Computers and Electronics in Agriculture 139 (2017) 41–55

Contents lists available at ScienceDirect

Computers and Electronics in Agriculture

journal homepage: www.elsevier.com/locate/compag

Original papers

Variation analysis in spectral indices of volatile chlorpyrifos and non-volatile imidacloprid in jujube (*Ziziphus jujuba* Mill.) using near-infrared hyperspectral imaging (NIR-HSI) and gas chromatograph-mass spectrometry (GC–MS)

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ARTICLE INFO

Article history:
Received 4 October 2016
Received in revised form 21 April 2017
Accepted 25 April 2017

Keywords:
Insecticide residuals
Hyperspectral imaging technique
Jujube fruit
Spectrum analysis
GC–MS

ABSTRACT

Two pesticides in terms of chlorpyrifos and imidacloprid contaminating edible jujube fruits were determined using hyperspectral imaging (900–1700 nm) and gas chromatograph-mass spectrometry (GC–MS). Hyperspectral images of jujube samples contaminated by pesticides at different concentrations were collected. Their spectral data extracted in reflectance (R_S), absorbance (A_S), exponent (E_S) and Kubelka–Munck (K-M_S), were respectively used to develop partial least squares discriminant analysis (PLSDA) and locally weighted partial least square regression (LWPLSR) models. Based on these spectral parameters, corresponding models defined as A_S-PLSDA and E_S-PLSDA acquired optimal results, with correlation coefficients of cross-validation (R_{CV}) of more than 0.900 for recognition of chlorpyrifos concentrations and R_{CV} of over 0.713 for identification of concentrations of the imidacloprid. The E_S-LWPLSR model obtained the best R_{CV} of 0.864 for quantitative determination of chlorpyrifos residuals, and the best R_{CV} of 0.885 for determination of imidacloprid residuals. The feature wavelengths were selected based on the automatic weighted least squares and gap segment derivative (AWLS-GSD) coupled with regression coefficient (RC) method. The better performance was obtained by the resulting simplified E_S-AWLS-GSD-RC-LWPLSR model established using only eight characteristic wavelengths, with R_{CV} of 0.757, RMSECV of 3.75×10^{-3} for chlorpyrifos residuals, and R_{CV} of 0.898, RMSECV of 0.311×10^{-3} for imidacloprid residuals. To summarize, hyperspectral imaging technology shows a great potential to predict pesticide residuals of jujube fruit.

1. Introduction

As a species of *Ziziphus* in the buckthorn family, jujube fruit is high in polysaccharides, organic acids, proteins, vitamin C, minerals, and polyphenols, and can be eaten freshly or consumed in processed foods, such as jujube slice and ingredient of tea (Gao et al., 2013). For quality and safety reasons, techniques such as drying (Cui et al., 2008; Yang et al., 2017; Pu and Sun, 2016) and cooling (Sun and Hu, 2003; Wang and Sun, 2002a,b; Sun and Wang, 2000; Sun, 1997; McDonald et al., 2000; Sun and Brosnan, 1999; Zheng and Sun, 2004; Wang and Sun, 2004) commonly used in keeping agricultural and food products can be used. In addition, development of effective ways for safety detection is also necessary. Due to its extensive cultivation, the jujube is mainly distributed in Asia (e.g. China, India) and south-eastern Europe (e.g. Spain, Italy). Immature jujube fruits are of smooth green color, and their colors become brown-red when they are ripe (Wojdyło et al., 2016). Before the harvest, insect infestations (e.g. *Ancylis sativa* Liu) can have a serious impact on the quality and the yield of jujube fruit (Wang et al., 2011a). Pesticides such as chlorpyrifos (an organophosphate insecticide) and imidacloprid (a nicotinic insecticide) are widely used in protecting jujubes from insect invasion. The specific structures of chlorpyrifos and imidacloprid are shown in Fig. 1. The chlorpyrifos (melting point: 42.5–43 °C) is a volatile pesticide that can act on the nervous system of insects by inhibiting acetylcholinesterase while the imidacloprid (melting point: 143.8 °C) is a sparingly volatile insecticide which prevents acetylcholine from transmitting impulses between nerves, both

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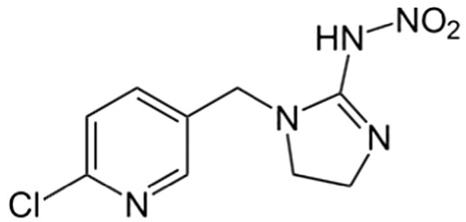
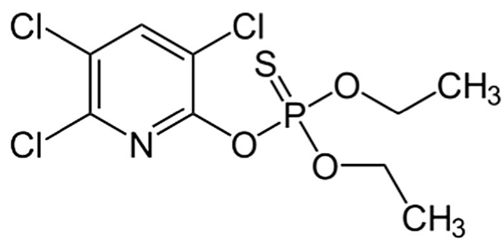
http://dx.doi.org/10.1016/j.compag.2017.04.017
0168-1699/

Chlorpyrifos



O,O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate

Imidacloprid



N-{1-[(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl}nitramide

Fig. 1. Structures of chlorpyrifos and imidacloprid.

resulting in the death of insect (Li et al., 2012; Pope et al., 1991). In the agricultural production, pesticides are usually overused, intentionally or unintentionally. The storage period of fresh jujube fruits is short in natural conditions. Sometimes, they are even purchased after being sprayed with pesticides for only a few days. With the improvement of consciousness of food safety and health of consumers, more and more attention has been focused on the detection of pesticide residuals of agricultural products. Over the past decades, many effective technologies, such as supercritical fluid chromatography (SFC), immunoassay method, liquid chromatography (LC) and gas chromatography-mass spectrometry (GC–MS), were applied to determine pesticide residuals (Wang et al., 2014; Campillo et al., 2013; Tao et al., 2014; Garcia-Febrero et al., 2014). However, these expensive, complicated and time-wasting methods are not suitable for real-time detection of insecticide residuals. Therefore, it is necessary and of vital importance to develop rapid, reliable and lower-cost measure techniques for evaluation of pesticide residuals.

A lot of researches have been conducted to explore the potential of various non-destructive inspection technologies, such as machine vision, electronic noses, acoustic techniques, and spectroscopic techniques, for the assessment of food quality (Alexandrakis et al., 2012; Karoui and Blecker, 2011; Cubero et al., 2011; Magwaza et al., 2012; Kamruzzaman et al., 2015; Cheng et al., 2013; Macrelli et al., 2013; Huang et al., 2014; Pan et al., 2011; Rogel-Castillo et al., 2016). Among them, spectroscopic techniques relying on simple and non-invasive approaches have drawn great attention (Cheng et al., 2013; Su et al., 2017). Spectroscopy technologies including near infrared spectroscopy, Raman Spectroscopy, terahertz time-domain spectroscopy and laser-induced breakdown spectroscopy, have proven useful to measuring pesticide residuals in agricultural products such as pepper, fruits, cereal (Liu et al., 2013; Sánchez et al., 2010; Chen et al., 2015; Ma and Dong, 2014). However, one of the major drawbacks of these spectroscopic methods is that the spectrum is collected from a single point or from a small portion of the tested sample which could not guarantee the data accuracy and representativeness. In contrast, the hyperspectral imaging is regarded as a great potential technique to solve the above defect (Wei et al., 2014; Rady et al., 2015; Zhu et al., 2014; Pu et al., 2015a; Cheng and Sun, 2015a; Kamruzzaman et al., 2012). With the computer vision (Jackman et al., 2009; Du and Sun, 2005; Sun and Brosnan, 2003; Jackman et al., 2011), the hyperspectral imaging is an advanced spectroscopic technique with the merit of rapid and non-invasive detection and can acquire spatially distributed spectral information at each pixel of an object (Zhang et al., 2016; Menesatti et al., 2009; Liu et al., 2014a,b; Rodríguez-Pulido et al., 2013; Lorente et al., 2013; Liu and Ngadi, 2013; Cen et al., 2014; Karimi et al., 2012; Zhang et al., 2017; Kamruzzaman et al., 2016; Sun, 2016; Xie et al., 2016). This technology has been widely used for the inspection of internal and external quality and safety of food products (Ma et al., 2016; Su and Sun, 2016a,b; Elmasry et al., 2012; Feng and Sun, 2013; Kamruzzaman et al., 2013; Barbin et al., 2013; Feng et al., 2013; Wu and Sun, 2013; ElMasry et al., 2013; Cheng and Sun, 2015b; Xiong et al., 2015; Cheng et al., 2015; Pu et al., 2015b; Cheng et al., 2016b). The feature information contained in the mass spectral images acquired from an imaging system can be further processed and extracted to effectively evaluate relevant quality attributes of agricultural products. In the multivariate analysis, the variable selection is to select a small subset of significant wavelengths that carries the most important spectral information (Wu et al., 2012). The reduction of highly relevant variables can optimize the predictive capability of a calibration model. Moreover, the effective selection of feature wavelengths saves the total time of data analysis, which can make the developed model more suitable for real-time quality detection. The efficient approaches, such as genetic algorithm (GA), competitive adaptive reweighted sampling (CARS), principal component analysis (PCA), and successive projection algorithm (SPA), have been extensively used in hyperspectral imaging to select feature wavelengths for the quality determination of agricultural foods (Cheng et al., 2016; Yu et al., 2014a; Liu et al., 2014; Qin et al., 2013; Dissing et al., 2013; ElMasry and Wold, 2008). As for jujube fruit, the hyperspectral imaging was effectively used to determine the soluble solids content (SSC) based on the back propagation artificial neural network (BPANN) model developed using five feature wavelengths from reflectance spectra (He et al., 2013). Additionally, the jujube samples with insect infestation, bruise, and crack were also successfully detected using reflectance hyperspectral imaging and chemometric algorithms (Liu et al., 2016; Wu et al., 2016; Yu et al., 2014b; Wang et al., 2011b). However, only a few studies were carried out to analyze pesticide residuals in jujube fruits based on hyperspectral imaging.

Accordingly, the aim of this study was to determine two pesticides in terms of volatile chlorpyrifos and non-volatile imidacloprid using the hyperspectral imaging technology combined with the GC–MS. The detailed objective of this research was (1) detecting the spectral variation of three concentrations of pesticide, (2) developing full-wavelength models for determination of pesticide residuals using the data of reflectance spectra (R_S), absorbance spectra (A_S), exponent spectra (E_S) and Kubelka–Munck spectra (K-M_S), (3) evaluating the effectiveness of different pre-treatment methods for spectral data analysis, (4) comparing the accuracy of different models for identification of different concentrations of pesticide; (5) determining the relevant variable selection approach for assessing pesticide residuals. Although the detection of artificially contaminated fruit is common, the variation analysis of these four spectral indices was carried out for the first time. Moreover, as the concentration of the hazardous substance is a process of dynamic change during storage due to their volatilities, the actual values of pesticide residuals from artificially contaminated jujube in this study were measured by the GC–MS after being stored at room temperature and in a ventilated place for 12 h. Besides,