THE TRACE ELEMENTS OF CHLORPYRIFOS AND MALATHION PESTICIDES ON GUAVA FRUIT USING LASER INDUCED BREAKDOWN SPECTROSCOPY

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I dedicated my thesis to the most important person in my life
who never give up helping me
in many ways

To my beloved father,

Abu Hanifah Nok Man Bin Harun

And

To my beloved mother,

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Also not forgotten to,

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) is an analytical technique used for identification of elements by analysing the emission line spectrum produced by a sample. LIBS is implemented as analytical technique for this study because it requires minimal sample preparation, fast result and non-destructive technique compared to other commercial detection techniques such as gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), Raman spectroscopy, and inductively coupled plasma (ICP) that need long experimental process, complicated sample preparation, and destructive to sample. In this research, LIBS technique was deployed for determination of presence pesticides on guava fruit. The experimental setup consists of Q-switched Nd:YAG laser operating at 1064 nm (139 mJ per pulse) and fiber optical cable was connected with HR4000 spectrometer in order to collect the atomic emission light. Different pesticide concentrations (1, 10, 100, and 1000 ppm) were prepared for calibration curve analysis in determination of limit of detection (LOD) and limit of quantification (LOQ). LIBS technique was able to detect the pesticide elements on guava sample such as phosphorus at wavelength of 253.56 nm and 255.33 nm. The different pesticide concentrations resulted to the proportional changes of pesticide element intensity such as phosphorus and carbon. LOD and LOQ were also measured with minimum value of 0.7 and 1.4 mg/L, respectively. Principal component analysis (PCA) implemented in the study was able to classify the group of pesticide at different concentrations with variance 95%. In conclusion, the combination of LIBS and PCA method has potential for detection of pesticides at different concentrations.

ABSTRAK

Spektroskopi leraian aruhan laser (LIBS) adalah teknik analisis yang digunakan untuk mengenalpasti unsur-unsur dengan menganalisis spektrum garis pancaran yang dihasilkan oleh suatu sampel. LIBS dilaksanakan sebagai teknik analisis untuk kajian ini kerana ia memerlukan penyediaan sampel yang minimum, dapatan yang cepat, dan teknik tidak-musnah berbanding teknik-teknik pengesanan yang lain seperti kromatografi gas-spektrometer jisim (GC-MS), kromatografi cecair prestasi tinggi (HPLC), spektroskopi Raman, dan plasma gandingan aruhan (ICP) yang memerlukan proses eksperimen yang panjang, penyediaan sampel yang rumit, dan pemusnahan sampel. Dalam kajian ini, teknik LIBS digunakan untuk mengenalpasti kehadiran racun serangga pada buah jambu batu. Peralatan eksperimen terdiri daripada laser Nd:YAG bersuis-Q beroperasi pada 1064 nm (139 mJ per denyut) dan kabel gentian optik disambungkan dengan spektrometer HR4000 untuk mengumpulkan cahaya pancaran atom. Pelbagai kepekatan racun serangga (1, 10, 100, dan 1000 ppm) disediakan untuk analisis lengkung penentukuran dalam menentukan had pengesanan (LOD) dan had kuantifikasi (LOQ). Teknik LIBS berupaya untuk mengesan unsur-unsur racun serangga seperti fosforus pada panjang gelombang 253.56 nm dan 255.33 nm. Pelbagai kepekatan racun serangga menghasilkan perubahan yang berkadar terus dengan keamatan unsur racun serangga seperti fosforus dan karbon. LOD dan LOQ masing-masing diukur dengan nilai minimum adalah 0.7 dan 1.4 mg/L. Analisis komponen utama (PCA) yang digunakan dalam kajian ini berupaya untuk klasifikasi kumpulan racun serangga pada pelbagai kepekatan dengan varians 95%. Sebagai kesimpulan, penggabungan LIBS dan kaedah PCA mempunyai keupayaan untuk mengesan racun serangga pada pelbagai kepekatan.

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LIST OF ABBREVATIONS

AChE	-	Acetycholinesterase Enzyme
ADI	-	Acceptable Daily Intake
AOP	-	Advanced Oxidation Process
ChE	-	Cholinesterase Enzyme
CNS	-	Central Nerve System
FAO	-	Food and Agricultural Organization
FDA	-	Food and Drug Administration
FOC	-	Fiber Optical Cable
FSA	-	Food Safety Authority
GC-MS	-	Gas Chromatography – Mass Spectrometer
HPLC	-	High Performance Liquid Chromatography
ICP	-	Inductively Coupled Plasma
IPC	-	Integrated Pest Control
IPM	-	Integrated Pest Management
LIBS	-	Laser - Induced Breakdown Spectroscopy
LLE	-	Liquid Liquid Extraction
LOD	-	Limit of Detection
LOQ	-	Limit of Quantification
MAD	-	Malaysian Agricultural Department
MEPS	-	Micro – Extraction in Packet Sorbets
MRL	-	Maximum Residue Limit
Nd: YAG	-	Neodyium: Yttrium Aluminum Garnet
OCP	-	Organochlorine Pesticide
OES	-	Optical Emission Spectrometer

OPP	-	Organophosphorus Pesticide
PCA	-	Principal Component Analysis
QuEChERS	-	Quick, Easy, Cheap, Effective, Rugged, and Safe
SERS	-	Surface Enhanced Raman Spectroscopy
SPE	-	Solid Phase Extraction
WHO	-	World Health Organization

LIST OF SYMBOLS

χ	-	Data matrix
$\sum$	-	Covariance matrix
μ	-	Mean
D	-	Mean-centering data
C	-	Concentration
h	-	Planck's constant
I	-	Intensity
k	-	Constant
N	-	Number of samples or datas
P	-	Power
S	-	Slope
υ	-	Frequency
W	-	Lower dimensional space of PCA
E	-	Energy of photon
Z	-	Singular value decomposition (SVD) matrix
σ	-	Standard deviation
τ_p	-	Laser pulse duration
Y	-	Projected data
V	-	Eigenvectors
λ	-	Eigenvalues

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The application of a pesticide in agriculture has been introduced since ancient time to kill and control any unwanted pest species from destroying the plants. The first generation of pesticide formulated with petroleum oil, heavy metals, and fumigant hydrogen cyanide was used liberally until nineteen-sixties [1]. Acute in toxicity that caused an adverse effect to human health and animals, and polluted the environment are the reasons of this pesticide is banned. Due to that case, the scientist has reformulated the pesticide using an active ingredient from synthetic organic compound which is less toxic than the previous pesticide. Dichloro-diphenyl-trichloroethane (DDT) was the example of synthetic organic pesticide that synthesized by a German scientist, Ziedler. Although it is less in toxic, but having long degradation process had forbidden DDT pesticide to be used in many countries to overcome the environmental pollution, crop damage, and diseases to humans and animals [2]. As a result, pesticide had re-improved its formula and reproduced back to meet the safety and quality requirements. Pesticide acts as chemical and biological agent to protect the plants from pest infestation at the beginning plantation process until the storage. Low in cost and provide fourfold return money, and resulting in high crop production and quality have indirectly increased the pesticide demand for agriculture around the world including Malaysia.

A Swiss physician and alchemist, Paracelsus (1493-1541) had said that all chemical substances are safe when a right dose is applied. The authorities such as Food and Agriculture Organization (FAO), World Health Organization (WHO), Food Safety Authority (FSA), Food and Drug Administration (FDA), and more, has developed a close working contact with food agencies around the world to implement food control system to provide consumer protection and ensure that all food through the processing methods and stages are safe, wholesome and fit for human consumption. Food safety and quality are referring to all-hazard caused by food that injures the health of the consumer either chronic or acute, and the nutritional and product values of the food, respectively. The examples of those hazards are diarrhea, excessive sweating, and any kinds of abnormal body behavior after consumption or even death. The food quality has both positive and negative attributes. Positive attributes consist of product origin, color, flavor, texture, and processing food methods, while, food spoilage, contamination of filth and chemicals, discoloration, and off-odors are the example of negative attributes [3]. In fact, consumers are tends to look food in terms of color, flavor, and texture without realized the food is safe to be consumed or not. Therefore, a food code which is a collection of standards, guidelines, and codes of practice, was introduced by Codex Alimentarius Commission to be implemented by the government, industries, and farmers for fair trade, food safety and quality, and to control the residual pesticide contents. Integrated pest management (IPM) or integrated pest control (IPC) is a proper guideline for pesticide use. Maximum residue level (MRL) and acceptable daily intake (ADI) are introduced for measurement of the safe amount of residual pesticide on food products, and the specific amount of pesticide residue that can be ingested by the humans in daily basis over a lifetime without health risk, respectively.

Even though the pesticide safety precautions were explained to industries and workers, but there are few industries and workers whose still ignore the importance of food safety and only think about to earn more profits and reduced the production costs. A small mistake such as improper agricultural practices, poor hygiene at all processing and preparation stages, misused of pesticides, inadequate or improper storage, and harvest before pesticide degradation ends, can cause food contamination of high residual pesticide. On May 2016, J. D. Heyes reported in Natural News about the contamination of apple juice with herbicide due to misuse of banned pesticide. Such herbicide that is persistent caused the adverse effects to consumers and the environment. Another article from the Associated Press on January 13, 2012 has written about the pollution of contaminated orange juice products from the polluted orange fruits with Carbendazim. It shows that pesticide chemicals can occur in chain, described as farm-to-table continuum, and may continuously affect the consumer. This may be due to the food cleaning process being overlooked or not done by industries or unprofessional pesticide handling which are the major reasons of pesticide-related illness never stop taking place around the world in every year [4,5].

Pesticide residue is the pesticide that remaining on food products after pluck out process. The amount of residue is depending on the physicochemical properties of the pesticide and crop, the rate of pesticide application, the pre-harvest intervals, and the plant cultivation methods [6]. Human and animals are easily get affected by pesticide residue because of its characteristics that transparent and odourless to all senses. High amount of pesticide residue are harmful to be consumed and may cause food hazard issues. Malaysia besides of other countries like China, Cambodia, India, and so forth also experienced the pesticide-food hazard issues. In March 2016, pesticide-food hazard case is reported by Sinar Newspaper in Malaysia about the poisoning of organophosphate pesticide to a few stall eaters at Siputeh, Ipoh which happen due to the improper pesticide handling. The incident poisoned almost a hundred consumers with symptoms such as dizziness, vomiting, diarrhoea, excessive sweating, and excessive salivation. One patient has reported death due to the inability of the brain to receive the oxygen. Hence, a fast detector tools for detection of pesticide residue on food products to assure the consumer health from the dangers of pesticide chemical is indispensable.

Determination of residual pesticide on any materials is not a new thing and had been first studied in 1933 of measuring the residue of rotenone [7]. Detection technique evolved in the following years starting from gas chromatography (GC), to mass spectrometry (MS), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), Raman spectroscopy, and next, inductively coupled plasma (ICP) [8,9]. Those are multi-residue methods that are commonly used in industrial and laboratories for identification of toxic elements in food materials. Intricate sample preparations, destructive the sample, lots of experimental process and expensive experimental costs are the cons of these techniques.

Fast, reliable, and in-situ detection techniques are imperative for laboratory and field use. Laser-induced breakdown spectroscopy or known as LIBS is a type of detection system that fulfil the criteria of little sample preparation, simple manual handling, non-demanding experiment conditions, micro-destructive technique, portable for field use and low experimental cost. In previous years, LIBS is rarely used for analysis of complex samples like blood plasma, food, drugs, and even pesticide due to sample matrices and lack of understanding the plasma properties. Currently, improvement in LIBS has deployed it to many field area such as archaeology, medical, geology and much more. The examples of analysis of these fields are as follows; analysis of age of archaeological ceramic and metal artefacts [10], determination of Wilson's disease through human liver analysis [11], identification of the abundant minerals on the surface of rocks [12], and so on [13–18].

An analytical LIBS signal is produced by the interaction of laser and sample. The LIBS signal is suitable for both qualitative and quantitative analysis by eliminating the instrumental interferences, the retention time for shift correction, selectivity, and chromatographic separation abilities. However, the data coming from such analytical techniques are very complex and difficult to resolve and interpret [19]. Therefore, the contribution of mathematical and statistical approach such as Principal Component Analysis (PCA) is helpful for better qualitative and quantitative analysis.

In this project, LIBS is deployed as fast pesticide residue detection system onto food products since the application of LIBS for pesticide detection is still new and become a great interest to many researchers. A psidium guajava or well known as guava is a food product that will be used in this study due to its nutritional benefits, flavour, and popularity among Malaysians. Malathion and Chlorpyrifos pesticide are chosen because they are the type of pesticide that commonly used by local farmers. Chemometrics method which is PCA will be implement in LIBS analysis to improve the separation quality of the complex sample and provide a powerful approach in a pattern of recognition and classification. A study by Zhao X. *et al.* had successfully demonstrated the potential of chemometrics technique in classification of various concentrations of detergent residues on food utensils [20].

1.2 Problem Statement

The determination of pesticide on fresh fruit may seem difficult for commercial detection techniques due to the weakness of these techniques. GC-MS, HPLC, Raman Spectroscopy, and ICP are those commercial analytical techniques that required long and complex experimental procedures, consumed high experimental costs, destructive to sample and produced much waste. Therefore, application of simple analytical technique for pesticide determination had become a great interest in this study.

The spectral lines produced by LIBS signal are able to classify the pesticide samples by comparing the intensity level of each pesticide elements. However, classifying the pesticide samples for many data may seem complex because of high noise contribution. Hence, combination of LIBS and chemometrics analysis may provide great potential in identification and classification of pesticide samples.

1.3 Research Question

The fast, in-situ, simple and micro-destructive detection technique is suitable for laboratories and field use. The technique can reduce the experimental costs and pollution to environment because required least equipment and minimal experimental process which consists of three experimental steps; 1) sample preparations, 2) detection and 3) analysis. Furthermore, the diameter of a laser beam for LIBS which is about 1-2 mm will cause micro damage to the sample with no side effect if eaten by a person. Studies by M. Dell'Aglio *et al.* had unveiled the potential of LIBS in monitoring the heavy metals with accuracy is acceptable for analytical method [21]. Hence, LIBS technique is deployed in this study to achieve the goals of the study.

Introducing the mathematical and statistical approach, or chemometrics analysis in LIBS helps reducing the noise interception as well as enhance the accuracy of LIBS. A study by Rahul Agrawal *et al.* had suggested for LIBS to couple with chemometrics analysis for better discrimination and classification of the adulterated and non-adulterated sample [22]. Hu *et al.* had proved that the combination of LIBS with chemometrics method may be an instant diagnostic tool to discriminate samples with different matrixes such as different concentrations of copper in food products [23]. Thus, principal component analysis (PCA) is deployed in this study for coupling with LIBS technique to discriminate between four different concentrations of pesticide ratios (1:1, 1:10, 1:100, and 1:1000) on fruit sample.

1.4 Objectives

In this study, a plasma generates on a sample surface is developed by the interaction of laser with the sample. The objectives of the study are:

1. To trace the elements of Chlorpyrifos and Malathion pesticide and element of guava using LIBS technique.

2. To determine the limit of detection (LOD) and limit of quantification (LOQ) of LIBS technique.
3. To classify the clean and treated guava at different pesticide concentrations through PCA method.

1.5 Research Scope

Q-switched Nd: YAG pulsed laser is deployed to induce the sample breakdown and generate a plasma on the sample surface. The experimental setup consists of the laser system, optical emission spectrometer (OES), a light collector, and guava sample. Lights emitted from plasma contained important information for elemental analysis. Laser characteristics such as beam laser (1.0 ± 0.1 mm), wavelength (1064 nm), and laser energy (139 ± 1 mJ), spectrometer gate window (40µs), and focal point from lens to sample (9.6 ± 0.1 cm) were adjusted for optimized plasma formation. The focused study is dealing with guava sample treated with four different pesticide concentration ratios (1:1, 1:10, 1:100, and 1:1000) for determination of limit of detection (LOD) and limit of quantification (LOQ). In addition to discriminate between treated guava and clean guava through PCA method. The spectral lines are observed and collected from the wavelength range of 200 nm to 650 nm regarding to the spectrometer used. However, there is limit for LIBS in which it is not suitable for detection of small element concentration.

1.6 Research Significance

The outcome of this study is important in introducing a fast, simple, and non-destructive technique in determination of pesticide residues on fresh food sample. Generally, there been efforts made to demonstrate the potential of LIBS in determination of pesticide residues on fresh food sample. However, the methods still have their limitations. Thus, introducing a guava fruit as a sample in LIBS will become a new features for LIBS technique. Combination of LIBS technique with PCA method will provide an automatic discrimination between uncontaminated and contaminated food.

Fast, in-situ, micro-destructive, easy for laboratory and field used, and less production of chemical waste in LIBS technique can become a new interest for the research industries in Malaysia.

1.7 Thesis Outline

Chapter one presents a brief background on the subject matter and overview of techniques used for detection of pesticide residues on matter of study as well the significance of laser-induced breakdown spectroscopy (LIBS). Chapter two provides a comprehensive literature review and theoretical background of the matter of study such as guava fruit and Malathion and Chlorpyrifos pesticide. The chemical and physical characteristics, and degradation factors of pesticides were also discussed in this chapter. The basic principle and mechanism of LIBS method is also presented in this chapter. Chapter three presents in detail the research methodology, which comprises the experimental set up, sample preparation methods for a substrate and pesticide solutions for different concentrations, and method for application of pesticide on guava skin. Furthermore, steps for principle component analysis (PCA) method is also present in such chapter. Chapter four highlight the result between the spectrum lines of clean guava sample and pesticide-treated guava sample. Afterward, the effect on the intensity levels for elemental line is reported as the pesticide concentration changes. The chemical and physical properties, and degradation factors of the pesticide are required for the changes that occurred. In addition, the result for classification of treated guava at different concentrations using PCA method were presented in this chapter. Chapter five concludes the thesis with deduction inferred from the results.

REFERENCES

1. Gary, C., Beatrice, A.G., Lee, H.H., Dalia, M.S., C.Ross, A., in:, *A Rev. Sci. Lit. As It Pertain. to Gulf War Illnesses Vol. 8 Pestic.*, RAND Corporations, Santa Monica, 2000, pp. 5–14.
2. Osborn, D., Pesticides in Modern Agriculture. *Environ. Impacts Mod. Agric.* 2012, 34, 111–128.
3. FAO/WHO, Assuring Food Safety and Quality: Guidelines for strenghtening national food control systems, vol. 76, 2003.
4. Bajwa, U., Sandhu, K.S., Effect of handling and processing on pesticide residues in food - a review. *J. Food Sci. Technol.* 2014, 51, 201–220.
5. Kaushik, G., Satya, S., Naik, S.N., Food processing a tool to pesticide residue dissipation - A review. *Food Res. Int.* 2009, 42, 26–40.
6. Fujita, M., Iijima, K., Evaluation of factors affecting pesticide residue levels in Japanese raw agricultural commodities. *J. Pestic. Sci.* 2013, 38, 169–170.
7. Sawyer, L.D., in:, Congress US (Ed.), *Pestic. residue food Technol. Detect.*, DIANE, 1988, pp. 112–121.
8. Watanabe, M., Ohta, Y., Licang, S., Motoyama, N., Kikuchi, J., Profiling contents of water-soluble metabolites and mineral nutrients to evaluate the effects of pesticides and organic and chemical fertilizers on tomato fruit quality. *Food Chem.* 2015, 169, 387–395.
9. Vongsvivut, J., Robertson, G., Mcnaughton, D., Surface-enhanced Raman spectroscopic analysis of fonofos pesticide adsorbed on silver and gold nanoparticles. *J. Raman Spectrosc.* 2010, 41, 1137–1148.
10. Melessanaki, K., Mateo, M., Ferrence, S.C., Betancourt, P.P., Anglos, D., The application of LIBS for the analysis of archaeological ceramic and metal artifacts. *Appl. Surf Sci.* 2002, 198, 156–163.

11. Grolmusová, Z., Horňáčková, M., Plavčan, J., Kopáni, M., et al., Laser induced breakdown spectroscopy of human liver samples with Wilson's disease. *Eur. Phys. J. Appl. Phys.* 2013, 63, p1–p7.

12. Khajehzadeh, N., Kauppinen, T.K., Fast mineral identification using elemental LIBS technique. *IFAC-PapersOnLine* 2015, 48, 119–124.

13. Hamzaoui, S., Khleifia, R., Jaïdane, N., Lakhdar, Z. Ben, Quantitative analysis of pathological nails using laser-induced breakdown spectroscopy (LIBS) technique. *Lasers Med. Sci.* 2011, 26, 79–83.

14. Gondal, M.A., Hussain, T., Yamani, Z.H., Baig, M.A., On-line monitoring of remediation process of chromium polluted soil using LIBS. *J. Hazard. Mater.* 2009, 163, 1265–1271.

15. Buckley, S.G., in:, Singh JP, Thakur SN (Eds.), *Laser-Induced Break. Spectrosc.*, Elsevier B.V., 2007, pp. 313–324.

16. Costa, V.C., Aquino, F.W.B., Paranhos, C.M., Pereira-Filho, E.R., Identification and classification of polymer e-waste using laser-induced breakdown spectroscopy (LIBS) and chemometric tools. *Polym. Test.* 2017, 59, 390–395.

17. Singh, V.K., Rai, V., Rai, A.K., Variational study of the constituents of cholesterol stones by laser-induced breakdown spectroscopy. *Lasers Med. Sci.* 2009, 24, 27–33.

18. Gondal, M. a, Dastageer, A., Maslehuddin, M., Alnehmi, a J., Al-Amoudi, O.S.B., Sensitivity enhancement at 594.8 nm atomic transition of Cl I for chloride detection in the reinforced concrete using LIBS. *J. Environ. Sci. Heal. Part A* 2011, 46, 198–203.

19. Liang, Y.-Z., Xie, P., Chan, K., Quality control of herbal medicines. *J. Chromatogr. B* 2004, 812, 53–70.

20. Zhao, X., Dong, D., Zheng, W., Jiao, L., Han, P., The application of laser-induced breakdown spectroscopy in domestic detergent residues detection. *RSC Adv.* 2015, 5, 89164–89170.

21. Dell'Aglio, M., Gaudiuso, R., Senesi, G.S., De Giacomo, A., et al., Monitoring of Cr, Cu, Pb, V and Zn in polluted soils by laser induced

breakdown spectroscopy (LIBS). *J. Environ. Monit.* 2011, 13, 1422–1426.

22. Agrawal, R., Pathak, A., Rai, A., Rai, G., An Approach of Laser-Induced Breakdown Spectroscopy to Detect Toxic Metals in Crushed Ice Ball. *ISRN Anal. Chem.* 2013, 2013, 1–9.

23. Hu, H., Huang, L., Liu, M., Chen, T., et al., Nondestructive Determination of Cu Residue in Orange Peel by Laser Induced Breakdown Spectroscopy. *Plasma Sci. Technol.* 2015, 17, 711–715.

24. Swirski, E., Ben-Dov, Y., Wysoki, M., in:, Ben-Dov Y, Hodgson CJ (Eds.), *Soft Scale Insects - Their Biol. Nat. Enemies Control*, Elsevier Science B.V, 1997, pp. 255–263.

25. Yusof, S., in:, *Encycl. Food Sci. Nutr.*, 2003, pp. 2985–2992.

26. Soliman, K.M., Changes in concentration of pesticide residues in potatoes during washing and home preparation. *Food Chem. Toxicol.* 2001, 39, 887–891.

27. Cengiz, M.F., Certel, M., Residue contents of captan and procymidone applied on tomatoes grown in greenhouses and their reduction by duration of a pre-harvest interval and post-harvest culinary applications. *Food Chem.* 2007, 100, 1611–1619.

28. Abou-Arab, A.A.K., Behavior of pesticides in tomatoes during commercial and home preparation. *Food Chem.* 1999, 65, 509–514.

29. Uchôa-thomaz, A.M.A., Sousa, E.C., Carioca, J.O.B., Morais, S.M. De, et al., Chemical composition, fatty acid profile and bioactive compounds of guava seeds (Psidium guajava L.). *Food Sci. Technol.* 2014, 34, 485–492.

30. Malaysia, J.P., Panduan Penggunaan Racun Perosak Bagi Tanaman Tertentu, Perpustakaan Negara Malaysia, Malaysia, 2017.

31. Selenothrips, J., Red-banded thrips. *Dep. Agric. Fish.* 2018, 1–2.

32. Malaysia, U.P., Buku Panduan Tanaman Jambu Batu, Universiti Putra Malaysia, Malaysia, 2011.

33. FOA, International Code of Conduct on the Distribution and Use of Pesticides, FOA, Rome, Italy, 2005.

34. Zacharia, T.J., in:, Stoytcheva DM (Ed.), *Pestic. Mod. World-Trends Pestic. Anal.*, vol. 1873, InTech, 1996, pp. 1–19.

35. Horsak, R.D., Bedient, P.B., Hamilton, M.C., Thomas, F. Ben, in:, D. Morrison R, L. Murphy B (Eds.), *Environ. Forensics Contam. Specif. Guid.*, Elsevier Inc., 2005, pp. 144–165.

36. National Pesticide Information Center, Phyrethrins - General Fact Sheet. *Environ. Prot.* 1967, 1–3.

37. Pesticides, B., Synthetic Pyrethroids, Beyond Pesticides, Washington DC, 2000.

38. Eto, M., Organophosphorus pesticides: Organic and biological chemistry, CRC Press Taylor & Francis Group, New York, 2018.

39. Chawla, P., Kaushik, R., Shiva Swaraj, V.J., Kumar, N., Organophosphorus pesticides residues in food and their colorimetric detection. *Environ. Nanotechnology, Monit. Manag.* 2018, 10, 292–307.

40. English, B.A., Webster, A.A., in:, Robertson D, Biaggioni I, Burnstock G, A. Low P, F.R. Paton J (Eds.), *Prim. Auton. Nerv. Syst.*, Elsevier Inc., 2012, pp. 631–634.

41. Brown, B.J., Marten, G.G., in:, G. Marten G (Ed.), *Tradit. Agric. Southeast Asia A Hum. Ecol. Perspect.*, Avalon Publishing, Colorado, 1986, pp. 241–272.

42. Yek, M.S., in:, FOA (Ed.), *Asia Reg. Work. Implementation, Monit. Obs. Int. Code Conduct Distrib. Use Pestic.*, RAP Publication 2005/29, Bangkok, Thailand, 2005, pp. 1–9.

43. Abdullah, M.P., Othman, M.R., Ishak, A., Nabhan, K.J., Detection of pesticides residues in water samples from organic and conventional paddy fields of Ledang, Johor, Malaysia. *AIP Conf. Proc.* 2016, 1784, 1–6.

44. Ali, A., Shaari, N., Mismanagement of Chemical Agriculture in Malaysia from Legal Perspective. *Procedia Econ. Financ.* 2015, 31, 640–650.

45. Hassan, R., Pesawah Di Sabak Bernam Terdedah Kepada Kesan Racun Serangga. *Univ. Kebangs. Malaysia* 2012, 1–6.

46. Pohanish, R.P., in:, *Sittig's Handb. Pestic. Agric. Chem.*, William Andrew Publishing, New York, 2015, pp. 91–195.

47. John, E.M., Shaike, J.M., Chlorpyrifos: pollution and remediation. *Environ. Chem. Lett.* 2015, 13, 269–291.

48. Wu, J., Xiao, Z., Ge, Y., Zhang, Y., et al., Degradation behavior and products of malathion and chlorpyrifos spiked in apple juice by ultrasonic treatment. *Ultrason. Sonochem.* 2009, 17, 72–77.

49. Pohanish, R.P., in:, *Sittig's Handb. Pestic. Agric. Chem.*, William Andrew Publishing, New York, 2015, pp. 518–597.

50. Büyüksönmez, F., Rynk, R., Hess, T.F., Bechinski, E., et al., Occurrence , Degradation and Fate of Pesticides During Composting. *Compost Sci. Util.* 1999, 7, 66–82.

51. El-Helow, E.R., Badawy, M.E.I., Mabrouk, M.E.M., Mohamed, E.A.H., El-Beshlawy, Y.M., Biodegradation of Chlorpyrifos by a Newly Isolated Bacillus subtilis Strain, Y242. *Bioremediat. J.* 2013, 17, 113–123.

52. Mugni, H., Demetrio, P., Paracampo, A., Pardi, M., et al., Toxicity persistence in runoff water and soil in experimental soybean plots following chlorpyrifos application. *Bull. Environ. Contam. Toxicol.* 2012, 89, 208–212.

53. Rawn, D.F.K., Quade, S.C., Sun, W., Smith, M., Captan residue reduction in apples as a result of rinsing and peeling. *Elsevier Sci. Ltd* 2008, 109, 790–796.

54. Chavarri, M.J., Herrera, A., Arino, A., The decrease in pesticides in fruit and vegetables during commercial processing. *Int. J. Food Sci. Technol.* 2005, 40, 205–211.

55. Bonnechère, A., Hanot, V., Jolie, R., Hendrickx, M., et al., Effect of household and industrial processing on levels of five pesticide residues and two degradation products in spinach. *Food Control* 2012, 25, 397–406.

56. Zohair, A., Behaviour of some organophosphorus and organochlorine pesticides in potatoes during soaking in different solutions. *Food Chem. Toxicol.* 2001, 39, 751–755.

57. Ticha, J., Hajslova, J., Jech, M., Honzicek, J., et al., Changes of pesticide residues in apples during cold storage. *Elsevier Sci. Ltd* 2008, 19, 247–256.

58. Sytze Elzinga, J.C.R.N.S., Determination of Pesticide Residues in Cannabis Smoke. *J Toxicol* 2013, 2013.

59. Han, J., Fang, P., Xu, X., Li-zheng, X., Shen, H., Study of the pesticides distribution in peel , pulp and paper bag and the safety of pear bagging. *Food Control* 2015, 54, 338–346.

60. Chandra, Anil. N. Mahindrakar, Mukesh Kumar, L. P. shinde, S., Determination of Pesticide Residue in Fruits Local Market Nanded, India. *Int. J. Adv. Res.* 2014, 2, 1075–1082.

61. Zhao, L., Ge, J., Liu, F., Jiang, N., Effects of storage and processing on residue levels of chlorpyrifos in soybeans. *Food Chem.* 2014, 150, 182–186.

62. Paranthaman, R., Sudha, A., Kumaravel, S., Determination of pesticide residues in banana by using high performance liquid chromatography and gas chromatography-mass spectrometry. *Am. J. Biochem. Biotechnol.* 2012, 8, 1–6.

63. Islam, S., Hossain, M.S., Nahar, N., Mosihuzzaman, M., Mamun, M.I.R., Application of high performance liquid chromatography to the analysis of pesticide residues in eggplants. *J. Appl. Sci.* 2009, 9, 973–977.

64. López-Fernández, R. Rial-Otero, J. Simal-Gandara, O., Factors governing the removal of mancozeb residues from lettuces with washing solutions. *Food Control* 2013, 34, 530–538.

65. Bumbrah, G.S., Sharma, R.M., Raman spectroscopy – Basic principle , instrumentation and selected applications for the characterization of drugs of abuse. *Egypt. J. Forensic Sci.* 2016, 6, 209–215.

66. Zhang, P.X., Zhou, X., Cheng, A.Y.S., Fang, Y., Raman Spectra from Pesticides on the Surface of Fruits Raman Spectra from Pesticides on the Surface of Fruits. *J. Phys. Conf. Ser.* 2006, 28, 7–11.

67. Dowgiallo, A., Guenther, D., Detection of Pesticide Residue on Fruit Surfaces Using Surface Enhanced Raman Spectroscopy. *Ocean Opt.* 2017, 1–8.

68. Lin, L., Dong, T., Nie, P., Qu, F., He, Y., Rapid Determination of Thiabendazole Pesticides in. *Sensors* 2018, 18, 1–14.

69. Wuilloud, R.G., Shah, M., Kannamkumarath, S.S., Altamirano, J.C., The

potential of inductively coupled plasma-mass spectrometric detection for capillary electrophoretic. *Electrophoresis* 2005, 26, 1598–1605.

70. Laursen, K.H., Schjoerring, J.K., Olesen, J.E., Askegaard, M., et al., Multielemental Fingerprinting as a Tool for Authentication of Organic Wheat, Barley, Faba Bean, and Potato. *J. Agric. Food Chem.* 2011, 59, 4385–4396.

71. Zhang, Z., Kong, F., Vardhanabhuti, B., Mustapha, A., Lin, M., Detection of Engineered Silver Nanoparticle Contamination in Pears. *J. Agric. Food Chem.* 2012, 60, 10762–10767.

72. Zhang, Z., Guo, H., Carlisle, T., Mukherjee, A., et al., Evaluation of Postharvest Washing on AgNPs Removal from Spinach Leaves. *J. Agric. Food Chem.* 2016, 64, 6916–6922.

73. González-Martin, I. Revilla, E.V. Betances-Salcedo, A.M. Vivar-Quintana, M.I., Pesticide Residues and Heavy Metals in Commercially Processed Propolis. *Microchem. J.* 2018, 18, 1–28.

74. Fernandes, V.C., Domingues, V.F., Mateus, N., Delerue-Matos, C., Determination of pesticides in fruit and fruit juices by chromatographic methods. An overview. *J. Chromatogr. Sci.* 2011, 49, 715–30.

75. Dell'Oro, D., Casamassima, F., Gesualdo, G., Iammarino, M., et al., Determination of pyrethroids in chicken egg samples: Development and validation of a confirmatory analytical method by gas chromatography/mass spectrometry. *Int. J. Food Sci. Technol.* 2014, 49, 1391–1400.

76. Melo, L.F.C., Collins, C.H., Jardim, I.C.S.F., High-performance liquid chromatographic determination of pesticides in tomatoes using laboratory-made NH-2 and C-18 solid-phase extraction materials. *J. Chromatogr. A* 2005, 1073, 75–81.

77. Salami, F.H., Queiroz, M.E.C., Microextraction in packed sorbent for the determination of pesticides in honey samples by gas chromatography coupled to mass spectrometry. *J. Chromatogr. Sci.* 2013, 51, 899–904.

78. Putri, D., Aryana, N., Aristiawan, Y., Styarini, D., Screening of the presence organophosphates and organochlorines pesticide residues in vegetables and fruits using gas chromatography-mass spectrometry. *AIP Conf.* 2017, 1803, 1–

8.

79. Lehotay, B.S.J., Majors, R.E., Anastassiades, M., QuEChERS , a Sample Preparation Technique that Is " Catching On ": An Up-to-Date Interview with the Inventors. *LCGC North Am.* 2010, 28, 504–516.

80. Xu, M., Gao, Y., Han, X.X., Zhao, B., Detection of Pesticide Residues in Food Using Surface-Enhanced Raman Spectroscopy : A Review. *J. Agric. Food Chem.* 2017, 65, 6719–6726.

81. Yu, Z., Sun, J., Jing, M., Cao, X., et al., Determination of total tin and organotin compounds in shellfish by ICP-MS. *Food Chem.* 2010, 119, 364–367.

82. Nelson, J., Hopfer, H., Silva, F., Wilbur, S., et al., Evaluation of GC-ICP-MS / MS as a New Strategy for Specific Hetero-Atom Detection of Phosphorus, Sulfur, and Chlorine Determination in Foods. *J. Agric. Food Chem.* 2015, 63, 1–21.

83. Rai, P.K., Srivastava, A.K., Sharma, B., Dhar, P., et al., Use of Laser-Induced Breakdown Spectroscopy for the Detection of Glycemic Elements in Indian Medicinal Plants. *Evidence-based Complement. Altern. Med.* 2013, 2013, 1–9.

84. Labutin, T.A., Popov, A.M., Zaytsev, S.M., Zorov, N.B., et al., Determination of chlorine , sulfur and carbon in reinforced concrete structures by double-pulse laser-induced breakdown spectroscopy. *Spectrochim. Acta Part B At. Spectrosc.* 2014, 99, 94–100.

85. Kasem, M.A., Russo, E., Abdel, M., Influence of biological degradation and environmental effects on the interpretation of archeological bone samples with laser-induced breakdown spectroscopy. *J. Anal. At. Spectrom.* 2011, 26, 1733–1739.

86. Torrisi, L., Caridi, F., Giuffrida, L., Torrisi, A., et al., LAMQS analysis applied to ancient Egyptian bronze coins. *Nucl. Inst. Methods Phys. Res. B* 2010, 268, 1657–1664.

87. Rai, A.K., Yueh, F., Singh, J.P., Laser-induced breakdown spectroscopy of molten aluminum alloy. *Appl. Opt.* 2003, 42, 2078–2084.

88. Gondal, M. a., Hussain, T., Yamani, Z.H., Optimization of the LIBS

Parameters for Detection of Trace Metals in Petroleum Products. *Energy Sources, Part A Recover. Util. Environ. Eff.* 2008, 30, 441–451.

89. Bogaerts, A., Chen, Z., Effect of laser parameters on laser ablation and laser-induced plasma formation: A numerical modeling investigation. *Spectrochim. Acta - Part B At. Spectrosc.* 2005, 60, 1280–1307.

90. Bilge, G., Boyaci, I.H., Eseller, K.E., Tamer, U., Cakir, S., Analysis of bakery products by laser-induced breakdown spectroscopy. *Food Chem.* 2015, 181, 186–190.

91. Klement, W., Willens, R., Duwez, P., Non-Crystalline Structure in Solidified Gold-Silicon Alloys. *Nature* 1960, 187, 896–870.

92. Haley, D., Pratt, O., Basic principles of lasers. *Anaesth. Intensive Care Med.* 2017, 18, 648–650.

93. Noll, R., Laser Induced Brekdown Spectroscopy - Fundamentals and Applications, Springer Berlin Heidelberg, Germany, 2012.

94. David A. Cremers et al, Handbook of Laser-Induced Breakdown Spectroscopy, John Wiley & Sons, Ltd, 2013.

95. Ocean Optics, Series Spectrometers Installation and Operation Manual 2008, 1–35.

96. Vadillo, J.M., Laserna, J.J., Laser-induced plasma spectrometry: Truly a surface analytical tool. *Spectrochim. Acta - Part B At. Spectrosc.* 2004, 59, 147–161.

97. Kim, G., Kwak, J., Choi, J., Park, K., Detection of nutrient elements and contamination by pesticides in spinach and rice samples using laser-induced breakdown spectroscopy (LIBS). *J. Agric. Food Chem.* 2012, 60, 718–724.

98. Ma, F., Dong, D., A Measurement Method on Pesticide Residues of Apple Surface Based on Laser-Induced Breakdown Spectroscopy. *Food Anal. Methods* 2014, 7, 1858–1865.

99. Du, X., Dong, D., Zhao, X., Jiao, L., et al., Detection of pesticide residues on fruit surfaces using laser induced breakdown spectroscopy. *RSC Adv.* 2015, 5, 79956–79963.

100. Farooq, W.A., Rasool, K.G., Tawfik, W., Aldawood, A.S., Application of Laser Induced Breakdown Spectroscopy in Early Detection of Red Palm Weevil: (Rhynchophorus ferrugineus) Infestation in Date Palm. *Plasma Sci. Technol.* 2015, 17, 948–952.

101. Lei, W.Q., Haddad, J. El, Motto-Ros, V., Gilon-Delepine, N., et al., Comparative measurements of mineral elements in milk powders with laser-induced breakdown spectroscopy and inductively coupled plasma atomic emission spectroscopy. *Anal. Bioanal. Chem.* 2011, 400, 3303–3313.

102. Rai, P.K., Srivastava, A.K., Sharma, B., Dhar, P., et al., Use of laser-induced breakdown spectroscopy for the detection of glycemic elements in Indian medicinal plants. *Evidence-based Complement. Altern. Med.* 2013, 2013, 1–9.

103. Gaft, M., Nagli, L., Fasaki, I., Kompitsas, M., Wilsch, G., Laser-induced breakdown spectroscopy for on-line sulfur analyses of minerals in ambient conditions. *Spectrochim. Acta - Part B At. Spectrosc.* 2009, 64, 1098–1104.

104. Tharwat, A., Principal component analysis - a tutorial. *Int. J. Appl. Pattern Recognit.* 2016, 3, 197.

105. Eriksson, L., Johansson, E., Kettaneh-Wold, N., Trygg, C., et al., in:, *Multi-Megavariate Data Anal. Part 1, Basic Princ. Appl.*, Umetrics Academy, 2006, pp. 39–62.

106. Multari, R.A., Cremers, D.A., Scott, T., Kendrick, P., Detection of pesticides and dioxins in tissue fats and rendering oils using laser-induced breakdown spectroscopy (LIBS). *J. Agric. Food Chem.* 2013, 61, 2348–2357.

107. Kumar, R., Tripathi, D.K., Devanathan, A., Chauhan, D.K., Rai, A.K., In-Situ Monitoring of Chromium Uptake in Different Parts of the Wheat Seedling (Triticum aestivum) using Laser-Induced Breakdown Spectroscopy. *Spectrosc. Lett.* 2014, 47, 554–563.

108. Agrawal, R., Pathak, A.K., Rai, A.K., Rai, G.K., An Approach of Laser-Induced Breakdown Spectroscopy to Detect Toxic Metals in Crushed Ice Ball. *ISRN Anal. Chem.* 2013, 2013, 1–9.

109. Velioglu, H.M., Sezer, B., Bilge, G., Baytur, S.E., Boyaci, I.H., Identification of offal adulteration in beef by laser induced breakdown spectroscopy (LIBS).

Meat Sci. 2018, 138, 28–33.

110. Multari, R.A., Cremers, D.A., Dupre, J.A.M., Gustafson, J.E., Detection of biological contaminants on foods and food surfaces using laser-induced breakdown spectroscopy (LIBS). *J. Agric. Food Chem.* 2013, 61, 8687–8694.

111. Manhas, F., Pereira, V., Marcondes, D., Pereira, B., et al., Evaluation of the effects of Candidatus Liberibacter asiaticus on inoculated citrus plants using laser-induced breakdown spectroscopy (LIBS) and chemometrics tools. *Talanta* 2010, 83, 351–356.

112. Zhang, C., Shen, T., Liu, F., He, Y., Identification of Coffee Varieties Using Laser-Induced Breakdown Spectroscopy and Chemometrics. *Sensors* 2017, 18, 95.

113. Andrade, D.F., Guedes, W.N., Pereira, F.M.V., Detection of chemical elements related to impurities leached from raw sugarcane: Use of laser-induced breakdown spectroscopy (LIBS) and chemometrics. *Microchem. J.* 2018, 137, 443–448.

114. Sezer, B., Bilge, G., Boyaci, I.H., Capabilities and limitations of LIBS in food analysis. *Trends Anal. Chem.* 2017, 97, 345–353.

115. Choi, D., Gong, Y., Nam, S., Han, S., Yoo, J., Laser-Induced Breakdown Spectroscopy (LIBS) Analysis of Calcium Ions Dissolved in Water Using Filter Paper Substrates : An Ideal Internal Standard for Precision Improvement. *Appl. Spectrosc.* 2014, 68, 198–212.

116. Faizi, S., Electronic Configurations Intro. *LibreTexts* 2019, 1–9.

117. Pacheco, P., Arregui, E., Rangel, N., Sarmiento, R., Identification of metal elements by time-resolved LIBS technique in sediments lake the " Cisne " Identification of metal elements by time-resolved LIBS technique in sediments lake the " Cisne ." *J. Phys. Conf. Ser.* 2017, 786, 1–5.

118. Anabitarte, F., Cobo, A., Lopez-Higuera, J.M., Laser-Induced Breakdown Spectroscopy: Fundamentals, Applications, and Challenges. *ISRN Spectrosc.* 2012, 2012, 1–12.

119. Tran, M., Sun, Q., Smith, B.W., Winefordner, J.D., Determination of F, Cl, and Br in solid organic compounds by laser-induced plasma spectroscopy.

Appl. Spectrosc. 2001, 55, 739–744.

120. Zacharia, T.J., Identity , Physical and Chemical Properties of Pesticides. *Pestic. Mod. World-Trends Pestic. Anal.* 1996, 1873, 1–18.

121. Kumar, R., Tripathi, D.K., Devanathan, A., Chauhan, D.K., Rai, A.K., In-Situ Monitoring of Chromium Uptake in Different Parts of the Wheat Seedling (Triticum aestivum) using Laser-Induced Breakdown Spectroscopy. *Spectrosc. Lett.* 2014, 47, 554–563.

122. Liu, B., McConnell, L.L., Torrents, A., Hydrolysis of chlorpyrifos in natural waters of the Chesapeake Bay. *Chemosphere* 2001, 44, 1315–1323.

123. Ling, Y., Wang, H., Yong, W., Zhang, F., et al., The effects of washing and cooking on chlorpyrifos and its toxic metabolites in vegetables. *Food Control* 2011, 22, 54–58.

124. Duirk, S.E., Collette, T.W., Degradation of chlorpyrifos in aqueous chlorine solutions: Pathways, kinetics, and modeling. *Environ. Sci. Technol.* 2006, 40, 546–551.

125. Zhao, X., Hwang, H.M., A study of the degradation of organophosphorus pesticides in river waters and the identification of their degradation products by chromatography coupled with mass spectrometry. *Arch. Environ. Contam. Toxicol.* 2009, 56, 646–653.

126. Newhart, K., Environmental Fate of Malathion. *Acme* 2006, 1–20.

127. Uhrovčík Jozef, Strategy for determination of LOD and LOQ values – Some basic aspects. *Talanta* 2014, 119, 178–180.

128. Misselbrook, T.H., Clarkson, C.R., Pain, B.F., Relationship Between Concentration and Intensity of Odours for Pig Slurry and Broiler Houses. *J. agric. Engng Res.* 1993, 55, 163–169.

129. Liu, S., Tong, Z., Mu, X., Liu, B., et al., Detection of Abrin by Electrochemiluminescence Biosensor Based on Screen Printed Electrode. *Sensors* 2018, 357, 1–12.