



FTIR of Soils from Different Areas of China

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Fourier transform infrared spectroscopy (FTIR) was used to study five different types of soil. The results showed that the infrared spectra of soil were mainly composed of the absorption band of inorganic salts, such as carbonate, nitrate, phosphate, manganate, *etc.*, clay minerals and the organic matter. FTIR spectra of five types of soils are similar on the whole, but they present obvious difference in the range of 1600-750 cm^{-1} . According to the first derivative spectra of five types of soils, the differences were mainly found displaying in the range of 1440, 875 and 798-780 cm^{-1} . The first derivative data of the range of 1600-750 cm^{-1} were selected to use the Matlab 2010 to implement the principal component analysis, the contributing rates of the first two principal components had reached 90.14 %, which can reflect the main information in the spectra. The two-dimensional distribution was made by plotting these two principal components as scores plots, which provided a reliable and rapid method for the identification of soil type. It is demonstrated that FTIR technique is rapid, nondestructive, convenient, accurate and has a great potential for application.

Keywords: FTIR, Soil, Principal component analysis, Soil identification.

INTRODUCTION

Soil is not only the undertaker of crops production, but also provides a suitable ecological environment for human beings, which is the important carrier of biological survival. Currently, there are a large population with relatively little arable, in face of the great pressure of survival and development, preserving ecological environment, maintaining sustainable development of farmland are particularly important for soil research. Traditional laboratory methods of soil analysis are based on chemical analysis, which provide a strong support for soil study, but the analysis process is very complex since soil is a complex mixture of minerals, oxides, organic matter, microorganisms and other compounds. Meanwhile it can be achieved frequently under the condition of destructing the original samples and some indicators are difficult to reflect the actual circumstances of the soil, it can also generate great chemical pollution¹. In this regard, currently many new techniques and methods would be used to replace traditional soil analysis, infrared spectroscopy not only can reflect the material compositions and interactions of the soil system, but can also achieve rapid, nondestructive and sustainable development.

Spectroscopy, both in the near-infrared (NIR) and mid-infrared (MIR) ranges, is a promising technology for soil analysis, as reported by Gao², who had adopted near infrared spectroscopy technology to realize the analysis of soil nutrient.

Du¹ had studied on the mid-infrared photoacoustic spectroscopy of soil, Rossel *et al.*³ compared the merits of quantitative models of the soil parameters using the diffuse reflectance spectroscopy of visible, near infrared and mid-infrared respectively. But they only focused on soil limited to narrow areas. In this paper, soil collected from extensive areas in China, fourier transform infrared spectroscopy combined with principal component analysis (PCA) had been used to study on five different types of soil.

EXPERIMENTAL

Fourier transform infrared spectra were recorded using Frontier FTIR spectrometer (PerkinElmer, America) equipped with DTGS detector in the region of 4000-400 cm^{-1} at a resolution 4 cm^{-1} . Each spectrum was acquired by adding together 16 scans.

Fifty topsoil samples were collected from field of Luoyang, Henan province, Kunming, Yunnan province, Jining Shandong province, Baiyin, Gansu province and Huludao, Liaoning province. They were respectively aquic soil, red soil, brown soil, Loess and yellow soil. Ten samples of each soil type were collected, the powders of soil samples and KBr were placed in an oven for drying, the soil samples were grinded with KBr in the agate mortar after drying. Each pellet was composed of 1 mg of sample powder mixture with 150 mg of pure KBr dried powder and pressed into a disc. The reference spectrum

was acquired by collecting the spectrum of pure KBr disc, KBr background was subtracted from each raw spectrum. Spectral software OMNIC 8.0 was used for baseline correction, normalization and smoothing. The statistical software (Matlab 2010) was used to realize principal component analysis.

RESULTS AND DISCUSSION

Spectral characteristics of five types of soils: Fig. 1 showed the average infrared spectra of five types of soils. The FTIR spectra were similar on the whole. Clear absorption peaks were showed in several spectral regions, as follows: the absorption peak about 3700 cm^{-1} was attributed to the Si-O stretching vibration in kaolin⁴. The absorption peak near 3420 cm^{-1} was attributed to the -OH stretching vibration. The spectral absorption peak near 1630 cm^{-1} mainly showed the deformation vibration of H_2O ; the spectral peaks of soils a and e near 1440 cm^{-1} showed asymmetric stretching vibration⁵ of CO_3^{2-} . The absorption peak at about 1370 cm^{-1} was attributed to the bending vibration⁶ of NO_3^- . The spectral absorption peak near 1030 cm^{-1} was Si-O-Si stretching vibration of Kaolinite⁷. The weak peak at about 430 cm^{-1} was attributed to symmetric deformation vibration⁸ of PO_4^{3-} . The spectral peaks in the range of $850\text{--}840\text{ cm}^{-1}$, $920\text{--}890\text{ cm}^{-1}$ mainly showed the absorption region¹ of MnO_4^{2-} . The weak doublets at about 780 cm^{-1} , 798 cm^{-1} were attributed to Si-O-Si symmetric stretching vibration in silica⁹. The absorption peak at about 695 cm^{-1} was attributed to the -OH bending vibration. The absorption peak at about 525 cm^{-1} showed Si-O-Mg, Si-O-Al bending vibration¹⁰. The wave number near 470 cm^{-1} showed Si-O-Si bending vibration in silica⁹.

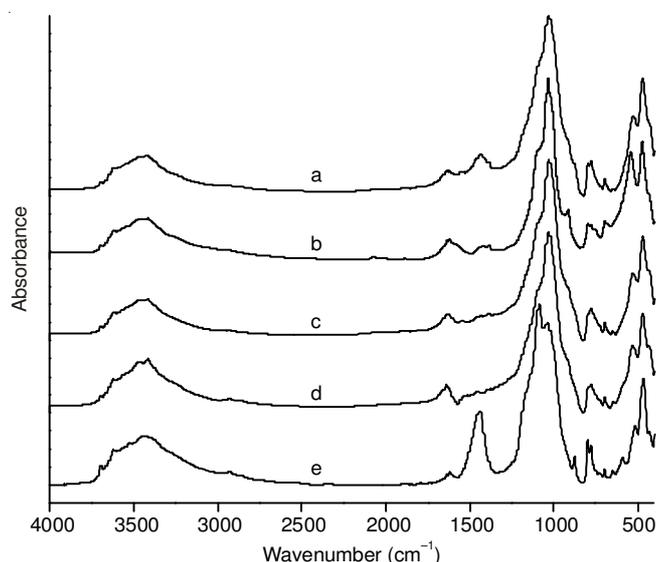


Fig. 1. FTIR spectra of five different types of soil: a. Aquic soil (Luoyang); b. Red soil (Chengong); c. Brown soil (Jining); d. Yellow soil (Huludao); e. Desert soil (Baiyin)

The spectral band near 2925 cm^{-1} were the absorption of organic matter¹¹. Fig. 1 showed that the absorption peak near 2925 cm^{-1} was relatively weak, which indicated that the content of organic matter was low in soil.

Quartz is the primary minerals, which is most difficult for weathering in the soil, the infrared spectra of soil near

$780, 799\text{ cm}^{-1}$ displayed the existence of double peak, which were attributed to Si-O-Si symmetric stretching vibration⁹, this double peak is composed of two characteristic absorption peaks of quartz. But from loess in baiyin to aquatic soil of Luoyang, the twin peaks gradually weakened, there was only a single peak near 780 cm^{-1} in brown soil of jining, which indicated that the weathering degree of soil increased gradually from loess to aquatic soil, until to brown soil, quartz had weathered severely, which had formed certain amount of amorphous oxide silicon¹².

First derivative spectra of five types of soils: Fig. 1 showed that the spectral differences were not obvious in the $1600\text{--}750\text{ cm}^{-1}$ region. As the derivative spectrum has higher resolution and can display more molecular information, so the first derivative spectrum was used for further distinguishing samples (Fig. 2). The first derivative average spectrum of sample a was different from the others at about 1440 cm^{-1} , which was attributed to the antisymmetric stretching vibration of CO_3^{2-} . The first derivative average spectrum of sample e was significantly different from the other four types of samples at about 875 cm^{-1} , which was attributed to the out-of-plane bending vibration of CO_3^{2-} in calcite. The first derivative average spectrum of sample b was significantly different from the others in the range of $798\text{--}780\text{ cm}^{-1}$, which could be attributed to Si-O-Si symmetrical stretching vibration in silica.

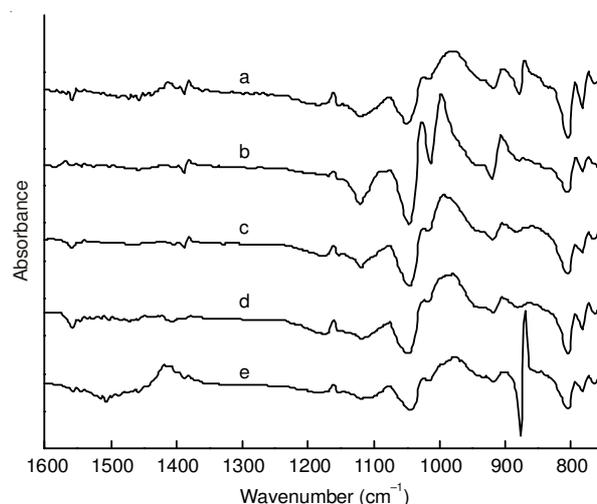


Fig. 2. First derivative spectra of five types of soil in the range of $1600\text{--}750\text{ cm}^{-1}$: a. Aquic soil (Luo yang); b. Red soil (Chengong); c. Brown soil (Ji ning); d. Yellow soil (Hu ludao); e. Desert soil (Bai yin)

Principal component analysis: The principal component analysis can not only reduce the data dimensionality, but also determine each sample belonging to which classes by scores scatter plot¹³. The first derivative spectra in the range of $1600\text{--}500\text{ cm}^{-1}$ were selected to use Matlab 2010 to perform the principal component analysis. The corresponding eigenvalues and the contribution rates of the first four principal components were showed in Table-1.

As can be seen from Table-1, the contributing rate of PC1 was 73.08 %, the contributing rate of PC2 was 15.87 %, the contributing rate of PC3 was 6.70 %. The cumulative contributing rates of the first three principal components had reached 95.65 %, which contained 95.65 % spectrum information of

TABLE-1
EIGENVALUES AND CONTRIBUTING RATE
OF PRINCIPAL COMPONENTS

PC	Eigen values	Contributing rate (%)	Cumulative contributing rates (%)
PC1	3.34	82.84	82.84
PC2	0.29	7.30	90.14
PC3	0.24	5.82	95.96

all, so the first three principal components could be used to show the similar relation between the samples.

Analysis of FTIR loading plots was showed in Fig. 3, two positive absorption band are observed in the range of 1470-1420 and 980-960 cm^{-1} , which belonged to the sensitive feature areas of PC1; from the loadings plot of PC2, there was a higher degree of correlation in the range of 1160-1140 cm^{-1} , 985-975 cm^{-1} ; from the loadings plot of PC3, two positive absorption band are observed in the range of 1450-1430 and 1095-1085 cm^{-1} , which indicated a higher correlation. The results showed that the first three principal components could be used to characterize the similarity of different soil samples, which also had certain feasibility and reliability.

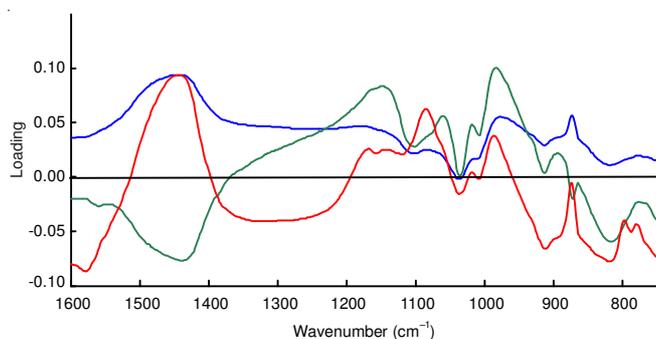


Fig. 3. PCA loadings plot (1600-750 cm^{-1}): 1. Loading PC1; 2. Loading PC2; 3. Loading PC3

Fig. 4 showed the two-dimensional score plots of PC1 and PC2, it can be seen that the soil samples of aquatic soil, red soil and loess could be significantly separated. They were

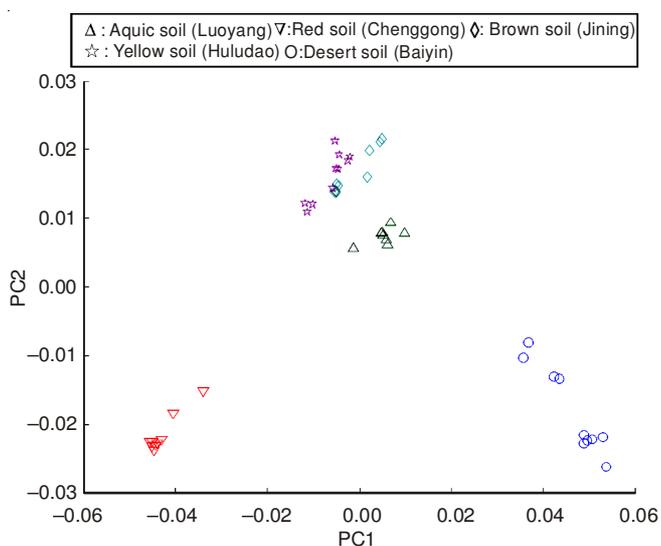


Fig. 4. Principal component analysis scores plots of fifty samples on the first derivative (1600-750 cm^{-1})

sui generis, but the clustering effect of loess in Baiyin was not very good, some samples of yellow soil and brown soil mixed together, thus they could not be well distinguished, but all the samples were better clustered and identified by the two-dimensional score plots on the whole, which can provide a reliable method for the soil identification.

Conclusion

Five different types of soils had been studied by Fourier transform infrared spectra, the results showed that the absorption band of infrared spectrum were mainly composed of inorganic salts, such as carbonates, nitrates, phosphates, manganate, etc., clay minerals and organic matter, the first derivative data of the range of 1600-750 cm^{-1} were selected to use Matlab 2010 to perform the principal component analysis, the contribution rates of the first three principal components and the principal component analysis loadings plot can reflect the main information in the spectra. The two-dimensional score plots is plotted by the first two principal components to classify the soil type. The results indicated that this distribution could be applied to distinguish soil type reliably, meanwhile, it showed that FTIR technique might be used to study the soil, which owns the advantages of rapid and convenient measurement, nondestructive testing and accuracy.

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