Invited Paper

Terahertz spectroscopy properties of trace crude oil in quartz sand

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Abstract: The purpose of this article is to classify the types of crude oils from different regions and oil-quartz sand mixture with different oil content with terahertz time-domain spectroscopy (THz-TDS). Multivariate statistical methods, including cluster analysis (CA) and principal component analysis (PCA), are used to build models between THz parameters and crude oils from different regions. The sample absorbance first increases and then decreases with the increase of oil content, revealing that the THz response is caused by the cracks and oil content simultaneously. When the oil content is smaller than the critical concentration, the existence of cracks makes more scattering; meanwhile, the more the oil content is , the larger the THz absorption becomes when the oil content is larger than the critical concentration. Consequently, the combination of THz technology as well as multivariate statistical methods could be an effective method for rapid identification of crude oils content and the geographical locations of crude oils.

Keywords: Terahertz time-domain spectroscopy, Crude oil, Trace, Multivariate statistical methods

Doi:

1. Introduction

Petroleum, chemical industry, metallurgy and other industries commonly produced oily wastewater [1, 2]. Billions of tons of oily wastewater are discharged into the ocean, causing grievous waste of resources and environmental pollution [3]. Quartz sand, widely used as a technical and economical filter medium, is significant for oil-water mixtures treatment [4, 5]. Therefore, the oil content in quartz sand will directly affect its filtration performance.

Previously, terahertz (THz) wave is a kind of wave between millimeter wave and infrared light [6]. It is extremely sensitive to the vibration of organic macromolecules, so it is often used to distinguish the oil content and the type of oil in stones [7-13]. In this work, oil-sandstone with different kinds of crude oils and different oil content were detected using THz time-domain spectroscopy (THz-TDS). Absorption coefficient spectra were calculated to conform the differences of oil content. Multivariate statistical methods such as cluster analysis (CA) and principal component analysis (PCA) were used to classify the crude oil, which realized the characterization of the type and content of crude oil in quartz sand. It provides a new method and a new idea for monitoring oil leakage.

2. Experimental methods

Ten kinds of crude oils, numbered from 1 to 10, are received from several oil fields in China. As shown in Fig. 1, 0.2 *g* selected crude oil is diluted in acetone by 10,000 *times* to obtain a mixed solution with a crude oil concentration C of 200 *ppm*. The 0.5-5 *g* solution is mixed with 5 *g* quartz sand in 50 *mL* acetone, which is stirred for 5 *min*. Then the mixture is dried at 70 ^{o}C for 20 *min* to evaporate the acetone, and cools to room temperature. Thus the quartz sand-crude oil mixtures are prepared with the oil concentrations of 20-200 *ppm*, respectively.

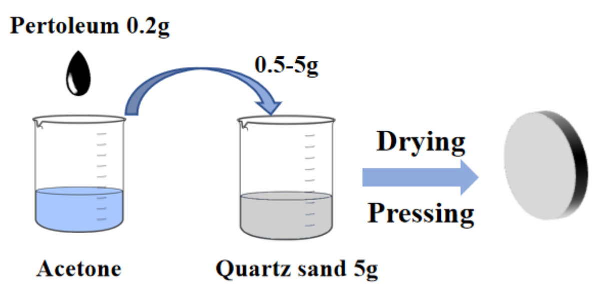

Fig. 1 The flow chart of sample preparation.

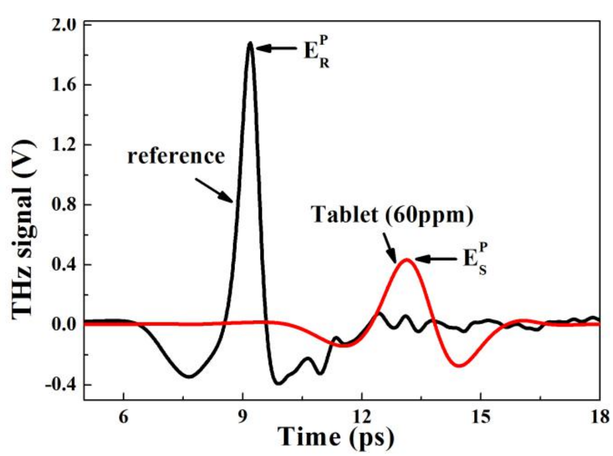

Fig. 2 THz-TDS of the reference and tablet with 60 *ppm* crude oil.

To conduct THz experiment, the quartz sand-crude oil mixture is compacted to a tablet with a diameter of 30 *mm* and a thickness d of ~2 *mm* under 20 *MPa*. Tablet samples are analyzed using THz-TDS. Figure 2 shows the change of THz field signal over time after THz pulse is transmitted in the 60 *ppm* crude oil tablet. Comparing with the peak intensity E^{P}_{R} (=1.89 *V*) of reference spectrum, there is a significant attenuation of the peak intensity E^{P}_{S} (=0.44 *V*) in the

THz-TDS of the selected tablet, indicating an evident absorption of the substances in the THz range.

3. Result and discussion

Figure 3 depicts the frequency-dependent absorption spectra of selected tablets with different crude oils (40 *ppm*) at a frequency range of 0.2 *THz*–0.7 *THz*. There are no significant absorption characteristics in the effective frequency range. Although a slight difference was observed in the spectra these spectra are still highly overlapped. In order to establish a more accurate model between crude oils and THz spectra, and more directly and effectively realize the determination of crude oil in different regions, CA and PCA are adopted to analyze and display the classification of crude oil.

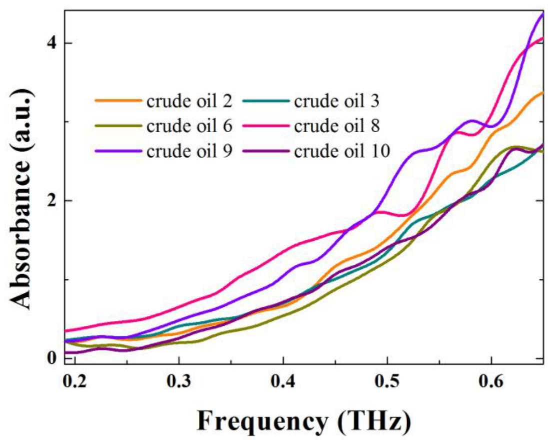

Fig. 3 THz absorbance spectra of tablets in a frequency range from 0.2 *THz* to 0.7 *THz*, respectively.

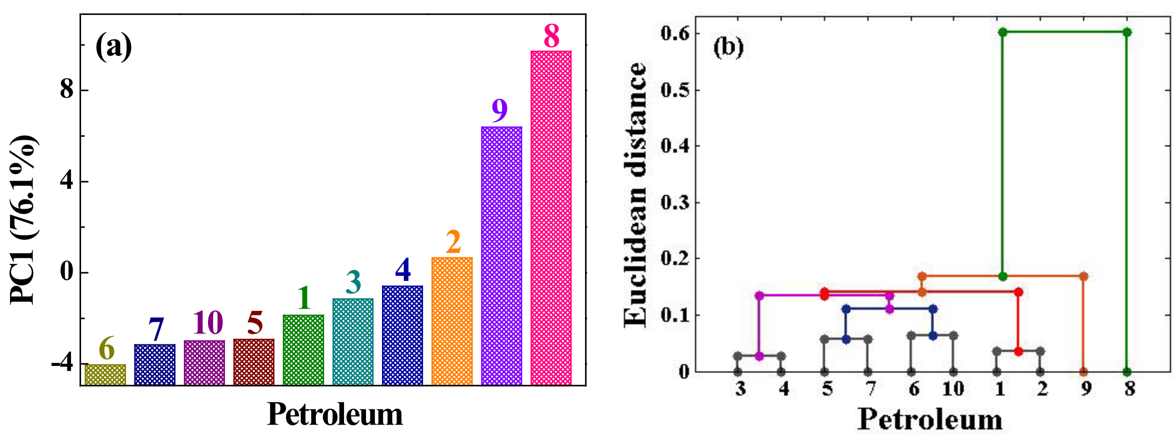

Fig. 4 (a) The PC1 score histogram and (b) Euclidean distance dendrogram calculated with absorption coefficient data.

The absorption coefficient spectra data are input into PCA and CA methods, and the calculation results are shown in Figure 4, which are respectively PC1 fraction histogram and CA entropy diagram. The PC1 of the data set describes 76% of the variance in the data. The greater the deviation of similar PC1 score in the sample is, the greater the differences there are. Crude oil 8 shows a great particularity in the calculation process of CA and PCA. The distance between crude oil 8 and other crude oil reaches the maximum, and its PC1 score is in a leading position relative to other kinds of crude oil. From Figure 4, it can be inferred that crude oil 5, 6, 7, 10 have some similarities due to their small distances and similar PC1 scores.

The relationship between δ and concentration C is plotted in Figure 5, where $\delta = d^{-1}E^{P}_{R}/E^{P}_{S}$. A 10% decrease from 1.50 to 1.32 mm^{-1} is observed in δ with increasing C from 0 to 80 *ppm*, and then δ monotonically increases from 1.32 mm^{-1} at 80 *ppm* to 1.50 mm^{-1} at 200 *ppm*, respectively.

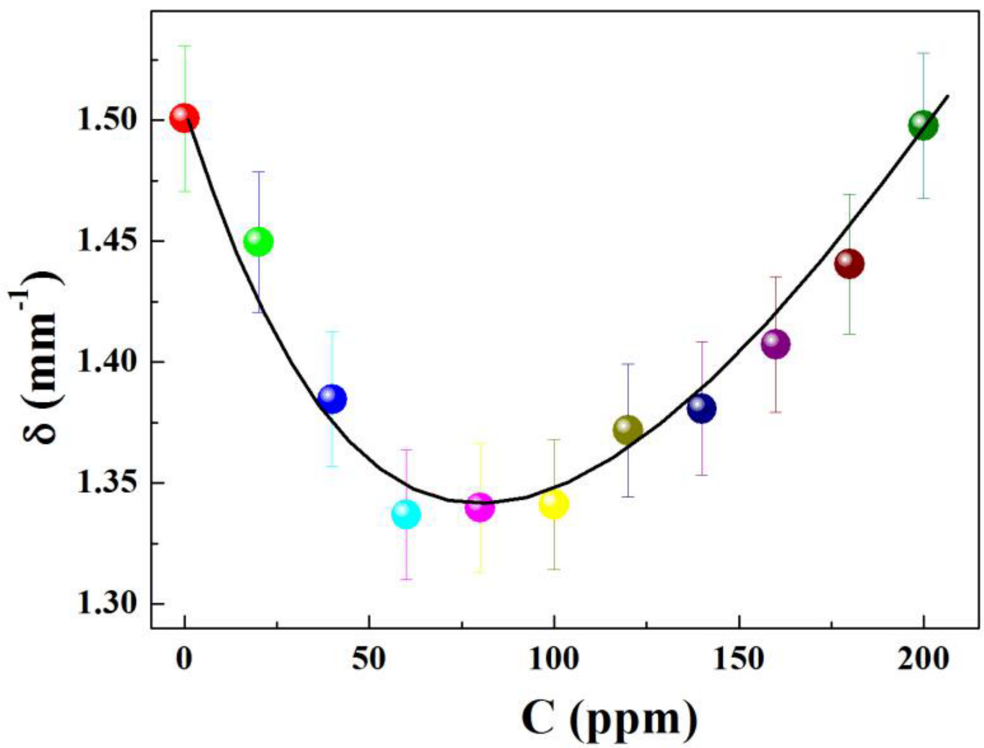

Fig. 5 Variation of δ ($=d^{-1}E^{P}_{R}/E^{P}_{S}$) with concentration C.

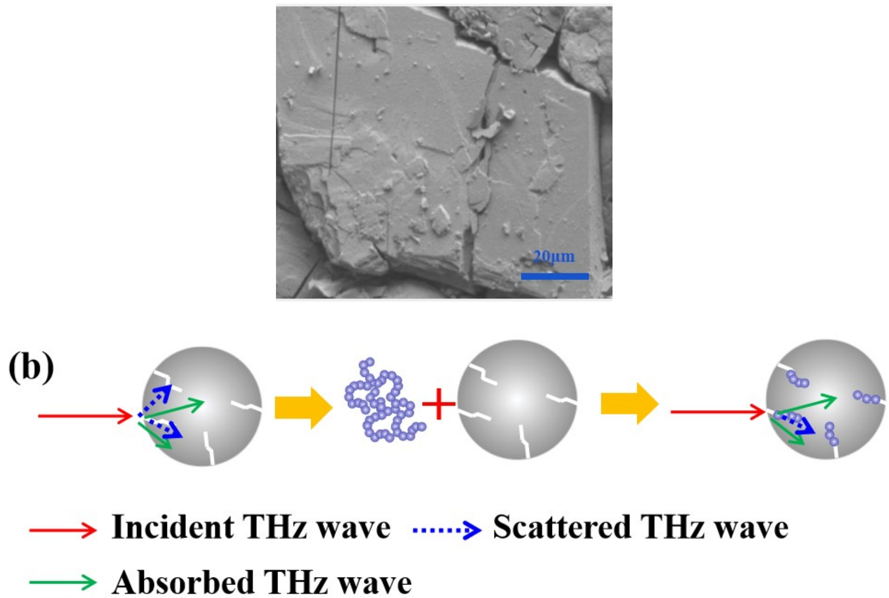

Fig. 6 (a) SEM image of quartz sand; (b) Schematic diagram of THz scattering.

In order to confirm the cause of this phenomenon, the quartz sand particles are tested by Scanning electron microscopy (SEM). SEM imaged the quartz sand particle contained abundant defect micro-fractures as shown in Figure 6(a). Different types and degrees of diagenesis significantly reshape the pore structure (size and shape, size distribution, and connectivity). Mechanical and chemical compaction, cementation and authigenic clay content are the main factors affecting pore volume-controlling, while matrix particles, cement dissolution and fracturing are the most important factors to improve porosity. Since the interaction with oil molecules is strong, the surface of the quartz sand is consequently rather oleophilic, which can adsorb the oil and makes it enter the fracture of quartz sand particles (Figure 6(b)).

Quartz sand particles are lipophilicity which makes it feasible for the oil to be fully adsorbed [14]. The sample of larger particles has greater porosity and greater scattering intensity [15]. Due to the small defects in the rock particles, the polar substances in crude oil will be adsorbed in the cracks of the rock particles, and the THz wave scattering in the sample will be reduced due to the decrease of porosity of the sample. Accordingly the δ decreased to a minimum of 1.32 mm^{-1} at ~80 *ppm*. With the further increase of crude oil content, the additional crude oil is located in the micro-fractures of quartz sand, improving the absorbance of the tablets [16]. The two factors compete with each other, leading to the phenomenon that the absorbance decreases first and then increases with crude oil concentration in tablets.

4. Conclusions

In summary, different trace amounts of crude oil mixtured with quartz sand can be quantitatively recognized by THz-TDS. CA can be combined with PCA for characterizing the trace of crude oil from different areas. The absorbance first increased and then decreased with the increase of oil content due to the adsorption effect of quartz sand on crude oil. Therefore, THz technique and multivariate statistical method is a potential choice for quantitative and qualitative identification of crude oil.

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