

## Quantitative determination of sulfur content in diesel using THz-TDS technology

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**Abstract:** The frequency-dependent absorption characteristics of diesels with different sulfur content have been studied in the spectral range of 0.2-1.5 THz by the terahertz time-domain spectroscopy (THz-TDS). The absorption coefficient presented a regular change with the THz frequency and sulfur content, and the absorption coefficient increases with the frequency at the same concentration, vice versa. A nonlinear multivariate model was established and the sulfur content in diesel can be confirmed easily by means of the measured THz frequency-dependent absorption coefficient. The results made the quantitative analysis of sulfur content in diesel possible by THz-TDS technology and indicated the bright future in practical application.

**Key words:** spectroscopy; sulfur content; THz time-domain spectroscopy; diesel

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## 运用太赫兹时域光谱技术定量分析柴油的含硫量

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**摘要:** 测量柴油样品的太赫兹时域光谱并对其含硫量进行了定量计算. 在0.2~1.5 THz范围内, 柴油的吸收系数随着太赫兹频率和硫含量呈规律性递增. 基于这一变化关系建立起了硫含量与太赫兹吸收系数和频率的多元非线性模型, 通过测量柴油的太赫兹光谱代入此模型即可计算出柴油的硫含量. 这一结果为太赫兹时域光谱技术应用与柴油含硫量的无损快速检测奠定了理论基础, 显示出巨大的应用前景.

**关键词:** 光谱学; 硫含量; 太赫兹时域光谱; 柴油

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### Introduction

Sulfur in diesel fuel leads directly to emission of SO<sub>2</sub> and sulfate particulate matter (PM) which endanger public health and welfare. Furthermore, the sulfur compounds in the exhaust gases of diesel engines can significantly impair the emission control technology designed to meet NO<sub>x</sub> and PM emission standards<sup>[1]</sup>.

The sulfur contents in clean diesel oil are re-

quired to be less than 500 mg/kg (0.05%). But due to the complexity of sulfur compound isomers, people have to adopt laborious and time-consuming combination technologies in the analysis of diesel oil. So there is an urgent need for a method to quickly determine the concentration of sulfur in diesel oil<sup>[2-4]</sup>.

In this paper, Terahertz spectroscopy has been used to research the sulfur content in diesel. Terahertz spectroscopy contains rich physical, chemical, and

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structural information of the materials. Most low-frequency vibrational and rotational spectra of organics and related compounds lie in this frequency range. Recently, there has been a remarkable effort in employing terahertz time-domain spectroscopy (THz-TDS) for investigating the properties of materials, including environment pollutants, semiconductors, polymers, explosive materials, oil-water complexes, and gases<sup>[5-7]</sup>. This paper illustrated the feasibility of quantitative analysis of sulfur content in diesel by THz-TDS.

## 1 Materials and method

A repetition rate of 80 MHz, diode-pump mode-locked Ti:sapphire laser (MaiTai, Spectra Physics) provided the femtosecond pulses with duration of 100 fs and center wavelength of 810 nm<sup>[8-9]</sup>. A p-type InAs wafer with  $\langle 100 \rangle$  orientation was used as the THz emitter and a 2.8 mm-thick  $\langle 110 \rangle$  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 298 K. Here, the focus diameter of the THz beam is about 1 mm.

Certified reference materials of sulfur in diesel oil were used in this study with the selected different mass percents. These samples were prepared by adding amount of n-Dibutyl sulfide (DS) to low sulfur straight-run diesel oil, in which the form of organic sulfide is close to that in commercial diesel<sup>[10]</sup>. The samples are located in the focus of the two Si lens and are held in a 10 mm thickness polyethylene cells, which are transparent for visible light and has a low refractive index and THz absorption. Both the time-domain sample and reference spectra were obtained by testing the polyethylene cell holding the sample and empty cell, respectively. After applying fast Fourier transform, we will get the frequency-domain sample

and reference spectra and calculate the absorption characters of samples<sup>[11]</sup>.

## 2 Results and discussions

Figure 1 showed the THz absorption spectra in 0.2 ~ 1.5 THz for samples with different mass fraction of sulfur 0.05%, 0.5% and 1%, respectively. The three absorption curves showed the same trend of slow upward, comprehended to be the scattering of samples or wide and structureless absorption. The absorption coefficients at the same frequency presented regularly increasing with the concentration, indicating the absorption activity of diesel with different S content in THz region and the probability of the determination of S content based on the absorption effect of the samples.

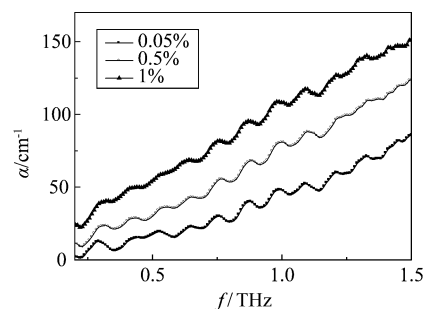


Fig. 1 Absorption coefficients of diesel with different sulfur content in 0.2 ~ 1.5 THz

图1 不同硫含量的柴油在0.2~1.5 THz波段的吸收系数

For the fact that absorption coefficient varied with both frequency and S concentration, the absorption data of the three samples were chosen to be the training set to establish a concentration-absorption model to reveal the relation between absorption coefficient  $a$ , S concentration and frequency. Placing the absorption curves to three-dimensional coordinate, as shown in the inset of Fig. 2, the absorption coefficient increased nonlinear with concentration and frequency.

Assuming that there was a curved surface running through the three curves, as shown in Fig. 2, it can be deduced that the diesels with various S concentration were all in this surface. As a result, the S concentration will be confirmed by putting its frequency-dependent absorption coefficient to this surface. A fitted dibasic regression curved surface equation with the Poly2D method then has been presented as below:

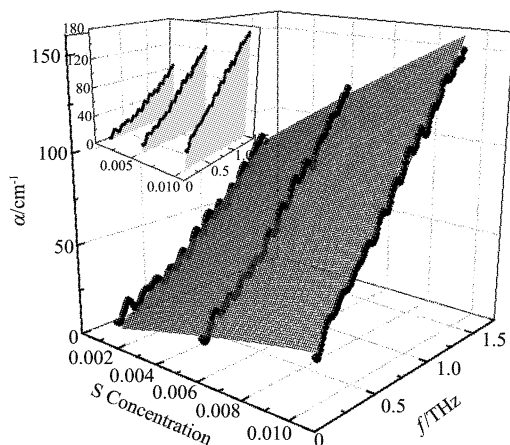


Fig. 2 Three-dimensional coordinate of absorption coefficients of diesels associated with frequency and concentration

图2 柴油吸收系数三维座标

$$F(x, y) = ax^2 + bx + cxy + dy + ey^2 + f, \quad (1)$$

where  $F(x, y)$  is the absorption coefficient,  $x$  is the S concentration and  $y$  is the frequency and the parameters are:  $a = -61\,219.543\,48$ ,  $b = 2\,808.856\,78$ ,  $c = 3\,933.860\,34$ ,  $d = 40.608\,46$ ,  $e = 12.596\,67$ ,  $f = -11.377\,21$ .

Figure 3 is the diagram of fitted and measured curves of 0.05%, 0.5% and 1% samples, in which the empty and solid icons are the measured and simulated spectra respective. Root mean square error (RMSE) and relative error (RE) of prediction were considered here, described in Eqs. (2-3).

$$\text{REME} = \sqrt{\frac{1}{N} \sum_{i=1}^N (F_{\text{calu}} - F_{\text{meas}})^2}, \quad (2)$$

$$\text{RE} = \frac{|F_{\text{calu}} - F_{\text{meas}}|}{F_{\text{meas}}} \times 100\%, \quad (3)$$

where  $N$  is the number of samples,  $F_{\text{calu}}$  and  $F_{\text{meas}}$  are the calculated and measured absorption coefficients, respectively. By Eqs. (2-3), the RMSE and RE were calculated as 3.5 and  $< 15\%$ , indicating the good agreement of simulated surface and measured curves.

To verify the performance of the fitted model, the THz absorption coefficients of diesel with the S concentration of 0.1%, as testing set, have been measured in 0.2 ~ 1.2 THz. Figure 4 is the obtained absorption curve in fitted curved surface, showing that the curve was nearly in the surface. Substituting the

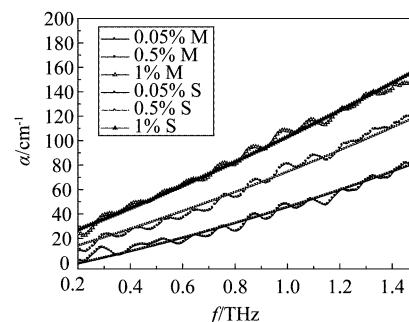


Fig. 3 The fitting and measured curves of 0.05%, 0.5% and 1% samples

图3 硫含量分别为0.05%、0.5%和1%的三种样品测量所得吸收曲线与计算曲线的对比

measured absorption coefficient and frequency into Eq. (1), the concentration of diesel can be calculated.

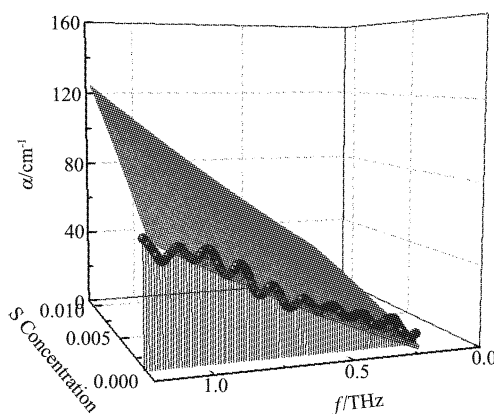


Fig. 4 the measured absorption curve of 0.1% sample in fitting curved surface

图4 硫含量为0.1%的样品吸收曲线在拟合曲面中的图示

Figure 5 is the result of calculation. The solid symbols are the known concentration and the empty symbol is the calculated one. In this figure, the four concentrations were presented and the calculated concentration was around the actual content of 0.1% closely, demonstrating a good agreement and the effectiveness of the built model. The RMSE and RE calculated by Eqs. (2-3) were 0.033% and  $< 20\%$ , showing certain residual. This may be originated from the oscillation in measured absorption spectra. To minimize the oscillation and improve the accuracy, the improvement of signal noise ratio and the influence of Fabry-Perot reflection should be considered in future<sup>[12]</sup>.

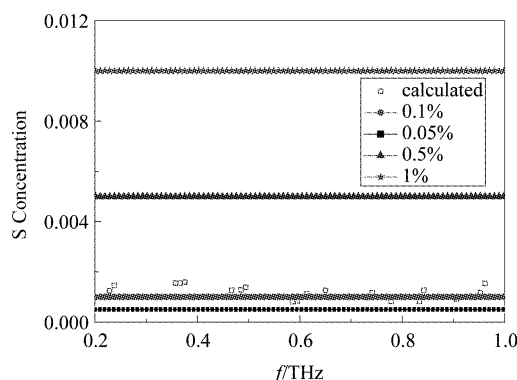


Fig. 5 the calculated concentration compared to the actual value of 0.1% sample

图5 样品计算所得硫含量与实际值的对比

From above, the S concentration of diesel will be confirmed easily by measuring its THz absorption spectroscopy. Comparing to the shortcomings of traditional analysis of expensive, laborious, and time-consuming, mentioned in Ref. 2-4, the THz-TDS technology needs 5 ~ 10 mL sample only and spend just 3 ~ 5 minutes. The low energy of 4.2 meV ensures THz a safety technology to prevent diesel from combustion or explosion when taking measurement.

### 3 Conclusions

The diesels with different sulfur content have been studied using THz-TDS technology. The terahertz absorption curves of four diesel samples are all in the same curved surface and the sulfur content of diesel was obtained by the built absorption-concentration model by measuring the absorption spectra. The investigations have illustrated that THz-TDS was an effective method to distinguish the diesels with different sulfur content and it will be a promising approach for sulfur concentration analysis no matter on line or field monitoring.

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