

DETECTION OF ELEMENTS IN SLIMMING TEA PRODUCT BY USING LASER
INDUCED BREAKDOWN SPECTROSCOPY

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To the people who loved me

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) has been applied to determine the element content in slimming tea product. A Q-switched Nd:YAG laser operating at 1064 nm and generating 93.7 mJ per pulses was employed to excite the pellet sample and the fluorescence emission was analyzed via spectrum analyzer. The induced spectral lines were compared with National Institute of Standards and Technology (NIST) database to identify the element. A commercial slimming tea was used as sample to be investigated whereas the natural tea leaves were used as control. The LIBS results showed that both slimming tea and natural tea leaves contain several elements including iron (Fe), sodium (Na), chromium (Cr), cobalt (Co), calcium (Ca), manganese (Mn), magnesium (Mg), silicon (Si), sulfur (S), titanium (Ti), nickel (Ni) and cesium (Cs). However, higher intensity of elements was found in slimming tea spectrum compared to natural tea leaves. The plasma temperatures calculated using Boltzmann plot were found to be 13588.95 K and 12319.50 K for slimming tea and tea leaves samples respectively whereas the electron density for slimming tea and tea leaves samples were $7.46 \times 10^{16} \text{ cm}^{-3}$ and $15.91 \times 10^{16} \text{ cm}^{-3}$, respectively. The plasma produced by this LIBS system was found to be in local thermodynamic equilibrium (LTE) condition after evaluating these plasma parameters. Quantitative analysis performed by using inductively coupled plasma mass spectroscopy (ICPMS) proved that the concentration of the elements is higher in slimming tea than in natural tea leaves.

ABSTRAK

Teknik spektroskopi leraian aruhan laser (LIBS) telah digunakan untuk menganalisis kandungan unsur di dalam produk teh pelangsingan. Sebuah laser suis-Q Nd:YAG beroperasi pada 1064 nm dan menjana 93.7 mJ per denyut telah digunakan untuk mengujakan sampel gentel dan pencucuran pendarfluor yang terhasil dianalisis melalui penganalisis spektrum. Garisan spektrum yang terhasil dibandingkan dengan data dari Institut Piawaian dan Teknologi Kebangsaan (NIST) untuk mengenal pasti unsur yang diwakilinya. Teh pelangsingan komersial digunakan sebagai sampel untuk dianalisis manakala daun teh semula jadi telah digunakan sebagai piawai. Hasil LIBS menunjukkan bahawa kedua-dua teh melangsingkan badan dan daun teh semula jadi mengandungi beberapa unsur logam berat termasuk ferum (Fe), natrium (Na), kromium (Cr), kobalt (Co), kalsium (Ca), silikon (Si), mangan (Mn), magnesium (Mg), sulfur (S), titanium (Ti), nikel (Ni) dan cesium (Cs). Walau bagaimanapun, kadar keamatan spektrum bagi teh pelangsingan badan adalah lebih tinggi berbanding daun teh semula jadi. Suhu plasma yang telah dihitung dengan menggunakan kaedah plot Boltzmann ialah 13588.95 K untuk teh pelangsingan badan dan 12319.50 K untuk daun teh semula jadi manakala ketumpatan elektron untuk teh pelangsingan badan dan daun teh semula jadi masing-masing ialah $7.46 \times 10^{16} \text{ cm}^{-3}$ dan $15.91 \times 10^{16} \text{ cm}^{-3}$. Plasma yang dihasilkan oleh sistem LIBS ini didapati berada dalam keadaan keseimbangan termodinamik setempat (LTE) selepas menilai parameter plasma. Analisis kuantitatif yang dilakukan menggunakan teknik plasma berganding aruhan spektrometri jisim (ICPMS) telah membuktikan bahawa kadar kepekatan unsur yang terkandung dalam teh pelangsingan badan adalah lebih tinggi berbanding daun teh semula jadi.

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LIST OF SYMBOLS

A_{ki}	-	transition probability
c	-	speed of light
C	-	carbon
Cd	-	cadmium
cm	-	centimeter
Co	-	cobalt
Cr	-	chromium
Cu	-	copper
Cs	-	cesium
E_k	-	upper level energy
eV	-	electron volt
Fe	-	iron
g	-	gram
g_k	-	upper level statistical weight
h	-	Plank constant
I	-	intensity
J	-	joule
k	-	Boltzmann's constant(8.617×10^{-5} eV K ⁻¹)
kN	-	kilo Newton
m	-	meter
mA	-	milliampere
Mg	-	Manganese
mJ	-	millijoule
μm	-	micrometer
mm	-	millimeter
Mn	-	manganese

<i>ms</i>	-	millisecond
Na	-	sodium
Ni	-	nickel
<i>n</i>	-	number density of emitting species
<i>nm</i>	-	nanometer
N_e	-	electron density
$N(T)$	-	total density
<i>ppm</i>	-	part per millions
<i>S</i>	-	slope of the calibration curve
<i>s</i>	-	second
σ	-	standard deviation of the background
S	-	Sulfur
Si	-	Silicon
<i>T</i>	-	temperature
Ti	-	Titanium
<i>U</i>	-	partition function
<i>V</i>	-	volt
λ	-	wavelength

LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
AES	-	Atomic Emission Spectroscopy
FDA	-	Food and Drug Administration
FOC	-	Fiber Optic Cable
HPLC	-	High Performance Liquid Chromatography
ICP	-	Inductively Coupled Plasma
ICPMS	-	Inductively Coupled Plasma Mass Spectroscopy
LIBS	-	Laser Induced Breakdown Spectroscopy
LOD	-	Limits of Detection
LTE	-	Local Thermodynamic Equilibrium
MPC	-	Maximum Permissible Concentration
Nd:YAG	-	Neodymium-Doped Yttrium Aluminum Garnet
NIST	-	National Institute of Standards and Technology

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CHAPTER 1

INTRODUCTION

1.1 Introduction

In this chapter researches regarding laser induced breakdown spectroscopy (LIBS) and slimming tea product will be reviewed. It also includes problem statement of the research together with objective and scope of the research.

1.2 Background of the Problem

The identification of elements in natural supplement is of vital importance to evaluate its nutritional status (Menet *et. al.*, 2004). Slimming tea comes in various brands and types with different variety of ingredients. Slimming tea differs from normal tea although its base ingredients are tea leaves which comes from the camellia sinensis plant. Many brands of slimming tea are available with varying strengths and benefits because most slimming teas contain some combination of stimulants, bulk fibers, diuretics and laxatives which comes from additional ingredients include herbs such as cassia, senna, peppermint, ginseng and fennel. By the identification of the contents of the nutritive elements in the slimming tea, one can estimate any nutritive deficiency or surplus which may have potential side effects on potential user.

Many researches have been done to determine some element content especially heavy metals in tea to investigate whether it exceeded the maximum permissible concentration (MPC). For example, Ahmad et al. (2012) revealed the presence of mineral metals (Zn, Fe, Mn and Cu) and toxic metals (Ni, Pb and Cd) in tea products available in Pakistan. In Nigeria, bioaccumulation of heavy metals (Zn, Cd, Cu and Pb) in tea products was investigated by Achudume and Owoeye (2010). Contamination tea can indirectly affecting weight loss because its based ingredient is *Camellia sinensis*.

1.3 Problem Statement

There are many research focusing on tea leaves but less research on slimming tea products due to less attention on detection and composition analysis in health field. Slimming tea products are widely available in Malaysia and consumers can easily buy them at the nearby store or through online shopping. Consumers are eager to have slim body even there are certain products that did not give any compositional information. Many of them think that all slimming tea products contain herbs that will stimulate body weight but unfortunately not all products contain the same herbs and probably there are just regular teas. Thus, it was important to discriminate slimming tea with natural tea leaves. The most common practice to analyze plant is by using chemical technique, either ICP, AAS, HPLC and other but in the recent years laser induced breakdown spectroscopy (LIBS) have also been used in plant studies. In this study, we proposed analysis slimming tea by using laser induced breakdown technique.

1.4 Significant of the Research

It is important to determine the content in slimming tea product to help in making the manufacturers and consumers aware of the danger and harmful element it may contain. The knowledge of the elements in the slimming tea is also important to determine safety level, whether the concentration each of the element is under the permissible limit.

1.5 Objectives of the Research

The main objective of the project is to analyze the content of slimming tea. In order to achieve this goal the following works are accomplished;

- i. To detect the constituents of original natural tea leaves and slimming tea product
- ii. To calibrate the heavy metal in the tea leave matrix
- iii. To calculate the characterization of plasma in tea leave and slimming tea product
- iv. To determine the concentration of selected elements in natural tea leaves and slimming tea product

1.6 Scope of the Research

Tea leave from Cameron highland was used as a control or reference. Several sample of slimming teas were purchase from retail shops and super market. All the teas are processed into powder to form pellet. The teas are analyzed using LIBS technique. A Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser was employed to form plasma, and Maya spectrometer was used to analyze the fluorescence of plasma intensity.

REFERENCES

- Ahmad, S., Khader, J. A., Gilani, S. S., Khan, S., Noor, S., Ullah, R., Hussain, I., Kanwal, F., Ullah, H. and Shah, Z. (2012). Determination of Mineral and Toxic Heavy Elements in Different Brands of Black Tea of Pakistan. *African Journal of Pharmacy and Pharmacology*. 6(15), 1194-1196.
- Achudume, A. S. and Owoeye, D. (2010). Quantitative Assessment of Heavy Metals in Some Tea Marketed in Nigeria. *Health*. 2(9), 1097-1100.
- Anderson, H. (2010). Retrieved from <http://www.microscopemaster.com/scanning-electron-microscope.html>. Advantages and Disadvantages in Imaging Components and Applications.
- Babushok, V., Junior, F. L., Gottfried, J. and Richardson, M. C. (2006). Double Pulse Laser Ablation and Plasma: Laser Induced Breakdown Spectroscopy Signal Enhancement. *Spectrochimica Acta Part B*. 61(9), 999-1014.
- Baudelet, M. and Smith, B. W. (2013). The First Years of Laser-Induced Breakdown Spectroscopy. *Analytical Atomic Spectrometry*. 28, 624-629.
- Baudelet, M., Yu, J., Bossu, M., Jovelet, J., Wolf, J. P., Amodeo, T., Frejafon, E. and Laloi, P. (2006). Discrimination of Microbiological Samples Using Femtosecond Laser-Induced Breakdown Spectroscopy. *Applied Physics Letters*. 89, 163903(1-3).
- Beldjilal, S., Borivent, D., Mercadier, L., Mothe, E., Clair, G. and Hermann, J. (2010). Evaluation of Minor Element Concentrations in Potatoes Using Laser-Induced Breakdown Spectroscopy. *Spectrochimica Acta Part B*. 65, 727-733.

- Boussaidi, S. (2012). Characterization of Laser-Induced Plasma of Water Extracted From Orange Juice. *Analytical Letters*. 45, 1928-1935.
- Burakov, V. S., Tarasenko, N. V., Nedelko, M. I., Kononov, V. A., Vasilev, N. N. and Isakov, S. N. (2009). Analysis of Lead and Sulfur in Environmental Samples by Double Pulse Laser Induced Breakdown Spectroscopy. *Spectrochimica Acta Part B*. 64, 141-146.
- Carmona, N., Oujja, M., Gaspard, S., Garcia-Heras, M., Villegas, M. A. and Castillejo, M. (2007). Lead Determination in Glasses by Laser-Induced Breakdown Spectroscopy. *Spectrochimica Acta Part B*. 62, 94-100.
- Evert, A. (2009). Iron in Diet. Retrieved July 27, 2014 from <http://www.nlm.nih.gov/medlineplus/ency/article/002422.html>.
- Garcimuno, M., Diaz Pace, D. M. and Bertucelli, G. (2013). Laser-Induced Breakdown Spectroscopy for Quantitative Analysis of Copper in Algae. *Optic & Laser Technology*. 47, 26-30.
- Gibaek, K., Jihyun, K., Jeunghwan, C. and Kihong, P. (2012). Detection of Nutrient Elements and Contamination by Pesticides in Spinach and Rice Samples Using Laser-Induced Breakdown Spectroscopy (LIBS). *Journal of Agricultural & Food Chemistry*. 60, 718-724.
- Junior, D. S., Nunes, L. C., Carvalho, G. G. A., Gomes, M. S., Souza, P. F., Leme, F. O., Santos, L. G. C. and Krug F. J. (2012). Laser-Induced Breakdown Spectroscopy for Analysis of Plant Materials: A Review. *Spectrochimica Acta Part B*. 71-72, 3-13.
- Karak, T. and Bhagat, R. M. (2010). Trace Elements in Tea Leaves, Made Tea and Tea Infusion: A Review. *Food Research International*. 43, 2234-2252.
- Kumar, A., Nair, A. G. C., Reddy, A. V. R. and Garg, A. N. (2005). Availability of Essential Elements in Indian and US Tea Brands. *Food Chemistry*. 89, 441-448.

- Lee, W. B., Wu, J. Y., Lee, Y. I. and Sneddon, J. (2004). Recent Applications of Laser-Induced Breakdown Spectrometry: A Review of Material Approaches. *Applied Spectroscopy*. 39, 27-97.
- Liu, Y., Penczak, J. S. and Gordon, R. J. (2010). Nanosecond Polarization-Resolved Laser-Induced Breakdown Spectroscopy. *Optic Letters*. 35(2), 112-114.
- Maiga, A., Diallo, D., Bye, R. and Paulsen, B. S. (2005). Determination of Some Toxic and Essential metal Ions in Medicinal and Edible Plants from Mali. *Journal of Agricultural and Food Chemistry*. 53, 2316-2321.
- Menet, M. C., Sang, S., Yang, C. S., Ho, C. T. and Rosen, R. T. (2004). Analysis of Theaflavins and Thearubigins from Black Tea Extract by MALDI-TOF Mass Spectrometry. *Journal of Agricultural and Food Chemistry*. 52, 2455-2461.
- Michel, A. P. M. and Chave, A. D. (2007). Analysis of Laser-Induced Breakdown Spectroscopy Spectra: The Case for Extreme Value Statistics. *Spectrochimica Acta Part B*. 62, 1370-1378.
- Noll, R., Sturm, V., Aydin, U., Eilers, D., Gehlen, C., Hohne, M., Lamott, A., Makowe, J. and Vrenegor, J. (2008). Laser-Induced Breakdown Spectroscopy – From Research to Industry, New Frontiers for Process Control. *Spectrochimica Acta Part B*. 63(10), 1159-1166.
- Nunes L. C., Braga, J. W. B., Trevizan, L. C., Souza, P. F., Carvalho, G. G. A., Junior, D. S., Poppi, R. J. and Krug, F. J. (2010). Optimization and Validation of a LIBS Method for the Determination of Macro and Micronutrients in Sugar Cane Leaves. *Journal of Analytical Atomic Spectrometry*. 25, 1453-1460.
- Nunes, L. C., Silva, G. A., Trevizan, L. C., Junior, D. S., Poppi, R. J. and Krug, F. J. (2009). Simultaneous Optimization by Neuro-Genetic Approach for Analysis of Plant Materials by Laser Induced Breakdown Spectroscopy. *Spectrochimica Acta Part B*. 64, 565-572.
- Pandhija, S. and Rai, A. K. (2008). Laser-Induced Breakdown Spectroscopy: A Versatile Tool for Monitoring Traces in Materials. *Pramana-Journal of Physics*. 70(3), 553-563.

- Pouzar, M., Cernohorsky, T., Prusova, M., Prokopcakova, P. and Krejcova, A. (2009). LIBS Analysis of Crop Plants. *Journal of Analytical Atomic Spectrometry*. 24, 953-957.
- Pytlakowska, K., Kita, A., Janoska, P., Polowniak, M. and Kozik, V. (2012). Multi-Element Analysis of Mineral and Trace Elements in Medicinal herbs and Their Infusions. *Food Chemistry*. 135, 494-501.
- Tokalioglu, S. (2012). Determination of Trace Elements in Commonly Consumed Medicinal Herbs by ICP-MS and Multivariate Analysis. *Food Chemistry*. 134, 2504-2508.
- Unnikrishnan, V. K., Alti, K., Nayak, R., Bernard, R., Kartha, V. B., Santhosh, C., Gupta, G. P. and Suri, B. M. (2010). Spectroscopy of Laser-produced Plasmas: Setting Up of High Performance Laser-Induced Breakdown Spectroscopy System. *Pramana-Journal of Physics*. 75(6), 1145-1150.
- Weidman, M., Baudelet, M., Palanco, S., Sigman, M., Dagdigian, P. and Richardson M. (2010). Laser-Induced Breakdown Spectroscopy of Copper with a 2 μ m Thulium Fiber Laser. *Optic Express*. 18, 7905-7910.
- Wilsch, G., Weritz, F., Schaurich, D. and Wiggerhauser, H. (2005). Determination of Chloride Content in Concrete Structures with Laser-Induced Breakdown Spectroscopy. *Construction and Building Materials*. 19, 724-730.