IMPACT OF LASER ENERGY AND GATE DELAY ON SELF-ABSORPTION OF EMISSION LINES IN LASER INDUCED PLASMA SPECTROSCOPY

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UNIVERSITI TEKNOLOGI MALAYSIA
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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Philosophy

Faculty of Science
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My sincere thesis dedication goes to;

My beloved parents,
Abah and Ma

and my siblings,

A big thank you for giving me great external force and support!
ACKNOWLEDGEMENT

First and foremost, all praises to Allah S.W.T for His Blessings and guidance for giving me the inspiration to embark on this research and instilling me the strength to see this thesis become reality.

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Lastly, to all my friends, thanks for being helpful and gave me the supports.
Laser-induced plasma spectroscopy (LIPS) is a spectroscopy that utilizes laser induced plasma as an emission source. The most challenging part in dealing with emission lines is the self-absorption (SA) which distorts the profile and reduces emission intensity of the spectrum. Resonant lines are most prominent lines of an element in the spectrum and at the same time most prone to SA. This project focuses on the impact of experimental parameters; laser energy and gate delay on the SA coefficient of emission lines which depends on two plasma parameter namely electron temperature, $T_e$ and electron density, $N_e$. A sample made of Al, Mn and Zn embedded in KBr matrix was irradiated with Nd:YAG laser and the plasma signals were recorded using optical spectrometer attached to a delay unit. The atomic and ionic spectral lines of Al, Mn and Zn were observed in the spectra. The lines were verified using references and National Institute of Standards and Technology (NIST) database. Resonant lines are Al I 256.4 nm, Al I 265.6 nm, Al I 308.2 nm, Mn I 403.3 nm, Mn II 259.4 nm and Mn II 260.1 nm. The laser energy was varied from 5 to 650 mJ at a fixed gate delay of 3.75 μs, meanwhile, the gate delay was varied from 0 to 23.75 μs at a fixed laser energy of 650 mJ. The intensity of the emission lines was found increasing in response to higher laser energy. The emission lines of Al, Mn and Zn was found initially increased in intensity within first 1 μs, but then it decreased as the increasing delay time. $T_e$ was calculated using the intensity ratio method applied on Mn I 257.6 nm and Mn I 422.5 nm emission lines and $N_e$ was determined using Stark broadening method of H$_\alpha$-line 656.3 nm. The SA coefficient was calculated for both experimental parameters, by using resonant lines Al I 308.2 nm and Mn II 259.4 nm, and non-resonant lines; Al I 309.1 nm and Mn I 257.6 nm. SA coefficient has variation from 0 to 1. The maximum value of the coefficient indicates that the emission lines is free from SA. The SA coefficient was found to increase from 0.3 to 0.9 as the laser energy increased resulting from rise in $T_e$ and $N_e$ of the plasma. Meanwhile, the increasing gate delay caused the SA coefficient to decrease from 0.9 to 0.1, where the emission lines are more prone to SA. This is due to the decreasing of $T_e$ and $N_e$. This work has emphasized on implementation of higher laser energy and shorter gate delay of LIPS experimental parameters as response to SA coefficient. It will save time and effort and lead to reliable plasma diagnostics, as well as pioneers in studying plasma opacity.
Spektroskopi plasma aruhan laser (LIPS) ialah satu spektroskopi yang menggunakan plasma aruhan laser sebagai sumber pancaran. Bahagian paling mencabar berkaitan garis pancaran ialah penswaserapan (SA) yang mana merencatkan profil dan mengurangkan intensiti pancaran spektrum. Garis resonans adalah garis yang paling menonjol bagi unsur dalam spektrum dan pada masa yang sama paling cenderung kepada SA. Projek ini memfokuskan impak parameter eksperimen; tenaga laser dan pintu penangguhan terhadap koefisien SA garis pancaran yang bergantung kepada dua parameter plasma iaitu suhu elektron, Te dan ketumpatan elektron, Ne. Satu sampel diperbuat daripada Al, Mn dan Zn tertanam di dalam matriks KBr telah dipancarkan dengan laser Nd: YAG dan signal plasma direkodkan menggunakan spektrometer optik yang disambungkan kepada satu unit penangguhan. Garis spektrum atom dan ion Al, Mn dan Zn diperhatikan dalam spektrum.

Garis ini disahkan menggunakan rujukan dan pangkalan data National Institute of Standards and Technology (NIST). Garis resonans adalah Al I 256.4 nm, Al I 265.6 nm, Al I 308.2 nm, Mn I 403.3 nm, Mn II 259.4 nm dan Mn II 260.1 nm. Tenaga laser berubah daripada 5 kepada 650 mJ pada pintu penangguhan tetap 3.75 μs, sementara itu, pintu penangguhan diubah daripada 0 kepada 23.75 μs pada tenaga laser tetap 650 mJ. Intensiti garis pancaran didapati semakin meningkat sebagai tindak balas kepada peningkatan tenaga laser. Garis pancaran Al, Mn dan Zn didapati pada mulanya meningkat dalam 1 μs yang pertama tetapi selepas itu ia menurun sebagaimana pintu penangguhan meningkat. Te dikira menggunakan kaedah nisbah intensiti yang digunakan pada garis pancaran Mn I 257.6 nm dan Mn I 422.5 nm dan Ne telah ditentukan menggunakan kaedah perluasan Stark bagi garis pancaran Hα 656.3 nm. Koefisien SA dihitung untuk kedua-dua parameter eksperimen dengan menggunakan garis resonans; Al I 308.2 nm dan Mn II 259.4, dan garis tidak resonans; Al I 209.1 nm dan Mn II 257.6 nm. Koefisien SA mempunyai variasi daripada 0 hingga 1. Nilai maksimum koefisien menunjukkan bahawa garis pancaran bebas daripada SA. Koefisien SA didapati meningkat apabila tenaga laser meningkat daripada 0.3 kepada 0.9 berikutan peningkatan Te dan Ne plasma. Sementara itu, penangguhan pintu yang semakin meningkat menyebabkan koefisien SA menurun,daripada 0.9 kepada 0.1 dengan garis pancaran lebih cenderung kepada SA. Ini disebabkan oleh penurunan Te dan Ne. Kerja ini telah memberi penekanan kepada pelaksanaan tenaga laser yang lebih tinggi dan pintu penangguhan yang singkat dalam eksperimen parameter LIPS sebagai tindak balas kepada koefisien SA. Ia akan menjimatkan masa dan
usaha dan membawa kepada diagnostik plasma yang boleh dipercayai, serta perintis dalam mengkaji kelegapan plasma.
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CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter consists of the introduction to thesis, overview of the study, problem statement, objectives, scope, and research significance which are explained in respective sections.

1.1 Overview of Study

Laser-induced plasma spectroscopy (LIPS), also known as laser-induced breakdown spectroscopy (LIBS), is a spectroscopy that utilizes laser induced plasma as an emission source. LIPS reported to be a future plasma diagnostic tool as compared to established analytical atomic spectrometry. [1] It is a technique commonly used in identification of constituents of unknown sample by ablating a small amount of the sample into hot dense plasma and capturing its emission line spectrum. [1-5] The contribution of LIPS has been expanded to various applications, for instance, remote material assessment in nuclear power stations, [2,3] high-tech textile industry, [4] space exploration, [5,6] archaeological objects, [7,8] biomedical [9,10], forensic purposes, [11–16] agricultural development, [17–19] and so forth. Today, LIPS is
considered as an attractive and effective technique as it is a simple and offers fast multi-elemental analysis.

LIPS operates as an energetic laser pulse is focused onto a sample surface and a small amount of the material is ablated, vaporized and ionized into a plasma plume which radiates characteristic spectral lines. The ablated material compresses the surrounding atmosphere and leads to formation of a shock wave. During this process, a wide variety of phenomena including rapid local heating, melting and intense evaporation involved. Plasma plume formed above the sample surface due to the expansion of evaporated material. At initial stage of plasma evolution, Bremsstrahlung process is predominant, where the free electrons release energy upon deceleration while passing through the electric fields generated by nuclei. A significant amount of energy is transferred to the atoms and ions by collisions and hence collisional ionization takes place. Those electrons absorbed more energy from laser pulse producing more ions. It results in the formation of plasma, also known as breakdown plasma. The breakdown process is a threshold process which strongly depends on physical parameters such as ambient pressure and environment, laser parameters (including wavelength, pulse energy, pulse duration and irradiance) and the nature of material. These parameters can contribute towards the dynamical behaviour of the plasma. The emitted light from the excited species have distinguished spectral signatures of the matter that provides information to the plasma and the sample composition. Optical emission spectrometer is used to measure the emitting radiation. The light emission is characterized by a continuum spectrum containing discrete atomic/ionic lines. Neutral lines, ionic lines and the continuum emission decay with time. Generally, the continuum spectrum decay faster than the atomic lines allowing the possibility of detecting atomic lines with a good signal strength by varying the delay and the integration time of the detector gate. [1,2,19-24]

LIPS is an appealing technique in optical emission spectrometry (OES) due to its ability to perform multi-elemental analysis of a wide variety of samples as liquid, solid, gas and aerosols. [2,22,23] From the aspect of spectrochemical analysis of elements, LIPS has many advantages over other conventional spectroscopic techniques
because the plasma is formed by focused optical radiation. [24] LIPS signals can give out the elemental composition in multi-elemental samples. Generally, the advantage of LIPS highlights that the sample preparation is either not necessary or very minimal. [25–27] It is also an almost non-destructive [28,29] and contactless technique [23] that provides direct characterization of the sample. LIPS has powerful capability in carrying out remote on line and in-situ analysis of the samples particularly situated in the hostile and harsh environments. [23]

Some of the disadvantages of LIPS technique is due to current hardware and software restrictions and fundamental physical processes. It has low precision and depends on operational parameters and ambient conditions. [22,30,31] In addition, self-absorption (SA) poses a big challenge in LIPS analysis. It is the absorption of radiation within the plasma which results in weaker signal than the original emission intensity. It can cause large error or even wrong estimations from the results more specifically when dealing with quantitative investigations. SA occurred as the plasma reabsorbs the light photons generated in prior emissions. [21-23] Thus, the results may not reflect the true condition of the plasma i.e., its composition, temperature and density.

There has been much activity on investigating the influencers of SA in laser induced plasmas in recent years. [18,20,30–54] The published works reports on exploring various conditions such as different elemental concentrations and samples, [19,41,42] ambient conditions i.e gas environment and pressure, [43–48] optimized laser parameters i.e type of laser, laser energies, and gate delay. [27,32,34,49,50] New approaches on reducing and correcting SA are also proposed by researchers [39,40,51–55] but these are not being widely utilized. Instead, researchers tend to work within the conditions which do not significantly favor self absorption.

Therefore, this study investigates the impact of experimental parameters; i.e., gate delay and laser energy on the self-absorption of emission lines and plotting calibration curves of aluminum (Al), manganese (Mn) and zinc (Zn) for a range of concentrations. A series of samples with known concentrations of aluminium (Al),
manganese (Mn) and zinc (Zn) are selected for the purpose of this study. Powders of these elements are mixed with KBr pressed to form hard pellets. The effect of variation in experimental parameters is then studied on plasma parameter and self-absorption of the emission lines.

1.2 Problem Statement

LIPS has more advantages compared to other contemporary analytical techniques for elemental analysis of a material. It is simple, fast and flexible, particularly useful for in-situ applications beyond laboratories. The selected emission lines from LIPS spectra have significant role in the quality of measurements. The most challenging part in dealing with emission lines is the self-absorption (SA). The actual spectrum might be affected by the self-absorption by distorting the profile and showing less emission intensity than the actual. Generally, resonant lines are most prominent lines of an element in the spectrum and at the same time most prone to SA. If such lines are utilized for investigations, the results will not be reflecting the actual value. This will affect the authenticity and reliability of LIPS measurements. In addition, these lines can provide vital information about SA of rest of the emission lines of the same element. The SA varies in response to the variation in experimental parameters such as time window of measurement, laser energy and ambient environment. The knowledge about optical thickness of emission lines under various experimental conditions is therefore of significant importance. Thus, this research is aimed to study the impact of gate delay and laser energy on self-absorption of resonant and non-resonant emission lines of Mn, Al and Zn from laboratory prepared samples in order to find out experimental conditions which are most favourable in obtaining signal with minimal self-absorption.
1.3 Objectives

The general objective of this research is the investigation of the effect of experimental conditions on SA of emission lines in response to experimental parameters. The impact of laser energy and temporal window measurements will be studied.

Specific objectives of the study are;

1. To identify and select resonant and non-resonant spectral lines of aluminium (Al), manganese (Mn) and zinc (Zn) in LIPS spectra.
2. Optimization of experimental parameters for quantitative measurements
3. To calculate electron temperature and electron density of plasma as response to laser energy and gate delay
4. To calculate SA coefficient of selected spectral lines at different laser energies and gate delays.
5. To plot and improve the linearity of calibration curves of Al, Mn and Zn at optimized experimental parameters.

1.4 Scope of Study

This study is focusing on the self-absorption of emission lines of Al, Mn and Zn from the LIPS spectra of laboratory prepared samples. Pelletized samples were prepared in the laboratory with known concentrations of Al, Mn and Zn in potassium bromide (KBr) matrix. Experiments were performed to study the influence of temporal window of measurement (0 – 23.75 μs) and laser energy (0 - 650 mJ). These parameters are of fundamental importance for LIPS investigations in natural environment.
Most suitable mathematical procedures (found in literature) applied to the experimental data for estimation of plasma conditions and self-absorption in spectral lines. For spectroscopic data of emission lines, our main source was NIST atomic spectral database besides published literature. Resonants and non-resonants lines from the spectra are identified. Plasma parameters (electron density, plasma temperature) are calculated to acquire knowledge about plasma conditions that also influence the SA of emission lines. Electron temperature is calculated using Intensity Ratio Method and electron density is calculated using Stark broadening Method. SA coefficient is calculated as response to different laser energies and gate delays. Calibration curves are plotted using intensity of spectral lines of each of the elements and the effect of standard and local normalization is investigated on linearity of the plots.

1.5 Significance of Study

This research is significant from both fundamental and application perspective. Self-absorption of emission lines raises issues in fundamental investigations of plasma and also makes the quantitative estimation of sample composition difficult. This work will contribute to the understanding of SA as response to laser energy and date delay. Special emphasis is on resonant lines which are most prone to self-absorption, if resonant lines are free from self-absorption under certain experimental conditions, other lines (non-resonant) can safely be considered optically thin. By estimating the magnitude of self-absorption, one can easily select suitable experimental to expect acceptable results for specific investigations. With the knowledge of SA coefficient, a correction factor can be introduced for accurate plasma diagnostics. It will save significant amount of precious time and efforts to produce reliable plasma diagnostics.
This will open up doors in studying plasma opacity from various unexplored perspectives.

1.6 Thesis Structure and Organization

This thesis is divided into five chapters. Chapter 2 will furnish a review on relevant published literature. The description of this LIPS technique includes its history, pros and cons, and prominent applications. In the next section, working principle of LIPS is discussed, which includes laser ablation, plasma formation, spectral emission lines and self-absorption phenomenon. In the following section, experimental parameters that would affect the investigation are explained, which consists of laser energy, gate delay, target material and ambient environment. In the last section of Chapter 2, plasma parameters i.e. electron temperature and electron density are discussed. Various researches on the determination of self-absorption are included.

In Chapter 3, methodology used in this research is explained in detail. It includes details on sample preparation and experimental procedures.

Chapter 4 provides the results obtained from this investigation. The influence of experimental parameters i.e. gate delay and laser energy on SA of spectral lines is discussed in detail. Plasma parameters are also calculated and their relationship with variation in experimental parameters and effects on SA is also explained. Calibration curves are drawn using intensity of spectral lines of Al, Zn and Mn against respective elemental concentration. Prominent improvement in linearity of plots is demonstrated by applying local normalization which is developed during this investigation.
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