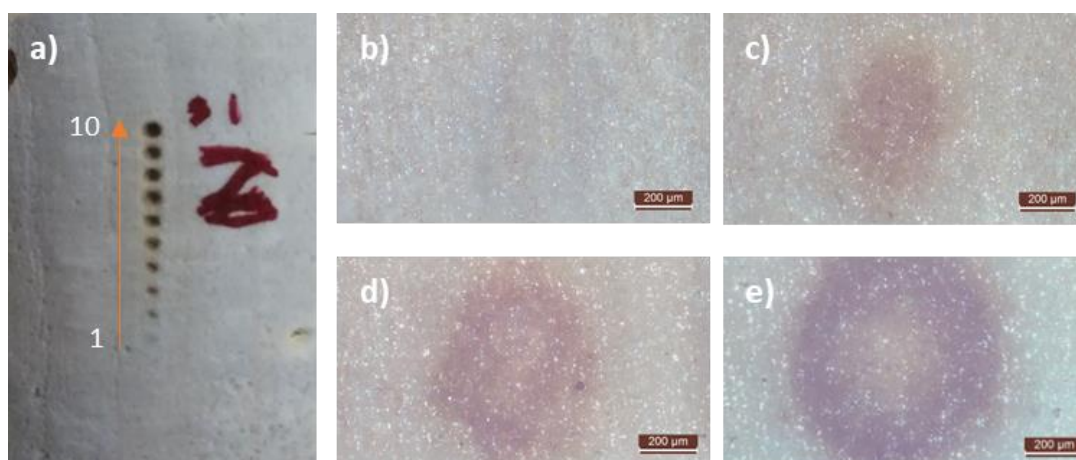


Figure I.2 – Naked eye photo of craters caused by 1 to 10 shots, b) microscope view of craters caused by 1, c) 3, d) 5 and e) 10 shots.

Despite the damage being visible at naked eye, the craters are smaller than 1 mm when firing up to 10 shots, making them smaller than most natural holes present in cork stoppers that can go up to a few millimetres and smaller than burn marks done for cosmetic purposes. In this context, it is possible that, depending on the size of the analysed region, a cork stopper might still be usable, especially after the parameters' optimisation.

While the obtained results seem positive, they urge further tests. The damage created using LIBS also propagates in depth, and its extension deserves attention. Not only it will give a more detailed picture of the dimensions of the craters, but it will also give a representation of how deep each shot is, giving knowledge of how much is being analysed at each spectrum. Plus, each coating will react differently to the laser shots. All this, however, is more suited to be performed in a dedicated LIBS system designed to analyse cork stoppers.

1.3.2. Identification of different types of treatments

For LIBS to be a viable option to analyse the coatings, it needs to be able to identify the type of coating across different types of cork stoppers. EGITRON made 10 different types of samples available for this purpose:

- 3 sets of natural cork stoppers, one without surface treatment, one with paraffin and one with both paraffin and silicone;
- 3 sets of natural cork stoppers with a pre-treatment of polyvinylidene chloride (PVC), one with no additional treatment, one with paraffin and one with both paraffin and silicone;
- 2 sets of technical cork stoppers, also known as champagne cork stoppers, one without surface treatment and one with silicone;
- 2 sets of micro-agglomerated cork stoppers, one without surface treatment and one with silicone.

For each type of sample, 15 spots were analysed along 3 lines of 5 points with a spacing of 2 mm between them. For the first spot of each line, 5 shots were performed for a subsequent depth study, the rest of the spots being analysed by a single shot. Pulse energies were not fixed, changing between samples to obtain the most intense signal while attempting to avoid saturation. The obtained spectra were submitted to a baseline removal using an asymmetric least squares algorithm[312,313], with examples for each samples being displayed in Figure 1.3.

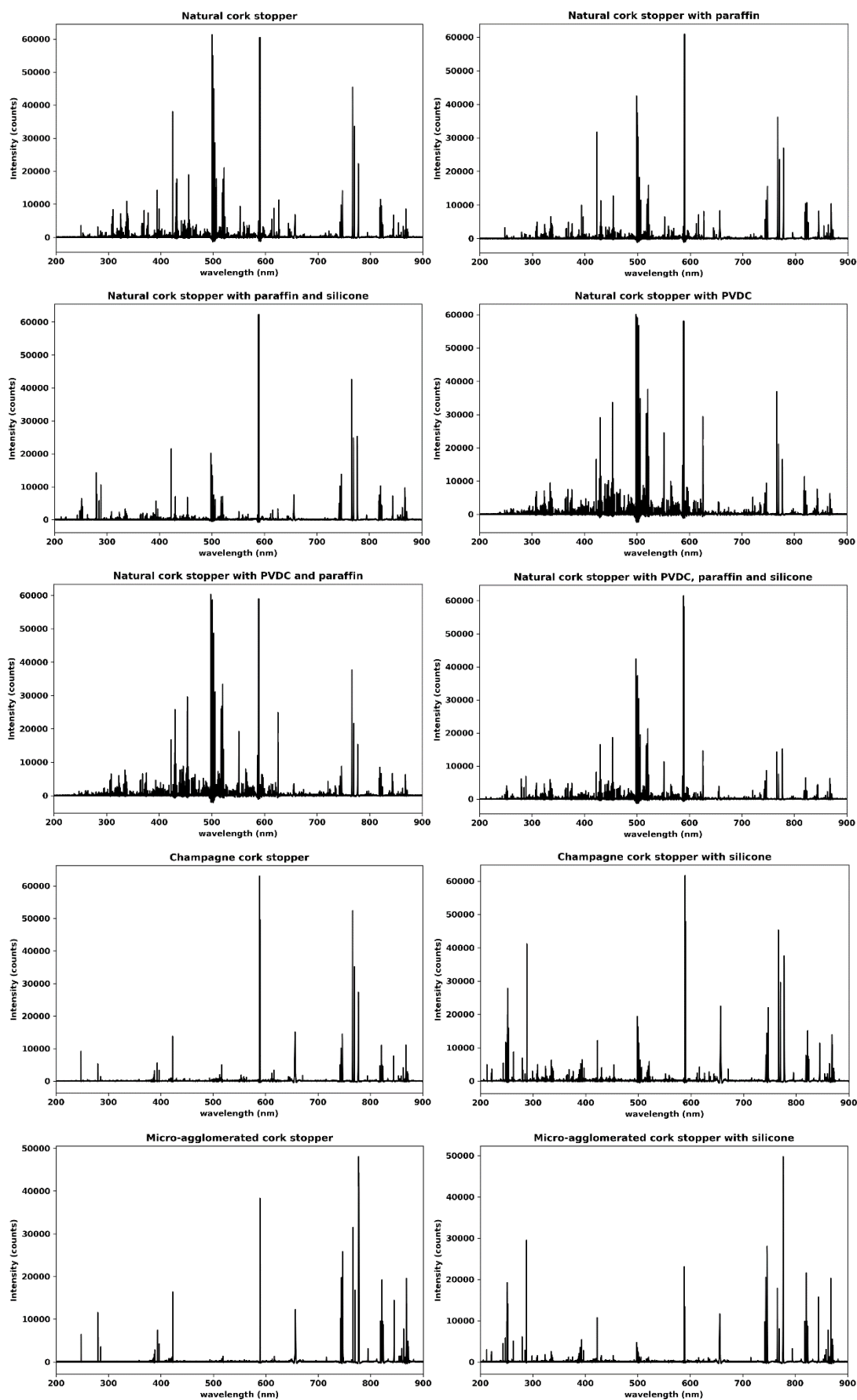


Figure I.3 – Examples of spectra for each type of sample.

Looking first at the samples prepared in natural cork stoppers, at first glance, it is hard to identify which lines truly distinguish the different samples. But, by searching for exclusive lines from the compositions of paraffin, silicone and PVDC, this task can be achieved. In the case of the PVDC, the exclusive lines should be related to its exclusive element Cl. Indeed, when comparing samples with and without PVDC, the 837.6 nm is able to distinguish both cases. In the case of silicone, its exclusive element is Si and its 288.2 nm line marks the difference between samples with and without silicone, including the champagne and micro-agglomerated cork stoppers cases. However, for the paraffin case, there is no exclusive element that a cork stopper does not already contain, making the two cases similar in terms of presence of lines. Despite this, the spectra are still different, as when lines related to C and H are compared to lines of other elements present in the cork stoppers, the proportion of their intensities changes, opening the possibility to identify the presence of paraffin with a more complex analysis.

While it is possible to identify the type of coating using a single shot, it does not provide information about its thickness and uniformity. Since the technique is micro-destructive, it should be able to ablate a portion of the coating with each shot, which means that a thicker coating will require a larger number of shots to reach past the coating. In principle, the spectral signature should diminish until it digs past the coating, using the 5 shots per spot this was confirmed as seen in the example of Figure I.4.

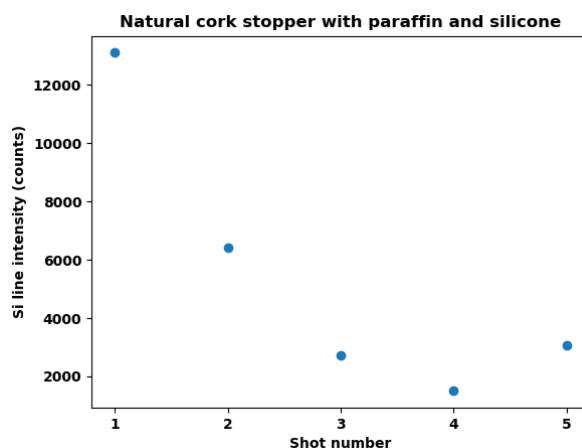


Figure I.4 – Example of the variation of the intensity of the 288.2 nm Si line with the consecutive shots in the same spot.

I.3.3. Mapping untreated areas

To unbiasedly verify the potential of LIBS to analyse coatings deposited on cork stoppers a blind test was performed. EGITRON prepared a batch of cork stoppers that were submitted to surface treatments of paraffin and silicone while having a mask with

an unknown geometrical shaped stucked to them (Figure A.1 in Attachments) aside from the one in the cork stopper number 16 for optimisation purposes.

For this analysis, several samples were analysed with different grids of points using a pulse energy of 25 mJ to see if LIBS could image the untreated areas shaped like the mask they held during treatment. Table I.1 presents the parameters of the analysis of each sample and the estimated times of analysis, which were high due to the lack of automation.

Table I.1 – Analysed samples and their respective measurement parameters.

Cork stopper	Columns	Lines	Step size (mm x mm)	Number of shots per point	Time of analysis (hours)
1	23	14	2x2	6	3.5
16	23	15	2x2	6	4
17	22	18	2x2	6	4
22	21	10	2x2	2	2.5
25	22	13	2x2	6	4
37	22	15	2x2	6	3.75
46	22	13	2x2	6	4.25
52	44	31	1x1	6	20

Due to paraffin needing a more complex analysis, this study focused on silicone only. Using the intensity of the 288.2 nm Si line, Figure I.5 to Figure I.12 present resulting maps for all samples comparing the low Si intensity areas to the real shapes of the masks that shielded their respective cork stopper.

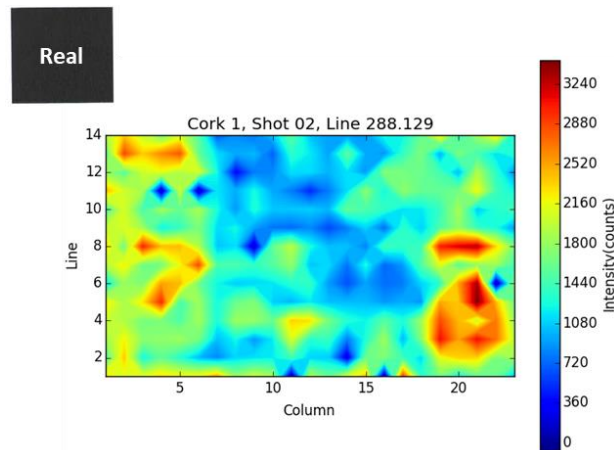


Figure I.5 – Si map for cork stopper 1.

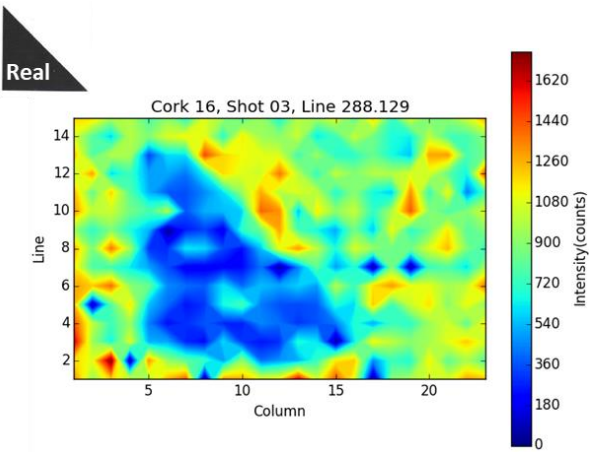


Figure I.6 – Si map for cork stopper 16.

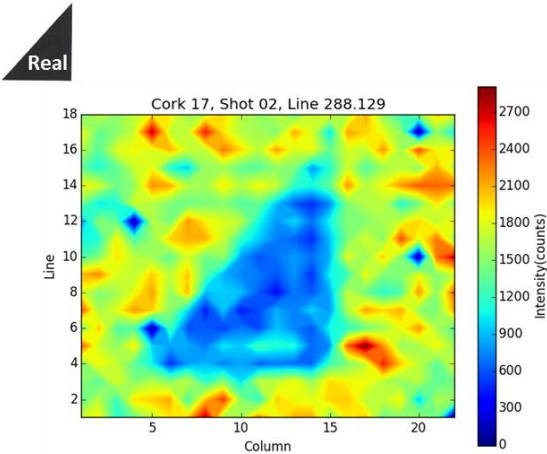


Figure I.7 – Si map for cork stopper 17.

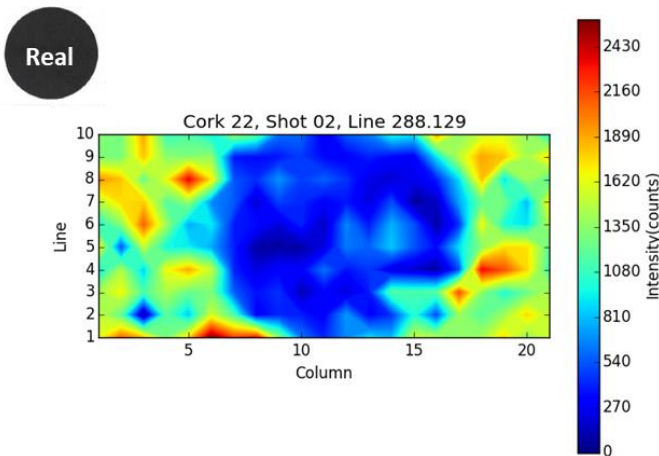


Figure I.8 – Si map for cork stopper 22.

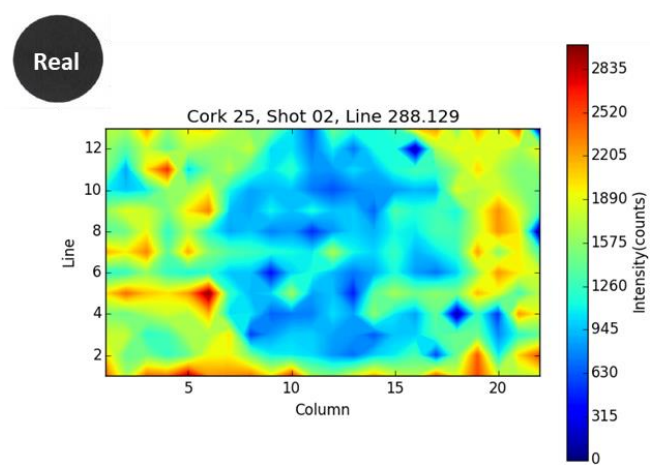


Figure I.9 – Si map for cork stopper 25.

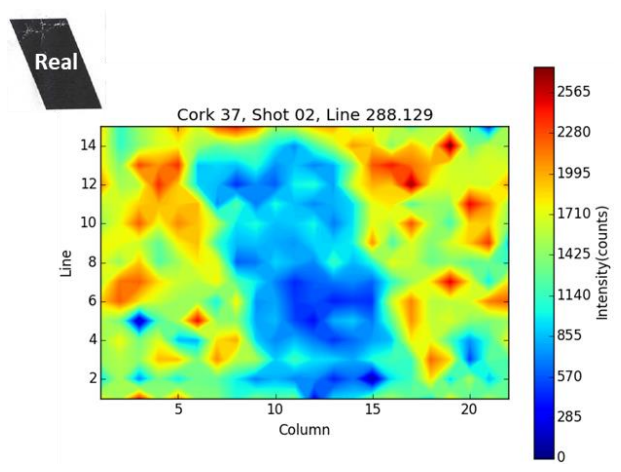


Figure I.10 – Si map for cork stopper 37.

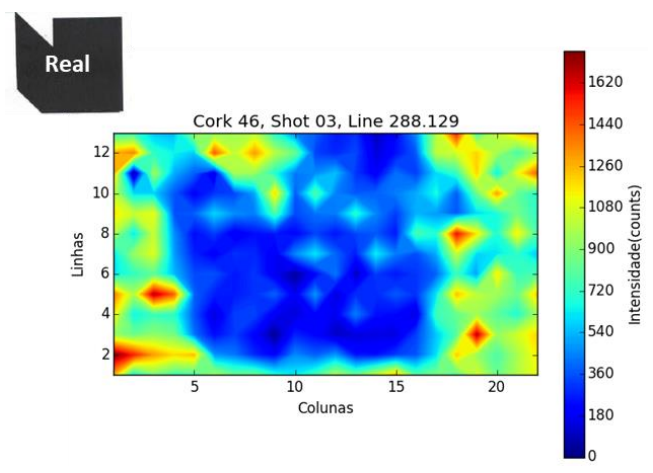


Figure I.11 – Si map for cork stopper 46.

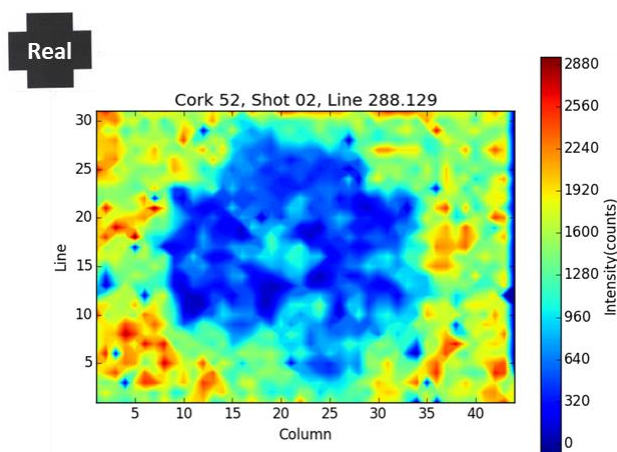


Figure I.12 – Si map for cork stopper 52.

Despite some issues with resolution and contamination, LIBS was capable of imaging all masks analysed with a small degree of error. Besides, by observing maps of the same sample related to different shot numbers in Figure I.13, it is possible to perceive that the Si intensity of the treated area starts to converge to the values at the untreated area, confirming yet again that it could be a potential metric to estimate the thickness of coatings.

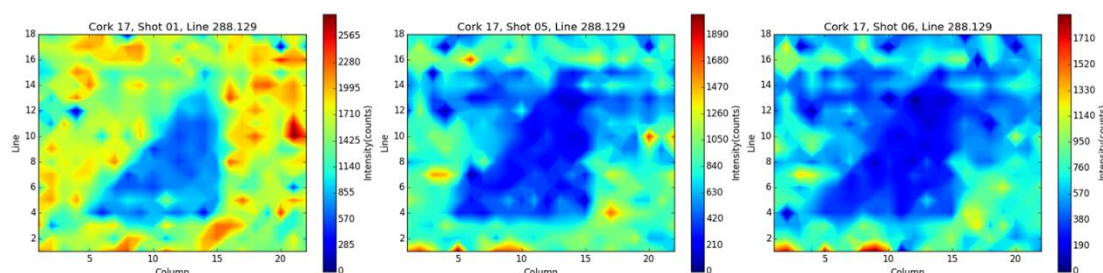


Figure I.13 – Comparison of the Si maps of the cork stopper 17 for shots 1, 5 and 6.

I.4. Conclusion

In this preliminary study, the LIBS technique was tested to see if it was a viable tool to evaluate coatings resulting from surface treatments on cork stoppers. As a micro-destructive technique, it is expected that the damage caused by an analysis should be negligible. From the analysis of the spectra, it is possible to detect the presence of paraffin, silicone and PVDC coatings, from which the first could require a more complex methodology for better results. The technique was then submitted to a blind test, where it was successful in mapping treated and untreated areas and, when combined with a depth analysis, LIBS has shown to be a viable candidate for attaining the thickness and uniformity of at least silicone coatings.

Annex II

Fibre laser pulse design predictor

II.1. Introduction

Apart from the default pulse profiles already programmed, the fibre laser used in this thesis allows for its user to design pulses in the time domain up to 320 ns. However, due to the limitations of the amplifier, the efficiency of the output will drop if the input leads to saturation, making the output laser shape a distorted version of the input laser shape (Figure 5.8).

To take full advantage of the laser capabilities, a way to achieve the desired pulse shape is required. With this in mind, a study was conducted to study how the saturation decays the emitted signal and a Python script was developed to be able to preview the necessary input for the desired output.

II.2. Saturation study

Within the fibre laser's features, a pulse is designed by assigning power values up to 64 steps of 5 ns segments, values which can range between 0 a 1023, the latter being the highest. In order to analyse how the saturation affects an inputted pulse over time, seven pulses of 300 ns with different constant powers (square shaped) were applied to the laser and their outputs were acquired using a costume photodetector (Figure II.1).

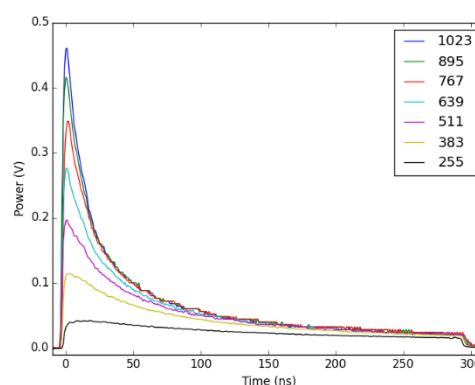


Figure II.1 – Output laser pulses resulting from the seven square shaped pulse inputs with different input powers.

At first glance, the decay section of the resulting pulses appears to follow an exponential curve, however, through several attempts of fitting no parameters could correctly fit the decays. Instead, fits were achieved for all but the two weakest pulses following:

$$P = a(t - d)^{-c} + b, c > 0, \quad (II.1)$$

where P is the pulse power, t is time and a , b , c and d are the parameters of the curves. Having failed to fit the weakest two studied pulses and the remaining having different curve parameters, including at the exponential c , it is safe to say that the saturation behaviour greatly changes with the inputted power and it is not simply proportional, suggesting that the outputted power at a given instant is dependent on the available power and inputted power at the previous instant besides the inputted power at that given instant.

Also worth mentioning is the relation between the first input power and the peak power. This is showcased in Figure II.2, where it clear that there isn't a direct correspondence between the two percentagewise. The fit, while only valid for inputs over 255, allows for a estimation for all the other non-tested input powers.

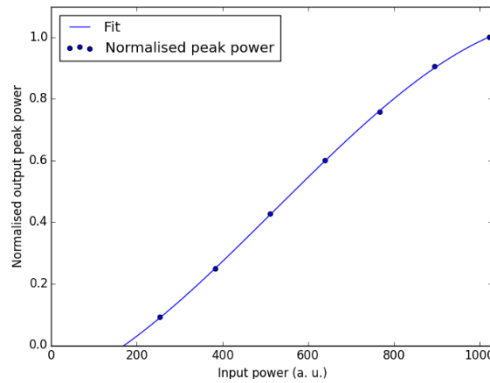


Figure II.2 – Relation between input power and output peak power and its cubic fitting.

Another aspect of the saturation is the laser's recovery from its effects within the timeframe for pulse design. For this study, 12 double square pulses of 30 ns with different time delays between the end of the first and the start of the second pulse were inputted into the laser. Figure II.3 presents some of the resulting pulses.

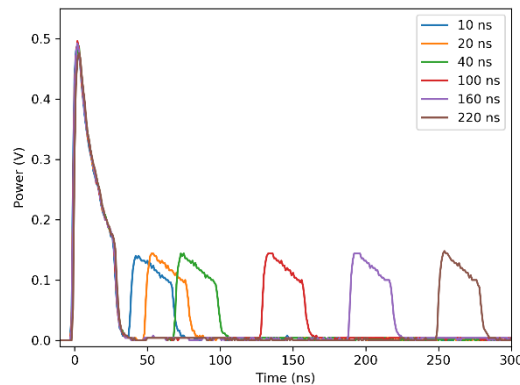


Figure II.3 – Some of the output double pulses.

Again, by analysing the peak power, it is possible to get an idea of how the amplifier is regenerating (Figure II.4).

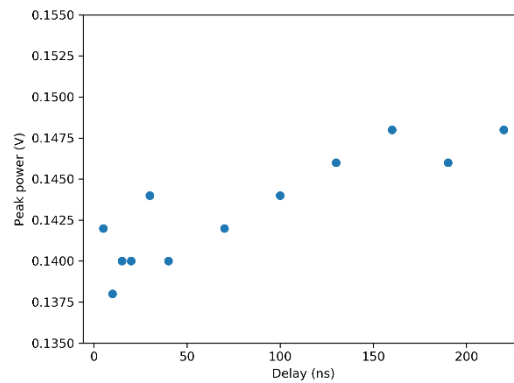


Figure II.4 – Peak power of the second pulse dependence on the delay.

Within the limits of the acquisition resolution, it can be seen that there is an increase in the peak power the more the two pulses are separated in time, meaning that the effects of saturation have reduced enough for them to be noticeable and can potentially be taken into account in a design prediction.

II.3. Concept

The idea behind the design predictor is the estimation of available power for a given 5 ns instant to assess the correct power input for the desired power output. This estimation is dependent on the previous instant's input and available power, the latter also being dependent on the prior one, in a recursive manner. The decay in available power when using a certain input can be extracted from its output pulse decay and its true percentage of power related to the maximum input. For example, by combining the pulses in Figure II.1 and the percentage of the peak powers from Figure II.2, one can obtain the decay in available power for the input powers (Figure II.5).

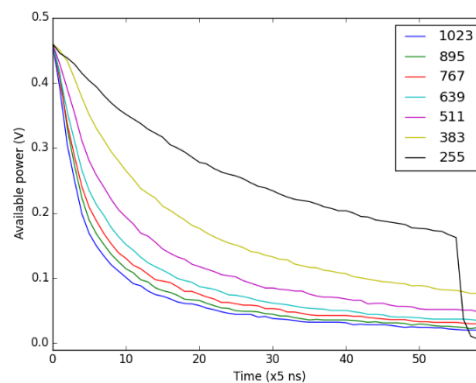


Figure II.5 – Estimated available power at each instant.

Ideally, these decays could be obtained experimentally for all the input powers, but it would be very time consuming. Instead, they can be obtained by analysing the average available power at each instant in relation to the input power, extrapolating using a gaussian fit.

With all the decays of available power determined, the predictor can receive the shape of the desired output (Figure II.6). Knowing the available power at the start, the predictor will attempt each power input, search its output power, estimate the available power at the next instant and calculate the best next input power to obtain a ratio of output powers between the second and first instants as similar as possible to the ratio of the desired output between the same two instants. This process is then repeated for all instants that are included in the desired output that was fed to the predictor. The predictor then creates a list of possible pulses for every possible first power input, which include several options with different energies, but may also include some unviable options that started with a too high of a first input power, that led to a saturation that deformed the shape, usually easy to detect due to the use of multiple maximum power inputs in a row.

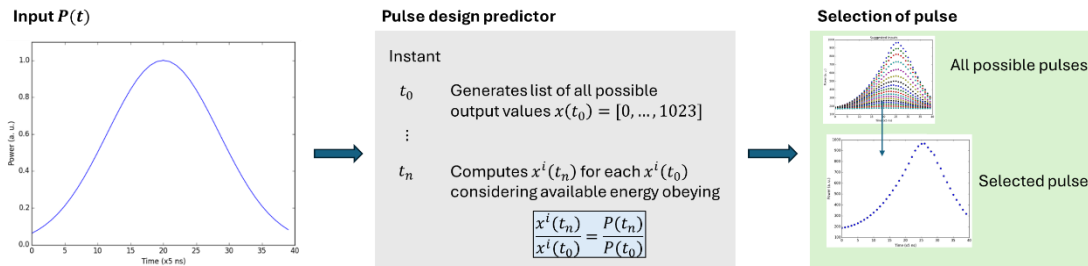


Figure II.6 – Schematic of the pulse design predictor operation process.

II.4. Results

A few shapes were attempted using the developed predictor. Figure II.7 presents the desired output (gaussian with a FWHM of 100 ns), the suggested input of the predictor and a comparison between the resulting pulse measured and the fibre laser's default "Gaussian 100 ns" pulse measured using a custom photodetector.

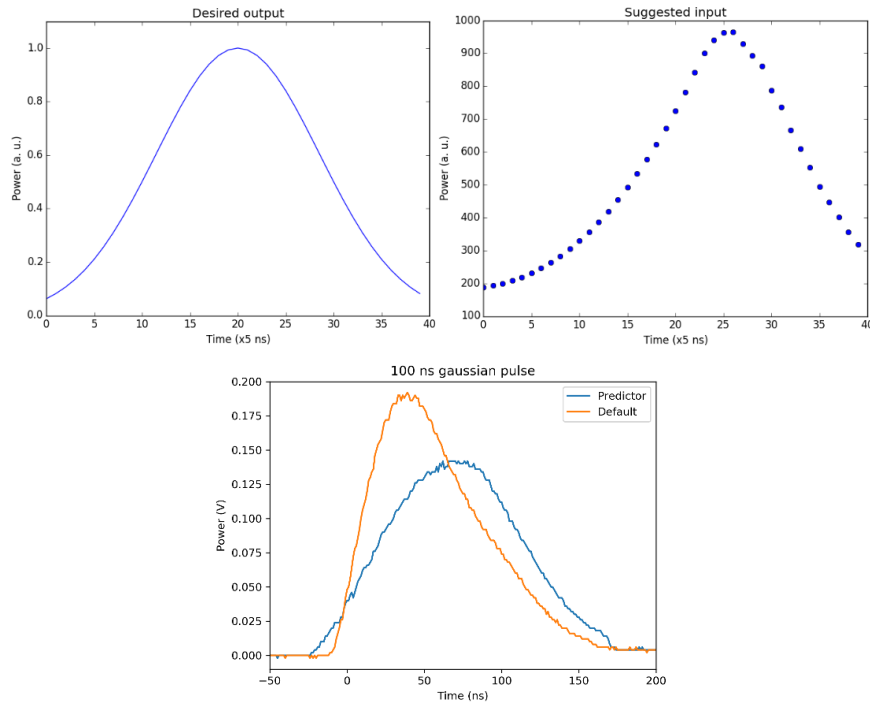


Figure II.7 – (Top left) Wanted output, (Top right) predicted input and (Bottom) comparison of the output pulses of the predictor and the default “Gaussian 100 ns” pulse.

Other examples include square pulses as seen in Figure 5.9 and ramp-shaped pulses (Figure II.8).

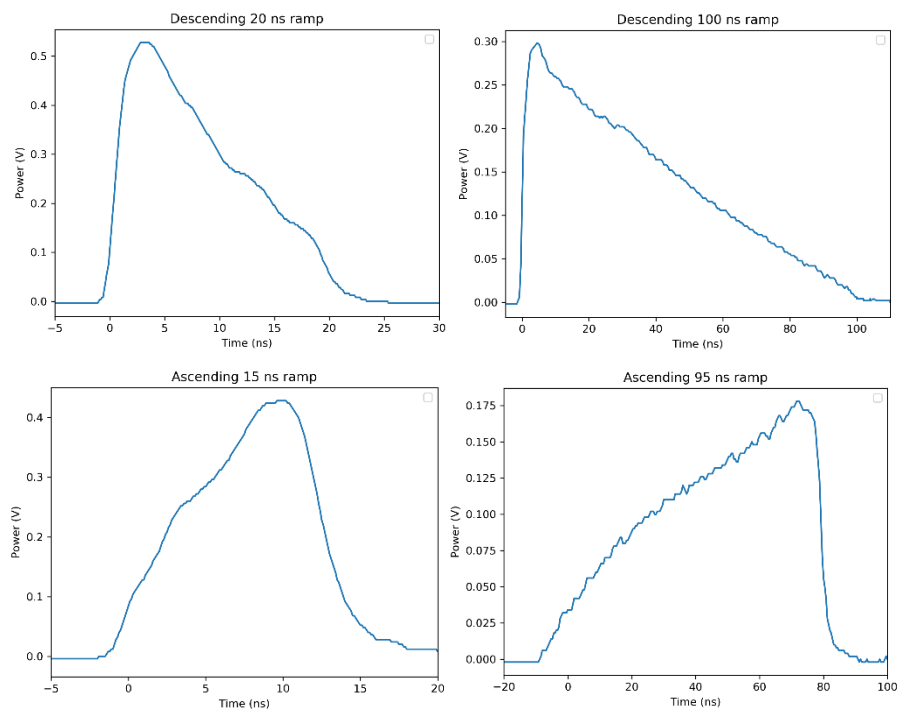


Figure II.8 – Ramp-shaped pulses.

II.5. Conclusion

A python script was created to predict the shape of the pulse to be given to the fibre laser to obtain the desired pulse shape at its output. It was successful in designing input shapes to obtain square-shaped pulses, gaussians and even ramps. The quality of the output works better with longer pulses, as shorter ones can be more deformed due to the lack of temporal resolution. The predictor is also heavily reliant on the decay study, meaning that better results can be obtained when dealing with lower powers if more decay curves are obtained for that power region. This also means that a new laser or an upgraded version with more energy output would need fresh new studies for this concept to properly predict the correct inputs.

Annex III

Industrial implementation

To advance the industrialisation of the CorkSurf system, it was sent to the industrial partner, EGITRON, for further upgrades in automation and adherence to industrial standards. The goal was to showcase the prototype to industry stakeholders. The upgraded system was then delivered to CTCOR, the technological centre for cork, to certify the new tool. This constitutes a demonstration in a relevant environment, scaling up in the Technology Readiness Level (TRL6).

The LIBS system was sent to EGITRON for final additions and improvements before public unveiling. One of these additions was a sample feeding system, developed by Azevedos Indústrias (Figure III.1). This system contains periodic sample holders designed to reduce contact and contamination. When a new cork stopper is to be analysed, a pneumatic tweezer transfers it to the sample holder. Additionally, a touch screen was integrated to run analyses and display results. For safe operation, the laser's interlock, located in the laser's trigger box was connected to all of the system's access point, including the feeding system's hatch, ensuring the laser disables itself if any door is opened during emission. This safety feature is complemented by warning lights and an emergency button. Further improvements included better cable management, optimised hardware placement, including the power switch and USB connections for external devices.

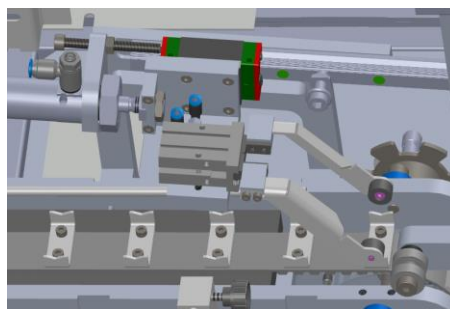


Figure III.1 – 3D drawing of the sample feeding system.

Software-wise, the system also received upgrades. EGITRON automated their most recent hardware additions, complementing the existing framework. They finished incorporating the vision system into the overall system, enabling image-based analysis of the samples' surface to identify the best spots for LIBS analysis, avoiding problematic areas such as natural craters on the cork stoppers. This vision system outputs

coordinates that replace the previously used grid protocol. For user operation, a new graphical interface was developed using JavaScript, which communicates with the PLC. Although there was an intention to readapt all Python scripts, time constraints only allowed the adaptation of the script related to the laser. The remaining Python scripts were rewritten into two executables: one to control the PDG and the other to manage the spectrometer, retrieve spectra, analyse data, and output results to a file for the main JavaScript software to read.

A photo of the system during public presentation is shown in Figure III.2. The system was showcased at the EGITRON quality conference, where it was revealed as a future product. It was displayed at the international scientific conference, Cork in Science and Applications 2023.



Figure III.2 – CorkSurf prototype at the EGITRON quality conference, keyboard only for the demonstration.

Currently, the LIBS system is at CTCOR for further testing with new samples. After installation, the optical alignment was examined and corrected for any misalignments due to transportation. Finally, the motorised rotation mount was replaced with a manual rotation mount, as it was intended to remain in a fixed position, and the half-wave plate was readjusted to set the pulse energy to 9 mJ.