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Method Development for Pesticide Determination in Paddy Rice Using Near Infrared Spectroscopy

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Abstract A growing world population leads to an increase in demand for agricultural products and food. In order to increase crop yield, pesticides have been extremely used, resulting in a high risk to environment and human health. A large number of pesticides are used on paddy rice field in Southeast Asia countries. Carbofuran is a highly toxic insecticide to vertebrates that has been illegally used on paddy field and other crops in developing country with a poor application and management. In order to maintain public health condition, the control and determination of pesticide residues in agricultural products is extremely needed. This study aimed to investigate the feasibility of near infrared (NIR) spectroscopy for a rapid determination of carbofuran in paddy rice. Thai jasmine paddy rice artificially contaminated with carbofuran ranging from 0-50 ppm was used as samples. The NIR measurements of the paddy rice were performed using reflectance FT-NIR spectroscopy as a nondestructive determination. The attempt to improve prediction efficiency of carbofuran residue was then performed using the dry-extract system for (near) infrared (DESIR) technique. The reflectance NIR spectra of DESIR samples were also obtained. For data analysis, partial least square (PLS) regression was used to develop a calibration model for the carbofuran prediction. It was found that the spectra of the contaminated paddy rice provided insufficiently accurate calibration results with coefficient of determination (R^2) of 0.87 and root mean square error of prediction (RMSEP) of 7.20 ppm. Superior prediction accuracy was obtained from the calibration model based on the spectra of DESIR samples (R^2 = 0.99, RMSEP = 3.05 ppm). It was concluded that NIR spectroscopy combined with DESIR technique had a potential to be a rapid and effective method for the determination of carbofuran in paddy rice. This method could become a powerful tool for coping with the environmental and health risk caused by a misuse or overuse of pesticides.

Keywords: Paddy rice, Pesticide, Carbofuran, Near infrared, Rapid method

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Introduction

Rice is one of staple foods in South and Southeast Asian countries. Yearly, yield of rice grain has been lost to insects, diseases and weeds. These problems lead to the use of pesticides for increasing agricultural productivity. Among the pesticides, carbamates are widely used in develop and developing countries to control agricultural pests (Huertas-Pérez *et al*., 2005; Martin and Shepherd, 2009). Carbofuran is a carbamate insecticide which is presently used in paddy fields. It is known to highly toxic to non-species, thus it has been restricted or banned for applying in export agricultural products in many counties (Otieno *et al*., 2010; Ramesh *et al*., 2015). Overspray and poor management of the pesticide paddy field may cause leave its residue on paddy rice and paddy field ecosystem. Accordingly, to maintain public health conditions and avoid the risk of being banned of the commodities, its residue concentration on agricultural products must be clarified.

In Thailand, the amount of pesticide residues on products is controlled by the National Bureau of Agricultural Commodity and Food Standards. The conventional measuring methods for detecting chemical residues involve gas chromatography (GC) and high performance liquid chromatography (HPLC) with post-column derivatization which are sensitive and reliable (Zan and Chantara, 2007; Tennakoon *et al*., 2013). However, these methods have some disadvantages of relatively expensive, complicated sample preparation, and enable sampling of only a few samples per batch.

For a decade, near infrared spectroscopy (NIRS) is a popular technique for quality evaluation of agricultural and food products (Nicoli *et al*., 2007; Bagchi *et al*., 2016; Numthuam *et al*., 2017). The advantages of NIRS include a rapidity, nondestructive measurement as well as a great potential for on-line analysis. For agricultural safety assessment, Saranwong and Kawano (2005) has introduced the dry-extract system for infrared (DESIR) technique for the rapid determination in ppm-level of fungicide contaminated on tomatoes The DESIR technique combined with NIR spectroscopy was also applied to determine pesticides residues on sample surfaces of mango and apple (Acharya *et al*., 2013). Therefore, it has a possibility to be used for the determination of trace amount of pesticide contamination in paddy rice and grains.

The aim of this study was to evaluate the feasibility of NIR spectroscopy combined with DESIR technique for determination of carbofuran contamination in paddy rice as a less sample preparation and rapid analyzing method.

Materials and methods

Carbofuran solution

A commercial carbofuran (Sigma-Aldrich, Germany) was used. Appropriate dilutions in deionize water were made in order to provide the solutions with different concentrations. A total of 20 concentration levels, from 0 to 50 ppm were prepared based on the amount of carbofuran. After preparation, the solutions were kept in amber vials and were preserved in a refrigerator in order to prevent chemical degradation prior to be used in the experiments.

Paddy rice samples

The organic Jasmin paddy rice was purchased from local rice mills in Phisanulok, Thailand. A 60 samples of rice bran were weighed 20 grams and then put into polyethylene bags for artificial contamination of carbofuran. A suspension of carbofuran in deionized water was applied on each sample using a spray bottle. The amount of carbofuran was varied using 20 different levels by adjusting the concentration of spraying suspension and the spraying volume (w/w), 3 replicates for each. Drying was performed by keeping the samples in the air-flow draft for 12 hours at room temperature. The paddy samples contaminated with carbofuran were transferred into quartz cup and then firstly scanned using FT-NIR spectrocopy.

After the first NIR measurement, 10 grams of scanned sample was divided into 50-mL test tube, extracted with 20 mL of ethylacetate by ultrasonic (Crest Ultrasonics, Malaysia) for 20 minutes, and then filtrated using 90-mm diameter paper filter No.1 (Whatman, International Ltd., China) from paddy rice sample. The filtrate containing carbofuran was used for preparation of DESIR sample.

DESIR samples

The DESIR preparation procedure was adapted from Saranwong and Kawano (2005). The solid substrate to be used as DESIR sample was the 47 mm diameter glass microfiber filter papers, model "GF/ C" (Whatman, International Ltd., UK). Two filter papers were placed in a 50-mm diameter Falcon disposal polystyrene Petri dish, and then 0.5 mL of the filtrate was dropped onto the middle of the papers. After that, ethylacetate from the filter paper was evaporated using the air flow drying method at room temperature for

1 hour. The dried filter paper containing carbofuran (called DESIR sample) was kept in desiccator for at least 1 hour before the NIR measurement.

NIR spectral acquisition and data analysis

A multi purpose analyzer (MPA) FT-NIR spectrometer (Bruker, Bremen, Germany) was used. Each sample was NIR-measured in the absorbance from 12000 to 4000 cm^{-1}. Firstly, NIR spectral acquisitions of contaminated paddy rice were performed in rotating-reflectance mode using a quartz cup as a sample holder. The NIR spectra were secondly acquired from the DESIR samples using an aluminum reflector in reflectance mode.

For data analysis, calibrations were performed by partial least squares (PLS) regression using the OPUS program version 7.2 (Bruker, Bremen, Germany). Pretreatment of standard normal variate method was performed to all spectral data before the calibrations. From the total of 60 contaminated paddy samples, 40 were used for construction of the calibration model and 20 were used to validate the developed calibration model.

Results and Discussion

Reflectance spectra of paddy rice and DESIR samples that contained various levels of carbofuran were shown in Fig.1. The strong absorption bands of water were observed in paddy rice spectra around 6840 cm^{-1} and 5190 cm^{-1} (Tsenkova *et al.*, 2001; Kesemsumran *et al.*, 2007), while those water bands were disappeared or became smaller in the spectra of DESIR samples (Fig. 1b). In order to examine the suitable sample presentation, spectra of paddy rice and DESIR samples were separately used for developing calibration models of contaminated carbofuran.

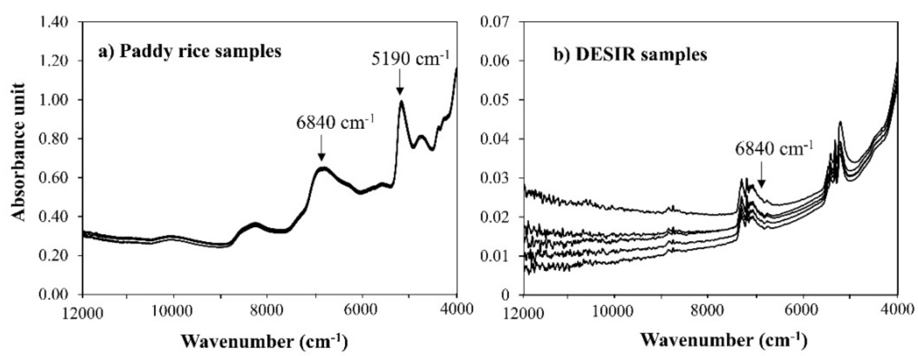

Fig 1. Original NIR spectra of (a) paddy rice samples and (b) DESIR samples.

PLS calibration results for predictions of carbofuran values are shown in Table 1. Noted from the lowest root-mean-square standard error of prediction (RMSEP) and the highest ratio of prediction to deviation (RPD) values, the non-destructive analysis using spectra of paddy rice provided inferior results than using the DESIR technique. The best PLS result for carbufuran prediction was from DESIR samples, which was RMSEP of 7.20 ppm and RPD of 6.62. The relation between the actual and the NIR-predicted carbofuran values for validation sets of paddy rice and DESIR samples are shown in Figure 2, which illustrated the better accuracy of DESIR samples.

Table 1. PLS calibration and validation results for carbofuran values of paddy rice and DESIR samples.

Sample	Rank	R^2	RMSEC	RMSEP	Bias	RPD	Region (cm^{-1})
Paddy rice	3	0.87	6.24	7.20	-1.81	2.28	9404–7498, 6102–5446
DESIR	8	0.99	1.39	3.05	1.05	6.62	6102–4243

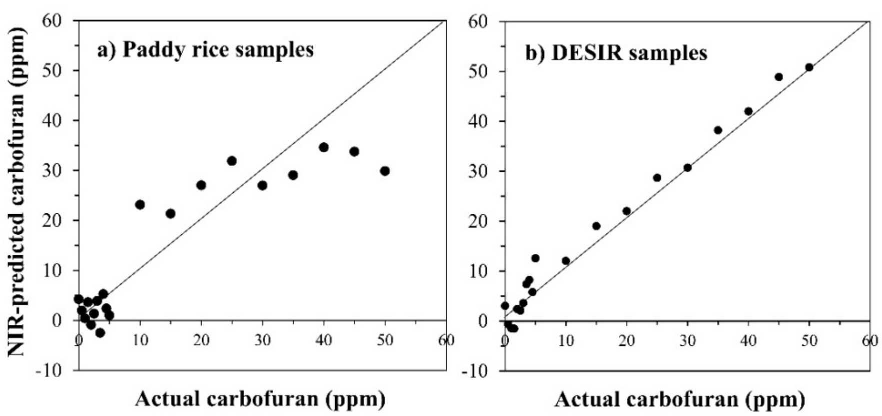

Figure 2: Scatter plots between actual and NIR-predicted values of cabofuran values in validation set of (a) paddy rice samples and (b) DESIR samples.

NIR regions of paddy rice spectra used for the carbofuran prediction were 9404–7498 cm^{-1} and 6102–5446 cm^{-1}, while the important regions used from DESIR spectra were shorter from 6102–4243 cm^{-1}. Intestingly, the region of 5446–4243 cm^{-1} could be noticed only in the model calibrated by DESIR spectra. The N-H bond in carbofuran molecular structure might play an important role since the absorbtion of vibrations of N-H bond were around 4690 and 4866 cm^{-1} (Osborne *et al*., 1993; Williams and Norris, 2001). These observed results indicated that the vital information for cabofuran prediction could expose after the elimination of chemical composition matrix of paddy rice and could improve the model prediction accuracy.

Conclusion

The study showed that NIR spectroscopy based on dry extract sample preparation was feasible to determine the carbofuran contamination in paddy rice. The performance of NIRS as a non-destructive measurement could support the use as a rapid rough screening tools.

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