Detection of pesticides residues in rapeseed oil by terahertz time domain spectroscopy

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Abstract. The absorption spectra of panax notoginseng and glycyrrhiza in the frequency range of 0.2~1.6THz has been measured with terahertz time-domin spectroscopy at room temperature. Simultaneously, the corresponding theoretical spectra were given by using density functional theory methods. It was found that the absorption peaks of the two molecules obtained by theoretical were in good agreement with the experimental results.

1. Introduction
Terahertz wave usually refers to the frequency range of 0.1 ~ 10THz in electromagnetic waves, which coincides with the energy between the molecular vibration and rotational energy transitions. Because of the macromolecules highly relevant nature of the spectroscopic properties in the scope of the THz band, the terahertz time-domain spectroscopy has received extensive attention in recent years [1-3].

In recent years, food safety problems occur frequently. Edible oil, which is one of the three major nutrients, is closely related to human life. People begin to pay attention to the safety of edible oil with the improvement of living standard. At present, edible oil inspection and detection depend largely on gas chromatography [4], and HPLC [5]. In order to guarantee food safety, there is an urgent need to develop a user-friendly, fast and effective test to identify the quality of edible oil. Although some of the methods mentioned above have high detection precision, the preprocessing technology such as purification and extraction is very complex. In this paper, we proposed a new detection method employing terahertz time-domain spectroscopy to investigate the pesticides residues in oil.

2. Theory analysis
The schematic diagram of the THz-TDS setup used in this experiment is shown in figure 1. A repetition rate of 80MHz, diode-pump mode-locked Ti:sapphire laser (MaiTai, Spectra Physics) provided the femtosecond pulses with duration of 100fs and center wavelength of 810nm. A p-type InAs wafer with <100> orientation was used as the THz emitter and a 2.8 mm-thick <110> ZnTe was employed as the sensor. A standard lock-in technology was used in this system. A femtosecond laser pulse was split into two beams. The pump beam was used to generate THz radiation and the probe beam acted as a gated detector to monitor the temporal waveform of THz field. A silicon lens and parabolic mirrors were used to collimate and focus the THz beam through free space onto the detector. A balanced photodiode detector detected the probe beam, and the signal was amplified by a lock-in amplifier and sent to the computer for processing. The THz beam path was purged with dry nitrogen to
minimize the absorption of water vapor and enhance the signal to noise ratio (SNR). The humidity was kept less than 1% and the temperature was kept at 298K. According to the figure, we can describe the Fresnel reflection ($R_{12}$) and transmission ($T_{12}$) coefficients of a THz wave at the interface of media 1 and media 2 in the time domain as follows:

$$T_{12} = \frac{2 \times \tilde{n}_1}{\tilde{n}_1 + \tilde{n}_2}$$
$$R_{12} = \frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_2 + \tilde{n}_1}$$

The transmission function of the first order Fabry-Perot can be given by

$$H_{\text{theory}} = \frac{(E_{\text{sam}}^1 (1) + E_{\text{sam}}^1 (2) + E_{\text{sam}}^1 (3))}{(E_{\text{ref}}^1 (1) + E_{\text{ref}}^1 (2) + E_{\text{ref}}^1 (3))}$$

$$H_{\text{experiment}} = \frac{E_{\text{sam}}}{E_{\text{ref}}}$$

We define the following error function

$$\text{Re}(\text{erf}) = \text{Re}(H_{\text{theory}}) - \text{Re}(H_{\text{experiment}})$$
$$\text{Im}(\text{erf}) = \text{Im}(H_{\text{theory}}) - \text{Im}(H_{\text{experiment}})$$

$$\text{Total}(\text{erf}) = \sum |\text{Re}(\text{erf})| + |\text{Im}(\text{erf})|$$

The optical path and thickness of the cuvette equal to 5mm and 1.2mm, respectively. The optical path of THz wave in cuvette is shown in figure 2.

Figure 1. A schematical THz-TDS system

Figure 2. Optical path figure of THz in cuvette
3. Experiment results

In order to detect pesticide ingredient in oil, we choose two samples as follows: Sample 1 (rapeseed oil), and Sample 2 (rapeseed oil + Imidacloprid). Figure 3 shows the terahertz time-domain spectra of the THz pulse traveling through reference and the pulse traveling through the small quartz cuvette with the two samples, respectively.

The refractive indices and the power absorption coefficients of the investigated two samples are calculated from the measured data by using Eqs. (1) ~ (3). There have three absorption peaks of rapeseed oil at 1.56THz, 1.45THz, and 1.35THz. For rapeseed oil/imidacloprid mixture, there have three absorption peaks at 1.58THz, 1.47THz, and 1.37THz. The refractive index decrease as the frequency increases.

![Figure 3. The time-domain spectra of reference and two sample](image1)

![Figure 4. Absorption spectra](image2)
4. Conclusion
We analyzed the absorption coefficient and refractive index of both the rapeseed oil and rapeseed oil/imidacloprid mixture in the frequency range from 0.2 to 1.6THz respectively. The results show that it is feasible to employ THz-TDS to identify imidacloprid in oil.

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