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Short communication

A new volatiles-based differentiation method of Chinese spirits using longpath gas-phase infrared spectroscopy

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ABSTRACT

The volatile compounds of different brands of Chinese spirits differ with respect to their composition and concentration. The infrared spectral characteristics of volatile gases from several brands of Chinese spirits were studied. We used a longpath gas cell to enhance the performance of the gas-phase infrared spectroscopy. Principal component analysis (PCA) was used for the discrimination of the different brands of spirits. It is demonstrated that different brands of Chinese spirits with the same flavour and from the same origin can be successfully differentiated.

1. Introduction

Chinese spirit is a popular drink in China for its special aroma. It has been verified by gas chromatography–mass spectrometry (GC–MS) that the volatile compounds from Chinese spirits include alcohols, esters and organic acid (Du, Fan, & Xu, 2011; Fan & Qian, 2006). The volatiles from several brands of Chinese spirits were studied by ambient glow discharge ionisation mass spectrometry and principal component analysis (PCA) and it was demonstrated that this method was able to differentiate different kinds of Chinese spirits without a pretreatment process (Zhen et al., 2013).

Gas-phase infrared spectroscopy is considered as an effective tool for the quantitative and qualitative measurement of unknown volatiles because most organic compounds have clear infrared fingerprint spectral characteristics (Griffiths & Haseth, 2007). Due to its high sensitivity, gas-phase infrared spectroscopy is also used for non-contact determination of trace gases and the remote detection of unknown gases (Bacsik, McGregor, & Mink, 2006; Barrancos et al., 2013; Love, Goff, Counce, Siebe, & Delgado, 1998; Ross & Todd, 2002). Researchers have used infrared spectrometer to measure the volatiles vaporised from food and fruits (Dong et al., 2013; Harren & Cristescu, 2013; Wang et al., 2013), and have demonstrated that it is possible to monitor the spoilage stages of fruits as the composition and concentration of the volatiles changed with deterioration.

Fourier transform infrared spectrometer (FTIR) is flexible in application and can even work in a remote-detection style (Griffiths & Haseth, 2007). There are some works that used infrared spectroscopy to analyse and classify different kinds of spirits, but all of these studies were based on liquid-phase samples (Li, Wei, Zhou, & Sun, 2008; Liua et al., 2008; McIntyre, Bilyk, Nordon, Colquhoun, & Littlejohn, 2011; Palma & Barroso, 2002; Picque et al., 2006; Yu, Ying, Fu, & Lu, 2006). In this study, we analysed the fingerprint infrared spectral characteristics of volatiles from different brands of Chinese spirits and were able to differentiate them using chemometric methods. To the best of our knowledge, this is the first study aiming differentiate spirits using gas-phase infrared spectroscopy based on the volatiles vaporised from the spirits.

2. Materials and methods

Table 1 shows the samples names, code names, flavours and origins of the spirits used in this study. All of the spirits names are commercial names. Nine different brands of Chinese spirits were used. The alcohol degrees of these spirits were between 35% and 53%. For the analysis, 100 µl spirit sample were diluted with 20 ml distilled water, and then placed into a sealed 1000 ml container. The absorbance infrared spectra of the gases can be described by Beer–Lambert law. Thus, it is possible to enhance the sensitivity of spectrometer by increasing the optical path of the measured gas (Griffiths & Haseth, 2007). For this reason, multi-reflecting mirrors were adopted to increase the optical path of the gas cell to 2 m. A mid-infrared light source was on one side of the gas cell, whilst the FTIR detector was on the other side. The optical layout of the experimental system is shown in Fig. 1. The sensitivity of the spectrometer was much enhanced by using longpath gas cell; more details on this can be found in another

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Table 1
Code name, flavour and geographical origin of spirit samples.

Spirit code	Spirit samples	Flavour	Geographical origin	Alcohol degree (%)
A	Guizhouchun (A)	Luzhou	Guizhou	35
B	Wuliangchun (B)	Luzhou	Sichuan	50
C	Fenjiu (C)	Fen	Shanxi	53
D	Kouzijiao (D)	Both Fen and Luzhou	Anhui	46
E	Gaoliang (E)	Fen	Taiwan	45
F	Red Star Erguotou (F)	Fen	Beijing	52
G	Luzhouteniang (G)	Luzhou	Sichuan	52
H	Wuliangye (H)	Luzhou	Sichuan	52
I	Jinliufu (I)	Luzhou	Sichuan	52

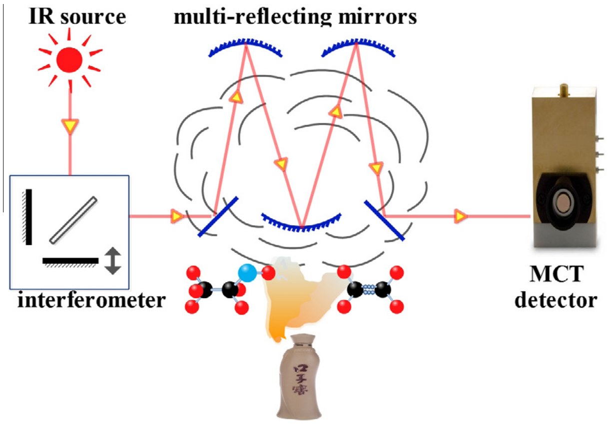

Fig. 1. Layout of the experimental system.

published study which used the same optical layout with this work (Dong et al., 2013), which used a same optical layout with this work. The container was sealed for 5 min before the experiment. The volatiles from spirits vaporise naturally at a temperature of 22 °C. The valotiles from the sample container was filled into the gas cell by the air pump (Dong et al., 2013). The spectrometer used in this study was a Vertex 70 (Bruker Ltd., Karlsruhe, Germany) with a liquid-nitrogen-cooled MCT detector. The light source was an air-cooled ceramic MIR/NIR light placed inside the spectrometer. The spectral range for the experiment was 600–4000 cm^{-1} with a resolution of 0.5 cm^{-1}. Four measurements were taken for each sample and 10 spectra were averaged for each measurement. The gas cell was a Cyclone™ C2 (Specac Ltd., UK). An 1 L vacuum pump, FY-1H 1 (ALUE Ltd., Shenyang, China), was used in this setup. Before measurements, a vacuum of gas cell was measured as background when the air was exhausted. Then, absorbance spectra were calculated for each time measurement. For statistical analysis, the spectra were collected and pretreated (baseline correction) using OPUS 7.0, and PCA analysis was performed using Unscrambler 9.7.

3. Results and discussions

Fig. 2 shows the spectral characteristics of the main components of the volatiles in Chinese spirits. Three infrared fingerprint absorbance spectra bands of ethanol can be observed, the peaks at 2830–3040 cm^{-1} (the peaks at 2979 cm^{-1} and 2906 cm^{-1} are two independent peaks), the peaks at 1000–1120 cm^{-1} and the peaks at 855–916 cm^{-1} (Linstrom & Mallard, 2013). These absorption bands can indicate the difference in the alcohol degree of the different brands of spirits. The alcohol degree of Guizhouchun, Kouzijiao and Red Star Ergoutou were estimated at 35%, 46% and 52%, respectively. As shown in Fig. 2, there were significant differences between these three kinds of spirits at 2830–3040 cm^{-1} and 1000–1120 cm^{-1} spectra. The absorbance bands at 1210–1280 cm^{-1} is mainly caused by esters (Linstrom & Mallard, 2013). Some esters contain acetic acid, such as ethyl acetate and methyl acetate, which have strong absorbance characteristics in this band. Chinese spirits are produced through different fermentation processes and materials, thus the ester concentrations are likely to be different. Thus, it is possible to differentiate brands of spirits according to this particular spectral band.

In our experiment, the absorption characteristics of ethanol and esters followed the same pattern for all the nine brands of spirits, and the intensities of the absorption peaks were different. However, because of the differences in raw materials and origins, the volatiles of some spirits may contain some components which are absent in other brands. Fig. 3 shows an absorption peak near 1178 cm^{-1}, which is observed in some brands of spirits and absent in other brands. This peak is probably caused by ethyl caproate or ethyl butyrate (Linstrom & Mallard, 2013). The alcohol content in Fenjiu and Luzhouteniang were close and therefore it is difficult to differentiate them according to ethanol characteristic spectral bands. However, Luzhouteniang has very obvious absorption peaks at 1178 cm^{-1}, which are not observed in the absorption spectra of Fenjiu. Besides, Luzhouteniang has weaker ester absorption bands at 1210–1280 cm^{-1} than Fenjiu. Therefore, Fenjiu and Luzhouteniang can be successfully differentiated according to the 1140–1300 cm^{-1} infrared spectral band. Fig. 3(b) demonstrates the difference between these two brands of spirits by PCA.

Various data can be classified with PCA through data dimension reduction (Gemperline, 2006). To demonstrate the ability of infrared spectroscopy to differentiate Chinese spirits more clearly, we analysed 7 brands of spirits with PCA, based on the 760–1300 cm^{-1} and 2600–3250 cm^{-1} bands. In this analysis, the major component number was set as 10, and the spectra were normalised before the analysis to reduce the baseline drift caused by the changes in the environmental temperature. Fig. 4 shows the PCA map of seven brands of Chinese spirits. Due to the fact that the alcohol degree of Guizhouchun was much lower (35%) than the other six types of spirits, Guizhouchun can be differentiated from the other types, including Wuliangchun and Luzhouteniang, which have the same flavours (called Luzhou) with Guizhouchun. Fenjiu and Red Star Erguotou were similar in terms of alcohol degree (53% and 52%, respectively), flavour and raw material (sorghum), but they could be distinguished easily by the infrared spectra combined with PCA. Wuliangchun and Luzhouteniang are both produced in Sichuan Province and they have the same flavour. As a result, most customers cannot distinguish between these two brands of spirits (Zhen et al., 2013), but they show obvious difference in the PCA map. As shown in Fig. 4, some regions slightly overlapped, for example in the case of Gaoliang and Red Star Ergoutou. Since there were big differences in the alcoholic content of the samples, we also excluded from the analysis the infrared