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Rapidly determinating the principal components of natural gas distilled from shale with terahertz spectroscopy

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HIGHLIGHTS

- The principal components of distillated gas were determined by THz-TDS.
- Different gas components can be directly distinguished by THz-TDS.
- THz combined with BPANN can be used to quantitatively determine the properties.
- THz-TDS could be an effective method in unconventional natural gas industry.

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ABSTRACT

It is undeniable that more and more simple and rapid techniques are necessary to satisfy the increasing need of the gas detection in unconventional natural gas industry. Terahertz (THz) technique, a recently developed spectral method, was used to realize the identification and determination of the principal gas components distilled from oil shale, including methane (CH_4), ethane (C_2H_6), carbon monoxide (CO) and carbon dioxide (CO_2). An obvious variation can be observed between the components after the measurement of THz. C_2H_6 represented the largest refraction property because of the highest time delay relative to the reference, followed by CO_2, CH_4 and CO in turn. In addition, back propagation artificial neural network was employed to quantitatively characterize the components' content and the total pressure of the four-component system. The correlation coefficient of the prediction set in the quantitative model equalled 0.9955. The results indicated that THz technique combined with mathematical method is an effective tool for gas detection and can be popularized in unconventional natural gas industry.

1. Introduction

As a kind of unconventional oil and gas resource, oil shale is deemed the replacing energy due to its rich reserves and the feasibility of extraction and utilization in twenty-first century [1,2]. Kerogen, a very significant component of oil shale, is a kind of complicated polymer mixtures and mostly composed of carbon, hydrogen and oxygen elements [3]. After being distilled at a higher temperature, the oil shale can generate shale oil; meanwhile, being similar to coal gas, the effluent gas can also act as a fuel resource. The gas distilled from shale, however, is very complex and need a further treatment before being transported to consumers in actual petroleum industry. Generally, the distilled gas includes methane (CH_4), ethane (C_2H_6), carbon monoxide (CO), carbon dioxide (CO_2) and so on. In addition, a common volume ratio of CH_4:C_2H_6:CO:CO_2 is found to be 1:1.5:1:6, but this concentration is not the same with all the cases and the concentration ratio is often variant in different distillation process. Consequently, the characterization of the principal components of distillated gas is necessary and a simple and rapid technique is needed to realize the qualitative and quantitative determination in oil shale industry [4–6].

As a recently arisen spectroscopic method, terahertz time domain spectroscopy (THz-TDS) method causes more and more attention and has been implied to kinds of fields, such as biochemistry, safety, medicine quality control, food, and petroleum [7–12].

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THz technique ranges from 0.1 to 10 THz and bridges the gap between infrared and microwave. This technology is not sensitive to the thermal background radiation and has relatively high signal-to-noise ratio (SNR > 1000). Also, it can provide rich information of inter- and intra-molecular vibration as well as rotation modes and give the amplitude and phase information of sample simultaneously. Moreover, THz causes little damage to sample due to its low photon energy; therefore, THz technique can be used for online nondestructive detection. As a contactless technique, the samples, such as unconventional gas and complicated gas mixtures, can be directly detected without any sample pretreatment [13]. Some successful application of THz technique can be observed in oil shale and gas detection. The evolutionary paths of kerogen was indicated and a set of oil and gas generation points were also characterized by THz-TDS technique [14]. With regard to gas detection, polar gas reflected great absorption effect in THz range and non-polar molecules has a relatively small absorption of THz pulse [15,16]. Due to the simple measurement conditions and rapid measurement process, THz spectroscopy can provide an indirect method for the characterization of physical properties of distilled gases based on refractive and absorption effect in THz frequency range. In addition, the differences of chemistry structure in distilled gases will generate significant diversity of vibration in inter- and intra-molecules, which THz radiation is much sensitive to. Hence, THz technique is very appropriate for the detection of gas distilled from oil shale due to the significance of distillation gas research and the advantages of THz technique in gas detection field.

In this research, the principal gas components distilled from oil shale, including CH_4, C_2H_6, CO and CO_2, were qualitatively identified and quantitatively determined using THz-TDS technique. Initially, the four gases reflected different response, especially the different time delay effect, indicating that qualitative identification of the principal components can be realized. Moreover, back propagation artificial neural network was used to build a quantitative model between the THz spectra and the components concentration as well as the total pressure of the four-component mixture system. The model reflected a high correlation between the actual and the predicted properties. Therefore, the research indicated that the THz technique combined with statistical method can be a new opportunity in unconventional natural gas industry.

2. Experimental methods

2.1. Experimental setup

The experimental setup used in this research is based on a conventional THz-TDS system with transmission geometry from Zomega Terahertz Corporation and a long-length gas cell made by ourselves. A Ti:sapphire laser is utilized with a center wavelength of 800 nm, a pulse width of 100 fs, and a repetition rate of 80 MHz. As shown in Fig. 1, the femtosecond (fs) laser beam is split into a pump beam and a detection beam. The pump beam generates the THz pulse at the emitter which is composed of a photo-conductive antenna. Then the THz pulse transmits the gas cell. After transmitting the delay stage, the detection laser beam meets the gas-characteristic-carried THz pulse at a 2.8 mm-thick ⟨1 1 0⟩ ZnTe and then the THz signal will be detected through a standard lock-in technology and displayed in a computer [17]. In this study, the gas samples were filled in a 50-cm-long multi-pass cell, which was attached on the top of a vacuum chamber. The gas cell was sealed with O-rings and 10-mm-thick polytetrafluoroethylene windows, which had little reflection and absorption effect in THz range. By the insertion of two flat mirrors, the THz wave was reflected into the cell so that the total path length of sample equalled 1 m. The pressure in the cell was monitored by a capacitance manometer [18]. To minimize the absorption of water vapor in air, the setup was purged with nitrogen at room temperature. In the THz-TDS system, an intelligent data sensor was used to test the detailed measurement temperature and relative humidity, and then these data will be displayed in the computer. The temperature and humidity were 294.6 ± 0.5 K and 0–0.5%, respectively in this experiment.

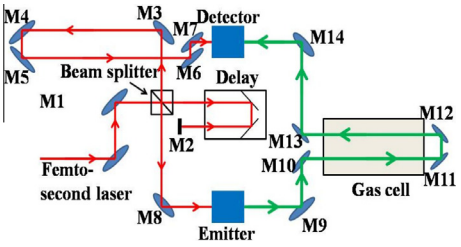

Fig. 1. THz-TDS setup for gas measurement.

2.2. Sample preparation

The measured samples in this study included methane (CH_4), ethane (C_2H_6), carbon monoxide (CO), and carbon dioxide (CO_2), all the purity of which exceeded 99.95%. To alleviate the influence of CO poisonousness, a mixture of CO and CO_2, the volume ratio of which is 1:3, was used in this research. Every kind of gas was firstly measured, and then the four-component gas mixtures were manufactured. The gas mixtures were obtained as following: the gas cell was filled with the first component, a second, third and fourth components were orderly introduced; then, the fourth component was gradually input into gas cell and the four-component mixture system with different ingredient concentration were obtained. All the corresponding parameter, such as pressure, can be displayed by the capacitance manometer.

2.3. Artificial neural networks (ANN)

ANN is a kind of normal mathematical statistical method which simulates the structure and function of the biological neural networks in human being brain. ANN can process the considered variables and learn from the present data, even when the noise exists. None of the priori models were required for ANN calculation. As shown in Fig. 2, a normal ANN algorithm included at least three layers: input, hidden, and output layer. The input layer receives and distributes a great deal of input information; the hidden layer captures the nonlinear relationship between the inputs and outputs; then an output layer produces the calculated data from hidden layer. A network with too few hidden nodes is always not enough to differentiate the complex input formation and predicted

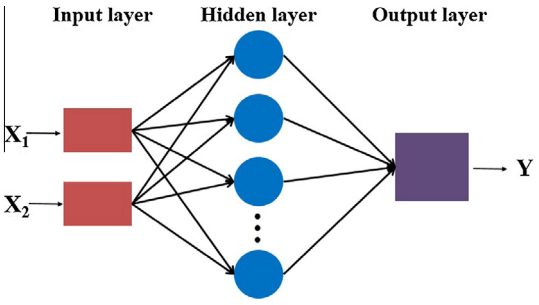

Fig. 2. Schematic diagram of ANN.