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Application of terahertz time-domain spectroscopy combined with chemometrics to quantitative analysis of imidacloprid in rice samples

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ABSTRACT

Terahertz time-domain spectroscopy (THz-TDS) has been utilized as an effective tool for quantitative analysis of imidacloprid in rice powder samples. Unlike previous studies, our method for sample preparation was mixing imidacloprid with rice powder instead of polyethylene. Then, terahertz time domain transmission spectra of these mixed samples were measured and the absorption coefficient spectra of the samples with frequency range extending from 0.3 to 1.7 THz were obtained. Asymmetric least square (AsLS) method was utilized to correct the slope baselines that are presented in THz absorption coefficient spectra and improve signal-to-noise ratio of THz spectra. Chemometrics methods, including partial least squares (PLS), support vector regression (SVR), interval partial least squares (iPLS), and backward interval partial least squares (biPLS), were used for quantitative model building and prediction. To achieve a reliable and unbiased estimation, bootstrapped Latin partition was chosen as an approach for statistical cross-validation. Results showed that the mean value of root mean square error of prediction (RMSEP) for PLS (0.5%) is smaller than SVR (0.7%), these two methods were based on the whole absorption coefficient spectra. In addition, PLS performed a better performance with a lower RMSEP (0.3%) based on the THz absorption coefficient spectra after AsLS baseline correction. Alternatively, two methods for variable selection, namely iPLS and biPLS, yielded models with improved predictions. Comparing with conventional PLS and SVR, the mean values of RMSEP were 0.4% (iPLS) and 0.3% (biPLS) by selecting the informative frequency ranges. The results demonstrated that an accurate quantitative analysis of imidacloprid in rice powder samples could be achieved by terahertz time-domain transmission spectroscopy combined with chemometrics. Furthermore, these results demonstrate that THz time-domain spectroscopy can be used for quantitative determinations of other pesticides in other agricultural products.

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1. Introduction

In modern agriculture, various pesticides have been used increasingly to improve crop yields. In the meantime, pesticides also bring about unintended adverse effects on the environment and non-target organisms, such as humans [1]. Thereby, environmental pollution and health problems caused by pesticide residues have attracted significant attention. Imidacloprid, which is 1-[(6-chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimie as the chemical name, has been one of the most widely used neonicotinoid insecticides for recent decades [2]. Research has reported that exaggeration of the toxic properties and deleterious effects caused by imidacloprid can be fatal for humans as well as animals [3]. Previous reports about the detection of pesticides, including imidacloprid, are mainly focused on liquid or gas chromatography usually with mass spectrometric detection [4–6]. Even though the chromatographic approaches have advantages of detecting pesticides with a lower detecting level, plenty of time has to be spent on sample pretreatment and working conditions should be optimized. Therefore, a supplement for chromatography is required to improve the detection efficiency. Spectroscopy has been used as supplement for chromatography because of its merits like simple pretreatment, fast and effective detection. Investigation on determining pesticides by spectroscopic methods like infrared and Raman spectroscopy were also reported in recent years [7,8]. Except for many conventional spectroscopic methods, terahertz spectroscopy, as a novel spectroscopic technique developed in recent decades, has shown a great potential as a crucial method for food process monitoring and quality control [18].

Typically, terahertz refers to the frequency range of 0.1–10 THz ($1\ THz = 10^{12}\ Hz$), which is a special frequency range between the far-infrared and microwave electromagnetic regimes. In recent years, THz spectroscopy was developed as a powerful tool for probing many physical phenomena such as vibrational modes, including phonon, rotational and vibrational transitions [9,10], and intermolecular and intra-molecular interactions [11,12]. More essentially, it has been indicated that terahertz spectroscopy is suitable for interrogating molecular motions [13] and probing increased number of vibrational states [14] with the generation of milliwatts terahertz power based on dendrimer. Unlike conventional mid- and far-infrared spectroscopy, the THz spectra can characterize the collective behavior of molecules in their environment and identify polymorphisms and chirality [11]. Also, THz spectroscopy uses coherent sources and ultrafast sensitive detectors [15,16], which can provide a higher signal-to-noise ratio and better dynamic range than the infrared spectroscopy [17]. Compared with near-infrared spectroscopy (NIRS) which has been widely applied in food process monitoring and quality control, terahertz spectroscopy has distinct advantages that it can depict the unique absorption features for different materials by calculating their absorption coefficients, and penetrate many organic materials like plastics, textile and paper [17]. Hence, terahertz spectroscopy and imaging is regarded as a promise technique for chemicals analysis and mapping, food safety [18-20]. Terahertz time-domain spectroscopy (THz-TDS) has been the most commonly used mode in the field of THz spectroscopic application [11]. By coupling with chemometric methods, such as partial least squares (PLS) and artificial neural networks (ANN), THz-TDS enables to perform qualitative and quantitative analyses with speed and accuracy [21–25] and, thus, offers a possibility to apply THz-TDS into practical food process monitoring and quality control, such as antibiotic detection [26–29], pesticides detection [21,22,30]. In the area of pesticides detection, Wang et al. have provided a possibility that exploiting THz-TDS to quantitatively analyze nitrofen [21] and thiabendazole [30] based on the matrix of polyethylene (PE). Nevertheless, in order to verify the applicable capability of THz-TDS during practical work, the measurements of other food matrices are necessary. Hua et al. [22] used THz-TDS to quantitatively and qualitatively analyze three pesticides in food matrices, including sticky rice powder samples. Concentrations of pesticides, which range from 0% to 75% (w/w), were analyzed based on the absorption coefficients of one absorption peak. Although such method can provide a good availability for predicting concentrations of pesticide, other crucial information of pesticide within terahertz region were not mentioned and investigated concentrations should be much lower.

Unbiased evaluation of regression models is crucial, especially when chemometrics methods are exploited to increasingly complex data sets that are under-determined [31]. In many cases, evaluations were based on the random division of samples into calibration and prediction sets. However, such split may not be considered as a sound method for unbiased evaluating the performance of constructed models, especially when a small number of samples were used. Because such split would not make the most use of all data to estimate the constructed model and prediction error was given without enough statistical significance. It has been accepted that both the number of samples and variation spanned by data samples can influence the model greatly. An available approach for validation and comparing regression and classification models is the bootstrapped Latin partition method [32], in which the relative proportion of the class or dependent variable distribution are maintained between training and prediction sets. By using bootstrapped Latin partitions to estimate calibration and regression models, bounds on the average prediction rates are obtained. According to recent reports, the Latin partition method has been successfully used to estimate the diagnosis of cervical carcinomas [33] and identification of official rhubarb samples [34] combined with THz-TDS.

In this paper, rice powder samples with spiked various amount of imidacloprid were prepared to tablet formats, the measurements of imidacloprid in rice matrix were implemented in a laboratory-built THz-TDS system with transmission mode. Apart from conventional multivariate calibration methods, e.g. PLS and SVR, the asymmetric least squares (AsLS) baseline correction method was used to alleviate the slope background that can be commonly observed in THz absorption coefficient spectra due to scattering [35,36] and may exert a negative influence on quantitative analysis. Variable selection was considered to

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