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Qualitative and quantitative identification of nitrofen in terahertz region

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ABSTRACT

Terahertz time domain spectroscopy (THz-TDS) has been utilized as an available tool for the identification and analysis of compounds owing to its unique characters. The THz spectrum of nitrofen was detected and the comparison with other two solid pesticides (thiacloprid and acetamipyrid) was provided to demonstrate pesticide's unique characteristics in THz region. For the quantitative analysis of pesticide, we applied THz-TDS to detect nitrofen mixtures with different weight ratios, and employed partial least squares (PLS), interval PLS (iPLS), moving window PLS (mwPLS) and backward interval PLS (biPLS) algorithms to achieve the best analysis accuracy through a variable selection. The regression models were optimized by root mean square error of cross validation (RMSECV) in the calibration set, and the performance of models was evaluated according to the root mean square error of prediction (RMSEP) and correlation coefficient (R). Compared with the results of the other three methods, the biPLS model acquired the best performance with RMSEP = 0.4064, R = 0.9995.

1. Introduction

Nitrofen, chemical name: 2, 4-dechlorophenylp-nitrophenylether, molecular formula: $C_{12}H_7C_{l2}NO_3$, is a faint yellow acicular crystal. It is one of selective herbicides, which has been widely used to prevent annual weeds from growing in vegetable gardens. Some researches focus on the detection techniques relying on IR or Raman spectroscopy, or mass spectrometry coupled with chromatography [1–3]. Also, many analytical methods have been developed for resolving their multi component mixtures [4].

The infrared spectroscopy is widely used to conduct qualitative analysis because of its sensitivity to scatter effect and heat radiation [3]. THz spectroscopy (frequency from 0.1 THz to 10 THz, 1 THz = 10^{12} Hz) can supply rich information of intra-molecular modes and inter-molecular modes arising from hydrogen bonding stretches, Van der Waals force and some torsion vibrations [5,6], besides, Terahertz wave is harmless to human health and environment. THz spectroscopy and imaging provide a powerful tool for the characterization of materials, including semiconductors and bio-molecules. Many recent papers have focused on nondestructive testing, medical diagnosis and chemical analysis [7–10]. Additionally, THz spectroscopy was increasingly used to conduct quantitative analysis in chemical multi-component mixtures [11–15].

For these quantitative works mentioned above, THz spectral data calibrations are often made with classic regression and multiple regression methods, such as partial least squares (PLS) [16] and artificial neural net (ANN) [17]. However, absorption intensity is linear with the content of samples, thus linear methods are widely used in calibration analysis, and PLS is an effective and reliable regression method among these methods. Variable selection is usually performed in PLS analysis [18], to remove nosy regions. However, the recent literatures referring to THz spectroscopy seldom apply the variable selection to obtain the superior analysis accuracy.

In this paper, the THz spectra of nitrofen and other two solid materials (thiacloprid and acetamipyrid) are presented, and their unique spectral features can be used for identifying. In addition, four linear techniques for building a calibration model with a variable selection, namely partial least squares (PLS), interval PLS (iPLS), moving window PLS (mwPLS) and backward interval PLS (biPLS), are used for the evaluation of nitrofen content based on the THz spectroscopy data from 0.3 to 1.6 THz, and a comparison of the performances of the four regression techniques with various model interval widths was provided, which are shown by the root mean square error of cross-validation (RMSECV) for the calibration set and the root mean square error of prediction (RMSEP) and the correlation coefficient (R) for the prediction set.

2. Theory and experiment

2.1. Experimental approach

The THz-TDS set-up developed by Zomega was used to collect the material spectral data shown in Fig. 1. A Ti:sapphire laser (Femtosource) provides 100 fs pulses with a repetition rate of 80 MHz. The terahertz emitter is a coplanar strip line antenna fabricated on a semi-insulating

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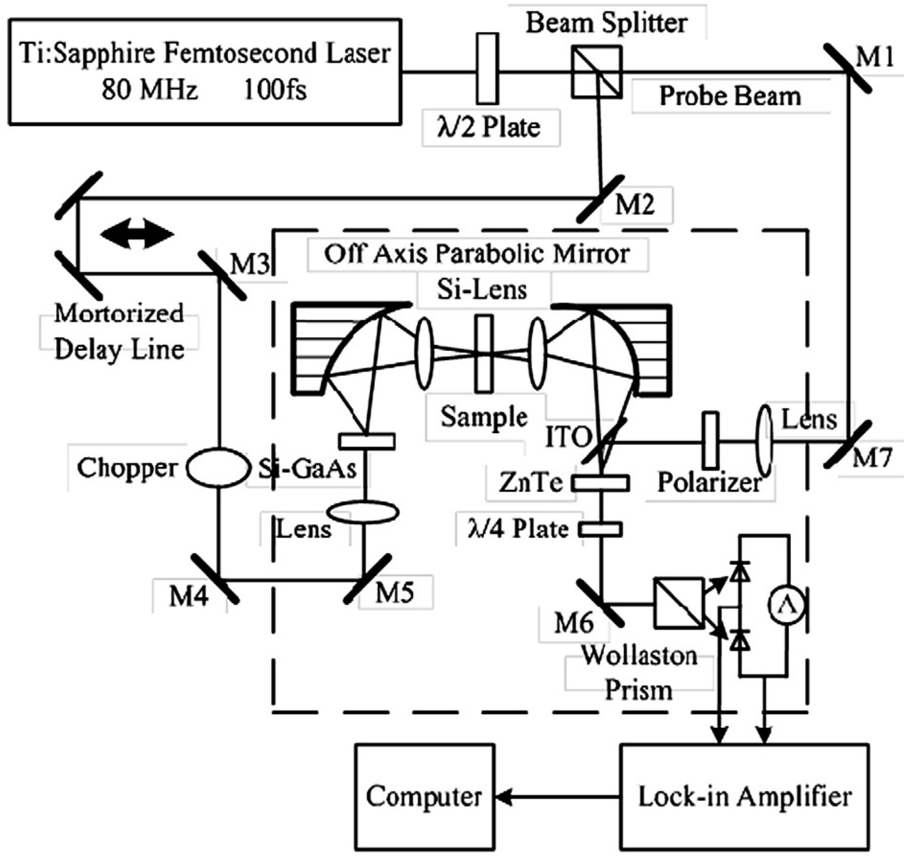

Fig. 1. Schematic of the THz-TDS setup.

(SI) GaAs wafer. The bias voltage between the coplanar strip lines of the emitter antenna is 30 V. An aplanatic hyper-hemispherical silicon lens is attached to the back of the THz emitter to increase the coupling efficiency of the terahertz pulse from the antenna to free space. Two highly resistive silicon lenses are used for focusing the THz beam to samples with a spot size of less than 2 mm diameter. The detector crystal is ZnTe with a thickness of 0.5 mm and is gated by 1 mW probe beam pulses [19].

Nitrofen, thiacloprid and acetamipyrid were supplied by Tokyo Chemical Industry Co. Ltd. and AccuStandard, with the purities of 98%, 99% and 99.5%. The three materials for qualitative comparison were mixed with polyethylene by a turbine mixer and pressed into samples with a pressure of 15 MPa and the weight ratio of 1:1, and their thicknesses were 1.178, 1.227 and 1.185 mm correspondingly. With respect to quantitative data, nitrofen and polyethylene mixtures (14 samples) were prepared with thicknesses from 1.178 to 1.600 mm, and the content range of nitrofen was 0–51.84% (w/w). Experiments were carried out at room temperature (294 K) and a circumstance of nitrogen with humidity of about 0.1%. For the THz spectral data of 14 samples, ten samples were selected as the calibration set to build a regression model, and the other four samples were regarded as the prediction set to evaluate the regression model.

2.2. Terahertz spectroscopy

The THz spectra were recorded with time window of about 25 ps corresponding to the resolution 0.04 THz. Each final sample spectrum resulted from the average of three time detections. By comparing the amplitude spectrum of a sample to the reference signal with no sample, we could determine the material properties of the samples. The refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$, respectively

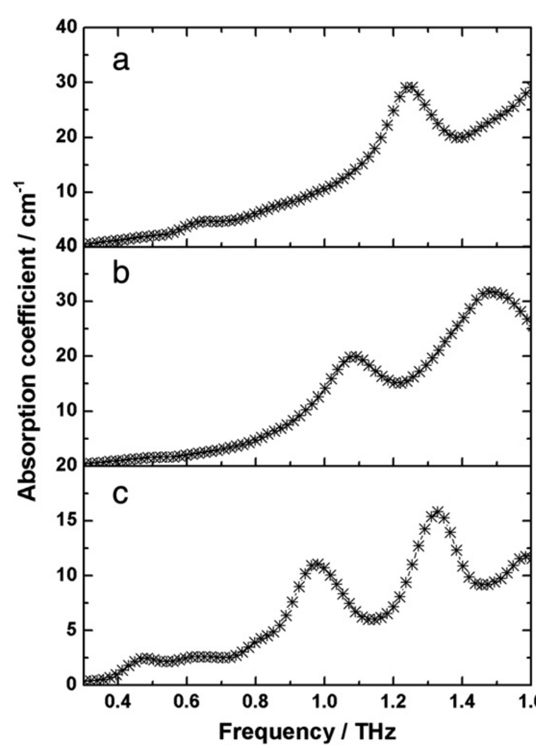

Fig. 2. The THz spectra of the three materials from 0.3 to 1.6 THz (thiacloprid (a), acetamipyrid (b) and nitrofen (c)).