SIMULTANEOUS DOUBLE PULSE ENHANCED LASER INDUCED BREAKDOWN SPECTROSCOPIC DETECTION OF TRACE HEAVY METALS IN HERBS

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I dedicate this thesis to my ***loving Mother***, who wanted me the most to pursue higher education and supported me in every respect by all means.

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is a versatile technique. It has enormous potential for in-situ elemental analysis of virtually any kind of material. Undesired fluctuations in analytical conditions seriously influence its quantitative measurements. Double Simultaneous Pulse (DSP) configuration is introduced in this work that can potentially minimize the influence of error factors and improve repeatability as well as detection limit. Its performance is compared with conventional Single Pulse (SP) LIBS configuration in a series of experiments performed under controlled environments of air and argon. Herbal samples Ficus Deltoidea, Phaleria Macrocarpa and Strobilanthes Crispus are utilized as investigative materials. Nd:YAG laser (1064 nm, 6 ns, 544 mJ) and Ocean Optics HR4000 spectrometer are employed for laser induced breakdown spectroscopic studies. Mg, Ca, Pb and Cu are quantified in samples through both configurations of LIBS. Better line profiles, emission intensities, signal-to-noise ratios (SNRs) and signal-to-background ratios (SBRs) are observed with DSP configuration. Electron density and plasma temperatures obtained from DSP configuration are slightly higher than those obtained with SP configuration. Comparatively, DSP configuration performs better in the estimation of heavy metal concentrations. Linear correlations of the calibration plots, limits of detection (LODs), relative standard deviation (RSD) and Errors of Prediction are generally improved. Minimum LODs obtained for Pb, Cu, Mg and Ca are 38.63 μg/g, 47.75 μg/g, 8.92 μg/g and 8.72 μg/g respectively. Minimum values of root mean square error of prediction (RMSEP) in the measurements, as yielded from SP and DSP configurations, are 83.13 μg/g and 43.13 μg/g respectively. Smaller errors and better repeatability are found as special traits of argon while smaller LOD is that of air environment. In this study DSP outperforms SP configuration at several fronts in both environments. It concludes that DSP can be a better alternative configuration of LIBS for quantification of heavy metals in herbal plants.

ABSTRAK

Spektroskopi pecahan teraruh laser (LIBS) adalah satu teknik yang serba boleh. Ia mempunyai potensi yang cerah untuk menganalisis unsur ditempat asal hampir semua jenis bahan. Perubahan yang tidak dikehendaki semasa menganalisis memberi kesan yang serius dalam pengukuran kuantitatif. Konfigurasi dua denyut serentak (DSP) diperkenalkan dalam kerja-kerja ini yang berpotensi mengurangkan pengaruh faktor kesilapan dan meningkatkan kebolehulangan dan juga had pengesanan. Pencapaiannya dibandingkan dengan konfigurasi konvensional denyut tunggal (SP) LIBS dalam satu siri kajian yang dilaksanakan dalam persekitaran yang terkawal didalam udara dan gas argon. Sampel herba Ficus Deltoidea, Mahkota dewa dan Strobilanthes crispus digunakan sebagai bahan kajian. Nd: YAG laser (1064 nm, 6 ns, 544 mJ) dan spektrometer ‘Ocean Optics HR4000’ digunakan untuk kajian spektroskopi pecahan teraruh laser. Mg, Ca, Pb dan Cu dalam sampel dikuantitikan melalui kedua-dua konfigurasi LIBS. Profil garis, keamatan pancaran, nisbah isyarat kepada hingar (SNRs) dan nisbah isyarat kepada latar belakang (SBRs) yang lebih baik dapat diperhatikan dengan konfigurasi DSP. Ketumpatan elektron dan suhu plasma yang diperolehi daripada konfigurasi DSP adalah tinggi sedikit daripada apa yang diperolehi dengan konfigurasi SP. Secara perbandingan, konfigurasi DSP melakukan yang lebih baik dalam anggaran kepekatan logam berat. Korelasi linear plot penentukuran, had pengesanan (LODs), sisihan piawai relatif (RSD) dan ralat daripada ramalan umumnya bertambah baik. Had pengesanan minima yang diperolehi bagi Pb, Cu, Mg dan Ca adalah masing-masing 38.63 μg/g, 47.75 μg/g, 8.92 μg/g dan 8.72 μg/g. Nilai minimum ralat punca min kuasa dua daripada ramalan (RMSEP) dalam pengukuran adalah masing-masing 83.13 μg/g dan 43.13 μg/g sebagai dapatan dari konfigurasi SP dan DSP. Ralat yang lebih kecil dan kebolehulangan yang lebih baik diperolehi sebagai ciri-ciri khas argon manakala LOD kecil bagi persekitaran udara. Kajian ini menunjukkan bahawa konfigurasi DSP melebihi prestasi SP di pelbagai bidang dalam kedua-dua persekitaran. Dapat disimpulkan bahawa konfigurasi dua denyut serentak DSP boleh menjadi tetapan alternatif LIBS yang lebih baik untuk kuantifikasi logam berat dalam tumbuhan herba

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LIST OF ABBREVIATIONS

DSP - Double simultaneous pulses
FAAS - Flame atomic absorption spectroscopy
FWHM - Full width at half maximum
IB - Inverse bremsstrahlung
ICP-MS - Inductively coupled plasma-mass spectroscopy
ICP-OES - Inductively coupled plasma-optical emission spectroscopy
LOD - Limit of detection
MRE - Maximum relative error
PI - Photo ionization
RMSEP - Root mean square error of prediction
RSD - Relative standard deviation
SD - Standard deviation
SP - Single pulse
XRF - X-Ray fluorescence

LIST OF SYMBOLS

A_0-A_9 - Samples of *Strobilanthes Crispus*

A - Einstein ‘s *A* coefficient/ Transition probability

α - Absorptivity

B_0-B_9 - Samples of *Phaleria Macrocarpa*

C - Speed of light

C_0-C_8 - Samples of *Ficus Deltoidea*

Ca - Calcium

$C_{nom,s}$ - Nominal concentration of prediction sample

$C_{pre,s}$ - Predicted concentration of sample ‘s’

C_p - Specific heat

Cu - Copper

D - Thermal diffusivity

ε - Emissivity

E - Laser energy

E_{atom} - Upper level energy of atomic transition

E_i - Energy of the transition level

E_{ion} - Upper level energy of ionic transition

g - Statistical weight of an energy level

I - Spectral line intensity

k - Boltzmann Constant

L_v - Latent heat of vaporization

m - Slope of the plot

m_e - Mass of electron

Mg - Magnesium

N - Number of prediction samples

n	-	Population density of an energy level
n_e	-	Electron Density
Pb	-	Lead
R	-	Surface reflectivity
R^2	-	Coefficient of determination
Γ	-	Wavenumber
σ	-	Standard deviation
Δt	-	Pulse duration
T_0	-	Room temperature
T_b	-	Boiling point
T_e	-	Electron temperature
$U(T)$	-	Partition function
V^+	-	Ionization potential
w	-	Electron impact parameter
ω	-	FWHM
λ	-	Wavelength
$\Delta\lambda_D$	-	Doppler’s width

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CHAPTER 1

INTRODUCTION

1.1 Background

Laser-Induced Breakdown Spectroscopy has shown great promise in the field of elemental detection. Over last few years intense scientific activity is observed in the study of LIBS [1, 2]. It will not be an exaggeration to call it the most versatile currently available technique for elemental analysis. The reason is its potential advantages of simple experimental setup, very little or no sample preparation, applicability in all environments, multi-elemental detection and low detection limits etc. LIBS is capable of fast multi-elemental analysis, one measurement merely takes fraction of a second. Lateral and depth profiling are further advantages that other techniques lack.

LIBS has capacity of elemental analysis of organic materials besides metals, alloys, explosives etc. [3-6]. Beyond laboratory research, it has also found place in industry for specific applications [7].

Malaysia is rich in tropical herbs and herbal medicines are appreciated by the population. Plants do absorb harmful elements from their polluted surroundings [8, 9] that may reach up to human toxicity levels [10]. If used in medicine, instead of being beneficial these can be harmful for a consumer if consumed over a long period of time or above safety limits. Therefore, it is of key importance to detect and measure the quantity of heavy metals in herbal plants before their usage. Not only the toxic metals, but the detection of beneficial metals or nutrients is also important. Various techniques like ICP-OES, ICP-MS, AAS and XRF are being employed for such analyses [11-13]. These techniques are rather complicated expansive and time consuming. In addition, acid digestion for sample preparation and chemical wastes are further disadvantages. Not much work is yet reported for monitoring of elemental composition of herbs or herbal medicines through non chemical methods.

LIBS can be an extremely useful analytical tool for this application. For the implementation of LIBS to its full potential for elemental analyses of herbal plants, a few aspects of LIBS are required to be improved. It has got some limitations. These are due to the environments in which the source is often deployed, and it is difficult to control the ablated mass, ambient atmosphere and the laser parameters, which accumulatively affect the emission signal from plasma [14]. It imposes limits on the accuracy and hence efficiency of the LIBS method. It is less likely to have identical conditions for each laser pulse, therefore reproducibility becomes an issue with LIBS in practical cases particularly for organic samples. In addition, matrix of the sample strongly influences LIBS measurements. Both physical and chemical matrix effects are really important to take into account for precise measurements [15].

By resolving these issues, overwhelming potential of LIBS can be brought into applications of rapid elemental analysis. Till date, LIBS as a technique, is improved through double pulse configuration (described in Chapter 3) and the efficiency is being enhanced by data processing techniques such as presented in [16, 17]. It is very sensitive configuration and requires the involvement of two pulsed lasers that makes it a rather delicate and expensive system. Therefore, an alternative method that is economical and efficient in performance would be highly appreciable.

In this work we have explored an economical and simplistic approach for reducing errors and increasing repeatability of the quantitative measurements of heavy metals in plant samples. By means of splitting one laser beam into two and ablating two sample sites simultaneously the influence of sources of errors can be reduced and precision can be increased by several folds.

1.2 Problem statement

LIBS is a highly potential technique for elemental analysis. It is strong in qualitative analysis. While for quantitative analysis, in non-time gated application, its measurements often suffer from lack of precision. It is highly sensitive to sample parameters and analytical environment. Even subtle variations in sampling conditions can reflect in measurements. Addressing these issues, to mitigate or ideally to eliminate them, will bring new endeavors to LIBS applications. A robust method is required to overcome the influence of interfering factors in LIBS measurements. We propose an alternative configuration i.e., Double Simultaneous Pulse for LIBS. It can potentially reduce undesired interferences in the signal and improve precision of measurements. Additionally, LIBS can be an excellent technique for monitoring the content of nutritious and toxic heavy metals in herbal plants. Its application can replace the tediousness of chemical analysis with convenience of fast measurements without even sample preparation.

1.3 Objectives

The current research embarks on the following objectives

i. Designing and construction of a laboratory LIBS system modifiable among Single Pulse and Double Simultaneous Pulse configurations.
ii. Determination of heavy metal concentrations in herbal plants with SP and DSP configurations of LIBS.
iii. Evaluation of the performance of Single Pulse and Double Simultaneous Pulse configurations for quantitative measurements under various experimental conditions.

1.4 Scope of study

Keeping in view the potential capabilities of LIBS and problems in achieving precision in measurements, the present study has been taken up to design and build a LIBS system in the DSP configuration. This configuration is proposed for enhancing the performance of LIBS. Its performance will be compared with a conventional configuration i.e., SP-LIBS under similar experimental conditions.

Due to the importance of monitoring the heavy metal concentrations in herbal plants, locally available herbs will be utilized in the investigation. Sample preparation procedures will be performed in the laboratory. Exploring the best sampling procedures and parameters from selection of leaves till compaction into the pellet form is included in the scope of this work. Maintaining similar quality of all samples is one of our basic interests.

Experiments with two configurations of LIBS will be carried out. A variety of experimental conditions will applied to explore and compare the performance of Single Pulse and Double Simultaneous Pulse configurations under similar circumstances. Ambient atmospheric conditions (160-1000 mbar of air and argon) and laser energies (100 mJ, 200 mJ, and 270 mJ) will be basic exploratory parameters in this study.

Quantitative investigations will embark on two objectives (i) investigations of the differences in plasma parameters obtained with both configurations & (ii) accuracy and precision levels obtained in estimation of heavy metal concentrations in herbal samples through both of the LIBS configurations. The approach of studies is towards exploring the performance of SP- and DSP configurations for accurate and precise estimation of heavy metal concentrations in herbal plants.

1.5 Significance of the study

This study encompasses the intention of socio-economic benefits by application of science for welfare of the people. The current study has been carried out at laboratory level but can be extended to the field with appropriate portable equipment.

Since sample preparation is not an essential procedure and very short analysis time, LIBS can be utilized for in-field monitoring of the chemical composition of herbal plants/medicines in a rapid manner. A number of studies of LIBS on elemental analyses of plant samples are published in recent years [18-20]. However, to the best of our knowledge there is none from Malaysia. Since Malaysia is rich in tropical herbs, the application of this analytical technique would be of great benefit.

As an extension, this study can be applied for a wide range of food applications from raw food to the market products.

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