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Chinese vinegar classification *via* volatiles using long-optical-path infrared spectroscopy and chemometrics

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ABSTRACT

Different brands of Chinese vinegar are similar in appearance, color and aroma, making their discrimination difficult. The compositions and concentrations of the volatiles released from different vinegars vary by raw material and brewing process and thus offer a means to discriminate vinegars. In this study, we enhanced the detection sensitivity of the infrared spectrometer by extending its optical path. We measured the infrared spectra of the volatiles from 5 brands of Chinese vinegar and observed the spectral characteristics corresponding to alcohols, esters, acids, furfural, etc. Different brands of Chinese vinegar had obviously different infrared spectra and could be classified through chemometrics analysis. Furthermore, we established classification models and demonstrated their effectiveness for classifying different brands of vinegar. This study demonstrates that long-optical-path infrared spectroscopy has the ability to discriminate Chinese vinegars with the advantages that it is fast and non-destructive and eliminates the need for sampling.

1. Introduction

Chinese vinegars are a traditional condiment derived primarily from grain and used frequently in food production and cooking (Li et al., 2005). Most customers cannot easily discriminate between different brands of Chinese vinegar because they have similar appearances and tastes. Taking advantage of this fact, some sellers illegally use low-price vinegars to cheat customers (Zou et al., 2012). However, commonly used analytical methods struggle to discriminate between vinegars because they have similar chemical compositions (Zou et al., 2012). The classification of different brands of Chinese vinegar has recently attracted increasing concern from both customers and the Chinese government (Zou et al., 2003, 2012).

Chinese vinegars have high volatility. The volatiles released from vinegars vary in composition and concentration depending on the raw materials and processes used in the vinegar production and allow the discrimination of different brands (Wang et al., 2012; Zou et al., 2003). Researchers have studied the volatiles from Chinese vinegars and found that they have high contents of alcohols, esters, and furfural, among others (Li et al., 2005; Miao et al., 2010; Wang et al., 2012). GC–MS is the most commonly used method for the volatiles analysis of food, but it requires complex sampling processes and long analysis times (Acree & Teranishi, 1993; Cirlini et al., 2011; Hui, 2010; Pizarro et al., 2008; Schamp & Dirinck, 1982; Wang et al., 2012). Zou et al. successfully classified two types of Chinese vinegar using E-nose and chemometrics methods (Zou et al., 2003). However, E-noses are usually used in laboratory tests but not in on-line measurements because of their high price and complex operation (Keshri et al., 1998; Magan & Evans, 2000; Zou et al., 2002).

Infrared spectroscopy is an effective tool for analyzing unknown gases and has been widely used in qualitative and quantitative measurements of automobile exhaust (Sebih et al., 2010; White et al., 2011; Yamamoto et al., 2011), harmful gas leaks (Harig et al., 2005, 2007; Li et al., 2002) and greenhouse gas emissions (Gardiner et al., 2008; Geibel et al., 2010; TsanChang et al., 2000), among other applications. Compared with GC–MS and many other laboratory analytical methods, infrared spectroscopy is more flexible and can realize non-destructive, real-time and continuous tests as well as remote-sensing measurements (Bacsik et al., 2006; Marshall et al., 1994; Ross & Todd, 2002). In previous works, we used multi-reflecting mirrors to increase the optical path of a common FTIR (Fourier transform infrared spectroscopy) system, studied the volatiles released from grapes and strawberries and observed the spectral characteristics corresponding to alcohols, esters, etc. (Dong et al., 2013, 2014a, 2014b; Wenzhong et al., 2013). The results revealed that it is possible to classify fruit spoilage stages *via* their volatiles using infrared spectroscopy.

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In this study, we analyzed the volatiles released from Chinese vinegars and tried to discriminate different brands of vinegar using long-optical-path infrared spectroscopy combined with chemometrics methods. To the best of our knowledge, this is the first study to discriminate vinegars based on the infrared spectra of their volatiles. The aims of this study were: (1) to observe the compositions of the volatiles from Chinese vinegars and their spectral characteristics, (2) to study the spectral differences in the volatiles from different brands of vinegar, and (3) to determine whether infrared spectroscopy can be used for the discrimination of Chinese vinegars.

2. Materials and methods

2.1. Experimental materials

We used 5 typical types of Chinese vinegars, Siyanjing, Baoning, Hengshun, Zhenjiang and Longmen. The vinegar code, raw material, geographical origins, flavor, as well as the brewing processes of each type of the vinegar sample are shown in Table 1. Both Hengshun and Siyanjing were produced in Shanxi province, while Longmen in Beijing, Baoning in Sichuan and Zhenjiang in Jiangsu province.

2.2. Experimental setup

A V70 FTIR spectrometer (Bruker Ltd., Germany) was used with a liquid-nitrogen-cooled MCT detector and a ceramic mid-infrared light source. The spectral range of the spectrometer was 400–4400 cm^{-1} with a resolution of 0.5 cm^{-1}. A Cyclone C2 gas cell (Specac Ltd., UK.) was used and its optical path was extended to 2 m by using 6 reflecting mirrors. We used a 1 L vacuum pump, FY-1H (ALUE Ltd., Shenyang, China), to exhaust gases from the gas cell. Our previous study demonstrated that the long-optical-path FTIR system was much more sensitive than the common one (Dong et al., 2013).

2.3. Spectral measurement

We moved the Chinese vinegar samples to some identical containers using a pipette and heated in 40 °C water for 30 min. Then the vapors released from the vinegars were exhausted from the containers to the gas cell and their infrared spectra were collected. In the experiment, 65 bottles of vinegars of each type were used. Each sample was prepared from one separate bottle, and therefore 65 spectra for each type of vinegar were collected. Then, 25 samples of each types of vinegar were used as calibration sets (125 spectra in total), and 40 samples were used as prediction sets (200 spectra in total). Absorbance spectra were calculated using the spectra in vacuum as a reference. The procedure of exhausting gases from the container to the gas cell was described in our previous publication (Dong et al., 2013, 2014a, 2014b).

2.4. Spectral data processing

The original absorbance spectral data was collected using OPUS 7.0 software. Some spectral pre-treatment methods, such as baseline correction and smoothing, were performed in Python 2.6. Unscramber 9.7 was used to realize PCA (Principal Component Analysis) analysis and to establish SIMCA (Soft Independent Modeling of Class Analogy) and PLS-DA (Partial Least Squires Discrimination Analysis) model. The figures were plotted in SigmaPlot 12.0 software.

3. Results and discussion

3.1. Spectral characteristics of the vapors from Chinese vinegars

Fig. 1 shows the infrared spectrum of the vapors released from a typical Chinese vinegar, Zhenjiang. As observed from Fig. 1 and our previous study, the infrared spectrum of the vapors from Chinese vinegar was similar to that from Chinese spirits (Dong et al., 2014a, 2014b), which may be due to the similar raw materials and brewing processes used for both. In this study, we observed the spectral characteristics of some major compositions in Chinese vinegars, includes alcohols, acetic acid, furfural, esters and 2,3-butanedione. The major volatile components in Chinese vinegars verified in previous literatures and in this study were shown in Table 2.

Three main spectral characteristic bands for alcohols, namely, 3100–2750 cm^{-1}, 1150–950 cm^{-1} and 950–800 cm^{-1}, were also present in the spectra of the vapors from vinegar, such as that from Chinese spirits Acetic acid is known to be a major acid component of the vapors from Chinese vinegar. The two characteristic peaks at 2700 cm^{-1} and 1180 cm^{-1} may correspond to acetic acid. Furfural is also known to be present in the vapors of Chinese vinegars. We believe that two spectral characteristics were related to furfural: the wide spectral peak at 1300–840 cm^{-1}, which may be due to both furfural and esters, and the peak at 1020 cm^{-1}, which overlapped with the spectral characteristics of alcohols at 1150–950 cm^{-1}. Previous studies based on GC–MS demonstrated that 2,3-butanedione is a major component in the aroma of Chinese vinegars. We believe that the absorbance peaks at 1110 cm^{-1} may be due to 2,3-butanedione (Fig. 1(c)), which exhibited strong absorbance characteristics despite overlapping with the alcohol peaks. This feature was not present in the spectra of the vapors from Chinese spirits (Dong et al., 2014a, 2014b). Previous studies also found many other components in the vapors from Chinese vinegars that were not observed in the current experiment (Li et al., 2005; Miao et al., 2010; Wang et al., 2012), which may be due to both the weak absorbance characteristics of these components and the overlap with other strong absorbance peaks.

Therefore, it can be studied from Table 2 that most major compositions in the volatiles from vinegars that verified by GC–MS method can also be measured using long optical path infrared

Table 1
Code name, geographical origin and raw materials of the vinegar samples.

Vinegar code	Vinegar sample name	Geographical origin	Raw materials	Flavor	Brewing processes
B	Baoning	Nanchong, Sichuan	Wheat bran, wheat and rice	Bran-vinegar	Using traditional medicine and low temperature fermentation, sealed for 6–12 months
H	Hengshun	Jinzhong, Shanxi	Sorghum, wheat bran, barley and peas	Aged vinegar	Traditional Shanxi vinegar brewing process combined with Zhenjiang aromatic vinegar brewing process
L	Longmen	Beijing	Rice and wheat bran	Rice vinegar	Traditional clinker brewing, without steamed material
S	Siyanjing	Jinzhong, Shanxi	Sorghum, barley and peas	Aged vinegar	Brewing acetic acid with high temperature and solid materials
Z	Zhenjiang	Zhenjiang, Jiangsu	Glutinous rice and rice	Aromatic vinegar	Solid material brewing, wine brewing, making fermented grains and drench vinegar, last for 70 days