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# Acoustic Spectroscopy of Laser-Induced Plasma

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TO APPLY FOR THE DEGREE OF DOCTOR

by MARKÉTA BOSÁKOVÁ

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# Acoustic Spectroscopy of Laser-Induced Plasma

por MARKÉTA BOSÁKOVÁ

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Las referencias de los artículos en los que la doctoranda figura como primera autora y que avalan la presente Tesis Doctoral se detallan a continuación de acuerdo a su orden cronológico de publicación:

**Markéta Bosáková**, Pablo Purohit, César Alvarez-Llamas, Javier Moros, Karel Novotný, Javier Laserna. A systematic evaluation on the impact of sample-related and environmental factors in the analytical performance of acoustic emission from laser-induced plasmas. *Analytica Chimica Acta*. **2022**, 1225, 340224.

**Markéta Bosáková**, Javier Moros, Pablo Purohit, César Alvarez-Llamas, Karel Novotný, Javier Laserna. Chemical and acoustical mixed-mapping of geological materials from laser-induced plasmas: A comprehensive approach to differentiate mineral phases. *Analytical Chemistry*. **2024**, 96, 17444–17452

**Markéta Bosáková**, Karel Novotný, Javier Moros, Javier Laserna. Acoustic signal in overcoming the matrix effect in LIBS: Toward reliable applicability. *Spectrochimica Acta Part B: Atomic Spectroscopy*. **2025**, 226, 107140.

**Markéta Bosáková**, Javier Moros, José M. Vadillo, Karel Novotný, J. Javier Laserna. Surveying the acoustics from laser-induced plasmas under non-standard atmospheric conditions: Implications for extraterrestrial missions. *Spectrochimica Acta Part B: Atomic Spectroscopy*. **2025**, 234, 107320.

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UNIVERSIDAD DE MÁLAGA

FACULTY OF SCIENCE

# Acoustic spectroscopy of laser-induced plasma

Doctoral thesis

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# Bibliographic Entry

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# Abstract

This dissertation presents a novel strategy for the incorporation of acoustic signals in laser-induced breakdown spectroscopy. In recent years, there has been an increasing focus on the fusion of diverse analytical approaches to enhance qualitative and quantitative analyses. A notable approach involves the utilisation of the acoustic signal generated by the laser-matter interaction between the sample and the laser pulse, a technique that has been employed by the Mars 2020 mission rover Perseverance. This dissertation aims to explicate several acoustic-spectroscopic phenomena that establish novel, systematic scientific foundations for the final complementarity of these methods.

The initial section is dedicated to the examination of the influence of the physico-chemical properties of the samples on the acoustic and emission signals, with additional consideration of the impact of the positioning of the acoustic receiver, in this case, a commercially available condenser microphone.

The subsequent section explores the practical application of this knowledge, with a particular focus on the field of geology, emphasising the domain of chemical acoustic-emission mapping. It has been demonstrated that the acoustic signal provides highly accurate and precise distribution maps with respect to the sample composition, complementing the chemical maps obtained from emission spectra.

In the third part, the focus was on the influence of instrumentation on acoustic-emission signal. The study investigated the influence of the ablation source wavelength and different types of microphones, with a particular emphasis on MEMS microphones (micro-electro-mechanical systems). These microphones are characterised by good compactness, robustness, small size and a wide choice according to the required acoustic-mechanical properties. The section was further expanded to consider the acoustic-emission analysis of nano- and microlayers, where the acoustic signal yielded results analogous to those of the emission signal.

In the final section, the focus was directed towards the examination of the effects of altering atmospheric conditions, with the primary objective being the imitation of the atmospheric conditions that prevail on Mars. This approach was undertaken to achieve a more accurate approximation of the real conditions in which the Perseverance rover is currently

operating. This involves monitoring variations in temperature (-40 to 20°C), ambient gas pressure modifications (1 to 30 mbar $CO_2$) and the composition of the surrounding atmosphere (Ar, Air, $N_2$, $CO_2$).

The four sections of this dissertation constitute the pioneering systematic acoustic-emission study of its kind, thereby providing invaluable insights for the future application of the LIBS-LIPAc (Laser-Induced Plasma Spectroscopy & Laser-Induced Plasma Acoustic) method in real-world research in harsh and extraterrestrial environments.

# Resumen

La espectroscopia acústica de plasma inducido por láser (LIPAc) representa una prometedora herramienta analítica complementaria a la espectroscopia óptica de emisión para la caracterización de materiales. El propósito de este estudio es examinar de manera sistemática la incidencia de las propiedades fisicoquímicas de las muestras y las condiciones ambientales en las variaciones de la señal acústica generada durante la formación de plasmas láser. Para ello se ha cuantificado el impacto de diversos factores, tales como la geometría de la muestra, la estructura interna, el color, la porosidad y las condiciones externas, en la calidad y el valor analítico de la señal acústica registrada.

En la primera fase del estudio, correspondiente con el primer artículo publicado, se investigaron muestras de aleación de aluminio de idéntica composición con diferentes diámetros y espesores. La evaluación de la respuesta acústica permitió identificar varios segmentos, cada uno de ellos asociado a una serie de fenómenos. Se constató que el primer segmento de la onda acústica no se ve afectado por las dimensiones de la muestra y refleja principalmente la interacción entre el láser y el material. En consecuencia, este segmento puede servir como un parámetro robusto para identificar variaciones entre materiales. Por contra, los segmentos posteriores de la señal manifestaban variaciones atribuidas a las vibraciones mecánicas y las resonancias inducidas por la geometría de la muestra, así como vinculadas al entorno en el que se encontraba la muestra.

Otros experimentos se centraron en la evaluación de la respuesta acústica procedentes de plasmas generados sobre muestras de idénticas dimensiones pero que manifestaban distinta coloración, a partir de la variable pigmentación de una resina epoxídica. Las discrepancias en las manifestaciones acústicas se atribuyeron, en este caso, a la disparidad en la absorción de la radiación láser a una longitud de onda de 1064 nm, en función de las propiedades ópticas de los pigmentos y el epoxi. Asimismo, se evidenció un impacto notable en las muestras con diversa porosidad interna, generadas mediante tecnología de impresión tridimensional. A mayor porosidad, mayor amplitud de la señal acústica, lo que se atribuyó a cambios en las propiedades mecánicas debido a la diferencia de densidad.

Otros factores circunstanciales, como la superficie sobre la que se localizaba la muestra de interés (arena, piedra, espuma absorbente), así como las coordenadas del dispositivo

receptor (distancia y altura del micrófono con respecto al punto de generación del evento plasmático) y el ángulo de incidencia del láser con respecto a la muestra, también mostraron tener un impacto significativo en las señales acústicas registradas. En esta ocasión, el análisis de la onda acústica reveló la existencia de interferencias, reflexiones y ecos en los segmentos posteriores de la señal que dificultaban la interpretación directa de los datos. Sin embargo, el primer segmento de la onda acústica se comprobó que era independiente de las condiciones externas.

En conclusión, la primera publicación permitió demostrar que las señales LIPAc ofrecen un conjunto rico de información sobre la naturaleza de la muestra, así como sobre su morfología y propiedades físicas. La interpretación de los datos acústicos requiere, ineludiblemente, un control preciso de las condiciones experimentales. Sin embargo, los métodos LIPAc, debidamente calibrados, pueden servir de valioso complemento a las técnicas ópticas tradicionales, como es el caso de la LIBS. Este estudio constituye un avance significativo hacia la implementación práctica de la técnica en el ámbito del análisis químico de materiales sólidos, incluso en condiciones de campo.

El segundo artículo expone una nueva aproximación metodológica para la cartografía óptica-acústica simultánea de materiales geológicos basada en plasmas inducidos por láser, cuyo propósito es mejorar la resolución de aquellas fases minerales de difícil distinción simplemente a partir de espectroscopía óptica. Mediante la combinación de dos enfoques analíticos complementarios —la espectroscopia de plasma inducidos por láser (LIBS, por sus siglas en inglés) y LIPAc—, se produce una imagen mejorada de la superficie de la muestra al incorporar información química y física a nivel micrométrico.

Los datos ópticos obtenidos mediante LIBS proporcionan un mapa de la distribución de los elementos (por ejemplo, Al, Fe, Ca, Ti, Cr), mientras que los datos acústicos reflejan las propiedades físicas de la superficie, tales como la densidad, la dureza, la compacidad y la absorción de la radiación (García, 2020). La combinación resultante de estos datos puede revelar la estructura interna de las rocas, el polimorfismo de los minerales y la historia geológica de cada sección de la muestra. La metodología ha sido aplicada en una variedad de materiales geológicos, incluyendo calcopirita, galena, bauxita y un nódulo septario, que representan rocas multifásicas complejas con diversos orígenes.

Los resultados obtenidos evidencian que el método en cuestión posee la capacidad de identificar zonas que exhiben una composición química equivalente, pero que presentan disparidades en sus propiedades físicas. Esta observación sugiere la presencia de diversas formas polimórficas de minerales. A modo ilustrativo, la disparidad en la respuesta acústica de áreas con idéntico contenido de Al podría atribuirse a la presencia de estructuras cristalinas divergentes, tales como la gibbsita frente a la boehmita. En el nódulo septario, se observaron bloques que evidenciaban la presencia de diferentes fases de carbono orgánico, en forma de grafito, e inorgánico, como carbonato. Este hallazgo sugiere que dichos bloques se formaron en múltiples etapas y que los procesos microbiológicos pudieron haber ejercido una influencia significativa durante la diagénesis.

En el marco del montaje experimental, se implementó la técnica de ablación por láser (1064 nm, 50 mJ) para la generación de plasmas en la superficie de las muestras. La emisión óptica del plasma se detectó mediante un espectrómetro óptico, mientras que el registro de ondas acústicas se realizó de manera simultánea por medio de un micrófono de condensador. La adquisición de la información se llevó a cabo mediante la interrogación de una matriz de puntos análisis solapados un 75% en uno de sus ejes, con el propósito de incrementar la resolución espacial. Posteriormente, se generaron los denominados «poliedros multiespectrales», entendidos como una geometría combinada que aunaba por superposición los mapas elementales (tantos como elementos se identificaban en la muestra) y el mapa acústico, todos ellos normalizados para no sesgar la respuesta de ninguna de las modalidades espectrales.

Esta técnica ha demostrado ser una herramienta poderosa para el análisis detallado de la superficie de las rocas, complementando, en incluso en algunos aspectos superando, a métodos establecidos como la espectroscopia Raman o la difracción de rayos X. En virtud de su robustez e independencia de la preparación de muestras, el método resulta igualmente adecuado para aplicaciones de campo y exploración planetaria. A modo ilustrativo, en el contexto de misiones de exploración planetaria, como la misión MARS2020 de la Administración Nacional de Aeronáutica y el Espacio (NASA, por sus siglas en inglés), en la que el instrumento SuperCam a bordo del vehículo robotizado PERSEVERANCE lleva un micrófono que, en ocasiones, actúa conjuntamente con la técnica LIBS. La combinación sinérgica de la luz del plasma inducido por láser y el sonido que lo acompaña ofrece una nueva dimensión al campo del análisis mineralógico.

LIBS es un método analítico atractivo para el análisis químico de sólidos debido a su naturaleza sin contacto, sus mínimos requisitos de preparación de muestras y su capacidad de mapeo espacial. No obstante, la precisión y reproducibilidad de la señal se ven afectadas significativamente por los denominados efectos de matriz, que corresponden a fenómenos derivados de las propiedades físicas y químicas de los materiales analizados. Estos efectos interfieren en la consistencia de la señal. El tercer artículo expone un nuevo enfoque para mitigar dichos efectos mediante el empleo de LIPAc para la corrección de la señal LIBS.

El estudio aborda de manera sistemática la influencia de diversos factores en la naturaleza de la señal acústica, desde variables asociadas a la generación de la fuente acústica, tales como la longitud de onda del pulso láser y su energía) hasta las características de los dispositivos utilizados para el registro de la señal (el tipo de micrófono), pasando por las propiedades de la superficie de la muestra. La comparación de distintos tipos de micrófono (basados en la tecnología MEMS ─ Micro-Electro-Mechanic Systems, por sus siglas en inglés ─ y de condensador electret) demostró que los micrófonos MEMS proporcionan un registro más estable y preciso de las señales acústicas, siendo el de tipo "In-Car Sound" (ICS, por sus siglas en inglés) el que proporcionó la mejor respuesta se consideró para las consiguientes mediciones. Asimismo, se evidenció que la fluencia del láser (energía por unidad de superficie) desempeña un papel crucial: si supera significativamente el umbral de ablación del material, las disparidades entre las señales acústicas se minimizan, esto es, los plasmas reportan prácticamente cantidades idénticas de energía acústica, lo que complica notablemente la diferenciación entre materiales.

En el ámbito de la aplicación práctica, la técnica fue examinada en diversas tipologías de muestras. De un laso, una muestra artificial sintética, consistente en una probeta cilíndrica de aluminio, cuya superficie, finamente pulida, se recubrió parcialmente con una capa de cobre de 1 μm de espesor. Al tiempo, la muestra se sometió parcialmente a un chorro de arena, disponiéndose de 4 cuadrantes bien definidos: aluminio bruto pulido, aluminio recubierto con cobre y sus homólogos rugosos. De otro lado, una muestra real, una estructura geológica formada por el mineral galena embebido en una matriz de calcita. En el caso de la muestra de aluminio, se observaron variaciones en la amplitud de las ondas acústicas entre la superficie bruta de aluminio y la recubierta de cobre. En cambio, los resultados acústicos no revelaron visiblemente ninguna diferencia física relacionada con la rugosidad de la superficie. Por el contrario, sorprendentemente se identificó que el mapeo químico mediante LIBS mostraba distribuciones dispares de Cu en la superficie de la muestra de aluminio, en función de la naturaleza, atómica o iónica, de la línea de emisión considerada. Esta disparidad, fruto del efecto matriz, consiguió eliminarse parcialmente utilizando la señal LIPAc para corregir la señal LIBS. Idénticos resultados se obtuvieron en la evaluación de la muestra de galena. La corrección mediante las señales acústicas permitió una mejor catalogación de la sección mineral de galena frente a la sección de calcita.

En conclusión, el presente estudio evidencia que la integración de señales acústicas y ópticas resulta en una contribución significativa al incremento de la fiabilidad cualitativa y cuantitativa de las mediciones LIBS. La corrección acústica se presenta como una herramienta robusta, sencilla y eficaz para suprimir los efectos de matriz y, por tanto, proporcionar un análisis químico más preciso de materiales heterogéneos. Este método ha mostrado mucho potencial a escala de laboratorio, pero no se descarta su futura aplicación en medidas de campo.

El cuarto artículo se centra en una investigación exhaustiva del impacto de las condiciones atmosféricas no convencionales sobre la señal LIPAc. El desarrollo de las evaluaciones convencionales de LIPAc se enmarcan predominantemente en entornos controlados de laboratorio, caracterizados por mantener condiciones constantes de presión, temperatura y composición del gas. En el presente estudio, se aborda en la comprensión de los fundamentos del comportamiento de dichas señales acústicas en entornos realistas y dinámicos, que difieren de las condiciones de referencia estándar. El propósito de la presente investigación fue cuantificar la influencia de variaciones en la presión (en un rango entre 1 y 30 mbar), la temperatura (en un rango entre -20 °C a +50 °C) y la composición atmosférica ($CO_2$, Ar, $N_2$ y aire) de la atmósfera sobre la forma de onda y la calidad de las respuestas acústicas detectadas.

La metodología propuesta se ha fundamentado en la recreación de diversas combinaciones de presiones, temperaturas y composición atmosférica en una cámara de vacío térmico (TVC). El plasma láser se generó mediante la utilización de un láser de Nd:YAG (1064 nm), mientras que las señales acústicas fueron registradas por micrófonos

MEMS de alta sensibilidad. Cada configuración atmosférica fue sometida a una adquisición sistemática de datos, incluida la forma de onda, la amplitud, el espectro de frecuencias y el retardo temporal de la respuesta acústica fundamental.

Los resultados obtenidos han evidenciado que las variaciones en la presión ejercen un impacto significativo en la amplitud y la propagación de la señal acústica. A medida que se incrementa la presión, se observa una atenuación más pronunciada y un desplazamiento de la banda de frecuencias hacia frecuencias armónicas más elevadas. En contraste, las presiones más bajas conducen a reverberaciones más prolongadas y a un espectro de ondas más difuso en el tiempo, lo que dificulta el análisis inequívoco del pulso de plasma. Los efectos de la temperatura se manifiestan a través de diversas velocidades de propagación del sonido y variaciones en las características de amortiguación (Meyer, 2019). Específicamente, en los extremos de -20 °C y +50 °C, se observan cambios significativos en la estabilidad de la amplitud de la señal (Meyer et al., 2021). Las alteraciones en la composición de la atmósfera, tales como el incremento de dióxido de carbono ($CO_2$) o de gases inertes, han ocasionado variaciones en la velocidad de generación y extinción del plasma, lo cual se manifiesta en una «huella dactilar» espectral distinta de la respuesta acústica.

El estudio sugiere la implementación de LIPAc en la investigación planetaria, con un enfoque particular en Marte, caracterizado por la baja presión y temperatura de su atmósfera mayoritariamente de $CO_2$. Los resultados obtenidos evidencian que, para una interpretación adecuada de los datos recabados por el instrumento SuperCam, resulta imperativo considerar los efectos atmosféricos en cada medida.

La presente Tesis describe una aplicación inédita e innovadora de LIPAc, en el contexto de la investigación desarrollada en la misión MARS2020, en conjunción con otro método basado en láser, la espectrometría de masas con plasma de acoplamiento inductivo por ablación láser (LA-ICP-MS).

Una parte sustancial de la investigación que involucra esta Tesis se ha centrado en el uso de LIPAc y su aplicación en condiciones extremas que simulan el entorno de Marte. El estudio se fundamenta en investigaciones previas en el ámbito de la LIBS, y se enriquece con nuevos experimentos llevados a cabo en la TVC en condiciones de 7 mbar de dióxido de carbono y -20 °C. El propósito de este estudio fue evaluar la eficacia del método LIBS-

LIPAc en la discriminación de diversos materiales de acuerdo a su respuesta acústica, particularmente en condiciones simuladas de entorno marciano, que emulan un contexto relevante para la exploración planetaria futura.

El análisis se llevó a cabo en siete muestras, que incluyeron cuatro cilindros de aluminio, dos piritas y una muestra de magnesita. La respuesta acústica se registró como la intensidad pico-valle de la primera onda de presión generada tras la ablación láser. Los resultados obtenidos evidencian una marcada diferenciación entre los materiales analizados, así como corroboran el hecho de que la ubicación de la muestra en el soporte no ejerce una influencia sustancial en la respuesta acústica, lo cual valida la notable estabilidad de la metodología desarrollada.

La combinación LIBS-LIPAc demostró el potencial para lograr una resolución más fina de las muestras. Si bien el procedimiento demanda una mayor autentificación en una serie más extensa de especímenes, los hallazgos apuntan a su factibilidad para la disolución de compuestos sin proximidad en circunstancias de misión planetaria.

# Declaration

I hereby affirm that this thesis, entitled "**Acoustic spectroscopy in laser-induced plasmas**" is my original work and has not been derived from the work of others unless such work has been referenced and acknowledged within my text. I hereby declare that I have completed my work independently under the supervision and guidance of Doc. Karel Novotný, Ph.D., Doc. Javier Moros and Prof. Javier Laserna. I have used the aforementioned sources and information cited in the thesis. The experimental results were obtained at the Department of Chemistry at Masaryk University, Czech Republic and UMA LASERLAB, Universidad de Málaga, Spain.

In Brno 9. 9. 2025 …..……………………………………………

Mgr. Markéta Bosáková

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# Original publications

The thesis is based on four accepted publications of the author of the dissertation (Markéta Bosáková, MB).

## Review article (annex 1)

**A systematic evaluation on the impact of sample-related and environmental factors in the analytical performance of acoustic emission from laser-induced plasmas**

**Markéta Bosáková**, Pablo Purohit, César Alvarez-Llamas, Javier Moros, Karel Novotný, and J. Javier Laserna

Analytica Chimica Acta (2022)

MB performed the experiments and data curation, formal analysis and investigation.

## Review article (annex 2)

**Chemical and Acoustical Mixed-Mapping of Geological Materials from Laser-Induced Plasmas: A Comprehensive Approach to Differentiate Mineral Phases**

**Markéta Bosáková**, Javier Moros, Pablo Purohit, César Alvarez-Llamas, Karel Novotný, and J. Javier Laserna

Analytical Chemistry (2024)

MB designed the study, performed the experiments and data analysis and revised the final version of the manuscript.

## Review article (annex 3)

### Acoustic signal in overcoming the matrix effect in LIBS: Toward reliable applicability

**Markéta Bosáková**, Karel Novotný, Javier Moros and J. Javier Laserna

Spectrochimica Acta Part B: Atomic Spectroscopy (2025)

MB designed the study, performed the experiments, wrote original draft, performer formal analysis and data curation and conceptualization of the final draft.

## Review article (annex 4)

### Surveying the acoustics from laser-induced plasmas under non-standard atmospheric conditions: Implications for extraterrestrial missions

**Markéta Bosáková**, Javier Moros, José M. Vadillo, Karel Novotný and J. Javier Laserna

Spectrochimica Acta Part B: Atomic Spectroscopy (2025)

MB contributed in in experiment design & measurement, methodology, investigation, formal analysis, data curation and review & editing of the draft.

# Table of Contents

# 1. Introduction

In recent years, there has been an increasing focus on the integration of diverse methodologies with the objective of enhancing the precision and efficiency of qualitative and quantitative analyses while concurrently reducing analysis time, the quantity of analysed sample and the necessity of its pretreatment.

Laser-induced breakdown spectroscopy (LIBS) is a cutting-edge analytical technique that has gained significant attention in the field due to its numerous advantages, including its speed, non-contact nature, minimal requirements for sample preparation and versatility in analysing a wide range of samples, whether solid, liquid, or gases. The fundamental principle of the method is based on the focalisation of a pulsed laser beam onto the surface of the sample, causing a small amount of material to evaporate and creating a short-lived plasma, accompanied by the creation of an acoustic shock-wave. The emission spectrum of the plasma then provides information about the atomic composition of the sample.

In recent years, significant developments have been witnessed in the field of LIBS, attributable to advanced detection systems, more powerful lasers, and sophisticated data processing algorithms (including machine learning). These enhancements have resulted in significant advancements in the sensitivity, accuracy, and quantitative capabilities of the method. LIBS is currently used in a wide range of fields, from metallurgy and geochemistry to forensic science, environmental monitoring, food science, and planetary exploration (e.g., NASA's Mars rover Perseverance mission). Furthermore, complementary approaches are being developed, such as the combination of LIBS with Raman spectroscopy, laser ablation coupled with mass spectrometry (LA-ICP-MS), which facilitates more profound material characterisation, and combination with plasma shock-wave analysis.

It is believed that the acoustic response of the analysed sample contains diverse additional information, which is complementary to the laser plasma-based techniques. Due to its complexity and robustness, it is believed that many sample, environmental and instrumentation factors are hidden in the acoustic signal, yet their contribution is crucial to fully understand and clearly identify the signal correctly. Once understood, laser plasma-based acoustics has the potential to become an invaluable, easily integrated tool for other plasma-based methods.

The analytical interdisciplinarity trend is most evident in the context of NASA's Mars 2020 mission, whose rover, Perseverance, is equipped with an array of scientific instruments designed for various Martian operations. In the context of my dissertation research, the SuperCam instrument on board the rover is of particular interest. The primary objective of the SuperCam is the chemical identification of Martian surface materials, with a focus on rocks, sand, and dust in the rover´s surroundings. The principal advantage of this instrument is its non-contact analytical approach, made possible by the use of laser-based methods, namely Raman spectroscopy, infrared spectroscopy and laser-induced plasma spectroscopy (LIBS), complemented by a microphone that records the acoustic response of the evolving plasma plume. However, even though Perseverance already records both the plasma emission and the acoustic signal, our knowledge of plasma acoustics is still limited. In order to comprehend it in detail and to propose the correct way of employing the plasma shock wave accompanying the plasma plume propagation, a systematic study is inevitable.

# 2. Objectives of the dissertation thesis

The main objective of the dissertation thesis was to understand and describe the behaviour of the laser-induced plasma acoustic (LIPAc) signal recorded simultaneously with the plasma emission for its potential to become a complementary method to laser-induced breakdown spectroscopy (LIBS).

In the first part of the study, the effect of the sample´s physical and chemical properties on the acoustic signal on well-controlled samples, resulting in the segmentation of the acoustic signal with respect to sample properties (used for further analyses), as well as the receiver´s characteristics, were defined. The second part was focused on applying the knowledge to real sample analysis – mapping of various mineralogical samples. Acoustic spectroscopy was shown as a powerful tool to distinguish minerals with close or even the same major elements composition (while altering physical-chemical properties such as density, hardness, crystallography, … in mineralogical samples), making it a fully complementary method to the LIBS signal.  The third subsection of experiments covered the instrumental alterations of the acoustic signal, suggesting the best experimental conditions. Additionally, verification of complementarity with another laser-plasma-based method, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), was additionally investigated with the same positive trend given by the preliminary results. The ultimate goal was to transfer all the knowledge to planetary-based research emphasising Martian conditions and their alterations (in question of atmospheric temperature, composition and pressure), which the Perseverance rover has to deal with daily.

# 3. Introduction to LIBS & LIPAc

Laser-induced breakdown spectroscopy (LIBS) is a rapid analytical technique based on the interaction between a high-energy laser pulse and the sample surface. The short laser pulse is tightly focused on the target, causing its instant overheating, vaporisation and ionisation, known as laser ablation. The rapid and high-temperature plasma expansion occurs simultaneously with the supersonic expansion, generating an acoustic shockwave that propagates through the ambient medium, typically air. Concurrently, the plasma radiation is captured by the spectrometer, meanwhile the acoustic shockwave can be recorded by the microphone. It has been demonstrated that both the plasma emission and the acoustic shockwave reflect the properties of the material under analysis. In recent years, laser-induced plasma acoustics (LIPAc) has gained importance in laser-based techniques, becoming a complementary method of plasma diagnostics. This development has accelerated the growth and general understanding of acoustic spectroscopy. To date, the LIBS has become a favoured method, primarily due to its significant advantages, including minimal sample preparation, real-time analysis, and the capacity to operate in harsh environments. This renders it useful in fields such as materials science and characterisation [1,2] environmental monitoring [3], biomedical diagnostics[4–7] and even space exploration [8].

Even though the LIBS-acoustic is one of the hot topics nowadays, the generally dominant trend is the interdisciplinarity and complementarity between the LIBS and other methods such as acoustic spectrometry or Raman spectroscopy. The fusion of later mentioned combines the non-destructive approach of the Raman spectroscopy providing information regarding the molecular structure, bonding and additionally even determines the crystal forms suitable not only to inorganic materials such as minerals but moreover to organic materials, with fast and mildly destructive elemental composition including the light elements in, by the principle, any solid, liquid and gas sample. The complementarity is exploited in characterising microplastics and detecting heavy metals from water sources [9], cultural heritage [10]characterisation of the biological samples [11], for mineral characteristics [12,13], enhanced by the artificial intelligence [14] or in planetary explorations [15].

Concurrently, the latter is one of the greatest propelling powers in plasma-based acoustics, led by NASA´s Martian exploration mission, with the SuperCam team in charge of the acoustic explorations. The currently ongoing mission Mars 2020 has deployed the

LIPAc along with other spectroscopy methods onboard the Perseverance rover, aiming to conduct geological research, mainly rocks and minerals identification [16,17]. Up to date, many publications have described acoustic spectroscopy as a promising tool for the independent information regarding the ablation process [18], enhanced discrimination capabilities of different mineral phases within altering atmospheric conditions[19], employment of the fast-fourrier transform (FFT) to differentiate chemically alike mineralogical phases [20] or even described the first acoustic responses obtained altogether with LIBS of geological targets at Jezero crater at Mars [21]. Nevertheless, the first attempts in engaging the acoustic signal in LIBS experiments were first introduced in 1988 based on the acoustic waves acting as an internal standard [22]. Ever since then, the plasma acoustic has been studied as a correlation parameter to the ablation rate [23], a normalisation parameter [24], a plasma expansion mechanism indicator [25], in steel classification [26] or a matrix effect suppressor in soil analysis [27].

# 4. Experimental section

## 4.1. Instrumentation

The chapter elucidates the experimental setup, its evolution, and the drawbacks encountered during the research. It is important to note that the experiments were conducted in two independent laboratories, each with a different configuration of instrumentation. The research was conducted at the UMA LASERLAB laboratory in Málaga, Spain, and the LIBS laboratory at Masaryk University in Brno, Czech Republic. The evolution of the setup is presented in chronological order and in general scope so as not to confuse the reader, yet all the specific instrumental parameters are described in detail in the enclosed articles.

In general, experimental setups consist of Nd:YAG laser as an excitation source (altering wavelengths, energies, fluences, manufacturers, etc.), focusing optics for the excitation laser, plasma collection optics and the optical fibres that lead the plasma light to the spectrometers and spectrometers (most commonly Avantes spectrometers of various ranges and number of channels, timing options, etc.). The microphone, which can be a commercial condenser mic, MEMS mic or electret mic, is another essential component. In addition to these components, the experimental setup also requires an AC/DC acoustic converter, such as a soundcard or oscilloscope, and a motorised sampler holder allowing alteration of the inter- and intra-sample positions.

The acoustic signal is a complex phenomenon for which a precise setup is required to record the real plasma shockwave with high accuracy. A fundamental principle that must be observed is to ensure that the distance between the sample and the microphone is shorter than that of any other closest subject. Secondly, the microphone must be positioned in close proximity to the optical path of the excitation laser, ensuring the accurate recording of the plasma shockwave in the same plane as the evolving plasma. The third rule is to design and build the anechoic chamber, covering the experiment and ensuring that the environment/background noise of the laboratory (laser power supply, noise from colleagues/traffic/...) doesn't affect the plasma recording.

In the initial configuration at UMA LASERLAB (used in articles 1 and 2), the experimental space was constrained by the dimensions of the optical table, necessitating the placement of the laser head externally to the table. The laser beam was directed to the anechoic chamber through an aperture in the acoustic absorbent (slightly wider in diameter than the original collinear laser beam, yet the smallest possible) and focused by the 100 cm focal length plane-convex quartz lens to the sample. It is imperative to note that, given this distance, a condenser microphone (Audix TR-40) was positioned at 50 cm, determined as the optimal distance between the microphone and the sample. It is also noteworthy that the plasma acoustic signal was digitalised by means of the QuadCapture (Roland) interface and recorded using the Audacity software. The plasma collection was positioned at a distance of 60 cm from the sample, in a quasi-collinear arrangement (10°) with respect to the excitation beam, in order to ensure optimal collection of the plasma light. The anechoic chamber (140 x 50 x 50 cm) has been constructed from an aluminium profile cage filled with acoustic absorbent material (polyurethane foam, total height of 40 mm, nub height of 30 mm, bulk density of 16.5 ± 1.0 kg·m$^{-3}$). The technical capability of the configuration was such that it permitted the examination of the effect of altering the position of the microphone in relation to the sample. This examination described the influence of modifying the height of the microphone, the mic-to-sample distance, and altering the angle of incidence between the microphone and the sample. This examination is described in detail in the Article 1.

The principal finding was the comprehension of the acoustic shockwave progression and defining the individual segments of the recorded signal. It was established that the initial (and concurrent maximum) peak-to-valley amplitude is indicative of laser-to-matter interactions. Utilising the experimental configuration, the anticipated echo times were determined through the application of equation 1 (where $d$ is the microphone-to-sample distance and $v_s$ is the speed of sound) and subsequently identified within the acoustic waveforms. However, a "direct" echo at 0.928 ms, corresponding to the 11 cm distance approximately, has been observed in the waveform, yet no subject has been placed at such a distance (fig. 1A). This finding prompted further investigation into plasma recording at varying mic-to-sample distances. Nevertheless, the direct echo remained unaltered, indicating an echo directly associated with the microphone. This hypothesis was corroborated through a closer examination of the microphone´s shape. As depicted in fig. 1B, the microphone has a tube-like construction with a slight enlargement of its diameter in the middle. Thus, the plasma acoustic signal propagates from the tip of the microphone alongside the body of the microphone, arriving at the enlargement where the signal is partially reflected to the tip of the microphone, resulting in the aforementioned direct echo.

$$t = \frac{2 \cdot d}{v_S} \qquad \text{(eq. 1)}$$

d … microphone-to-sample distance (m)

vs … speed of sound (m/s)

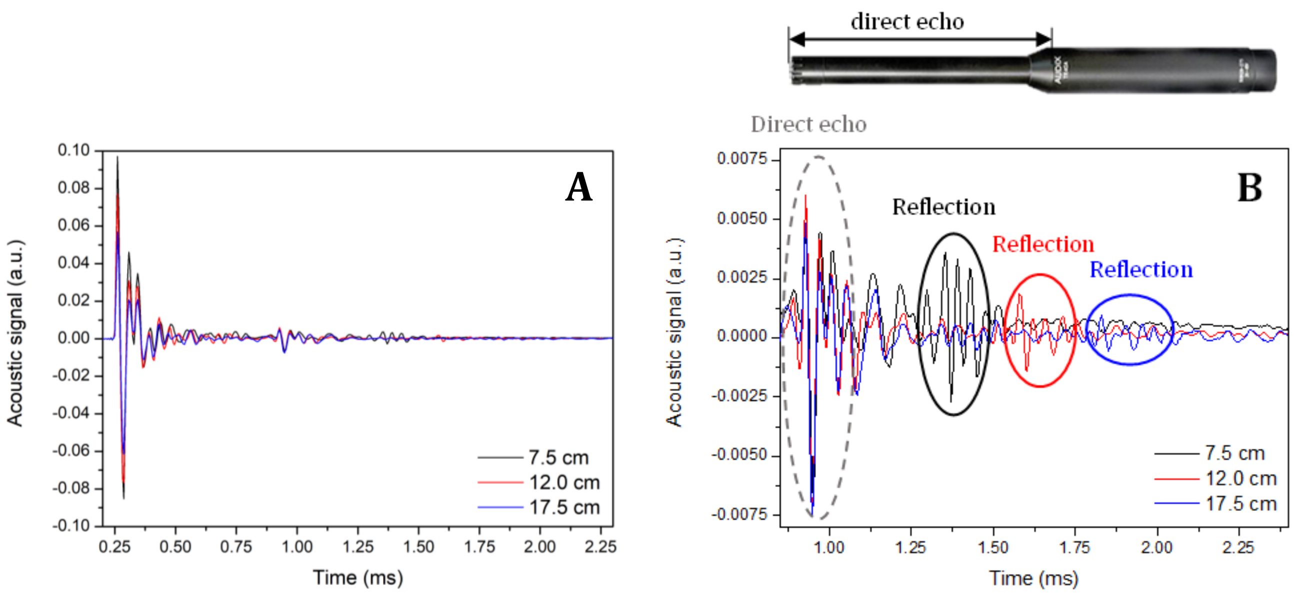


***Figure 1.*** *A) Plasma-acoustic distance-dependent spectra; B) Zoomed figure A with a photo of the mic with arrow demonstrating the propagation of the acoustic signal [28].*

The second setup was designed at the LIBS laboratory of Masaryk University. For this purpose, three pairs of new MEMS microphones with altered acoustic/electrical characteristics were procured: the ICS-40720 (TDK InvenSense), the SPM0687LR5H-1 (SiSonic™ SPM series by Knowles), and the SPU0410LR5H-QB (SiSonic™ SPU series by Knowles). In addition to these microphones, two MCE 100 electret capacitor microphone capsules were purchased. In order to incorporate the microphones into the setup itself, each of them has been soldered onto purpose lab-made printed circuit boards (PCBs). Two 3D-printed holder cases have been designed to power the microphone PCB with two AA batteries, and the BNC connector output port was mounted to directly connect the microphone to the oscilloscope (fig. 2). The specifics of the acoustic and electrical properties of the microphones, in addition to the outcomes of the plasma-acoustic experiments, are elucidated in Article 3.

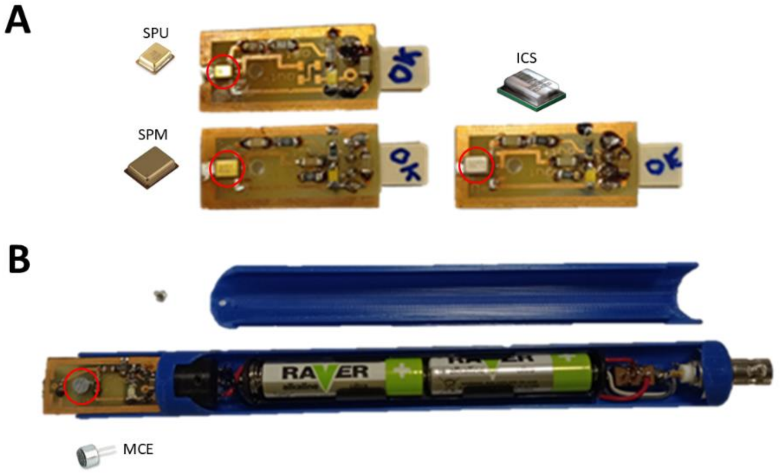


***Figure 2.*** *A) MEMS microphones solded to a PCB boards; B) 3D printed mic holder [29]*

Nevertheless, in comparison with the UMA LASERLAB configuration, the most significant challenge was to be found in the design of the optimum incorporation of the microphones into the pre-existing and space-restricted LIBS cage system, as illustrated schematically in figure 3. The initial approach involved the construction of a small anechoic chamber within the cage system, with the objective of mitigating echoes and background noises. The construction of a completely closed chamber was undertaken, utilising a HiLo-N40 broad-band acoustic absorber (comprising polyurethane foam with a total height of 40 mm, nub height of 30 mm, and bulk density of 16.5 ± 1.0 kg·m-3). This absorber was equipped with small apertures to allow for the entry of the laser beam, the collection optics, the sample, and two microphones. The microphones have been positioned within the chamber in close proximity to each other and to the plasma expansion, with the aim of optimising the plasma acoustic recording. The microphones were positioned at a distance of approximately 7 cm from the plasma, with the objective of preventing their saturation while ensuring that the shortest feasible measuring distance was maintained.

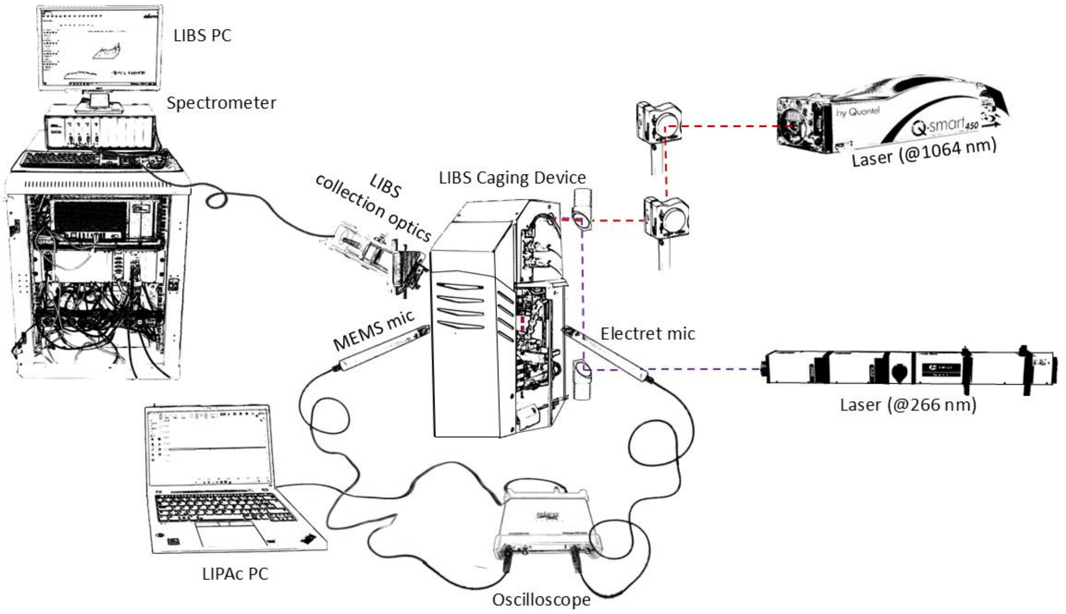
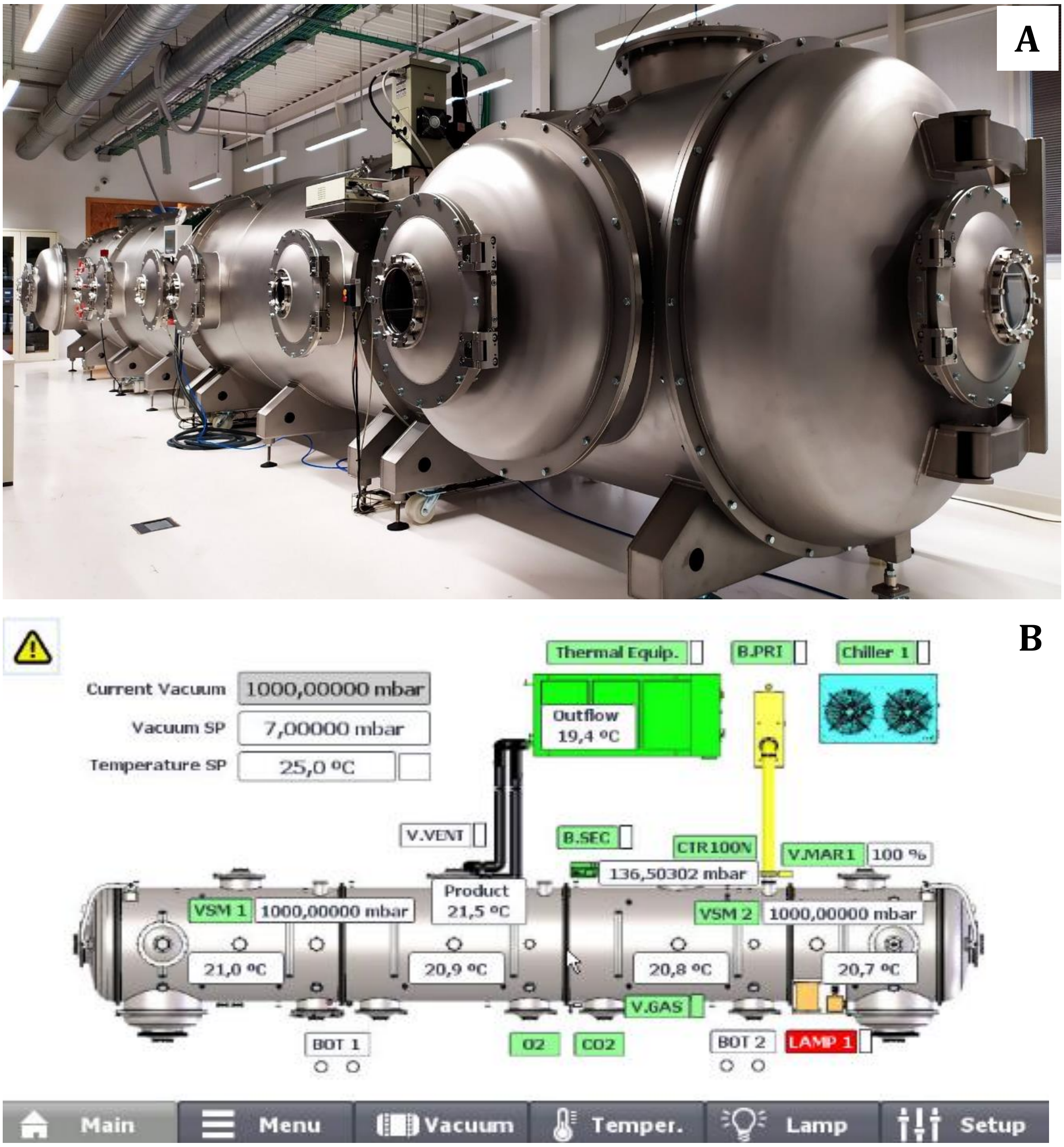


***Figure 3.*** *Scheme of the setup at MU lab [29]*

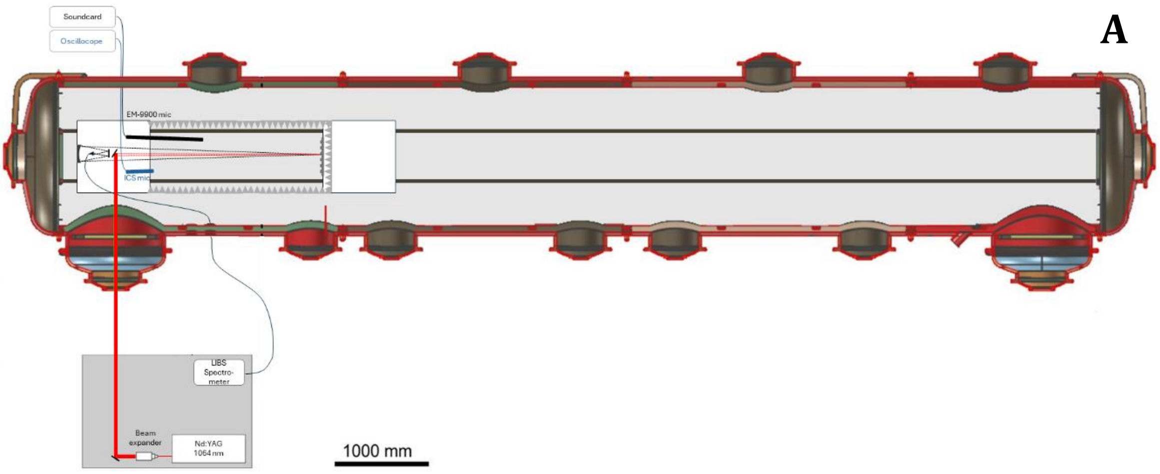
The third and final configuration has been developed to address the questions concerning the technology transfer from ambient Earth conditions to those on Mars or potentially other planets. To facilitate these experiments, a thermal vacuum chamber (TVC) at UMA LASERLAB has been used. The chamber was originally constructed to support NASA's Mars 2020 mission, encompassing not only LIBS-LIPAc measurements but also a range of other Martian Perseverance-related experiments. The TVC is a 12-metre-long and 2-metre-wide tube-like structure with multiple high-vacuum viewports and feed-throughs. The chamber (fig. 4A) is equipped with 12 doors, 13 feedthrough universal flanges, a high-vacuum system capable of generating pressure variations ranging from 1000 mbar to 10-3 mbar, a liquid cooling/heating system with a temperature range of -70 to 150°C, and an illumination system covering the VIS, UV-A, UV-B and UV-C regions. Additionally, the chamber is equipped with a gas inlet, enabling experiments to be conducted under varying atmospheric conditions. The entire system is controlled by its specialised computer unit, thereby enabling independent activation of each of the aforementioned temperature, pressure and gas systems, as well as simultaneous activation of all these systems (see figure 4B).



Current Vacuum 1000,00000 mbar
Vacuum SP 7,00000 mbar
Temperature SP 25,0 ºC
Outflow 19,4 ºC
136,50302 mbar
V.MAR1 100 %
VSM 1 1000,00000 mbar
Product 21,5 ºC
VSM 2 1000,00000 mbar
21,0 ºC
20,9 ºC
20,8 ºC
20,7 ºC

***Figure 4**. A) Photo of the thermal vacuum chamber (TVC) at UMA LASERLAB [30]; B) Control pannel of the TVC*

The primary technical challenge was installing the MEMS microphones and the commercial T-bone microphone into the chamber through a feedthrough. The primary challenge encountered with the MEMS microphone pertained to the technical design of the holder, necessitating the replacement of batteries with an external charger to ensure safe operation within the TVC under low vacuum and temperature conditions. Subsequent testing of all types of MEMS microphones under low-pressure conditions was undertaken to verify their suitability with the new extreme experimental conditions. Following this, the ICS mic (providing the best acoustic response thanks to its high sensitivity) was chosen for the following study. However, despite the microphone's capacity to record the plasma shockwave under low pressure, the signal-to-noise ratio deteriorated when low temperatures were applied, necessitating the use of the preamplifier (Omnitronic LH-045). Conversely, the second microphone, the condenser T-bone, exhibited generally lower sensitivity; however, its signal-to-noise ratio was enhanced and preamplified by the QuadCapture AC/DC converter. The two microphones were recording the plasma shockwave simultaneously, yet the MEMS microphone was connected to the oscilloscope (Tektronix DPO7104), and the condenser mic was connected to the soundcard. This configuration (fig. 5) enabled a comparative analysis of the two methods with respect to alterations in experimental conditions, as well as their suitability for subsequent experiments concerning data processing. It is noteworthy that under conditions of low pressure (lower than 5 mbar of $CO_2$ and -20°C), the signal from the condenser microphone became hidden in the background noise generated by the vacuum pumps, yet the background noise correction provided by the Audacity software was applied to the final data processing, revealing the plasma shockwave signal from the original recording.



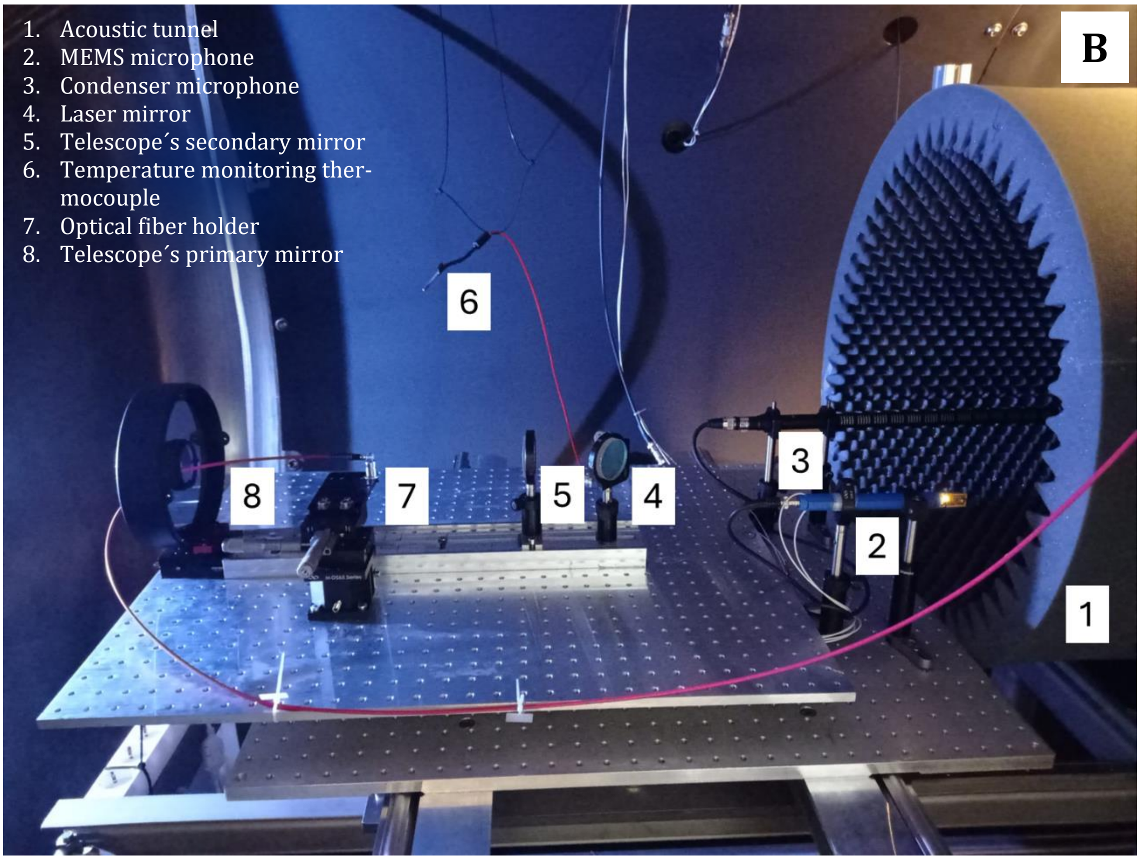


***Figure 5.*** *A) Experimental setup scheme of the TVC; B) photo of the optical train and microphone arrangement inside the TVC*

The second issue to be resolved was that of the isolation of the inner part of TVC. The microphones were positioned at a distance of two metres from the target, while the rails within the chamber and the inner thermal walls were situated approximately 50 centimetres away from the microphones and the sample holder. This configuration enabled multiple acoustic reflections and echoes. Finally, the alternative acoustic tunnel was employed. The construction of this tunnel involved the assembly of acoustic absorbent panels (the same type as in aforementioned setups), which were adhered and positioned within a custom-built aluminium support (fig. 6) along the entire optical/acoustic path from the sample to the microphones. Additionally, an anechoic housing was constructed to encompass the sample holder. This approach ensured that no reflections from the walls, rails, and other TVC components would disturb the plasma shockwaves' acoustic signal.

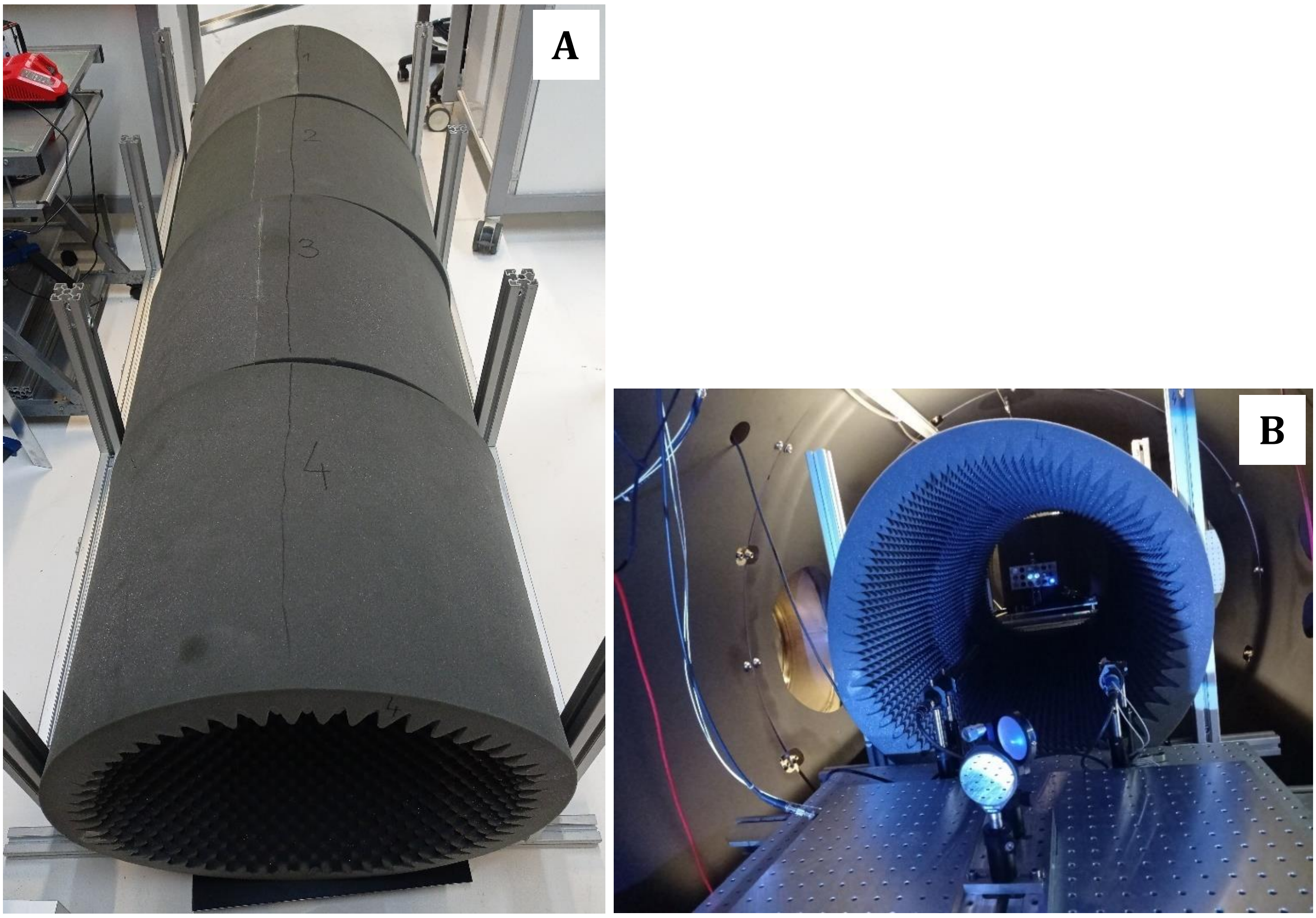


*__Figure 6.__ Photo of the acoustic tunnel and its aluminium-profile support system outside (A) and inside the TVC (B)*

The third complication has been characterised by a the plasma emission collection efficiency. The tip of the optical fibre was fixed at a distance of approximately 2.5 metres from the plasma plume. In order to obtain the greatest emission signal possible, a telescope was installed in collinear alignment on the optical table inside the TVC. However, effective plasma signal collection was problematic. Furthermore, significant signal losses were observed at the feed-through. In an effort to mitigate this effect, a 1000 µm wide optical fiber was employed for the collection of plasma images within the TVC. This fibre was SMA connected to the commercial Thorlabs ultra-high-vacuum feed-through port, SMA connected to the 4 x 600 µm optical fibre outside the TVC, and connected to the four channels CMOS Avantes spectrometer. Despite the substantial enhancement achieved, approximately one-third of the signal was still lost due to feedthrough leakage. It is also noteworthy that laser energy has been reduced by approximately 20%, attributable to energy dissipation at the TVC interface, specifically the viewport facilitating laser entry into the TVC. These two major losses have been compensated for by the use of higher laser energy at the laser head.

## 4.2. Samples

The main objective of the research endeavour was to enhance the classification of mineralogical and rock samples under Martian conditions. At the terminal stage of the research, the experimentally suggested concept was tested on real mineralogical samples. However, the initial experiments were conducted on homogeneous materials, with alterations to their physical-chemical properties.

In the initial study, the primary experiments were based on a series of aluminium cylinders with varying thickness and diameter. The second set of samples comprised artificially coloured epoxy cylinders, which were created to understand the effect of altering absorption coefficients on LIBS-LIPAc experiments. The third sample batch comprised 3D-printed cylinders, which were printed with different thicknesses of filaments and the density of these filaments per sample. The samples are illustrated fig. 8.

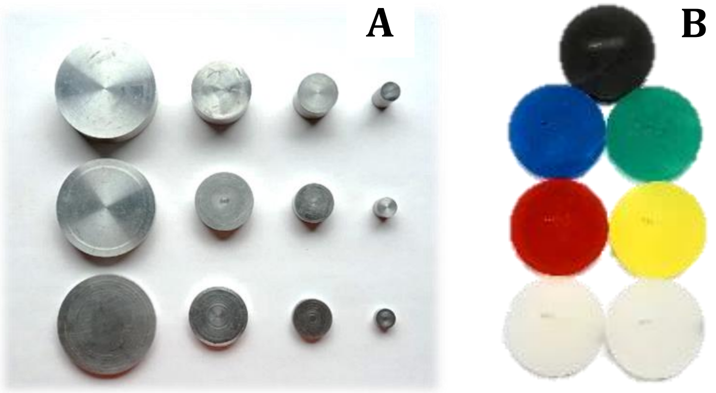


***Figure 8.*** *Batch of aluminium cylinders (A); Dyed epoxy resin (B) [28]*

The second study was based on authentic mineralogical specimens of chalcopyrite ($CuFeS_2$), galena (PbS), bauxite and septarian nodule (Fig. 9). As depicted in the accompanying photo, the chalcopyrite crystals are surrounded by quartz crystals on the top and meanwhile, the galena ore is enclosed by a calcite specimen (white crystals). The mineral samples were cut to provide a flat surface for analysis. All of these minerals were, however, individually embedded in epoxy resin (Ø 5 cm for septarian and chalcopyrite sample, Ø 3 cm for bauxite and galena sample) and conveniently polished from the resin on the surface to be analysed. This approach ensured optimal mounting on the sample holder and uniform experimental conditions. However, the movement of the stage could not be synchronised with the laser in an automatic manner, which constituted a significant issue that had to be resolved. In order to correct the final emission and acoustic maps, and to ensure a true overview, a strip of aluminium tape was placed around the sample, as shown in Figure 9. The strip allowed any misalignment between individually analysed lines to be accurately aligned.

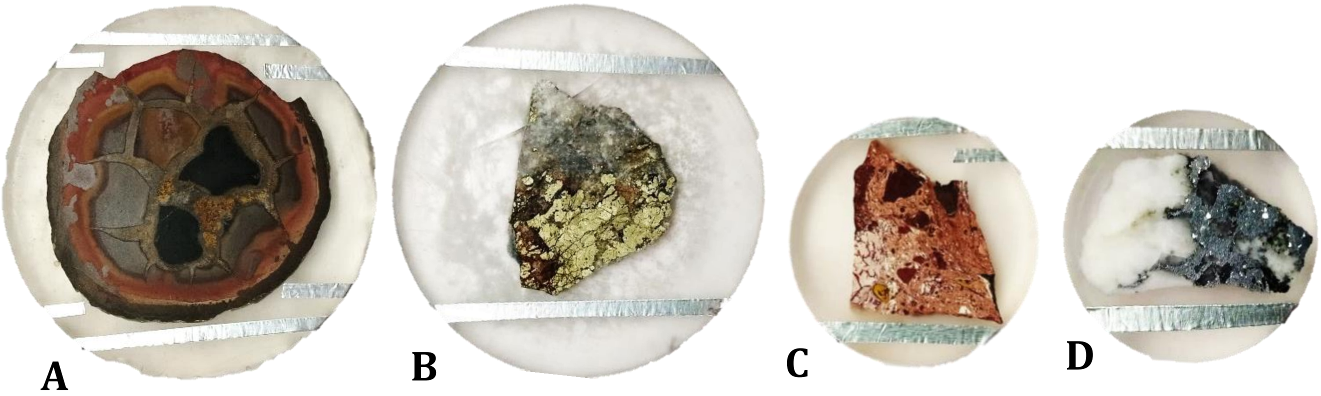


***Figure 9.*** *Photos of samples: septarian nodule (A); chalcopyrite (B); bauxite (C) and galena (D)*

The third study made use of samples from the preceding studies (galena and aluminium cylinders) for the purpose of comparative analysis. Conversely, a novel experiment was designed, encompassing a sample-related experiment. In this experiment, aluminium cylinders with variations in surface roughness were prepared. However, the LIBS-LIPAc analysis did not reveal any significant deviations in the signal, so the roughness of the sample was considered a non-selectable parameter and won't be commented on further. One of the most recent approaches employed in this research was the investigation of nano-deposited layers, for which two batches of samples were prepared. The initial batch of samples (fig. 10) was prepared by plasma deposition of a 1 μm copper layer on half of a 1 mm thick aluminium sample, 90°degrees rotated and partially blast-sanded, as previously outlined in Article 3. The same method was used to prepare the aluminium samples deposited by phosphorus-doped silicon layer. The second batch was created by dripping 20 μl droplets of solutions containing silver and gold nanoparticles, respectively (with different particle sizes from 20 to 80 nm), onto the surface of the aluminium cylinder and leaving it to dry in the air. In the end, a nanoparticle solution containing 80 nm gold nanoparticles (EM.GC40, BBI Solutions) has been selected for further analyses, altogether with two distinct 80 nm silver nanoparticles (AGCN80 silver nanospheres, nanoComposix Inc; EM.SC80, BBI Solutions). The same approach was used to prepare a sample with an increasing number of coatings of nanoparticles (from 1 to 7).

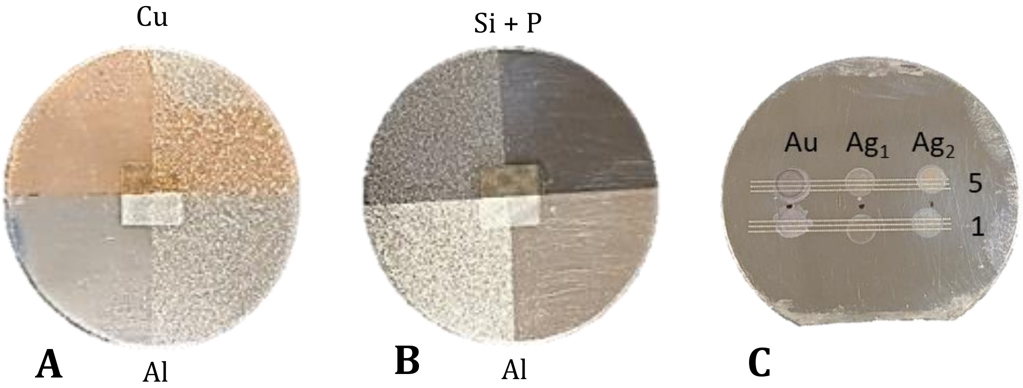


***Figure 10.*** *Photos of aluminium probes, partially covered by: nano-deposited layer of copper (A) and phosphorus-doped silicon (B); single and five layers of 20µl volumes of silver and gold nanoparticles (C)*

The fourth study entailed the application of the recently acquired knowledge to the Perseverance-like conditions. The study was principally based on our well-known aluminium cylinders as samples, complemented by a pure copper plate as a second well-characterised standard and pyrite mineral, representing a genuine Martian sample. The study concluded with the corroboration of the theory of mineral differentiation based on their plasma acoustic response, as evidenced by the analysis of four aluminium samples in comparison to one magnesite and two pyrite samples, as illustrated in figure. 11 in red, blue and green circles.

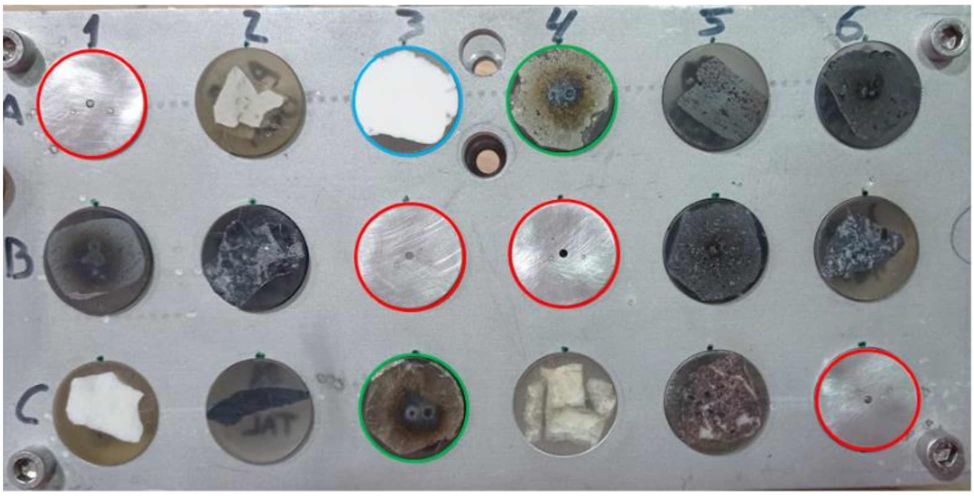


***Figure 11.*** *TVC sample holder with highlighted samples of aluminium (red), pyrite (green) and magnesite (blue)*

## 4.3. Acoustic data processing

In the context of plasma acoustic signal recording, two distinct approaches have been employed or, in certain instances, utilised in conjunction. The initial approach involved the utilisation of a soundcard system, whereas the second approach relied on an oscilloscope. It should be noted that each of these systems possesses its own set of advantages and disadvantages, as previously outlined. However, it is important to emphasise that these two recording systems necessitate divergent evaluation steps, which have been optimised in Matlab R2023R and Origin 8.6 software.

### 4.3.1. Soundcard recording

In our experiment, the audio interface Quad-Capture (Roland) was connected via USB to the sound card integrated with the PC and used to record the plasma acoustic signal using the free licensed Audacity software. This type of recording does not have the option of being triggered by the laser flash lamp or the spectrometer, which is a major encountered drawback. The recording must be switched on and off before and after analysis manually by the operator. In the case of multi-pulse analysis, all the plasma events are recorded in one file (fig. 13A), which has to be cut into individual pulses (in Matlab software) for further analysis (fig. 13B). The second disadvantage of the recording is the low maximum sampling rate of 192 kHz, which is limited by the audio Quad-capture interface and the sound card itself. The Audacity software offers an option to use a higher project rate. Nevertheless, this approach entails the computation of additional points by interpolation within the authentic acoustic signal, and consequently, the genuine experimental information may be misconducted. The alteration between the LIPAc signal within the same conditions and sample, varying only by the project rates chosen in Audacity software is depicted in fig. 14.

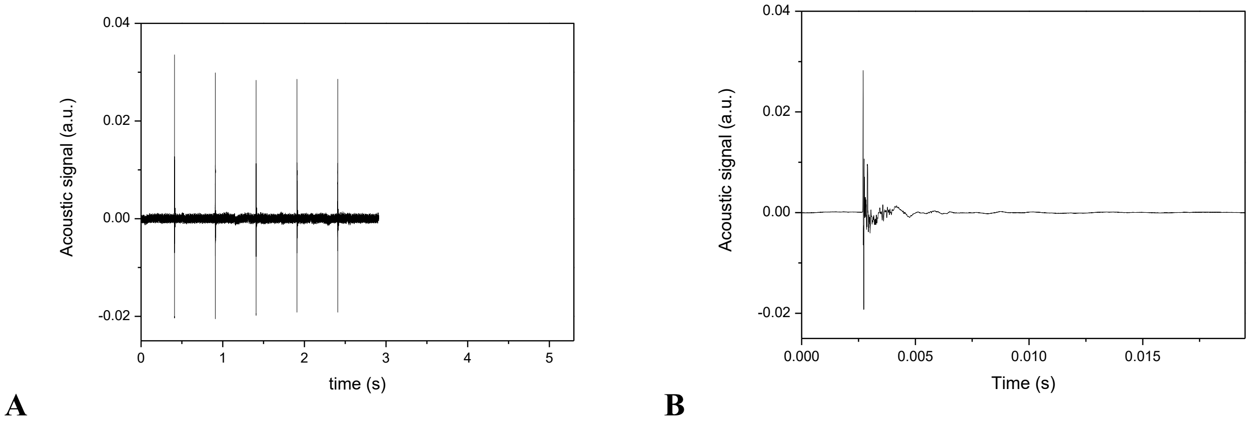


***Figure 13.*** *A) acoustic signal obtained from 10 successive laser pulses; B) acoustic signal of the first peak from spectrum A after separation into individual laser events*

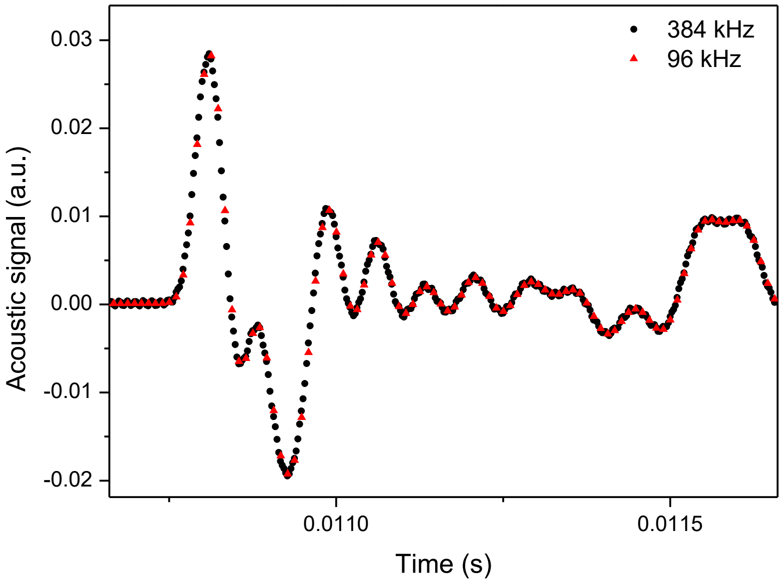


***Figure 14***. *LIPAc signal recorded with two different project rates in Audacity software*

The acoustic evaluation was based on the first peak-to-valley intensity. Prior to the signal analysis itself, the raw output file in WAV format was opened in Matlab software and processed in following steps. In the first one, the raw signal was segmented into individual peak signals (in the time domain) based on the laser repetition rate (mostly used 2 Hz), the total number of laser events and sampling rate defined by the Quad-capture converter. In the next step, within each segment, a customized script was implemented to identify and memorize the signal's maximum point, equivalent to the "peak" intensity, as well as the minimum point, designated as the "valley" intensity. The maximum and minimum values were then summed as absolute values. Furthermore, the raw signal was segmented into a final dataset comprising of n number of laser shots, with 1050 data points obtained prior to and 6450 data points subsequent to each pulse maximum. This process yielded n number spectra, each comprising 7500 data points (corresponding to 0.0195s in the time domain, thereby encompassing the complete acoustic response of the plasma propagation). In conclusion, the Origin software was utilised for the purpose of visualising the plasma waveforms, in addition to the creation of heat maps. This was undertaken for the purpose of facilitating further comparison with LIBS data. This approach facilitated a comparative analysis of the acoustic waveform among diverse samples.

### 4.3.2. Oscilloscope recording

The main advantage of the oscilloscope is its ability to record signals under well controlled conditions, including high resolution in terms of sampling rate, number of samples and time segment per laser shot, and the use of the laser as an external trigger, which allows the monitoring of the acoustic signal always with the same delay after the laser pulse. This is particularly useful in the fourth article of this thesis, as we were able to monitor not only the shape alterations of the acoustic waveform, but also the variable time delay of the sound transmission under changing temperature, pressure and atmospheric conditions. In addition, the exact delay allows us to calculate the actual temperature inside our TVC system.

The major disadvantage of this type of recording is the vast size of the saved files, especially in the case of successive multi-pulse analysis, where all the plasma shockwaves are saved one by one in a single file in txt format, which size is about 170 MB each (sampling rate of 5 mS/s, 10,000 samples per pulse, 100 pulses), which led to another script in Matlab to analyse these files time-efficiently. The first step is to define the number of shots in the file, the frame size corresponding to the samples per pulse and the file's location in the computer directory. In the second step, Matlab opens the txt file and separates the original file into a matrix of n columns, where n is the number of pulses. The next step is finding and noting the first pulse's first maximum and minimum peak amplitude (intensity). Based on the pixel number of the max and min value in the first pulse dataset, the intensities of max and min are found and memorised for all the remaining pulses. The rest of the data processing is the same as in the previous chapter on soundcard recording.

## 4.4. LIBS-LIPAc material differentiation under Martian conditions

The most recent series of experiments has been conceptualised in light of the accumulated knowledge and the strategic vision for Martian exploration. As demonstrated by the aforementioned theories and results, it was hypothesised that a sufficient distinction could be made between altering materials based exclusively on their plasma shock-wave acoustic response. In order to transfer the prediction model to the trustworthy reality, a set of seven samples was selected. These samples comprised four aluminium targets, two pyrite samples and one magnesite sample. These samples were inserted into the TVC sample holder, as illustrated in figure 19A. The materials were selected to provide evidence of specific anticipated challenges. For instance, four aluminium cylinders were selected as the most homogeneous and best-controlled material. At the same time, the holder positions were altered to verify the LIPAc signal intra-holder-position stability. Meanwhile, the pyrite and magnesite samples represented the real mineralogical systems with the greatest possible homogeneity. As previously referenced, the TVC sample holder was equipped with seven samples (highlighted) and was accompanied by additional mineralogical samples utilised to occupy the remaining positions within the holder (see figure 19A). This was done to validate the subsequent proposed study design. The experiment was conducted in a thermal-vacuum chamber at UMA LA-SERLAB, with the samples analysed at two fresh spots. The experiment was conducted in an atmosphere of 7 mbar of $CO_2$ at a temperature of -20 °C.

As demonstrated in figure 19B, the results of the LIPAc analysis are represented graphically based on the first peak-to-valley maximum intensity, as previously described in the relevant sections and articles. As demonstrated in the experiment, a clear resolution was evident between the aluminium, pyrite and magnesite samples, respectively. Furthermore, a significant correlation was identified between altering the aluminium sample positions within the sample holder. This observation serves to substantiate the negligible effect of sample position on its acoustic response.

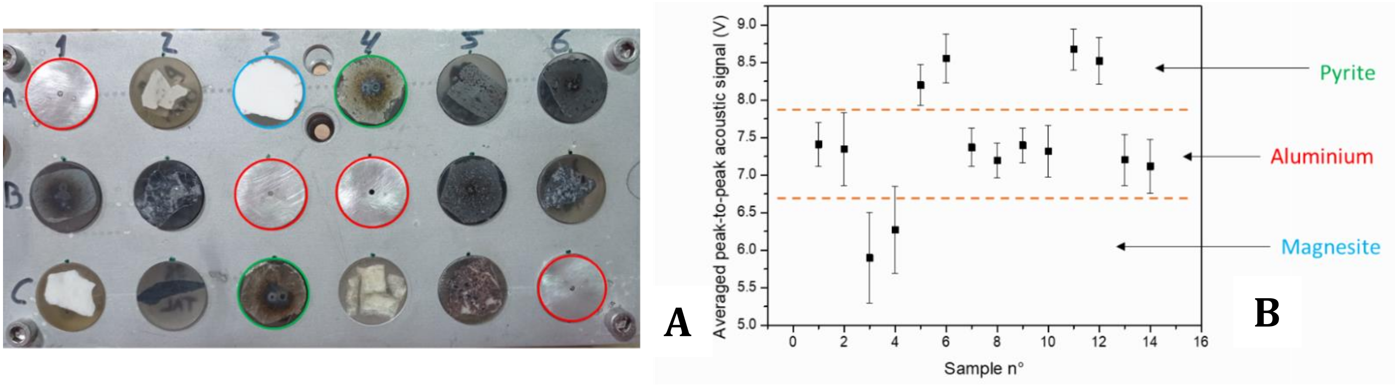


***Figure 19.*** *(left) Photo of the TVC sample holder with highlighted samples of aluminium (red), pyrite (green) and magnesite (blue); (right) LIPAc graphical differentiation of various materials under Martian conditions*

# 5. Conclusions

The dissertation thesis introduces the first systematic LIBS-acoustic study of its kind. The theories and overall progress between the LIBS-LIPAc (laser-induced breakdown spectroscopy & laser-induced plasma acoustics) is explained in detail in four thematically complex publications.

The initial publication was intended to facilitate a comprehensive understanding of the laser plasma-based acoustic signal, with a primary focus on the contribution of the signal from the samples, in conjunction with its surrounding environment and the receiver's coordinates. The target-based acoustic signal alterations were evaluated within a batch of aluminium cylinders varying in diameter and thickness, the dyed epoxy resin cylinders and 3D-printed cylinders of altering inner porosity. The study indicated that the acoustic signal may be segmented into specific segments, with each segment being influenced by particular parameters. The primary segment of the time-domain, defined as the magnitude of maximum peak-to-valley amplitude, exhibited a close correlation with laser-to-matter interactions, influenced by the physical-chemical properties of the studied sample, notwithstanding its size or sampling position. Consequently, this phenomenon was reflected in the secondary segment. The ultimate objective of this publication was to ascertain the impact of modifying the receiver's coordinates (particularly the microphone-to-ground position, the angle of incidence, and the distance between the microphone and the target) and the surrounding terrain effect. It is evident that these effects yield echoes and reflections, which correspond to more complex phenomena manifesting in the subsequent third segment of the plasma acoustic signal. Despite the absence of precise material characterisation in this study, the categorisation of the most prevalent phenomena has been introduced.

The second publication describes the LIBS-LIPAc application as a promising tool for geological identification. Firstly, the plasma emission elemental maps were constructed in order to demonstrate the distribution along the sample surface. In the subsequent step, the acoustic signal, based on the first peak-to-peak intensity, was employed to generate the complementary maps. As described in the first study, the complexity of the acoustic signal also encompasses the physical-chemical traits of the studied material, such as optical absorption of the laser light, the density of the sample, etc. This trait has been demonstrated to favour acoustic mapping over LIBS mapping. In instances where LIBS emission maps appear to be identical, despite differences in elemental composition or crystallography, acoustic maps can provide additional, complementary evidence.

The third publication has focused on instrumental influences of the LIPAc signal, namely the microphone used for plasma acoustic recording, as well as laser ablation parameters. The MEMS microphones were considered the most suitable for laser plasma recording for their superior audio recording quality. In the next step, the influence of the laser pulse wavelength on the LIPAc signal has been evaluated. Even though the ablation process depends significantly on the ablation laser source, the acoustic response of altering wavelength followed the same tendency and thus can be considered negligible, even from the evaluation point of view. However, the LIPAc signal, in particular the amplitude, has been observed to be strongly affected by the laser fluence. Furthermore, the acoustic signal has shown high sensitivity to alterations in the chemical-physical nature of the analysed target, demonstrated on a partially coated aluminium alloy cylinder and a geological sample of galena mineral. The most prominent is the acoustic-based correction of the matrix effects, leading to the elimination of discrepancies between spectral lines and thus enhancement of the LIBS mapping potential.

The fourth and final publication is concerned with the exploitation of the acoustic potential for extraterrestrial purposes in light of all recently acquired knowledge. The impact of modifying atmospheric composition, pressure and temperature, one at a time, while maintaining constant values for the other parameters, has been assessed. The acoustic signal intensity exhibited a strong correlation with the adiabatic index of the plasma environment. In addition, the LIPAc signal exhibits a close proximity in variation related to the altering atmospheric temperature and pressure, following the LIBS trend. It has been demonstrated that both the plasma plume and its shockwave are affected by thermal conductivity in an analogous manner.

Finally, the recent knowledge has been suggested to two applications. The first experiments conducted within the thermal-vacuum chamber effectively demonstrated the LIPAc's capacity to distinguish between different types of materials based on their plasma shockwave characteristics, irrespective of their position within the sample holder. Furthermore, the experiment was expanded to encompass Martian conditions, thereby demonstrating its capacity for stand-off analysis in extreme environments, also well-suited for planetary research.

# 6. Conclusiones

La presente Tesis doctoral aborda la primera investigación sistemática sobre la respuesta acústica que acompaña a los plasmas generados por láser (LIPAc) y la simbiosis analítica que supone con la espectroscopía de emisión óptica de plasmas inducidos por láser (LIBS). Los aspectos más fundamentales, así como la evolución de la complementariedad LIBS-LIPAc, y algunas de sus potenciales aplicaciones reales se explican detalladamente a lo largo de cuatro publicaciones científicas temáticamente complejas.

Las primeras investigaciones, integradas en la publicación inicial, buscaban comprender de forma exhaustiva qué variables y de qué manera podían condicionar la respuesta acústica de los plasmas, centrándose principalmente en propiedades relacionadas con la propia muestra, características del entorno de la muestra, y las coordenadas del dispositivo receptor respecto al punto de origen de la fuente acústica.

Las alteraciones de la señal acústica relacionadas con las características de la muestra se evaluaron sobre un conjunto de cilindros de aluminio de diámetro y grosor variables, en cilindros de resina epoxi teñidos con diferentes pigmentaciones y en cilindros impresos en 3D de porosidad interior variable. La evaluación de los resultados evidenció que la señal acústica, en su dominio temporal, puede fragmentarse en tres segmentos temporales específicos, y que cada segmento está gobernado por diversos parámetros particulares. El primer segmento, comprendiendo la onda acústica de pico N, esto es, la amplitud máxima de una onda sonora, específicamente la distancia entre el pico (valor de amplitud más alto) y el valle (valor de amplitud más bajo) de la onda, mostraba una estrecha correlación con la interacción láser-materia, influida por las propiedades físico-químicas de la muestra estudiada, independientemente de su tamaño o posición de muestreo. Una circunstancia que se corroboró a partir de los resultados obtenidos del análisis de las muestras coloreadas. Por el contrario, las dimensiones de la muestra reflejaban diferencias en el segmento secundario de la respuesta acústica. Finalmente, la naturaleza de la superficie donde queda localizada la muestra de análisis, así como las coordenadas del dispositivo detector acústico (en particular, distancia entre el micrófono y la fuente sonora, separación del micrófono con respecto a la superficie, y ángulo de captación con respecto a la incidencia del pulso láser para la generación del plasma) evidenciaron la generación de potenciales ecos y reflexiones, manifestándose de forma mucho más compleja en el tercer y más postrero segmento de la señal acústica del plasma. Si bien estas investigaciones permitieron categorizar algunos de los fenómenos más influyentes en la respuesta acústica d ellos plasmas producidos por láser, todavía ésta no estaba en disposición de considerarse una puntuación singular para la caracterización precisa de un material en particular.

Los siguientes estudios, refrendados en la segunda publicación, describen el acoplamiento de las modalidades LIBS y LIPAc y su aplicación como una herramienta prometedora para el análisis de material geológico. De un lado, la modalidad LIBS posibilitó construir mapas químicos a partir de las emisiones de los elementos presentes en los plasmas procedentes de la muestra, informando de la distribución elemental a lo largo de su superficie. Por otro lado, la modalidad LIPAc permitió generar un mapa acústico complementario de dicha superficie. Finalmente, el apilamiento de todos los mapas lograba generar una cartografía mucho más completa, englobando los rasgos químico-físicos, del material estudiado. Esta estrategia evidenció ser de extrema utilidad en aquellas circunstancias en la que las respuestas LIBS resultaban ser altamente similares, evidenciado así la complementariedad y el carácter distintivo que puede ofrecer la cartografía acústica hacia una categorización más exacta de los especímenes evaluados.

Otro conjunto de investigaciones, reflejadas en la tercera publicación, se centraron en las influencias instrumentales de la señal LIPAc, concretamente en los parámetros de ablación láser, responsables de la formación del plasma y con ello de la fuente sonora, así como en el micrófono utilizado para el registro de la repuesta acústica. Los micrófonos basados en la tecnología MEMS (Micro-Electro-Mechanic Systems, por sus siglas en inglés) se consideraron los más adecuados para la grabación de la acústica del plasma láser por su superior calidad de grabación. En lo que refiere a las variables vinculadas al proceso de ablación, la longitud de onda del pulso láser pareció no influir excesivamente en la señal LIPAc, al menos en lo que a perfil temporal se refiere. Por el contrario, la fluencia del láser mostró condicionar significativamente la amplitud en la señal LIPAc. Se identificó que cuanto más superaba la fluencia láser empleada el umbral de ablación de los componentes de la muestra, mayor similitud había en sus respuestas acústicas y más complicada resultaba su diferenciación. De igual modo, la señal LIPAc mostró su valía para la corrección de los efectos matriz que tanto influyen a las señales LIBS. El análisis de una muestra artificial consistente en una aleación de aluminio parcialmente recubierto con cobre y de una muestra geológica real integrada por un fragmento del mineral galena en una matriz de calcita, mostró que la cartografía LIBS puede conducir a una distribución elemental errónea en matrices multicomponente, según la naturaleza, atómica o iónica, de la línea de emisión que se utilice en la monitorización del elemento. De nuevo aquí, la señal LIPAc demostró la complementariedad que puede ofrecer a LIBS en lo que a exactitud se refiere.

Las últimas investigaciones, plasmadas en la cuarta y última publicación, abordan, a la luz de todos los conocimientos recientemente adquiridos la potencial futura explotación de la señal LIPAc en un ámbito extraterrestres. En ese sentido se evaluó, de forma monoparamétrica, el impacto de la alteración de diferentes propiedades de la atmósfera, desde su composición química hasta su presión y temperatura, en la respuesta acústica de los plasmas. La intensidad de la señal acústica mostró una fuerte correlación con el índice adiabático del entorno plasmático. Además, la señal LIPAc exhibe una gran proximidad en la variación relacionada con la alteración de la temperatura y presión atmosférica, siguiendo la tendencia de LIBS. Se ha demostrado que tanto la pluma de plasma como su onda de choque se ven afectadas por la conductividad térmica de forma análoga.

# 7. List of abbreviations

| | |
|---|---|
| a.u. | Arbitrary Units |
| AC/DC | Analog to Digital |
| EQM | Engineering and Qualification Model |
| FFT | Fast Fourier Transform |
| IR | Infrared |
| LIBS | Laser-Induced Plasma Spectroscopy |
| LIPAc | Laser-Induced Plasma Acoustic |
| MEMS | Micro-electromechanical systems |
| NASA | National Aeronautics and Space Administration |
| Nd:YAG | Neodymium-Doped Yttrium Aluminum Garnet |
| PCB | Printed Circuit Board |
| RMI | Remote Micro Imager |
| SPS | Spark Plasma Sintering |
| TVC | Thermal Vacuum Chamber |
| UV | Ultraviolet |
| VIS | Visible |
| VISIR | Visible and Infrared |
| WAV | Waveform Audio File Format |

# 8. Publications and presentations related to the dissertation thesis

## 8.1. List of publications

1. **BOSÁKOVÁ, Markéta**, Pablo PUROHIT, Cesar ALVAREZ-LLAMAS, Javier MOROS, Karel NOVOTNÝ and Javier LASERNA. A systematic evaluation on the impact of sample-related and environmental factors in the analytical performance of acoustic emission from laser-induced plasmas. Analytica Chimica Acta. Elsevier, 2022, roč. 1225, September, s. 1-9. ISSN 0003-2670. https://dx.doi.org/10.1016/j.aca.2022.340224.
2. **BOSÁKOVÁ, Markéta**, Javier MOROS, Pablo PUROHIT, Cesar ALVAREZ-LLAMAS and Javier LASERNA. Chemical and Acoustical Mixed-Mapping of Geological Materials from Laser-Induced Plasmas: A Comprehensive Approach to Differentiate Mineral Phases. Anal Chem 96 (2024) 17444–17452. https://doi.org/10.1021/acs.analchem.4c05214
3. **BOSÁKOVÁ, Markéta;** NOVOTNÝ, Karel; MOROS, Javier and LASERNA, Javier. Acoustic signal in overcoming the matrix effect in LIBS: Toward reliable applicability. Spectrochimica Acta Part B: Atomic Spectroscopy. 2025, 226. ISSN 05848547. https://doi.org/10.1016/j.sab.2025.107140
4. **BOSÁKOVÁ, Markéta**; MOROS, Javier; Vadillo, José Miguel; NOVOTNÝ, Karel; and LASERNA, Javier. Surveying the acoustics from laser-induced plasmas under non-standard atmospheric conditions: Implications for extraterrestrial missions. Spectrochimica Acta Part B: Atomic Spectroscopy. 2025, vol. 234, s. 107320. ISSN 0584-8547. https://doi.org/10.1016/j.sab.2025.107320

## 8.2. List of conference presentations & posters

1. **BOSÁKOVÁ, Markéta**, Karel NOVOTNÝ, Javier MOROS and Javier LASERNA. Acoustic &optical simultaneous spectroscopic data from laser-induced plasmas - the new informative mix to Mars and beyond. In XXVIII RNE & XII CIE Spectroscopy conference, Granada, 2024. Poster presentation.

2. **BOSÁKOVÁ, Markéta**, Karel NOVOTNÝ, Javier MOROS and Javier LASERNA. Acoustic &optical simultaneous spectroscopic data from laser-induced plasmas - the new informative mix to Mars and beyond. In III ES-LIBS conference, Granada, 2024. Poster presentation.

3. **BOSÁKOVÁ, Markéta**, Karel NOVOTNÝ, Javier MOROS and Javier LASERNA. Acoustic/optical emission spectroscopic hyphenated data from laser-induced plasmas. From the concept to the scene. In Czech - Slovak Spectroscopic Conference & Mössbauer Spectroscopy in Material Science, 2024. Oral presentation.

4. **BOSÁKOVÁ, Markéta**, Karel NOVOTNÝ, Javier MOROS and Javier LASERNA. Hyphenated acoustic/optical emission spectroscopic data from laser-induced sparks to geological material characterisation. In 12th Euro-Mediterranean Symposium on Laser-induced Breakdown Spectroscopy, 2023. Oral presentation. The presentation won the Outstanding Oral Presentation Award.

5. **BOSÁKOVÁ, Markéta**, Karel NOVOTNÝ, Javier MOROS and Javier LASERNA. Instrumental configuration effect on the LIBS acoustic signal response. In European Symposium on Analytical Spectrometry ESAS 2022 - 17th Czech - Slovak Spectroscopic Conference, 2022. Poster presentation.

6. **BOSÁKOVÁ, Markéta**, Pablo PUROHIT, César ÁLVAREZ-LLAMAS, Javier MOROS and Javier LASERNA. Exploring factors conditioning laser-induced acoustics and its potential as a LIBS-hyphenated technique. In 11th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy 2021. Poster presentation.

7. MOROS, Javier, **Markéta Bosáková**, S. Luna-Ramírez, F.J. López and Javier Laserna. Listening to laser plasmas of minerals: Research activities towards the analytical exploitation of the microphone onboard SuperCam for the Mars rover 2020. 51st Lunar and Planetary Science Conference 2020. Poster presentation.

# 9. Curriculum Vitae

**Personal data:**

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| Name: | Mgr. Markéta Bosáková |
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**Education:**

| | |
|---|---|
| 10/2021 – now: | Universidad de Málaga, ES |
| Type of study: | Doctoral degree programme |
| Faculty: | Faculty of Science |
| Programme: | Química y Tecnologías Químicas, Materiales y Nanotecnología (https://laser.uma.es/) |

| | |
|---|---|
| 09/2020 – now: | Masaryk University, Brno, CZ |
| Type of study: | Doctoral degree programme |
| Faculty: | Faculty of Science |
| Programme: | Chemistry |
| Specialisation: | Analytical chemistry (https://las.sci.muni.cz/) |

| | |
|---|---|
| 09/2018 - 09/2020 | Masaryk University, Master's degree programme in Analytical chemistry.<br>Degree conferred: **Mgr.**, in 2020 (passed with honour**).**<br>Diploma thesis: Study of acoustic signal in Laser Induced Breakdown Spectrometry |
| 09/2015 - 06/2018 | Masaryk University, Bachelor's degree programme in Biophysical Chemistry.<br>Bachelor thesis: Electrochemical oxidation of guanine and its methylated derivatives on graphite electrodes<br>Degree conferred: **Bc.**, in 2018. |

| | |
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| 01/2014 - 03/2014 | Kaplan International Languages - Adelaide (Australia)<br>10-week intensive course in IELTS preparation<br>Academic IELTS exam passed, the overall level: 6.5 |
| 09/2007 - 06/2015 | Wichterlovo gymnázium , Ostrava |

## Work experiences:

| | |
|---|---|
| 10/2024 – now | LIBS specialist at ATOMTRACE, a.s. |
| 02/2023 – 07/2024 | Researcher at UMA LASERLAB (Málaga, Spain)<br>Main goal: simultaneous analysis of laser-induced breakdown spectroscopy (LIBS) and acoustic spectroscopy of mineralogical samples under the Martian and other extreme conditions. System development, control, problem-solving; experiment design, data analysis and evaluation (Origin, Matlab) |
| 01-12/2022 | Researcher at Masaryk University<br>IGA grant: The study of surface morphology to acoustic response during laser ablation (MUNI/IGA/1258/2021)<br>Main goal: Exploring the instrumentation-related factors conditioning the acoustic signal in laser-induced plasmas, LIBS/acoustic analysis of the sample morphology modifications. Current LIBS system adjustments for simultaneous acoustic measurements, experimental design of the study, data analysis and evaluation (Origin, Matlab). |
| 02/2021 – 02/2022 | Researcher at UMA LASERLAB (Málaga, Spain)<br>Main goal: Exploring the sample and environment-related factors conditioning the acoustic signal in laser-induced plasmas and acoustic mapping of the sample surface. System development, control and problem-solving; experimental design, data analysis and evaluation (Origin). |
| 10/2020 - 02/2021 | Researcher at Masaryk University<br>Main goal: hyphenated LIBS-acoustics experiments at MU, building the setup and technical testing. |
| 09/2019 – 03/2020 | Researcher at UMA LASERLAB (Málaga, Spain)<br>Main goal: first LIBS/acoustic study in terrestrial conditions. New system construction and optimisation to obtain the best first preliminary emission-acoustic results. |

## Language skills & certificates:

English language – fluent
Spanish language – intermediate

| | |
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| 03/2016 | IELTS Academic exam (overall band score: 6.5), University of Adelaide, Australia (ID: 13AU008491BOSM100A) |

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| 07/2024 | SIELE (Servicio Internacional de Evaluación de la Lengua Española), Cervantes Escuela Internacional, Málaga, Spain (ID: WQpC1Ytgz5KZpIxqmWQSzQ==) |

Driving license:

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Interests:

Singing (active singer), playing the piano, dancing (modern, ballroom, folklore), equitation, skiing, windsurfing, inline and ice skating, hiking, and climbing.

# 10. References

[1] P. Purohit, C. Alvarez-Llamas, J. Moros, J.J. Laserna, Materials Characterization by Laser-Induced Plasma Acoustics and Spectroscopy, in: Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences, Springer International Publishing, Cham, 2022: pp. 283–313. https://doi.org/10.1007/978-3-031-14502-5_11.

[2] Z. Gajarska, L. Brunnbauer, H. Lohninger, A. Limbeck, Advanced Polymer Characterization, in: Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences, Springer International Publishing, Cham, 2022: pp. 253–281. https://doi.org/10.1007/978-3-031-14502-5_10.

[3] Y. Zhang, T. Zhang, H. Li, Application of laser-induced breakdown spectroscopy (LIBS) in environmental monitoring, Spectrochim Acta Part B At Spectrosc 181 (2021). https://doi.org/10.1016/j.sab.2021.106218.

[4] R. Zhang, S. Hu, C. Ma, T. Zhang, H. Li, Laser-induced breakdown spectroscopy (LIBS) in biomedical analysis, TrAC - Trends in Analytical Chemistry 181 (2024). https://doi.org/10.1016/j.trac.2024.117992.

[5] L. Sancey, V. Motto-Ros, B. Busser, Preclinical Evaluation of Nanoparticle Behavior in Biological Tissues, in: Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences, Springer International Publishing, Cham, 2022: pp. 131–138. https://doi.org/10.1007/978-3-031-14502-5_5.

[6] N. Sushkov, Qualitative Classification of Biological Materials, in: Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences, Springer International Publishing, Cham, 2022: pp. 165–203. https://doi.org/10.1007/978-3-031-14502-5_7.

[7] A. Metzinger, Z. Szoldán, Analysis of Forensic Trace Evidence, in: Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences, Springer International Publishing, Cham, 2022: pp. 223–251. https://doi.org/10.1007/978-3-031-14502-5_9.

[8] D.A. Cremers, Space Applications of LIBS, in: 2014: pp. 257–291. https://doi.org/10.1007/978-3-642-45085-3_10.

[9] P.S. Vaisakh, U.K. Adarsh, K. Amrutha, A.K. Warrier, V.B. Kartha, V.K. Unnikrishnan, Integrated LIBS-Raman spectroscopy: A comprehensive approach to monitor microplastics and heavy metal contamination in water resources, Environ Res 231 (2023). https://doi.org/10.1016/j.envres.2023.116198.

[10] J. Aramendia, L. Gómez-Nubla, S. Fdez-Ortiz de Vallejuelo, K. Castro, G. Arana, J.M. Madariaga, The combination of Raman imaging and LIBS for quantification of original and degradation materials in Cultural Heritage, Journal of Raman Spectroscopy 50 (2019) 193–201. https://doi.org/10.1002/jrs.5546.

[11] A.S. Anderson, H. Mukundan, R.E. McInroy, S.M. Clegg, Combined LIBS-Raman for remote detection and characterization of biological samples, in: Imaging, Manipulation, and Analysis of Biomolecules, Cells, and Tissues XIII, SPIE, 2015: p. 932811. https://doi.org/10.1117/12.2076832.

[12] S.K. Sharma, A.K. Misra, P.G. Lucey, R.C.F. Lentz, A combined remote Raman and LIBS instrument for characterizing minerals with 532 nm laser excitation,

Spectrochim Acta A Mol Biomol Spectrosc 73 (2009) 468–476. https://doi.org/10.1016/j.saa.2008.08.005.

[13] S. Choi, D. Kim, J. Yang, J.J. Yoh, Accuracy Enhancement of Raman Spectroscopy Using Complementary Laser-Induced Breakdown Spectroscopy (LIBS) with Geologically Mixed Samples, Appl Spectrosc 71 (2017) 678–685. https://doi.org/10.1177/0003702817691289.

[14] S. Julve-Gonzalez, J.A. Manrique, M. Veneranda, I. Reyes-Rodríguez, E. Pascual-Sanchez, A. Sanz-Arranz, M. Konstantinidis, E.A. Lalla, M.E. Charro, E. Rodriguez-Gutiez, J.M. Lopez-Rodríguez, J.F. Sanz-Requena, J. Delgado-Iglesias, M.A. Gonzalez, F. Rull, G. Lopez-Reyes, Machine learning methods applied to combined Raman and LIBS spectra: Implications for mineral discrimination in planetary missions, Journal of Raman Spectroscopy 54 (2023) 1353–1366. https://doi.org/10.1002/jrs.6611.

[15] A.K. Misra, S.K. Sharma, T.E. Acosta, D.E. Bates, Compact remote Raman and LIBS system for detection of minerals, water, ices, and atmospheric gases for planetary exploration, in: Next-Generation Spectroscopic Technologies IV, SPIE, 2011: p. 80320Q. https://doi.org/10.1117/12.884392.

[16] S. Maurice, R.C. Wiens, P. Bernardi, P. Caïs, S. Robinson, T. Nelson, O. Gasnault, J.M. Reess, M. Deleuze, F. Rull, J.A. Manrique, S. Abbaki, R.B. Anderson, Y. André, S.M. Angel, G. Arana, T. Battault, P. Beck, K. Benzerara, S. Bernard, J.P. Berthias, O. Beyssac, M. Bonafous, B. Bousquet, M. Boutillier, A. Cadu, K. Castro, F. Chapron, B. Chide, K. Clark, E. Clavé, S. Clegg, E. Cloutis, C. Collin, E.C. Cordoba, A. Cousin, J.C. Dameury, W. D'Anna, Y. Daydou, A. Debus, L. Deflores, E. Dehouck, D. Delapp, G. De Los Santos, C. Donny, A. Doressoundiram, G. Dromart, B. Dubois, A. Dufour, M. Dupieux, M. Egan, J. Ervin, C. Fabre, A. Fau, W. Fischer, O. Forni, T. Fouchet, J. Frydenvang, S. Gauffre, M. Gauthier, V. Gharakanian, O. Gilard, I. Gontijo, R. Gonzalez, D. Granena, J. Grotzinger, R. Hassen-Khodja, M. Heim, Y. Hello, G. Hervet, O. Humeau, X. Jacob, S. Jacquinod, J.R. Johnson, D. Kouach, G. Lacombe, N. Lanza, L. Lapauw, J. Laserna, J. Lasue, L. Le Deit, S. Le Mouélic, E. Le Comte, Q.M. Lee, C. Legett, R. Leveille, E. Lewin, C. Leyrat, G. Lopez-Reyes, R. Lorenz, B. Lucero, J.M. Madariaga, S. Madsen, M. Madsen, N. Mangold, F. Manni, J.F. Mariscal, J. Martinez-Frias, K. Mathieu, R. Mathon, K.P. McCabe, T. McConnochie, S.M. McLennan, J. Mekki, N. Melikechi, P.Y. Meslin, Y. Micheau, Y. Michel, J.M. Michel, D. Mimoun, A. Misra, G. Montagnac, C. Montaron, F. Montmessin, J. Moros, V. Mousset, Y. Morizet, N. Murdoch, R.T. Newell, H. Newsom, N. Nguyen Tuong, A.M. Ollila, G. Orttner, L. Oudda, L. Pares, J. Parisot, Y. Parot, R. Pérez, D. Pheav, L. Picot, P. Pilleri, C. Pilorget, P. Pinet, G. Pont, F. Poulet, C. Quantin-Nataf, B. Quertier, D. Rambaud, W. Rapin, P. Romano, L. Roucayrol, C. Royer, M. Ruellan, B.F. Sandoval, V. Sautter, M.J. Schoppers, S. Schröder, H.C. Seran, S.K. Sharma, P. Sobron, M. Sodki, A. Sournac, V. Sridhar, D. Standarovsky, S. Storms, N. Striebig, M. Tatat, M. Toplis, I. Torre-Fdez, N. Toulemont, C. Velasco, M. Veneranda, D. Venhaus, C. Virmontois, M. Viso, P. Willis, K.W. Wong, The SuperCam Instrument Suite on the Mars 2020 Rover: Science Objectives and Mast-Unit Description, Space Sci Rev 217 (2021). https://doi.org/10.1007/s11214-021-00807-w.

[17] R.C. Wiens, S. Maurice, S.H. Robinson, A.E. Nelson, P. Cais, P. Bernardi, R.T. Newell, S. Clegg, S.K. Sharma, S. Storms, J. Deming, D. Beckman, A.M. Ollila, O. Gasnault, R.B. Anderson, Y. André, S. Michael Angel, G. Arana, E. Auden, P. Beck, J. Becker, K. Benzerara, S. Bernard, O. Beyssac, L. Borges, B. Bousquet, K. Boyd, M. Caffrey, J. Carlson, K. Castro, J. Celis, B. Chide, K. Clark, E. Cloutis, E.C. Cordoba, A. Cousin, M. Dale, L. Deflores, D. Delapp, M. Deleuze, M. Dirmyer, C. Donny, G. Dromart, M. George Duran, M. Egan, J. Ervin, C. Fabre, A. Fau, W. Fischer, O. Forni, T. Fouchet, R. Fresquez, J. Frydenvang, D. Gasway, I. Gontijo, J. Grotzinger, X. Jacob, S. Jacquinod, J.R. Johnson, R.A. Klisiewicz, J. Lake, N. Lanza, J. Laserna, J. Lasue, S. Le Mouélic, C. Legett, R. Leveille, E. Lewin, G. Lopez-Reyes, R. Lorenz, E. Lorigny, S.P. Love, B. Lucero, J.M. Madariaga, M. Madsen, S. Madsen, N. Mangold, J.A. Manrique, J.P. Martinez, J. Martinez-Frias, K.P. McCabe, T.H. McConnochie, J.M. McGlown, S.M. McLennan, N. Melikechi, P.Y. Meslin, J.M. Michel, D. Mimoun, A. Misra, G. Montagnac, F. Montmessin, V. Mousset, N. Murdoch, H. Newsom, L.A. Ott, Z.R. Ousnamer, L. Pares, Y. Parot, R. Pawluczyk, C. Glen Peterson, P. Pilleri, P. Pinet, G. Pont, F. Poulet, C. Provost, B. Quertier, H. Quinn, W. Rapin, J.M. Reess, A.H. Regan, A.L. Reyes-Newell, P.J. Romano, C. Royer, F. Rull, B. Sandoval, J.H. Sarrao, V. Sautter, M.J. Schoppers, S. Schröder, D. Seitz, T. Shepherd, P. Sobron, B. Dubois, V. Sridhar, M.J. Toplis, I. Torre-Fdez, I.A. Trettel, M. Underwood, A. Valdez, J. Valdez, D. Venhaus, P. Willis, The SuperCam Instrument Suite on the NASA Mars 2020 Rover: Body Unit and Combined System Tests, Space Sci Rev 217 (2021). https://doi.org/10.1007/s11214-020-00777-5.

[18] B. Chide, S. Maurice, N. Murdoch, J. Lasue, B. Bousquet, X. Jacob, A. Cousin, O. Forni, O. Gasnault, P.Y. Meslin, J.F. Fronton, M. Bassas-Portús, A. Cadu, A. Sournac, D. Mimoun, R.C. Wiens, Listening to laser sparks: a link between Laser-Induced Breakdown Spectroscopy, acoustic measurements and crater morphology, Spectrochim Acta Part B At Spectrosc 153 (2019) 50–60. https://doi.org/10.1016/j.sab.2019.01.008.

[19] C. Alvarez-Llamas, P. Purohit, J. Moros, J. Laserna, LIBS-Acoustic Mid-Level Fusion Scheme for Mineral Differentiation under Terrestrial and Martian Atmospheric Conditions, Anal Chem 94 (2022) 1840–1849. https://doi.org/10.1021/acs.analchem.1c04792.

[20] C. Alvarez-Llamas, P. Purohit, J. Moros, J. Laserna, Differentiation of closely related mineral phases in Mars atmosphere using frequency domain laser-induced plasma acoustics, Anal Chim Acta 1226 (2022). https://doi.org/10.1016/j.aca.2022.340261.

[21] C. Alvarez-Llamas, J. Laserna, J. Moros, P. Purohit, L. García-Gómez, S.M. Angel, P. Bernardi, B. Bousquet, A. Cadu, E. Dauson, O. Forni, T. Fouchet, O. Gasnault, X. Jacob, G. Lacombe, N.L. Lanza, C. Larmat, J. Lasue, R.D. Lorenz, P.Y. Meslin, D. Mimoun, F. Montmessin, N. Murdoch, A.M. Ollila, P. Pilleri, N. Randazzo, A.L. Reyes-Newell, S. Schröder, A. Stott, J. Ten Cate, A. Udry, D. Vogt, S. Clegg, A. Cousin, S. Maurice, R.C. Wiens, The sound of geological targets on Mars from the absolute intensity of laser-induced sparks shock waves, Spectrochim Acta Part B At Spectrosc 205 (2023). https://doi.org/10.1016/j.sab.2023.106687.

[22] G. Chen, E.S. Yeung, Acoustic Signal as an Internal Standard for Quantitation in Laser-Generated Plumes, Br, 1988. https://pubs.acs.org/sharingguidelines.

[23] Acoustic in situ monitoring of excimer laser ablation of different ceramics, 1993.

[24] F. Anabitarte, L. Rodríguez-Cobo, J.-M. López-Higuera, A. Cobo, Normalization of laser-induced breakdown spectroscopy spectra using a plastic optical fiber light collector and acoustic sensor device, 2012.

[25] S. Conesa, S. Palanco, J.J. Laserna, Acoustic and optical emission during laser-induced plasma formation, Spectrochim Acta Part B At Spectrosc 59 (2004) 1395–1401. https://doi.org/10.1016/j.sab.2004.06.004.

[26] S. Xiong, N. Yang, H. Guan, G. Shi, M. Luo, Y. Deguchi, M. Cui, Combination of plasma acoustic emission signal and laser-induced breakdown spectroscopy for accurate classification of steel, Anal Chim Acta 1336 (2025). https://doi.org/10.1016/j.aca.2024.343496.

[27] Z. He, L. Liu, Z. Hao, Z. Xu, Q. Wang, Y. Lu, Z. Zhao, J. Shi, X. He, Matrix effect suppressing in the element analysis of soils by laser-induced breakdown spectroscopy with acoustic correction, Plasma Science and Technology 25 (2023). https://doi.org/10.1088/2058-6272/ace954.

[28] M. Bosáková, P. Purohit, C. Alvarez-Llamas, J. Moros, K. Novotný, J. Laserna, A systematic evaluation on the impact of sample-related and environmental factors in the analytical performance of acoustic emission from laser-induced plasmas, Anal Chim Acta 1225 (2022). https://doi.org/10.1016/j.aca.2022.340224.

[29] M. Bosáková, K. Novotný, J. Moros, J. Laserna, Acoustic signal in overcoming the matrix effect in LIBS: Toward reliable applicability, Spectrochim Acta Part B At Spectrosc 226 (2025). https://doi.org/10.1016/j.sab.2025.107140.

[30] M. Bosáková, J. Moros, J.M. Vadillo, K. Novotný, J.J. Laserna, Surveying the acoustics from laser-induced plasmas under non-standard atmospheric conditions: Implications for extraterrestrial missions, Spectrochim Acta Part B At Spectrosc 234 (2025) 107320. https://doi.org/10.1016/j.sab.2025.107320.

[31] https://periodictable.com/index.html, (n.d.).

[32] M.N. Polyanskiy, Refractive index info database of optical constants, Sci Data 11 (2024) 94. https://doi.org/10.1038/s41597-023-02898-2.

[33] S. Dengler, C. Kübel, A. Schwenke, G. Ritt, B. Eberle, Near- and off-resonant optical limiting properties of goldsilver alloy nanoparticles for intense nanosecond laser pulses, Journal of Optics (United Kingdom) 14 (2012). https://doi.org/10.1088/2040-8978/14/7/075203.

# Annex 1

## A systematic evaluation on the impact of sample-related and environmental factors in the analytical performance of acoustic emission from laser-induced plasmas

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Acoustics recordings from laser-induced plasmas are becoming increasingly regarded as a complementary source of information from the inspected sample. The propagation of these waves is susceptible to be modified by the physicochemical traits of the sample, thus yielding specific details that can be used for sorting and identification of targets. Still, the relative fragility of the acoustic wave poses major challenges to the applicability of laser-induced acoustics. Echoes and reflections sourcing from intrasample parameters as well as from interactions of the acoustic wave with the surroundings of the inspected target can dilute the analytical information directly related to the object contained within the recordings. The present work aims to experimentally scrutinize the impact of different parameters internal and external to the sample into the final acoustic signal from laser-induced plasmas in order to accurately use this information source for characterization purposes. Variables inherent to the sample such as dimensions, porosity and absorption coefficient, which guides the laser-matter coupling process, have been, for the first time, systematically studied using ad-hoc solids to thoroughly isolate their influence on the signal. Moreover, modulation of soundwave induced by the surroundings of the probed target and the anisotropy of the acoustic signal because of the angle at which the plasma is formed, have been evaluated.

# Annex 2

## Chemical and Acoustical Mixed-Mapping of Geological Materials from Laser-Induced Plasmas: A Comprehensive Approach to Differentiate Mineral Phases

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The acoustic wave produced alongside laser-induced plasmas can be used in conjunction with the recorded atomic spectra of plasma emission to expand the physicochemical information acquired from a single inspection event. Among the most interesting uses of acoustic information is the differentiation of mineral phases with similar optical responses coexisting in geological targets. In addition, laser-induced plasma acoustics (LIPAc) can provide data related to the inspected material's hardness, density, and compactness. In this paper, we present a dual acoustic–optic laser-based strategy for the generation of high-resolution surface images of mineral samples. By combining simultaneous multimodal LIBS (laser-induced breakdown spectroscopy) and LIPAc spectral data from laser-induced plasmas, we explore the mineralogical composition of rocks embedded in resin matrixes to distinguish their chemical composition as well as their crystal phases based on physical changes caused by the different spatial arrangements of the constituent atoms. The multispectral polyhedron created by merging singular optical maps, one per detected elements, and the coincidental acoustic map enhance the distinction between regions present within the matrix of a host rock as compared to the differentiation yielded by each technique when used separately. The chemical information guides the composition of the mineral phases in the host rock. Then, the physical information obtained from acoustics may reinforce the identification of the detected mineral phase, draw the geological history of the inspected section, and showcase possible transformations, mainly of polymorphic nature. To test the combination proposed herein, we also inspected a septarian nodule featuring an ensemble of mineral

phases with different origins. Mixed optical and acoustic responses from laser-produced plasmas of this complex sample allowed us to obtain more specific information. This approach constitutes a reliable and high-throughput tool for studying the surface of geological samples, which can substantially supplement well-established techniques for mineralogical analysis such as Raman spectroscopy and X-ray diffraction.

# Annex 3

## Acoustic signal in overcoming the matrix effect in LIBS: Toward reliable applicability

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The versatility of laser-induced breakdown spectroscopy (LIBS) resulting from its advantageous analytical characteristics is, unfortunately, still limited by challenges inherent to the fundamental principles of the method – the processes of laser ablation and laser-induced plasma generation. Unwanted effects (generally known as matrix effects) significantly decrease the analytical performance of LIBS, complicating quantification and impairing reproducibility. This study investigates acoustic signals accompanying plasmas (LIPAc) to overcome these limitations and enhance LIBS performance. The influence of instrumental (microphone types), operational (laser wavelength and fluence) and sample parameters on acoustic responses were evaluated. The results indicate that laser fluence strongly influences acoustic wave oscillation. When laser fluence substantially exceeds the breakdown thresholds of the different components in the matter, acoustic responses may become identical across various materials. On the other hand, proportionality in differences of acoustic signal is maintained for different microphones and laser wavelength settings.

Promising solutions for eliminating matrix effects on various surfaces were identified, but the suitability and efficiency may be highly dependent on the emission line used. This is demonstrated using the signals of atomic Cu(I) 324.74 nm and ionic Cu(II) 329.04 nm lines measured from an aluminum sample with a partially coppered and partially roughened surface. Acoustic maps of a galena ore sample demonstrate the applications of LIPAc in spatially resolved LIBS imaging and elemental mapping. These maps can help eliminate the discrepancy between the intensities of the calcium atomic line of Ca(I) at 422.67 nm measured from the galena mineral and calcium carbonate.

# Annex 4

## Surveying the acoustics from laser-induced plasmas under non-standard atmospheric conditions: Implications for extraterrestrial missions

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The snapping sound accompanying laser produced plasmas are standing out in recent times as a complementary source of information to the spectroscopic measurements, allowing to catalogue occurring processes as well as to categorize inspected samples. These promising uses are currently considered for the identification of geological material and the characterization of the Martian atmosphere by the SuperCam instrument and its microphone onboard the NASA Perseverance rover. The singularity of each laser plasma, combined with the effect of the different atmospheric environments in which its expansion can occur (composition, pressure, temperature, etc.) provides multiple scenarios that affect the analytical signals generated. Despite the extensive bibliography on the effects of the surrounding atmosphere on the optical emission of laser-induced plasmas, little has been studied about the acoustics derived out of them. The present work aims to systematically scrutinize the effect of the more common atmospheric variables like pressure, temperature and composition into the final acoustic signal from laser-induced plasmas to accurately use this information source.