Assessment for less than 20-ppm oil leakage in soil using terahertz wave

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Abstract

Although an accurate detection of trace oil leaks is of the utmost important for soil protection, the typically used techniques fail to provide rapid assessment of less than 20 parts per million (ppm) of oil in soil. Terahertz (THz) time-domain spectroscopy, an optical method with high sensitivity to polar organics, was used to characterize the content of crude oil in soils. A linear model was built between the concentration of crude oil and the THz attenuation coefficient, which predicted the limit of detection ranging from 4.11 to 16.2 ppm. Some organics, such as aromatic and aliphatic compounds, contribute to larger absorption in the THz range than minerals. Effective-medium theory was optimized to elucidate the crude oil content dependence of THz dielectric constants. Consequently, THz technology could be an effective method for detecting trace oil leakage in soil.

Keywords: Terahertz spectroscopy, oil leakage, soil, effective-medium theory.
Introduction

Water, air, and soil pollution have become the most serious environmental and ecological problems with the development of industry. Awareness of the human health impacts of environmental pollution is growing rapidly. Better governance and management of the environment are required to move toward sustainable environmental resource use. Soil pollution can endanger human health and lead to serious direct economic losses, among which oil pollution is one of the most important causes of soil pollution. Oil-spill pollution can affect soil and marine resources in numerous ways. Petroleum contains refractory organic toxic substances, heavy metals, etc., which can persist and become enriched for a long time, endangering fishery safety and human health. In the early stage of a spill, oil pollution is difficult to monitor due to the small amount of leakage. Therefore, detection of the occurrence of oil spills in a timely manner and accurate prediction of subsequent spreading is the key to realizing early warning of oil-spill-area detection automatically, intelligently, and quickly.

Common methods for monitoring crude-oil leakage include infrared spectroscopy, radar, remote sensing, fluorescence spectroscopy, and gas chromatography–mass spectrometry. In infrared images, oil-spill areas present a ‘hot’ characteristic due to their absorption of solar radiation being greater than their evaporation, while non-oil-spill areas present a ‘cold’ characteristic. Mineral oil spills floating on the sea surface are detectable by imaging radars because they dampen the short surface waves that are responsible for radar backscattering. In optical remote-sensing imagery, the contrast between surface oil and non-oil water comes from two sources. The first is the sun-glint effect, which enhances the contrast of the otherwise non-observable oil due to the wave-damping effect. The aromatic hydrocarbons contained in crude oil will fluoresce under the excitation of ultraviolet light, so the fluorescence spectrum is an effective method for detecting traces of crude oil. Optical properties of the oil-water contrast have been used to characterize oil spills in marine environments. A limitation of gas
chromatography–mass spectrometry is that it can only detect a single category of substance, such as total petroleum hydrocarbons.\(^1\)

Previous studies of the detection of crude oil have not dealt with concentrations of 20 ppm or less, and researchers have considered 100 ppm as a satisfactory limit of detection (LOD).\(^4\) Furthermore, the existing technical means cannot detect trace leakage of crude oil at concentrations of less than 20 ppm. Thus, a new technology is required to distinguish soil from crude oil. The newly developed spectroscopic method, known as terahertz (THz) spectroscopy, is very sensitive to inter- and intra-molecular interactions, including van der Waals forces and especially hydrogen bonds, which range from 0.1 to 10 THz and bridge the gap between microwave and infrared spectroscopy. Crude oils are primarily composed of a variety of liquid hydrocarbons, such as alkanes, cycloalkanes, aromatic hydrocarbons, and olefins. Since the macromolecular groups in these substances show strong absorption of THz waves, THz spectroscopy offers some unique advantages and has been used in the analysis and monitoring of various materials, such as coal, petroleum, and pollutants.\(^7,8\)

The aim of the essay is to explore the relationship between the concentration of crude oil and the THz attenuation coefficient. The THz parameters were different from each other due to the different sampling locations. Therefore, principal component analysis (PCA) and Mahalanobis distance (MD) were applied to evaluate the leaking crude oil in different regions at first. And a linear model was built, predicting the limit of detection ranging from 4.11 to 16.2 ppm. Effective-medium theory was optimized to elucidate the crude oil content dependence of THz dielectric constants.

**Experimental**

A schematic representation of the entire experimental process was shown in Figure 1(a). Soil samples were collected from three different sites: soil in the campus (soil A), soil in the hillside (soil B) and soil in the park (soil C). The soil exposed on the hillside contains less organic
matter and more particulate matter. The soil in the park is selected from the side of the trees and the soil structure is loose. The looser soil without trees in the campus was chosen as the C soil. Crude oil is taken from ten different oil field. The soil between 80-120 mesh is selected to pass through the screen, and the soil with a particle size between 100-120 μm is selected to eliminate the influence of the particle size on subsequent experiments. 0.2 g selected crude oil was diluted in acetone by 10,000 times to obtain a mixed solution with a crude oil concentration $C$ of 20 ppm. The 0.5-5 g solution was mixed with 5 g soil in 50 mL acetone, which was stirred for 5 min. Then the mixture was dried at 70 °C for 20 min to evaporate the acetone, and cooled to room temperature. Thus, the soil-crude oil mixtures were prepared with the oil concentrations of 20-200 ppm, respectively. The concentration interval is 20 ppm, which is for the calculation of the subsequent limit of detection.

The dried soil and polyethylene were mixed in a ratio of 1:1 (total weight 1.6 g), and the mixed powder is pressed into a compressed sheet with a diameter of 30 mm and a thickness of 1.8±0.5 mm. The sheet samples were then analyzed using a THz time-domain spectrum (THz-TDS)\textsuperscript{19}. The analyses were performed three times for each sample and the average value was used to calculate the optical parameters. The THz field signals of samples as functions of time are shown in Figure 1(b). The peak coordinates of the reference signal are $(t_0, E_{p0})$ which is (8.7 ps, 1.7 V). The time delay of the the soil without oil’s signal was $\sim$12.3 ps due to the refraction of the THz wave in the sample. Sample absorption has contributed to the decline in THz signal from 1.8 to 1.1 V. And the soil with 100 ppm oil’s signal value was $\sim$0.5 V due to the oil absorption.

**Results and Discussion**

From Figure 2(a), we can see the differences in attenuation coefficients between Areas A, B, and C. The red model, the blue model, and the black model represent the data of the soil form
areas A, b, and c, respectively. Attenuation coefficient was calculated using $E_{P-\text{Sam}}/E_{P-\text{Ref}}$, where $E_{P-\text{Sam}}$ is the sample peak value and $E_{P-\text{Ref}}$ is the reference signal peak value. Thus, 30 samples can be divided into three main categories. According to the PCA the PC1 score is between −7 and 1 for Area A in Figure 2(b), while it is between 1 and 15 for Area C. The PC2 score is between −6 and 0 for Area B. As shown in Figure 2(c), the MD in the cluster analysis (CA) was strongly dependent on the type of crude oil, e.g., samples 4 and 5 of Area A have the largest and smallest values of −0.138 and 0.0028, respectively. Samples 3 and 10 of Area B showed MDs of −0.116 and 0.009 see Figure 2(d). It is noted that the samples with different concentrations of crude oil in a single zone were distinguished by calculating the MD, since THz waves can sensitively detect the alkane and aromatic hydrocarbon contents in crude oil.

Furthermore, five groups of samples—A1, A2, A3, B3, and C3 were prepared by combining the soil in Areas A, B, and C and crude oil 1, 2, and 3, respectively. The crude-oil concentration was changed from 20 to 200 ppm. It was found that the attenuation coefficient of the THz signal further increases with successive increases in crude-oil concentration, as shown in Figure 3, the error bars in Figure 3(a) is 1%, and the error bars in Figure 3(b) is 0.5%. The formula for calculating the error bar is 0.5% or 1% of the value in the figure. The solid lines represented linear fitting to the data and the slopes $k$ were $1.58 \times 10^{-4}$, $3.04 \times 10^{-4}$, $3.06 \times 10^{-4}$, $5.17 \times 10^{-4}$, and $1.29 \times 10^{-4}$ with respective intercepts (Inc) of 1.13, 1.12, 1.24, 1.24, and 1.27 for A1, A2, A3, B3, and C3, respectively. The attenuation coefficient is mainly dependent on the oil content although the subtle changes were observed due to the soil-crude oil interactions differing from their locations and types. The LOD can be calculated to reach 13.4, 6.99, 6.94, 4.11, and 16.2 ppm for A1, A2, A3, B3, and C3, respectively, by $\text{LOD}=3\sigma/k$, where the THz spectral noise $\sigma$ is $7\times10^{-4}$ in our setup. As expected, THz spectroscopy quantitatively detected the leakage of trace crude oil at concentrations of less than 20 ppm, which is more than the sensitivities reported in the previous literature.
The powder-form structure contained in the sample is a composite medium of oil and soil. Hence, the optical properties of composite materials are often characterized by effective-medium theory (EMT), especially, the Bruggeman (BR) theory is more suitable for small particles randomly distributed and mixed to form an aggregate structure\textsuperscript{20,21}. Different from BR theory, a typically self-consistent model in which two elements are treated equally and their properties are determined self-consistently, in this case, the effective dielectric function of the composite is given by

\[ \beta f \left( \varepsilon_1 - \varepsilon_{\text{eff}} \right) \left( \varepsilon_1 + 2 \varepsilon_{\text{eff}} \right) + \left( 1 - f \right) \left( \varepsilon_2 - \varepsilon_{\text{eff}} \right) \left( \varepsilon_2 + 2 \varepsilon_{\text{eff}} \right) = 0 \]

where \( \beta \) is correction factor, \( f \) is the volume fracture of media 1, \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric constants of media 1 and 2, respectively, and \( \varepsilon_{\text{eff}} \) represents the effective dielectric function corresponding to the two composite dielectric materials. The effective dielectric functions for two-phase systems of A2 and B3 were obtained by solving the above equation as depicted in Figure 4. Based on the dielectric constants of ~10, 11, 2.81, and 2.35 for Oil 2, Oil 3, Soil A, and Soil B, respectively, from our THz-TDS measurements, good agreement is found with the calculations, confirming the linear dependence in Figure 3.

The present sample can be described as an isotropic matrix containing spherical inclusions that are isolated from each other, and our THz-TDS measurements are a result of the two-phase-mixture composite. Although the electromagnetic interactions between pure materials and host matrices are approximately taken into account, the BR model in the EMT approaches was failure in matching the experiment until a correction factor \( \beta \) was adopted. Note that the agreement between experimental results and fitting curves directly reveals the correction factor \( \beta \) of ~300 and 500 for A2 and B3, which heavily depends on the types of crude oil and soil. THz technology has been proved to be an effective tool in oil and gas optical engineering, such as qualitatively and quantitatively detection of crude oil and inflammable oil products\textsuperscript{16,17,22}. In fact, to date, a killer application for THz wave is being expected. Machine
learning within artificial intelligence, combining THz technology, could emerge as the method of choice for addressing these scientific and engineering questions in detecting trace oil leakage.

Conclusions

The findings of this study suggest that the THz-TDS technique is an effective method for detecting trace leakage in crude oil. There exist obvious differences among all kinds of oils in soil, with different soils exhibiting different attenuation coefficient spectra in the THz range. Two multivariate statistical methods, CA and PCA, were used to build qualitative models between oils and their THz spectra. This study establishes a quantitative framework for detecting the less than 20-ppm oil leakage in soil. In addition, the LOD for the THz spectral detection curve is 4.11–16.2 ppm. Therefore, the THz-TDS technique is a potential method of selection for the detection of less than 20-ppm oil leakage in soil.

Acknowledgements

We thank the National Nature Science Foundation of China (Nos. 11804392 and 11574401), the Science Foundation of China University of Petroleum, Beijing (Nos. 2462017YJRC029, 2462018BJC005 and yjs2017019) and the Beijing Natural Science Foundation (No. 1184016) for the financial support.

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Advance Publication by J-STAGE
Received September 10, 2019; Accepted November 11, 2019; Published online on November 22, 2019
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Figure Captions

Fig. 1  Schematic of experimental process and selected transmissive THz spectroscopy.

Fig. 2  Qualitative detection of trace soil pollution. (a) Attenuation coefficient of 10 kinds of crude oil mixed in three different areas; (b) two-dimensional scatter plot generated by PCA analysis of THz absorbance spectra of Areas A, B and C; (c) MD histogram of crude oil in (c) Areas A and (d) B.

Figure 3 Depends of the attenuation coefficient on the concentration C, which ranged from 20 ppm to 200 ppm at an interval of 20 ppm for (a) mixtures of No. 3 crude oil and soil of areas A, B and C with the intercepts of 1.24, 1.24, and 1.27, respectively; (b) mixtures of No. 1, 2 crude oil and soil of areas A with the intercepts of 1.13, 1.12.

Fig. 4  Experimental (symbols) dielectric constant $\varepsilon$ and calculated (lines) dielectric constant $\varepsilon_{\text{eff}}$ as a function of f for two-phase systems of A2 and B3 shown in Figure 3. Error bars were denoted.
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Figure 4 Experimental (symbols) dielectric constant $\varepsilon$ and calculated (lines) dielectric constant $\varepsilon_{\text{eff}}$ as a function of $f$ for two-phase systems of A2 and B3 shown in Figure 3. Error bars were denoted.