



Rapid qualitative and quantitative analysis of chlortetracycline hydrochloride and tetracycline hydrochloride in environmental samples based on terahertz frequency-domain spectroscopy

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ABSTRACT

Owing to the advantages of transient, broadband, low-energy, transmission and high frequency accuracy, terahertz frequency domain spectroscopy (THz-FDS) has been introduced and pioneered for determining chlortetracycline hydrochloride (CCH) and tetracycline hydrochloride (TCH) in environmental samples, such as chicken, rice and soils. Their THz fingerprint spectra were located in the range of 0.4–1.1 THz, with the peaks at 0.49, 0.60, 0.76, 0.90 and 1.03 THz for CCH and at 0.52, 0.67, 0.79, 0.92 and 1.05 THz for TCH, respectively. By simple pressing treatment, dry soil, chicken and rice samples spiked with standards can be used for direct analysis. For the quantitative analysis, partial least squares regression (PLSR) algorithms were utilized for optimizing the analysis accuracy, calculation and prediction. Lower root mean square error of cross validation (RMSECV < 0.1689), calibration (RMSEC < 0.0623), prediction (RMSEP < 0.1280) and higher correlation coefficient ($R > 0.9089$) for these two compounds in soil, chicken and rice samples have been obtained. Our results indicated that THz-FDS combined with PLSR model could be a useful analytical technique for monitoring CCH and TCH in environmental samples.

1. Introduction

Terahertz (THz) spectroscopic technique with the THz frequency region from 0.1 to 10 THz (1 THz = 10^{12} Hz) is an attractive and unique spectroscopic technique between the microwaves and infrared bands [1]. Due to its high penetrability, low ionization energy, fingerprint spectrum and coherence [2,3], THz spectroscopy has been widely studied in fields of biomedicine diagnosis [4,5], security inspection [6,7], environmental detection [8], astronomy and communication [9]. With the density functional theory, THz spectroscopy can be used to investigate the THz fingerprint spectrum of chemicals, such as caffeine and 3-acetylmorphine [10].

Beyond that, THz time-domain systems (THz-TDS) have been proven to be an available tool to analyze chemicals and to identify the differences on their structures [11–14]. For measuring a well-studied series of homologous alcohols, a planar Goubau line THz-TDS system integrated with a microfluidic measurement system [1] has been developed recently. Combined with chemometrics analysis, THz-TDS was also a suitable analytical technique for detecting chemicals, even in the

complex samples of rice and infant milk powder [15,16]. The great promise of THz spectroscopy in the qualitative and quantitative analysis of chemicals can be principally attributed to the fingerprint spectrum of molecules based on their characteristic vibrations [15,17].

Compared with THz-TDS, THz frequency-domain systems (THz-FDS) with continuous terahertz radiation and the flexible choice of the THz frequency can directly record the transmittance signals of chemicals without the conventional Fourier transform (FFT) processes [18]. In view of the advantages on high frequency accuracy and selective-targeting spectrum region, it is believed that THz-FDS could be a promising technique for chemical analysis [19]. However, up to now, due to THz-FDS is still in its infancy, few studies on THz-FDS have been reported in recent years.

As effective drugs for challenging microbial populations, antibiotics have been widely used for preventing and treating infections of animals and plants as well as for promoting growth in animal farming [20–22]. But their extensive usages have resulted in their widespread occurrence in natural ecosystems and led to a series of environmental problems [23–25]. A specific aftermath is the possible development on antibiotic

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resistant pathogens. Therefore, antibiotic pollution has become a pressing concern needed to be solved [26,27]. The routine analysis of antibiotics often relies on the methods involving gas chromatography (GC), high performance liquid chromatography (HPLC) and mass spectrometry (MS) which possess the advantages of good separation efficiency, superior sensitivity and high selectivity [28–30]. But it has to be noted that complex pretreatments are inevitable for these methods. Therefore, developing novel methods featured simple sample pretreatments, nondestruction as well as non-pollution is still a great challenge for monitoring these chemicals [31].

In this study, a THz-FDS method combined with simple pressing treatment has been firstly developed for analyzing chlortetracycline hydrochloride (CCH) and tetracycline hydrochloride (TCH) in chicken, rice and soil samples. The THz fingerprint spectra of CCH and TCH were predicted by the density functional theory (DFT). The analysis accuracy was optimized by using partial least squares regression (PLSR) algorithms and the performance of PLSR model was evaluated by the root mean square error of calibration (RMSEC), root-mean-square errors of cross-validation (RMSECV) and prediction (RMSEP), and correlation coefficient (R) of calibration model values.

2. Materials and methods

2.1. Materials and chemicals

CCH and TCH with the purities of 95% and 99% used in our experiments were provided by Beijing Solarbio Science & Technology Co., Ltd., Polyethylene powder (particle size: 40–48 μm) was supplied by Sigma-Aldrich. Chicken breast from chicks raised for 400 days old in Weifang City, China was freeze-dried under $-60\text{ }^\circ\text{C}$ for 48 h, and then crushed into smaller particles (200 mesh). Rice was purchased from Wumei supermarket in Zhejiang Province, China. Soil powders were obtained from the grassless ground in Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences. The rice and soil powders were sieved through the 200 mesh screens after dried at $60\text{ }^\circ\text{C}$ for 24 h. All chemical reagents used in the study were of analytical grade and all the experiments were done in triplicate.

To analyze the THz fingerprint spectra of CCH and TCH, their standards were mixed with polyethylene powder (1:1 by weight) and pressed into slices (13 mm in diameter and 0.65 mm in thickness) with a tablet machine (HY-12, Tianjin tianguang optical instrument Co. Ltd., China) under the pressure of 12 MPa for 2 min. Polyethylene powder was chosen in the tableting process is because of its high transparent to THz radiation, low interference to features and easy formation of slices [15,16]. To evaluate the performance of the developed method, a series of soil, chicken and rice powders spiked with CCH and TCH standards were ground to proper size with a mortar after weighing and mixing, and then the homogenized mixtures were compressed into series of slices according to the same protocol described above. The content range of the two chemicals was from 1% to 50%. The spectra in the range from 0.5 to 1.0 THz were selected as the calibration set to build PLSR models. The transmittances (T) of the samples were directly obtained from THz-FDS in this study and the absorbance (α) could be calculated by Eq. (1).

$$\alpha = -\ln T \quad (1)$$

where α is the absorbance of CCH and TCH in different environmental samples; T at any frequency was computed by comparing the photocurrent amplitude of the sample and reference at the same frequency.

2.2. Instrumentation

A commercial THz-FDS (TeraScan 1550, Toptica Photonics, Germany) system was employed to measure the THz spectra of the samples, as shown in Fig. 1. Two distributed feedback (DFB) lasers (0.05–1.2 THz with lasers #1 and #2;), THz transmitter, THz receiver,

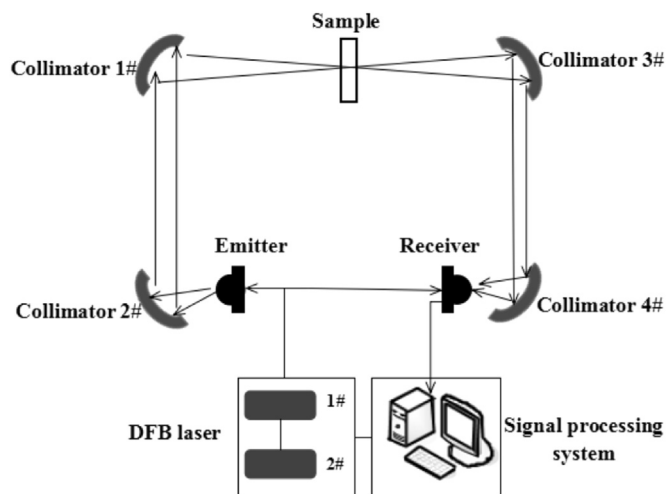


Fig. 1. Schematic of Terahertz frequency-domain spectroscopy system in experiment.

four collimators, sample cell and signal processing system were integrated in the system. Signals from THz transmitter propagated through the samples and was eventually imported into THz receiver connected to the computer. In this study, THz region for sample detection was settled in the range of 0.5–1.1 THz with the step of 0.04 GHz. Air was chosen as the reference and detected under the same detection conditions. The humidity was kept less than 4.0% and temperature was maintained at 293 K during the experiments.

2.3. The density functional theory (DFT) calculation and absorption feature analysis

In order to understand the observed THz absorption features from molecular structures, the isolated molecule ground state geometry optimization and frequency calculation were performed using the GAUSSIAN 09 Revision-D.01-SMP software package [32]. The optimized structures were confirmed through Gaussian view 5.0 software package. Fig. 2 shows their predicted molecular structures after the geometry optimization. DFT calculations with B3LYP/6-31G (d) were carried out to assign the vibrations of CCH and TCH.

2.4. Regression modeling and evaluation

The redundancy factors of THz spectral data obtained from the signal processing system were removed by the principal component analysis (PCA). PLSR were used to verify the data obtained from the experiment. The RMSEC, RMSECV, RMSEP and R values were chosen to evaluate the predictive ability of PLSR model [11,12,15]. It is proposed that higher R values and lower RMSEC, RMSECV and RMSEP values correspond to the better prediction accuracy for the model [33]. All of the calculations were carried out using the software of TQ analyst (version 8.3.0.125, Thermo Fisher Scientific Inc.) combined with Origin software (version 8.5, Origin Lab Corp.) for the mapping.

3. Results and discussion

3.1. THz spectra of CCH and TCH

The experimental and simulated THz absorbance spectra of CCH and TCH in the range of 0.4–1.1 THz were shown in Fig. 2. All the experiments were performed in triplicate, and the final THz spectra figure is an average of the three sets of data, with deviation less than 0.17. In Fig. 2, ϵ is epsilon, which represents the molar absorption coefficient. The simulated absorbance peak at 1.03 THz was in

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