Terahertz spectroscopic investigation of Chinese herbal medicine

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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-domain 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 [1-4]. Drug ingredients identification and quality control is the key for the widely used Chinese herbal medicine. In this paper, we investigate the terahertz spectra of two kinds of Chinese herbal medicines using terahertz time-domain spectroscopy (THz-TDS) as well as computationally using the B3LYP density functional theory (DFT) method. The research shows that THz-TDS technique can be used for the identification of panax notoginseng and glycyrrhiza, which provides guidance significance to further research using THz time-domain spectroscopy to identify other herbs.

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. The dynamic range was about 4000:1, and the spectral resolution was better than 60 GHz in the 0.2–1.8THz region.

The THz-TDS can be used to extract optical parameters such as the absorption coefficient and refractive index of the sample. The transmitted field, \( H = \frac{E_{\text{sam}}(\nu)}{E_{\text{ref}}(\nu)} \), is related to the complex refractive index \( N = n + ik \) by

\[
H = \frac{4N}{(1+ N)^2} e^{\frac{2\pi i (N-1)d}{c} \omega} = A e^{-i\phi}
\]

where \( \omega \) is the frequency of the THz wave, \( A \) the amplitude of the THz wave, \( \phi \) the phase difference between the sample and reference waveforms, and \( d \) the thickness of the sample. The multiple internal reflection is ignored in this equation under the condition \( K \ll n \), where \( K \) is the extinction coefficient. Hence the Fabry–Perot effect can be neglected. Thus, we can obtain the refractive index \( n \), absorption coefficient \( \alpha \), respectively:

\[
n = \frac{c\phi}{2\pi \omega} + 1
\]

\[
\alpha = \left( \frac{4\pi k\omega}{c} \right) = \frac{2}{d} \ln \left( \frac{4n}{A(n+1)^2} \right)
\]

Here, the panax notoginseng is named sample 1, and glycyrrhiza is named sample 2. To reduce the scattering effect of the sample, these samples were ground into fine particles and then pressed into pellets. The approximate pressure is 4500 PSI. The THz spectra of three kinds of POPs were measured with free space electro-optic sampling. We calculated the THz spectrum of the panax notoginseng and glycyrrhiza by using the method of DFT method. Optimization of the molecular structure was shown in figure 2.

![Figure 1. A schematical THz-TDS system](image)

### 3. Experiment results

The terahertz time-domain spectra and frequency domain spectrum of the terahertz pulse traveling through air and the pulse traveling through the four kinds of soil samples are shown in figure 3 and figure 4. Every pulse curve is the average of three individual measurements in order to increase the signal-to-noise ratio. The experimental results were redone more than 3 times, the results provided here are repeatable and credible. Figure 5 shows the absorption curves of panax notoginseng and glycyrrhiza. Panax notoginseng has three characteristic absorption peaks which are located at 1.29THz, 1.40THz and 1.51THz, while glycyrrhiza in the frequency of 1.56THz has a characteristic absorption peak. The theoretical calculation has a good accordance corresponding to each other with experimental spectra characteristic absorption peaks.
Figure 2. Molecular structure of panax notoginseng and glycyrrhiza

Figure 3. Measured terahertz time-domain spectra of reference and samples
4. Conclusion
We tested panax notoginseng and glycyrrhiza in frequency of 0.2 ~ 1.6THz. The experimental results and theoretical calculations are basically in accordance with each other. The results of this study provide a practical application of THz-TDS in the detection quality of Chinese herbal medicine.

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