ICBAA2017-17

DETECTION OF PESTICIDE PRESENCE ON ROUND CABBAGES USING VISIBLE SHORTWAVE NEAR INFRARED SPECTROSCOPY

Che Dini Maryani Ishkandar[1], Nazmi Mat Nawi[1,2], Rimfiel Janius[1,2], Norida Mazlan[3] and Chut Afifa Muhamad Radzi[1]

[1]*Department of Biological and Agricultural Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Selangor, Malaysia*
chedinimaryani@gmail.com, nazmimat@upm.edu.my, janius@upm.edu.my, Chutafifa.work@gmail.com*
[2]*Institute of Plantation Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor*
[3]*Department of Agriculture Technology, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Selangor, Malaysia*
noridamz@upm.edu.my

Abstract: Pesticides have long been used in cabbage industry to control pests. This study aimed to investigate the potential application of visible shortwave near infrared spectroscopy for detection of typical pesticide (deltamethrin) on round cabbages. In this study, a total of 60 round cabbages were used. The sample were divided into four batches. Three batches of round cabbage were sprayed with deltamethrin at three different concentrations level of pesticides namely low, medium and high with values of 0.08, 0.11 and 0.14 % (v/v), respectively. Spectral data of the cabbage samples were collected using visible shortwave near infrared spectrometer (VSWNIRS) with the wavelength range between 200 to 1100 nm. The spectral data was pretreated using multiple scattering correction (MSC) method in order to obtain optimal prediction values. Gas chromatography was used to determine the multi-residue limit (MRL) value of the samples. Calibration and prediction models were developed to correlate the spectral data with MRL values using partial least square regression (PLS) method. The calibration model produced the values of coefficient of determination (R^2) and root mean square errors (RMSEP) of 0.98 and 0.02, respectively. The prediction models gave good R^2 and RMSEC values of 0.94 and 0.04, respectively. These results demonstrated that the proposed spectroscopic measurement provide a promising technique for pesticide detection at different level of concentration on round cabbage.

***Keywords*:** gas chromatography, spectroscopy, MRL, pesticide residues, PLS, round cabbages

INTRODUCTION

Cabbage (*Brassicae oleracea var. capitata*) is one of the most important and widely cultivated vegetable because of its nutritional and economical values. The world's biggest cabbage producers are China, India, and Russia with the production amount around 32.8 Mt, 8.2 Mt and 3.3Mt, respectively (Chepkemoi, 2017). In Malaysia, the production of round cabbage in 2015 was 0.28 Mt with the production value about RM 3.3 million (DOSM, 2016). In addition, cabbage is good source of vitamins such as vitamin C and vitamin K (USDA, 2000).

However, cabbage cultivation is always exposed to a problem of pest infestations such as leafminers, thrips, whiteflies, cabbage maggots, beetles, true bugs and caterpillars (Carr, 1979). Cartwright et al. (1987) reported that the most prominent insect pest of cabbage crops is cabbage looper (Trichoplusia ni Hübner) and diamondback moth (*Plutella xylostella L).* Meanwhile in India, common insect pests on cabbage are diamondback moth (*Plutella xylostella*), webworm *(Hellula undalis),* head caterpillar *(Crocidolomia binotalis),* cabbage butterflies *(Pieris* brassicae), aphids (*Lipaphis erysim*i) and flea beetle (*Phyllotreta brassicae*) (Chaudhuri et al., 2001; Srinivasan and Murthy, 1991).

Typically, farmers use pesticides to manage the agricultural pests (Bommarco et al., 2011). However, it was reported that some farmers may overuse and apply pesticides rampantly as to satisfy the high demand of the vegetable (Jipanin et al., 2001). As a result, a very serious undesirable problem is increasing including food poisoning, contaminated market produces and environmental pollution. Pesticides have been examined in epidemiologic studies as environmental and risk factor for cancer (Teitelbaum, 2002). The contaminated vegetables in a market is dangerous because it can affect the consumer life and health (Lim, 1990).

Usually, the pesticide residues are measured in a laboratory using expensive technology such as gas chromatography with tandem mass spectrometry (GC-MS) (Osman, et al., 2010; Palenikova et al., 2015) and liquid chromatography with tandem mass spectrometry LS-MS (Alez et al., 2008; Kaczyñski and Lozowicka, (2016).

These measurement methods to detect pesticides presence in agricultural produce involves complex sample treatment as the vegetable need to be crushed and extract in order to obtain an aliquot. The sample is also needed to be brought back to a laboratory which will cause losses in cost and time. Thus, a new measurement method which is non-destructive is required for rapid screening of pesticide presence on cabbage samples.

One of the most promising non-destructive techniques to detect pesticide residue is by using spectroscopic method (Jamshidi et al. 2016). This technique is non-contaminant, low operating cost and fast response times compared with the conventional techniques (Montes et al. 2006). Furthermore, it also requires little or no sample preparation (Peng et al., 2012). Thus, this study was conducted to investigate the potential application of visible shortwave near infrared spectrometer to detect the pesticide presence on cabbage samples. The specific objective was to develop calibration and prediction models between multi-residue limit (MRL) values and spectral data.

METHODS

A total of 60 organic round cabbages were used in the experiment. Cabbage were brought from Cameron Highlands, Malaysia after one day of harvest. The average weight of cabbage sample is 1 kg. The samples were divided into four batches, where the first three batches were treated with deltamethrin pesticide at different concentrations namely low (0.08% (v/v)), medium (0.11% (v/v)) and high (0.14% (v/v)). The fourth batch was not treated with any pesticide. Deltamethrin ($C_{22}H_{19}Br_2NO_3$) belongs to a pyrethroids pesticide group. The pesticide was manually sprayed on cabbage samples by using knapsack sprayer with an average volume of 600 ml per sample. The nozzle sprayer was positioned vertically to the samples. Pesticides were sprayed on the round cabbages 24 hour before spectral scanning.

The reflectance spectra of each cabbage sample were collected using VSWNIR spectrometer (Ocean Optics HR4000, high resolution miniature fiber optic spectrometer with the charge-coupled device (CCD) detector. The spectrometer was sensitive in the VSWNIR spectrum at the wavelength range between 200 and 1100 nm with the optical resolution of 0.025 nm. The Spectrasuite software (Ocean Optic, Inc.) was used for collecting, viewing and processing the spectra.

The reflectance data were collected from the surfaces of cabbage samples at five different points. The individual sample was placed inside a custom made measuring box. The measuring box was used to enclose the sample and sensor from the ambient light which can affect the spectra (Guthrie & Walsh, 1997; Lu et al., 2000). The surface inside the box was painted black to minimize the influence of the background colour on the spectral data (Wu et al., 2008). The measurement distance between probe and sample was fixed at 5 mm.

After the spectral measurement, the samples were sent to the Department of Chemical, Petaling Jaya, Malaysia for the measurement of multi-residue limit (MRL) of deltamethrin with a reference method of gas chromatograpy (GC) analysis. The sample preparation and extraction for GC analysis were based on GC standard developed by FAO (2003); and Pakvilai et al. (2015). An Agilent 7890A gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) was used to measure the concentration of pesticide residue in each cabbage sample.

The raw spectral data obtained from the spectrometer contains noise, uncertainties, variability and unrecognised features of the sample information (Mohghimi et al., 2010). There are several types of preprocessing methods available for data treatment (Nawi et al., 2013). The spectral data obtained from the spectrometer need to undergo preprocessing to improve the accuracy and the reliability of the data (Cen & He, 2007). The spectral data of cabbage was treated using Savitzky-Golay method. All spectral data were preprocessed using Unscrambler X version 10.3 software (CAMO PROCESS, AS, Oslo, Norway).

RESULTS AND DISCUSSION

Typical reflectance spectra of cabbages at different pesticides concentration

The reflectance spectra in Figure 1 shows typical spectra of the cabbage samples with deltamethrin pesticide at different concentration (high, medium and low) and without deltamethrin applied. The trends of the curve were similar however a high concentration of pesticide gives low reflectance value. The difference of reflectance is due to the different chemical composition in each pesticide (Tano, 1996). Jamshidi et al., (2016) also reported the presence of pesticide gives the low value of spectra.

The difference between the spectra was observed in the visible region. There was a spectral peak at 682 nm due to chlorophyll of the cabbages absorbed the light source. This spectral peak can be used as an effective wavelength as it could show the difference of reflectance values in corresponding to different pesticide concentrations.

However, the high concentration pesticide shows the lowest reflectance value. It was noticed that the increase of sample reflectance value indicates pesticide free in the sample. The NIR region from 700 to 900 nm also shows the high concentration of pesticide has low reflectance value. This increase is more related to C-H bonding (María- teresa et al., 2010).

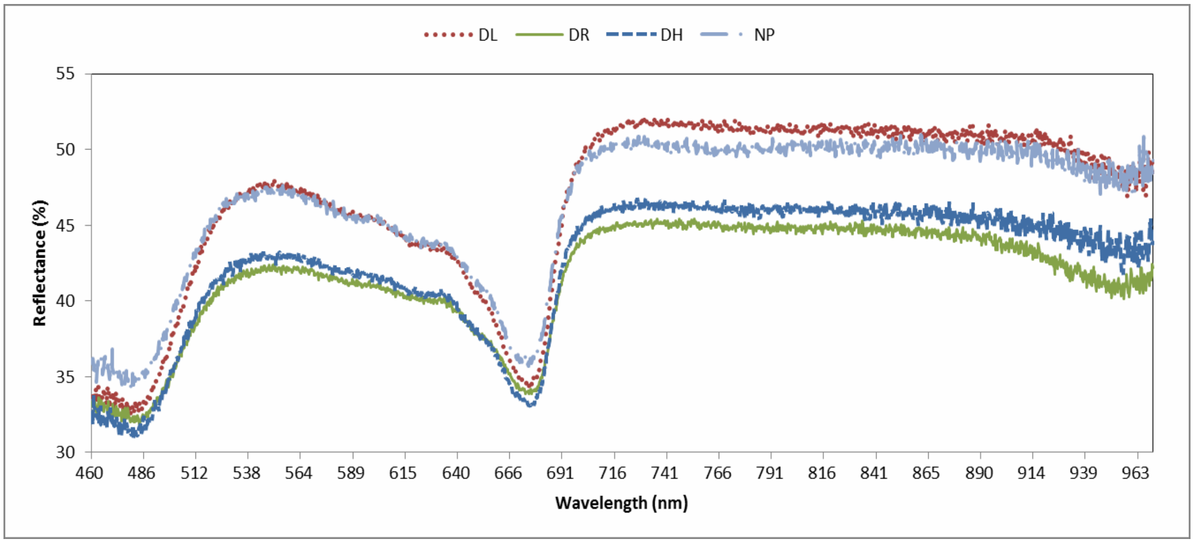

Figure 1: Typical spectra of cabbages at low (DL), medium (DM), high (DH) deltamethrin concentration and with no pesticide (NP).

Multi-Residue Limit (MRL) of cabbage samples

Table 1 show the results of MRL for different pesticide concentrations. The low concentration of pesticide sprayed on the cabbages gives a low concentration of MRL. According to Department of Agriculture, Malaysia (2015) the maximum permitted proportion of pesticide residue in food for deltamethrin is 0.2 mg/kg. The cabbage treated with high concentration of deltamethrin (DH) was above MRL value.

Table 1: MRL values for each pesticide concentration.

CONCENTRATION (% v/v)	MRL (mg/kg)
Deltamethrin Low (DL)	0.06
Deltamethrin Medium (DM)	0.17
Deltamethrin High (DH)	0.41
No Pesticide (NP)	0.00

Calibration and prediction model of cabbage sample

There were 75% of the samples used for the calibration model and 25% were used for the prediction model. The quality of both calibration and prediction models represented by the value of correlation of determination (R^2) for the samples were 0.98 and 0.94, respectively. It can be seen that correlation between MRL and spectral data had higher R^2 values for both calibration and prediction models.

CONCLUSIONS

This study showed the VSWNIR spectrometer has the potential to detect the presence of deltamethrin on cabbage samples at different concentrations. The result also showed that the cabbage with a high concentration of pesticide has low reflectance value compared to cabbage without pesticide treatment.

The correlation between MRL and the spectral data gave a good accuracy values for the both calibration and prediction models with R^2 values of 0.98 and 0.94, respectively. Thus, the portable spectroscopic

technique could potentially be used for fast, low-cost and non-destructive screening system to detect pesticide residues of the cabbages.

Acknowledgement

The authors acknowledge Ministry of Higher Education for providing a research grant (FRGS - Grant no.: 5524733) and Department of Biological and Agricultural Engineering, Faculty of Engineering, Universiti Putra Malaysia for providing facilities for the research.

REFERENCES

Carr, A., (1979). Color Handbook for Gardening Insects. Rodale Press*, Emmaus, PA*, 241.

Cartwright, B., Edelson, J.V., & Chambers, C., (1987). Composite action thresholds for the control of lepidopterous pests on fresh-market cabbage in the lower Rio Grande Valley of Texas. *J. Econ. Entomol*. 8, 175– 181.

Amin, I., & Lee, W. Y. (2005). Effect of different blanching times on antioxidant properties in selected cruciferous vegetables, 2314–2320. https://doi.org/10.1002/jsfa.2261.

Peng, Y., Li, Y., & Chen, J. (2012.). Optical Technologies for Determination of Pesticide Residue. *Infrared Spectroscopy - Materials Science, Engineering and Technology*, 455-466.

Bommarco, R., Miranda, F., & Bylund, H. (2011). Insecticides Suppress Natural Enemies and Increase Pest Damage in Cabbage. *Biological and Microbial Control*, 789-791.

Lim, G.S. (1990). Integrated Pest Management as an Alternative to Insecticide Overuse in Vegetables in Southeast Asia. 155-156.

Jipanin, J., Rahman, A.A., Jaimi, J.R., & Phua, P.K. (2001). Management of Pesticide Use on Vegetable Production: Role of Department of Agriculture Sabah. *6th SITE Research Seminar.*

Osman, K.A., Al-Humaid, A.M., Al-Rehiayani, S.M., & Al-Redhaiman, K.N. (2010). Monitoring of pesticide residues in vegetables marketed in Al-Qassim region, Saudi Arabia. *Ecotoxicology and Environmental Safety*, 1433-1439.

Palenikova, A., Martinez-Domingue, G., Arrebola, F. J., Romero-Gonzalez, R., Hrouzkova, S., & Frenich, A. G. (2015). Multifamily determination of pesticide residues in soya-based nutraceutical products by GC/MS-MS. *Food Chemistry*, 796-807.

Alez, R. R.-G., Frenich, A. G., & Mart´ınez, J. (2008). Multiresidue method for fast determination of pesticides in fruit juices by ultra-performance liquid chromatography coupled to tandem mass spectrometry*. Talanta*, 211-225.

Kaczyński, P., & Łozowicka, B. (2015). Liquid chromatographic determination of glyphosate and aminomethylphosphonic acid residues in rapeseed with MS/MS detection or derivatization/fluorescence detection. *Open Chem*, 1011-1019.

Guthrie, J & Walsh, KB (1997). 'NIR technology for melon brix measurement', In: Invited presentation to Fourth Australian Melon conference, October 16-18, 1997, Bundaberg.

Lu, R., Guyer, D., & Beaudry, R.M. (2000). Determination of firmness and sugar content of apple using NIR diffuse reflectance. *Journal of Texture Studie*s, 31, 615-630.

Wu, J., Liu, C., Chen, Y., Chen, Y. & Xu, Y., (2009). IFIP International Federation for Information Processing, Volume 295, Computer and Computing Technologies in Agriculture II, Volume 3, eds. D. Li, Z. Chunjiang, (Boston: Springer), pp. 2217.

Tano, J. (1996). Identity, Physical and Chemical Properties of Pesticides, 1873.

Food and Agriculture Organization/ World Health Organization (FAO/ WHO). (2003). Guidelines on Good Laboratory Practice in Residue Analysis. CAC/GL 40-1993.

USDA. (2000). Nutrition and your health: dietary guidelines for Americans. Home and Garden Bull. 232, U.S. Dept. Agr., Washington, D.C. (Website: www.usda.gov/cnpp).

Chaudhuri, N., Ghosh, S., Ghosh, J., Senapati, S.K., (2001). Incidence of insect pests of cabbage in relation to prevailing climatic conditions of Terai region. Indian J. Entomol. 63, 421–428.

Srinivasan, K., Murthy, P.N.K., (1991). Mustard plants trap major cabbage pests. Indian Farming 40, 11–12.

Peñuelas, J., & Filella, L. (1998). Visible and near-infrared reflectance techniques for diagnosing plant physiological status. *Trends in Plant Science*, 3(4), 151–156.

Montes, J. M., Utz, H. F., Schipprack, W., Kusterer, B., Muminovic, J., Paul, C. & Melchinger, A. E. (2006), 'Near-infrared spectroscopy on combine harvesters to measure maize grain dry matter content and quality parameters', *Plant Breeding* 125, 591-595.