Front. Optoelectron. 2018, 11(3): 256–260
https://doi.org/10.1007/s12200-018-0805-1

RESEARCH ARTICLE

Identifying $PM_{2.5}$ samples collected in different environment by using terahertz time-domain spectroscopy

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Abstract Particulate matter with the diameter of less than 2.5 μm ($PM_{2.5}$) is the most important causation of air pollution. In this study, $PM_{2.5}$ samples were collected in three different environment including ordinary atmospheric environment, lampblack environment and the environment with an air conditioning exhaust fan, and analyzed by using terahertz time-domain spectroscopy (THz-TDS). The linear regression analysis and the principal component analysis (PCA) are used to identify $PM_{2.5}$ samples collected in different environment. The results indicate that combining THz-TDS with statistical methods can serve as a contactless and efficient approach to identify air pollutants in different environment.

Keywords $PM_{2.5}$, terahertz time-domain spectroscopy (THz-TDS), statistical methods

1 Introduction

At present, atmospheric particulate matter (PM) is universally acknowledged to be the primary pollutant in the air. It is made up of a mixture of solid and aqueous species which dispersed in the aerosol system. PM can enter the atmosphere by anthropogenic and natural pathways [1]. In the past decades, city air pollution has become a global issue because of industrial expansion and traffic-related emission. $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) is a major contributor to air pollution. It has many special characteristics including small size, large area, and strong activity. $PM_{2.5}$ can reside long time and transmit large distance in air and it has adverse effects on human respiratory health as well as on air visibility [2,3]. The relationship between exposure to particles and adverse health effects is currently under close scrutiny. Many epidemiological studies corroborate the elevated risk for cardiovascular events associated with exposure to $PM_{2.5}$ such as myocardial infarction, stroke, arrhythmia, and heart failure exacerbation [4–6]. Therefore, reducing air pollution is one of the most important things for the government to protect the environment.

The composition of $PM_{2.5}$ is complicated. Both the levels and composition of ambient air $PM_{2.5}$ depend on the climatology, geography and the human activities [7]. Major contributors to $PM_{2.5}$ include organic carbon, elemental carbon, nitrate, sulfate and ammonium [8,9]. The source of air pollution mainly include emissions from vehicles, fired-coal, dust, industrial production and biomass burning [10]. Identifying the main sources of pollutants and distinguishing the main types of pollutants determine the efficiency of pollution protection. However, normal PM monitoring approaches are very sensitive to $PM_{2.5}$ concentrations, but identifying pollution sources remains challenging. With the developments of ultrashort pulse laser, semiconductors, and optical detectors, the terahertz time-domain spectroscopy (THz-TDS) has advanced rapidly. It has become an important tool for non-contact identification and classification of various materials [11–13]. Recently, terahertz (THz) technique drew a high attention due to a series of reports in application of pollutant. It was proved that the THz wave amplitude gradually decreased with the increase of $PM_{2.5}$ concentration and the absorbance of $PM_{2.5}$ increased. Moreover, a linear relationship was found between THz peak intensities and $PM_{2.5}$ mass. Based on the THz absorbance spectra of $PM_{2.5}$ samples, the two-dimensional correlation spectroscopy was used to study the elemental compositions of $PM_{2.5}$. When the $PM_{2.5}$ samples were collected in the first red-alert air pollution period and the normal high-pollution conditions, it was found that sulfate types were different by comparing features in synchronous and asynchronous plots of these spectra. We can conclude that the THz-TDS technique can be used to characterize $PM_{2.5}$ in the atmosphere [14–18].

Received January 29, 2018; accepted May 15, 2018

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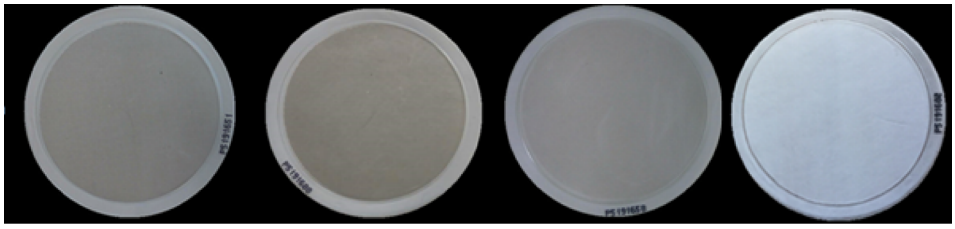

Fig. 1 $PM_{2.5}$ samples collected in different environment. (a) Ordinary atmospheric environment; (b) lampblack environment; (c) environment with an air conditioning exhaust fan; (d) blank filter

In this study, the $PM_{2.5}$ samples were collected from three different environment. And a basic study was performed about the THz dielectric effect of these samples. Accordingly analysis of the THz-TDS, using the linear regression modeling, linear relationship was found between THz peak intensities and $PM_{2.5}$ mass. However, the relationship is different when the environment where the samples were collected from is different. Principal component analysis (PCA) was applied to all of $PM_{2.5}$ sample spectra to identify the sources. The samples are clearly divided into three different groups in the principal component (PC) distributions.

2 Experimental methods

$PM_{2.5}$ samples were collected in three different environment including ordinary atmospheric environment, lampblack environment and the environment with an air conditioning exhaust fan. An air sampler (Minivol Tactical Air Sampler) was used to collect $PM_{2.5}$ samples and the air flow rate was set as 7 L/min. In the PM sampling mode, air was drawn through two separators that removes particles with aerodynamic diameters greater than 2.5 μm. The separators are designed for $PM_{2.5}$ with cut-offs of 10 and 2.5 μm. $PM_{2.5}$ samples for THz-TDS determination were collected on 47 mm diameter polytetrafluoroethylene (PTFE) filters with a polypropylene support ring. Each PTFE filter was weighed twice before and after the sampling of $PM_{2.5}$. So the mass of $PM_{2.5}$ can be calculated by subtracting the average of the pre-sampling weights from the average of the post-sampling weights. The $PM_{2.5}$ samples collected in three different environment and the filter without $PM_{2.5}$ were shown in Fig. 1.

In the experiment, a standard THz-TDS setup was used. Both the THz-TDS of samples and reference were obtained by testing the PTFE filters with and without $PM_{2.5}$. Fast Fourier transform (FFT) was used for deriving the THz frequency domain spectra (THz-FDS). According to the derived spectra, THz absorbance spectra can be calculated. Multivariate statistical method, specifically PCA, was adopted to identify the sources of $PM_{2.5}$ with the input of absorbance spectra. PCA can reduce the number of dimensions within the data and identify potential structure of large spectral data as well as groups. PCs, the results calculated by PCA, can reflect as much of overall variation as possible. PCA method has been applied in many fields.

3 Results and discussion

Figure 1 showed the $PM_{2.5}$ samples collected in three different environment and the filter without $PM_{2.5}$. The filters with $PM_{2.5}$ were different from the blank filter at color. However, it is impossible to identify the source of the $PM_{2.5}$ samples by their color. So we performed a basic study of THz dielectric effect of $PM_{2.5}$ samples with different mass collected in three different environment. Figure 2 showed the THz-TDS, the THz field signal amplitude as a function of time delay between pump and probe after the transmission of the THz pulse through the filters with and without $PM_{2.5}$. The air (in normal atmosphere) was also tested as a reference. The THz signal peak intensities of samples were smaller than that of blank filter and air. The result indicated that $PM_{2.5}$ had obvious absorption and showed district properties in THz range. However these spectra are still highly overlapped in Fig. 2. And we can't identify the $PM_{2.5}$ samples collected in different environment.

To identify the source of these different samples of

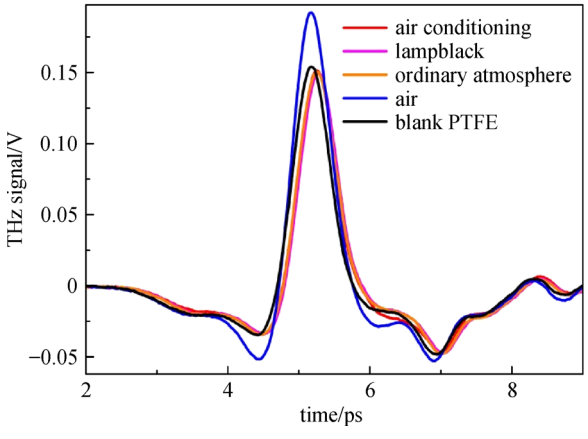

Fig. 2 THz-TDS of samples and air

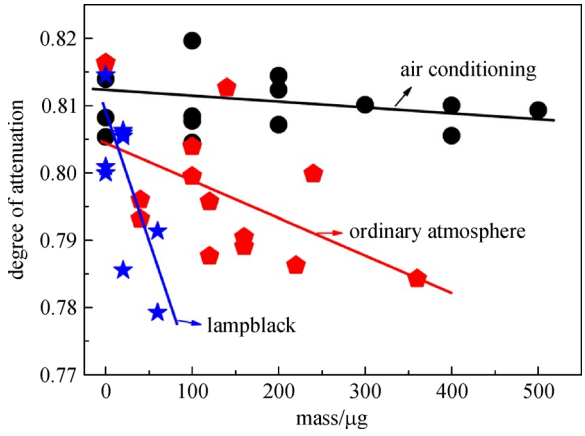

Fig. 3 $PM_{2.5}$ mass dependent the degree of attenuation

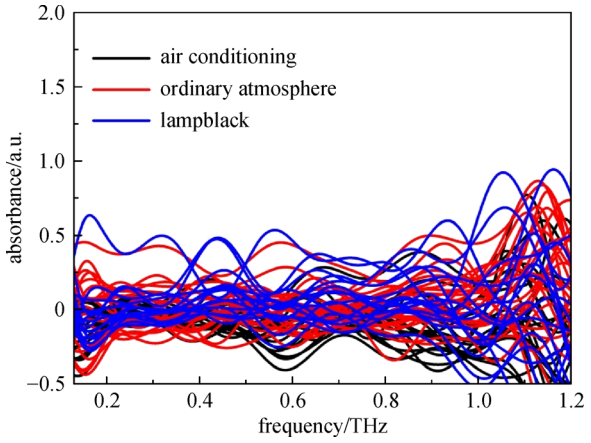

Fig. 4 Frequency dependence of the absorbance spectra for $PM_{2.5}$ samples collected in three different environment

$PM_{2.5}$, the peak intensity E_p of these spectra were used. The degree of THz signal attenuation were calculated by the peak intensity E_p of samples and air. And we described $PM_{2.5}$ mass dependent the degree of THz signal attenuation as shown in Fig. 3. It can be observed that the degree of THz signal attenuation decreased with the increase of $PM_{2.5}$ mass. According to the collected tendency, it can be proved that the degree of THz signal attenuation reflected linear relation with the mass of $PM_{2.5}$. However, the relationship between the degree of THz signal attenuation and $PM_{2.5}$ mass is different when the $PM_{2.5}$ samples were collected in different environment. The linear regression analysis was used to describe the three linear relation. When the samples were collected in the environment with an air conditioning exhaust fan, the linear function can be described as $y = -1.918\text{E}-06x + 0.81$. And when the samples collected in lampblack environment, it can be described as $y = -3.349\text{E}-04x + 0.0.806$. The linear function of the samples collected in ordinary atmospheric environment is $y = -4.4469\text{E}-05x + 0.807$. From the results of linear regression analysis, it can be found that the slopes of the three lines were different. According to this, we can identify the source of the $PM_{2.5}$.

Based on the THz-TDS, the THz frequency-domain spectroscopy (THz-FDS) can also be calculated by FFT. According to the formula $A = -\log(E_S(\omega)/E_R(\omega))$, where $E_S(\omega)$ and $E_R(\omega)$ were the amplitudes of the sample and reference in the FDS, the frequency dependent absorbance A spectra can be obtained. The frequency-dependent absorption spectra of the $PM_{2.5}$ samples collected in three different environment that we described above at a frequency range of 0.2 – 1.2 THz (i.e., the effective frequency range) was shown in Fig. 4. Because of the existence of excessive datapoints, the errobars are not shown in Fig. 4 to ensure that the spectra are clearer. As shown in Fig. 4, the absorbance values of the $PM_{2.5}$ samples varied in the frequency range from 0.2 to 1.2 THz. No sharp absorption features are observed in the effective frequency range. These spectra are still highly overlapped (Fig. 4). And they can be distinguished using other methods such as the PCA.

To detect and distinguish the spectra of $PM_{2.5}$ samples collected in different environment, the PCA is employed to cluster the $PM_{2.5}$ samples collected in the same environment by using THz absorbance spectra as the input. The spectral pretreatments are not performed. PCA is a widely used statistical analysis technique for dimension reduction achieved. PCA project a data set into a space defined by the PCs of the data. The PCs are related to the original variable and reflects the information about the samples. When the PC scores are plotted against each other, a two-dimensional or three-dimensional scoring space can be obtained [19]. The PCA score projection groups samples with similar characteristics together in the new coordinate system and provides a means to see if the sample types used can be differentiated. In this study, three groups of spectral absorbance data, each of which follows an ascending order according to $PM_{2.5}$ mass, were combined in the order of the environment with an air conditioning exhaust fan, ordinary atmospheric environment and lampblack environment. The first two PCs are employed here.

To determine the degree of separation of the feature vectors associated with the THz absorbance spectra from the $PM_{2.5}$ samples collected in different environment, the scores of PCs are used and plotted in Fig. 5, where the position of each sample is reported in a two-dimensional space for the two PCs (PC1 and PC2). The X and Y axes indicate the scores of PC1 and PC2. In Fig. 5, it can be shown that the first two PCs of the data account for 63.99% of the total variance within the data, i.e., PC1 explained 45.32% and PC2 18.66. And we found that the $PM_{2.5}$ samples collected in different environment demonstrate obvious divergence. Therefore, PCA is used to identify groups within the data and is performed on the scores of the first two PCs instead of on the original absorbance data to obtain suitable classification; thus, differentiating

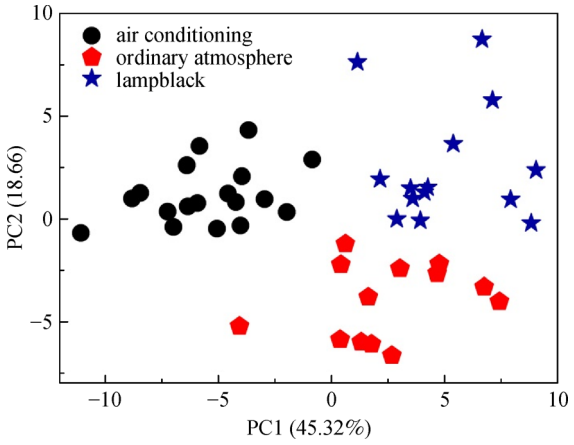

Fig. 5 Two-dimensional system of PC1 versus PC2 plot calculated by PC

the $PM_{2.5}$ samples collected in different environment is easier.

4 Conclusion

In this work, we verify qualitatively identifying $PM_{2.5}$ samples collected in different environment including ordinary atmospheric environment, lampblack environment and the environment with an air conditioning exhaust fan by using the terahertz time-domain spectroscopy. The linear regression analysis and the PCA were employed to classify the $PM_{2.5}$ samples collected in different environment. The results indicate that combining THz-TDS with statistical methods can serve as a contactless and efficient approach to identifying air pollutants in different environment.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 11574401) and the National Basic Research Program of China (No. 2014CB744302).

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