ANALYSING HEAVY METALS USING LASER INDUCED BREAKDOWN SPECTROSCOPY TECHNIQUE

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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Science (Physics)

Faculty Of Science
Universiti Teknologi Malaysia

NOVEMBER 2012

This thesis is specially dedicated to:

My beloved parents,

Badruzzaman bin Hamzah, Zaiton bt. Hitam

My supportive siblings,

Ammar, 'Umar and Fathymah

My dedicated lecturers,

and all my friends.

.....thanks......

ACKNOWLEDGEMENT

Alhamdulillah, first and foremost, all praise to Allah Almighty, for giving me the courage, strength, and patience to complete this work.

I would like to express my thanks to my supervisor, Prof Dr. Noriah Bidin for being inspiring, supporting, understanding and keep build up my spirit in order to help me finishing my study. Only Allah will repay your sincere kindness.

Thanks are also to Ms Shima and Ms Ruzilah for being kind to help me during my research process and helping me order anything needed for my research, thank you very much. To all my lab mates, especially Shafiq, Ezzaan, Maisarah, Aiza and Faizani thank you for being helpful during my research study in the lab. Thanks are also to my family Mak and Abah for financial support. I love you both so much.

To my soul friends, Ezza, Kaety, Mar, Izzah, Aimi, Sona, Nadia and Aina thanks for always with me whenever I down and made my stay in UTM such a joyful experience. For my new HON family, Dex, Gee, Peter, Eppy, Akir, Dee, Andre, Biena, Raja, Timah, Slay, Don, Apip, Jiji, Acap, Ben, Ajim, Paan, Nami, Sempit, Anep, Zaihan, Arep, Nuox, Ankel, Jing, Broz, Daoh, Amir, Mirul, Saleh, Sam, Nas, Ujang thank you for made my life more meaningful. I would like to thank to the brothers of Aie and Pian, for being understanding during this research.

Lastly, thanks for UTM for giving me opportunity to continue my study in this master degree.

ABSTRACT

Analyzing heavy metals in polluted water using conventional method by chemical technique is difficult because sample preparation involves a lot of chemical. As an alternative to overcome the drawback, laser induced breakdown spectroscopy is introduced. The aims of this project is to analyze heavy metals commonly found in sea water using a q-switched Nd:YAG laser. The laser was focused using two lenses, concave lens was used to diverge the beam and then bring to merge by camera lens with wide angle of 28 mm focal length. An optical breakdown occurred associated with plasma formation at the focal point. Heavy metal sample comprised of solid form and powder. The powder sample was deposited on glass slide by PVD technique. The heavy metal sample was located at the focal point in the air and exposed by laser in repetitive mode with frequency of 10 Hz. The plume plasma formation on the metal sample was visualized using CCD camera. The spectrum produced after laser-metal interactions were recorded via spectrum analyzer. The line spectra were manifested on the screen and analyzed by comparing to data base. Each line represents the element contained in the tested metal. The highest signal indicates the major element contains from the tested heavy metal. Finally, the analyzed heavy metals were summarized in a histogram for comparison purposes.

ABSTRAK

Menganalisis logam berat dalam air tercemar dengan menggunakan kaedah konvensional dengan teknik kimia adalah sukar kerana perlu menyediakan sampel dan melibatkan pelbagai bahan kimia. Sebagai alternatif untuk mengatasi masalah ini, laser mengaruhkan runtuhan spektroskopi diperkenalkan. Matlamat projek ini adalah untuk menganalisis logam berat biasanya dijumpai dalam air laut menggunakan q-suis laser Nd: YAG. Laser ditumpukan menggunakan dua kanta, satu kanta cekung bergabung dan lensa kamera yang mempunyai sudut lebar dan panjang focus 28mm. Satu runtuhan optik berlaku diikuti dengan pembentukan plasma pada titik fokus. Sampel logam berat terdiri daripada bahan pepejal dan serbuk. Sampel serbuk telah dienapkan di atas slaid kaca melalui teknik PVD. Sampel logam berat yang diletakkan dalam titik fokus di udara dan didedahkan dengan laser dalam mod berulang-ulang dengan frekuensi 10 Hz. Pembentukan gumpalan plasma atas sampel logam dirakam menggunakan kamera CCD. Spektrum yang dihasilkan selepas interaksi laser-logam telah dirakamkan melalui penganalisis spektrum. Garis spektrum telah dimanifestasikan pada skrin dan dianalisis dengan membandingkan dari pangkalan data. Setiap garis mewakili elemen yang terkandung dalam logam yang diuji. Isyarat tertinggi menandakan elemen utama yg dikandungi oleh logam berat yang diuji. Akhirnya logam berat yang dianalisis disenaraikan dalam histogram untuk tujuan perbandingan.

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LIST OF ABBREVIATIONS

CCD	-	Charge couple device
CHCs	-	Chlorinated hydrocarbons
CID	-	Charge injection device
CTD	-	Charge transfer detector
K	-	kelvin
LIBS	-	Laser induced breakdown spectroscopy
LIPS	-	Laser induced plasma spectroscopy
LTE	-	Local thermal equilibrium
Nd:YAG	-	Neodynium doped yttrium aluminium garnet
Nm	-	nanometer
PDA	-	Photodiode arrays detector
Pm	-	picometer
PMT	-	photomultiplier tube

LIST OF SYMBOLS

F_{min}	-	Minimum power density absorbed
d	-	Mass density
L_v	-	Latent heat of vaporation
t_e	-	Laser pulse duration
C	-	Heat capacity per unit mass
F	-	Power density
T_v	-	Vaporation temperature
T_0	-	Initial temperature
K	-	Thermal Conductivity
α	-	Coefficient of the absorption
T	-	Temperature
t	-	Time
χ	-	Depth in solid
T_s	-	Temperature on the surface
M	-	Ablated Mass

CHAPTER 1

INTRODUCTION

1.1 Overview

Due to rapid industrial growth, environmental pollution is increasing over the years, especially the contamination of soil and ground water with heavy metals such as aluminum, chromium, arsenic, lead, copper, nickel, beryllium, antimony, zinc, magnesium, cobalt etc. These heavy metals, even at low concentrations, are still toxic. These metals can get into human body by inhalation, ingestion, or skin absorption. It also can enter into human body when eating a crop that had been irrigated with untreated waste water, chemicals, industrial waste and effluents. If the heavy metals ions in the human body's tissues accumulate faster than the detoxification, the toxins will gradually build up.

According to the US Environmental Protection Agency (US EPA) reports, the exposure of excessive concentrations of the toxicity heavy metals such cadmium and mercury has produced bad health effects in public (Msaky and Calvert, 1990; Fergusson, 1990). These metals also have bad effect on ecosystem if there is no regular and proper detection, analysis, disposal and dispersal. It causes the dramatically rise in last 10 years on the exposure of these metals to human body (Fergusson, 1990; Islam *et.al*, 2007).

Keeping in view the above mentioned harmful effects of these metals, there is a need for rapid and precise determination of these metals in the environment. The interest for the development of new analytical techniques has increased in the recent years to assess and monitor the extent of environmental contamination in water resources, soil, and waste disposal sites. The available methods are too expensive and time-consuming because of the sample preparation and also required special chemical and reagent, so they are not cost effective (Rai *et.al*, 2001; Uhl *et.al*, 2001; Russell *et.al*, 2005).

Laser Induced Breakdown Spectroscopy (LIBS) is a simple technique that uses optical contact to the surface of the sample, therefore it is can be use as a simple and fast method to detect and qualify the contaminants in various samples. It is a new technique for element determination in environmental samples, metallic and non-metallic solid, liquid, gases, aerosol and biological samples (Rusak *et.al*, 1998; Samek *et.al*, 2001; Fichet et.al, 2001; Ying *et.al*, 2003; Russell *et.al*, 2005). Some elements can be measured using this technique simultaneously event at parts per million concentration level (Russell *et.al*, 2005).

In this LIBS technique, pulsed laser are applied to ablate the samples, as a result, it vaporized and ionized the sample in hot plasma and then it will be detected by the optical access and analyzed by the spectrometer. These elements are then identified by their spectral signatures. Till date, most of the work on quantitative and qualitative analysis using LIBS technique has been focused to solid samples and much less work has been carried out on liquid samples (Fichet *et.al*, 2001).

The main reason for less work on applications of this technique for analysis of liquid samples is that it is not easy to generate plasma. It could embrace many problems with laser-plasma generation mechanism in liquids, as compared with laser produced plasmas from solid samples. This is because of the density of liquid are lower than solid, and there will be shock waves associated together with the vaporization of the liquid sample and create aerosol above the liquid surface. The existence of the aerosols will disturb the laser that targeted to the sample and also will disturb the plasma emitted which is will detect by the spectrometer. These aerosols may disturb the incident laser radiations and plasma emitted light returning to the spectrometer. The laser pulse will induce bubbles inside the liquid which are not transparent to the laser induced plasma and it will affect the result (Fichet *et.al,* 2001).

Recent developments towards improving analytical capability of this technique have led to more applications of LIBS. However, still more efforts are required to improve the precision and the sensitivity of this technique (Lazic *et.al,* 2005). Some improvement in methodology is needed for its wide applications in terms of its efficiency and limits of detection.

In this research, LIBS's analytical capability is tried on solid samples. Spectrum pattern of heavy metals Al, Sb, Cd, Cu, In, Ni, Pb, Ag, Sn and Zn have been collected during this work. The LIBS spectra for each sample is then analyzed and characterized. Later, the results were compared with NIST data base. This work is as preliminary study to identify the spectrum signature and properties of a few heavy metal that have potential in inducing toxicity and danger to human and environment.

1.2 Problem Statement

In order to develop a new LIBS system, many other information and tasks need to be gathered and accomplished. One of crucial parts in the early stage in development process of the system is to prepare a standard identification and comparison purposes. Thus this project was conducted to analyze the spectra of some heavy metals that commonly found in the polluted water.

1.3 Research Objective

The main objective of this research is to study the spectroscopic properties of some heavy metals commonly found from water pollution. In order to achieve this goal, the following works are performed;

i. Identification of heavy metal samples.
ii. Fabrication of thin film sample by vapor deposition.
iii. Generation of laser induced breakdown on heavy metal sample.
iv. Detection of fluorescence emission spectrum.
v. Analysis and characterization of heavy metal spectrum.

1.4 Research Scope

In this project, a Q-switched Nd:YAG laser was used as a source of energy. A short focal length lens is placed along the beam path so that the plasma spark created on the focal point. The characterization of the laser beam will be carried out by using fiber optic that connected to USB 2000 spectrometer. The selected of heavy metal are include aluminium, antimony, cadmium, copper, indium, nickel, lead, silver, tin and zinc.

REFERENCES

Abdellatif, G. and Imam, H. (2002). A study of laser plasma parameters at different laser wavelength. *Spectrochimica Acta Part B.* 57: 1155-1165.

Allen, H.E., Huang, C.P., Bailey, G.W. and Bowers, A.R. (1995). *Metals speciation and contamination of soil,* Lewis Publishers, Boca Raton.

Andrzej, W. M., Vincenzo, P. and Israel, S. (2006). *Laser-induced breakdown spectroscopy: Fundamentals and Applications.* Cambridge University Press.

Bassiotis, I., Diamantopoulou, A., Giannoudakos, A., Kompitsas, M. and Roubani-Kalantzopoulou, F. (2001). Effect of experimental parameters in quantitative Analysis of steel alloys by laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B.,*56: 671-683.

Bekefi, G. (1976). *Principles of laser plasma,* John Wiley & Sons, New York.

Berman, L.M. and Wolf, P.J. (1998). Laser-induced breakdown spectroscopy of liquids: aqueous solutions of nickel and chlorinated hydrocarbons. *Appl. Spectrosc.,* 52: 438-443.

Boudjemai, S., Gasmi, T., Boushaki, R., Kasbadji, R. and Medjahed, F. (2004). Laser induced breakdown spectroscopy in water. *J. Appl. Sci. Environ.,* 8: 13 – 15.

Bolger, J.A. (2000). Semi-quantitative laser-induced breakdown spectroscopy for analysis of mineral drill core. *Appl. Spectrosc.,* 54:181-189.

Body, D. and Chadwick, B.L. (2001). Simultaneous elemental analysis system using laser induced breakdown spectroscopy. *Rev. Sci. Instrum.,* 72:1625-1629.

Cabalin, L.M. and Laserna, J.J. (1998). Experimental determination of laser-induced breakdown thresholds of metals under nanosecond Q-switched laser operation, *Spectrochimica Acta Part B.*, 53: 723-730.

Cho, H. H., Kim, Y. J., Soo Jo, Y., Arai N. and Lee Y. (2001). Application of laser induced breakdown spectrometry for direct determination of trace elements in starch based.

Corsi, M., Cristoforetti, G., Hidalgo, M., Legnaioli, S., Palleschi, V., Salvetti, A., Tognoni, E. and Vallebona, C. (2004). Three-dimensional analysis of laser-induced plasmas in single and double pulse configuration, *Spectrochimica Acta Part B*. 59: 723-735.

Cremers, D. A., Radziemski, L. J. and Loree, T. R. (1984). Spectrochemical analysis of liquids using the laser spark. *Appl. Spectrosc.,* 38 (5): 721-729.

Dahmain, F. (1992). Ablation scaling in laser-produced plasma with laser intensity, laser wavelength, and target atomic number. *Phys. Fluids B,* 4: 1585-1588.

Fergusson, J.E. (1990). The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamin Press, Oxford, p. 382-399.

Fiona, J., Wallis, Bruce, L., Chadwick, and Richard J.S. Morrison (2000). Analysis of lignite using laser-induced breakdown, Applied Spectroscopy, 54: 1231-1235.

Fredman, B. (1996). *Environmental Ecology (The impacts of pollution and other stresses on the ecosystem structure and function)* New York: Academic Press.

Gondal, M. A and Hussain, T. (2007). Determination of poisonous metals in Waste water collected from paint manufacturing plant using laser-induced breakdown spectroscopy. *Talanta*, 71: 73-80.

Gondal, M. A., Hussain, T., Yamani, Z. H. and Ahmed, Z. (2007). Determination of toxic metals in petroleum, cultivated land and ore samples using laser-induced breakdown spectroscopy, *Bull. Environ. Contam. Toxicol.,* 78: 270-274.

Gondal, M. A., Hussain, T., Yamani, Z. H., and Baig, M. A. (2006). Detection of heavy metals in Arabian crude oil residue using laser-induced break down spectroscopy. *Talanta,* 69: 1072-1078.

Gondal, M. A., Hussain, T., Yamani, Z. H., and Baig, M. A. (2007). The role of various binding materials for trace elemental analysis of powder samples using laser-induced breakdown spectroscopy. *Talanta,* 72: 642-649.

Gondal, M. A., Hussain, T., Yamani, Z. H., and Bakri, A.H. (2007). Study of hazardous metals in iron slag waste using laser-induced breakdown spectroscopy. *Journal of Environmental Science and Health Part A,* 42: 765-775.

Hussain, T., Gondal, M. A., Yamani Z. H. and Baig, M.A. (2007). Measurement of nutrients in greenhouse soil with laser-induced breakdown spectroscopy, *Environ. Monit. and Assess.,* 124: 131-139.

Islam, E., Xiao, Y., Zhen, H., and Qaisar, M. (2007). Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. *Jr. Zhejiang University Science B,* 8: 1-13.

Kennedy, P.K., Hammer, D. X. and Rockwell, B. A. (1997). Laser-induced breakdown in aqueous media, *Prog. Quantum electron.* 21: 155-248.

Kuzuya, M., Matsumoto, H., Takechi, H., Mikami, O. (1993). Effect of laser energy and atmosphere on the emission characteristics of laser-induced plasma, *Appl. Spectrosc.,* 47: 1659-1664.

Lazic, V., Colao, F., Fantoni, R. and Spizzicchino, V. (2005). Laser-induced breakdown spectroscopy in water: Improvement of the threshold by signal processing. *Spectrochimica Acta Part B,* 60: 1002-1013.

Lee, Y., Song, K. and Sneddon, J. (2000). *Laser-induced breakdown spectrometry.* Nova Sci. Pub., Inc. New York.

Lee, Y.I., Song, K. and Sceddon, J. (1997). *Laser-induced plasma in analytical atomic spectroscopy,* VCH Publishers: New York.

Martin M. Z. and Cheng, M. D. (2000). Detection of chromium aerosol using timeresolved laser-induced plasma spectroscopy. *Appl. Spectrosc.,* 54: 1279-1285.

Msaky, J.J. and Calvert, R. (1990). Adsorption behavior of copper and zinc in soils: influence of pH on adsorption characteristics. *Soil Sci.,* 150: 513-522.

Muller, K. and Stege, H. (2003). Evaluation of the analytical potential of the Laserinduced breakdown spectroscopy for the analysis of the historical glasses. *Archaeometry,* 45: 421-433.

Piepmeier, E.H., and Osten, D.E. (1971). Atmospheric influences on Q-switched laser sampling and resulting plumes. *Appl. Spectrosc.,* 25: 642-652.

Radziemski, L.J. (2002). From LASER to LIBS, the path of technology development, *Spectrochim. Acta, part B: Atom Spectrosc.,* 57: 1109-1113.

Rai, K.A., Zhang, H., Yueh, F.Y., Singh, J.P and Weisberg, A. (2001). Parametric study of a fiber optic laser-induced breakdown spectroscopy probe for analysis of aluminium alloys. *Spectrochimica Acta Part B.,* 56: 2371-2383.

Ready, J. F. (1971). *Effect of high power laser radiation:* New Academic Press, Inc.,New York.

Rusak, D.A., Castle, B.C., Smith, B.W. and Winefordner, J.D. (1998). Recent trends and the future of laser-induced breakdown spectroscopy. *Trends in Anal. Chem.,* 17: 453-461.

Russell, S. H., Frank, C. D., Andrzej, W. M., Kevin, L. M., Roy, A. W. and Patrick, D. F. (2005). Laser-induced breakdown spectroscopy (LIBS) – an emerging field-portable sensor technology for real-time, in-situ geochemical and environmental analysis. *Environment Analysis,* 5: 21-28.

Samek, O., Beddows, D.C.S., Telle, H. H., Kaiser, J., Liska M., Caceres J.O. and Gonzales U.A., (2001). Quantitative laser-induced breakdown spectroscopy analysis of calcified tissue samples, *Spectrochimica Acta Part B,* 56: 865-875.

Smith, D.C., and Meyerand, R.G. (1976). *Laser radiation induced gas breakdown in principles of laser plasma.* John Wiley & Sons, New York, 457-507.

Sneddon, J., Thiem, T.L. and Lee, Y.I. (1997). (edition). *Lasers in Analytical Atomic Spectroscopy,* VCH-John Wiley & Sons, 7th Avenue, New York.

Uhl, A., Loebe, K. and Kreuchwig L. (2001). Fast analysis of wood preservers using laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B.* 56: 795-806.

Ying M., Xia Y., Sun Y., Lu Q., Zhao M. and Liu X. (2003). Study of the plasma produced from laser ablation of a KTP crystal, *Appl. Surf. Science*, 207: 227-235.