

Quantitative determination of *n*-heptane and *n*-octane using terahertz time-domain spectroscopy with chemometrics methods

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Abstract This paper introduces the terahertz time-domain spectroscopy (THz-TDS) used for the quantitative detection of *n*-heptane volume ratios in 41 *n*-heptane and *n*-octane mixtures with the concentration range of 0–100% at the intervals of 2.5%. Among 41 samples, 33 were used for calibration and the remaining 8 for validation. Models of chemometrics methods, including partial least squares (PLS) and back propagation-artificial neural network (BP-ANN), were built between the THz-TDS and the *n*-heptane percentage. To evaluate the quality of the built models, we calculated the correlation coefficient (*R*) and root-mean-square errors (*RMSE*) of calibration and validation models. *R* and *RMSE* of two methods were close to 1 and 0 within acceptable levels, respectively, demonstrating that the combination of THz-TDS and chemometrics methods is a potential and promising tool for further quantitative detection of *n*-alkanes.

Keywords terahertz time-domain spectroscopy (THz-TDS), *n*-heptane, *n*-octane, partial least squares (PLS), back propagation-artificial neural network (BP-ANN)

1 Introduction

Alkane is an important kind of organics owing to its chemical structures and special components only including carbon and hydrogen atoms so that it reflects stable chemical properties. *N*-heptane and *n*-octane are normal kinds in the *n*-alkane group, which mainly originate from natural gas and petroleum. As the octane number of *n*-

heptane equals zero, it is one of the standard substances regulating antiknock performance of gasoline. The analysis with regard to the two similar and important components is significant to the further characterization in the research of gasoline. Because of the subtle differences of $-\text{CH}_2$ radical group between *n*-heptane and *n*-octane, conventional ways of qualitative and quantitative detection are very limited. Spectroscopic method such as infrared and Raman spectra can be used to detect *n*-heptane or *n*-octane in terms of the absorption responses, i.e., a few differences of the frequencies of LAM-1 and the observed and estimated frequencies of D-LAM between *n*-heptane and *n*-octane using Raman spectra [1–4].

Terahertz time-domain spectroscopy (THz-TDS), a recently developed spectroscopic method, possesses special advantages of analyzing subtle difference between two kinds of alkane. THz spectroscopy, whose electromagnetic spectrum region locates between the microwave and the infrared regions, can provide abundant information of inter- and intra-molecular vibrations. Moreover, THz wave causes little damage to alkane because of its low photon energy, and gives the amplitude and phase information simultaneously. Due to the above properties, THz-TDS has been applied to various fields [5–10].

It is meaningful to discuss the quantitative analysis of *n*-alkanes using THz-TDS with chemometrics methods, which proved to be significant for spectroscopic research. Partial least squares (PLS), a method for relating two data matrices by a linear multivariate model, can analyze the strongly collinear and noisy data [11]. Artificial neural network is a widely used method which imitates and simplifies some basic characteristics of human brain function. Back propagation-artificial neural network (BP-ANN) can store a lot of input-output mapping relationships without prior revealing the mathematical

equation describing the mapping relationships. BP-ANN is currently one of the most widely used artificial neural network models [12].

Previous report of THz-TDS for *n*-heptane and *n*-octane analysis described measurements of the THz dielectric properties of normal alkanes [13]. In this paper, we measured the THz spectra of 41 *n*-heptane and *n*-octane mixtures with the *n*-heptane volume ratio range between 0 and 100% (the intervals of 2.5%). Chemometrics models were built between *n*-heptane volume percentage and the THz frequency-spectra (THz-FDS) using PLS and BP-ANN methods. Relevant errors of the two methods kept within acceptable levels, demonstrating that the combination of THz-TDS and chemometrics methods would be a promising analytical tool for further quantitative detection of *n*-alkanes.

2 Experiments

2.1 Experimental setup

In this experiment, we utilized the THz spectrometer in the transmission mode to measure the THz-TDS of samples. The experimental setup is comprised of a THz-TDS system from Zomega Terahertz Corporation and a femtosecond Ti-sapphire laser. Relevant parameters and apparatus of THz-TDS are exactly the same as the ones discussed previously [5].

2.2 Sample preparation

The *n*-heptane and *n*-octane were purchased from A Johnson Matthey Company, with the purity of 99% and 98%, respectively. We prepared 41 *n*-heptane and *n*-octane mixtures with the *n*-heptane volume ratio of 0–100% at the intervals of 2.5%.

2.3 Data acquisition

The samples and references pulses were measured by scanning the quartz cells holding the mixtures and without anything, respectively. The thickness of quartz cell is 10 mm, shown in Fig. 1. To reduce the influence of water vapor in the air, the samples were scanned in the atmosphere of nitrogen at room temperature.

3 Results and discussion

The THz-TDS of all samples, shown in Fig. 2, are obtained by scanning the quartz cell holding the *n*-heptane (99%) and *n*-octane (98%) mixtures in the atmosphere of nitrogen at room temperature. Due to the same chemical structures of *n*-heptane and *n*-octane, the THz-TDS have similar THz amplitudes. However, mixtures reflect different time

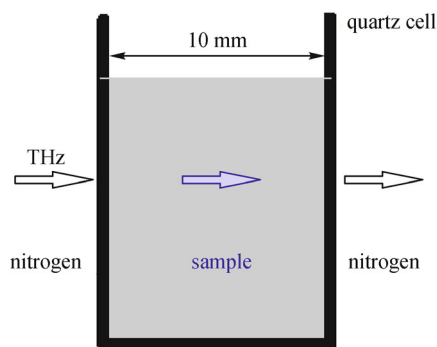


Fig. 1 Chart of the sample held in a quartz cell

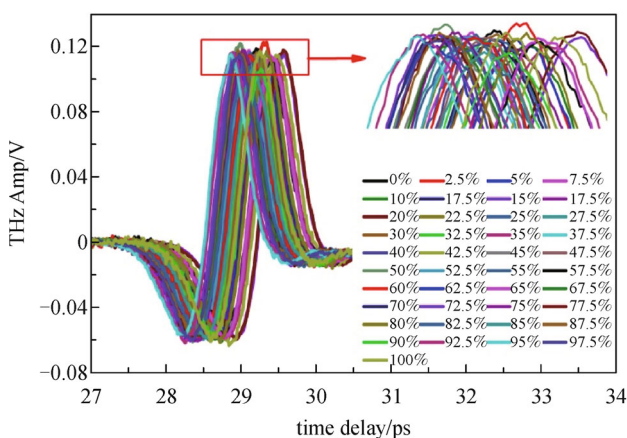


Fig. 2 THz-TDS of 41 *n*-heptane and *n*-octane mixtures at the intervals of 2.5%

delays of peaks, demonstrating that *n*-heptane and *n*-octane keep different dielectric properties caused by the differences of one methylene. We selected 20 samples and extracted their THz peaks' delay time versus the *n*-heptane volume ratio with a linear regression line, given in Fig. 3.

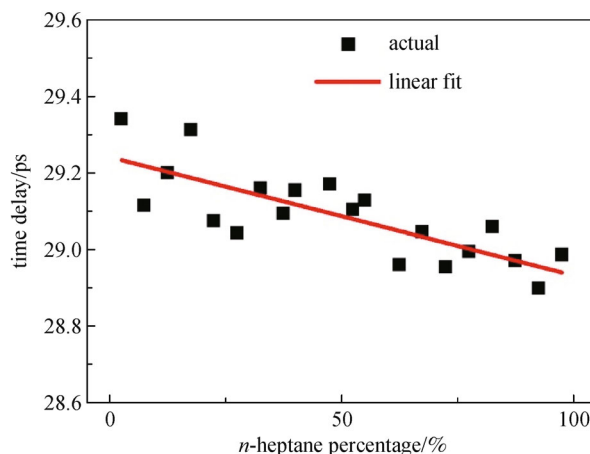


Fig. 3 Time delay versus *n*-heptane percentage of 20 selected samples

The results show that the peaks' delay time roughly decreases with the increased *n*-heptane ratio, but there exist several big deviations in the linear model possibly caused by the environmental and instrumental noises, as well as the little difference of quartz cells. The simple linear model can be improved by using chemometrics methods, which will be discussed later.

Figure 4 shows the THz-FDS of all samples in 0.2–2.5 THz range, calculated by fast Fourier transform (FFT). There exist two peaks at about 0.50 and 0.65 THz, but the similar wave forms and amplitudes which indicate the quantitative analysis cannot be done visually. To realize the quantitative determination of *n*-heptane volume ratio in the mixtures, we adopted two kinds of chemometrics methods, PLS and BP-ANN, to establish the models which are used to predict the unknown mixtures.

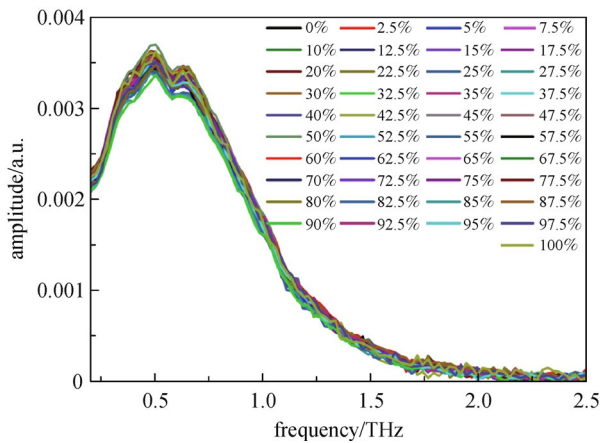


Fig. 4 THz-FDS of 41 *n*-heptane and *n*-octane mixtures at the intervals of 2.5%

Using appropriate parameters of the PLS and BP-ANN calibration models, 8 samples were predicted for validation. Figures 5 and 6 show the results of calibration and validation models calculated by PLS and BP-ANN respectively, with the reference lines representing zero residuals between the predicted and actual values. The

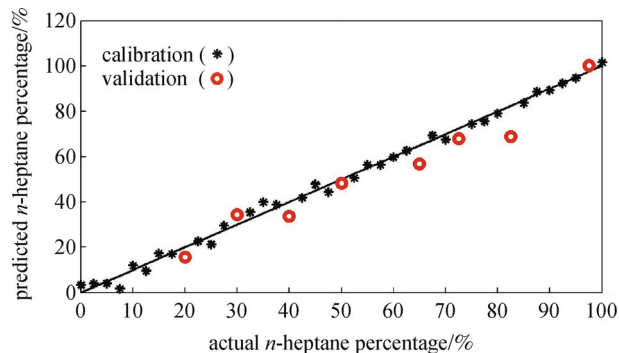


Fig. 5 Predicted *n*-heptane percentage versus actual *n*-heptane percentage from PLS models

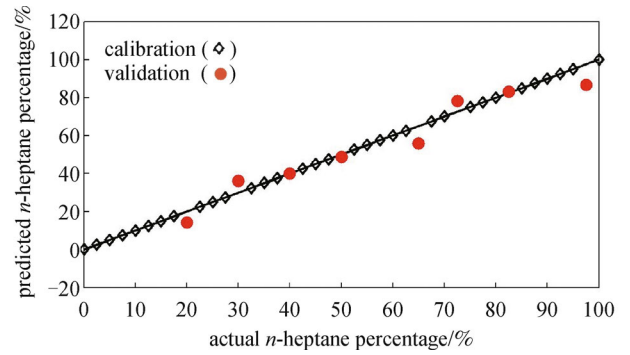


Fig. 6 Predicted *n*-heptane percentage versus actual *n*-heptane percentage from BP-ANN models

predicted *n*-heptane ratios were calculated from the PLS and BP-ANN models with the input of THz-FDS in 0.2–2.5 THz range, and none of the spectral pretreatments was used. The results of validation in Figs. 5 and 6 demonstrate the agreement between actual values and predicted values, which indicates that the PLS and BP-ANN methods can precisely determine the *n*-heptane concentrations in the *n*-heptane and *n*-octane mixtures.

To evaluate the performance of the calibration models and validation models, two kinds of errors are calculated in terms of correlation coefficient (R) and root-mean-square errors ($RMSE$) between the actual concentration of a sample and the predicted concentration of the same one. R is an index correlation determined by the degree of linear relationship between actual and predicted concentrations. $RMSE$ measures the deviation between actual and predicted values, and can give an indication of the precision of prediction. $RMSE$ is defined as

$$RMSE = \sqrt{\frac{\sum (C_{act} - C_{pre})^2}{n}}$$

where C_{act} is the actual concentration of a sample, C_{pre} is the predicted concentration of the same one, and n is the number of samples. The closer R and $RMSE$ are to 1 and 0, respectively, the higher the model prediction precision is.

The results of errors are listed in Table 1, which were calculated from Figs. 5 and 6, and all the errors keep within acceptable levels. All the calibration and validation models' correlation coefficients of two methods are greater than 0.97, and all the root-mean square errors are smaller than 7.0%. This experiment proved that the THz-TDS could serve as a reliable way to quantitatively detect the components of mixtures with chemometrics methods. Similar application of THz-TDS with chemometrics methods can be found in previous reports [14–16]. Quantitative determination of cyfluthrin in *n*-hexane was achieved by THz-TDS with four calibration methods, including simple linear regression (SLR), PLS, least-squares support vector machine (LS-SVM) and the combination of PLS and LS-SVM (PLS-LS-SVM),

Table 1 Errors of calibration and validation of two methods

	PLS		BP-ANN	
	calibration	validation	calibration	validation
<i>R</i>	0.9973	0.9764	0.9999	0.9716
<i>RMSE</i> /%	2.217	6.714	0.0003	6.21

where the average relative errors of prediction were about 10% [14]. In addition, PLS was used as the qualitative and quantitative detection methods of pesticides with THz-TDS and the relative errors of prediction were close to 5% [15]. In the field of pharmacy, numerous kinds of tablets were explored using THz-TDS with principal component regression (PCR) and PLS. Prediction results were in good agreement with the nominal concentration values, but the prediction errors fluctuated [16]. Our research, therefore, as well as some others' work discussed above demonstrates that THz-TDS combined with chemometrics methods would be an effective technique for quantitative analysis.

4 Conclusions

In summary, this research proves the feasibility of the combination of THz-TDS and chemometrics methods for the detection of *n*-heptane and *n*-octane mixtures. Chemometrics methods including PLS and BP-ANN were utilized to build the model between the actual *n*-heptane volume ratio and the predicted concentration of 41 mixtures based on their THz spectra. Results indicate that there exists a special relationship between the THz spectra and the *n*-heptane percentage, which could be extracted by appropriate methods of data analysis. This research may lead to a more widespread application of THz-TDS for quantitatively detecting organics with subtle chemical differences.

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