Determination of Chinese liquors from different geographic origins by combination of mass spectrometry and chemometric technique

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ABSTRACT

Determination of Chinese liquor from different geographic origins is benefit for controlling liquor quality and safeguarding the interests of consumers. In the study, 131 Chinese liquor samples were detected by the headspace (HS)-solid phase microextraction (SPME)-mass spectrometry (MS) technique, and then mass spectra data of samples were exported by the NIST 05 library. By combination of partial least squares discriminant analysis (PLS-DA) and stepwise linear discriminant analysis (SLDA) method, 32 characteristic ions were finally picked out and the prediction accuracy of SLDA was more than 97.7%. And then an artificial neural network (ANN) recognition model using the 32 ions as inputs and 8 groups different geographic origins as outputs was built, whose prediction accuracy was up to 100%.

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1. Introduction

Chinese liquor is one of the oldest distillates in the world. Compared with other spirits such as vodka, whiskey, and brandy, it has higher ethanol content (normally 40–55% vol.) (Fan & Qian, 2006a). Benefiting from its unique flavor, Chinese liquor is really popular in China. At present the Chinese consume more than 10 billion liters annually.

Sichuan, Guizhou, Shandong, Jiangsu, Anhui, and Henan provinces are the main producing regions in China, commanding more than 90% of the total liquor output. Many famous brand of Chinese liquor, such as Maotai, Wuliangye, Jiannanchun, Fenjiu, and Yanghe Daqu liquors, are distilled and bottled in these regions (Fan & Qian, 2006b). Because of differences in manufacturing practices, the aroma profiles of Chinese liquors are quite different. Currently the aroma type of liquor is a wide range including strong aroma, soy sauce aroma, light aroma, sweet honey, and miscellaneous types (Fan, Xu, & Qian, 2012). Various liquors mix in the market so that it is of great significance to find out an effective, economic, and robust technique to identify the geographic origin.

Nowadays, several analytical techniques were used for determination of the geographic origin of alcoholic beverage, such as mass spectrometry techniques, i.e. isotope ratio mass spectrometry (IRMS) (Dutra et al., 2011), inductively coupled plasma (ICP)-MS (Coetzee & Vanhaecke, 2005), MS-based electronic nose (EN) (Berna, Trowell, Clifford, Cynkar, & Cozzolino, 2009; Cynkar, Dambergs, Smith, & Cozzolino, 2010), electrospray ionization (ESI)–MS (Møller, Catharino, & Eberlin, 2005), and gas chromatography (GC)–MS (Masuda et al., 2010); spectroscopic techniques, including near-infrared spectroscopy (NIR) (Liu, Cozzolino, Cynkar, Gishen, & Colby, 2006), and fluorescence spectroscopy (Sádecká, Tóthová, & Májek, 2009; Tóthová, Žiak, & Sádecká, 2008); and other techniques, i.e. colorimetric artificial nose (Qin et al., 2012). Although the spectroscopic technique was a simple, rapid, and nondestructive method, its sensitivity was relatively low and was prone to interference between components possessing similar spectral regions (Luykx & van Ruth, 2008). So the method used broadly was still MS technique. Among these MS methods, major defect of IRMS method was the high cost of purchasing instrument, while ICP technique was nowadays used for total metal detection and the full capabilities had yet to be realized (Luykx & van Ruth, 2008). But the MS technique was used for discrimination of the geographic origin based on the ions information of components without chromatographic peaks separation and identification and quantification of volatile compounds (Cynkar et al., 2010; Møller et al., 2005). Meanwhile, the headspace (HS)-SPME could fast extract volatile compounds present at low concentrations in spirits without a preconcentration step

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(Jelen, Ziolkowska, & Kaczmarek, 2010). All these advantage obviously shortened the detection time.

Chemometric analysis methods, such as principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), and stepwise linear discriminant analysis (SLDA), were effectively used to discriminate the geographic origin of alcohol beverage (Cynkar et al., 2010; Jelen et al., 2010; Liu, et al., 2006; Møller et al., 2005; Sampaio, Reche, & Franco, 2008). They processed data obtained by effective equipment technique and overcame the resource limitations of detecting equipment to provide statistical separation of different categories.

The aim of this study was to show the effectiveness and feasibility of the HS-SPME-MS technique combined with chemometric analysis methods used to classify the Chinese liquors from different geographic origins.

2. Material and methods

2.1. Liquor samples

The 131 Chinese liquor samples with different aroma type and geographic origins were used in the study, including 12 Fenjiu (light aroma type, made in Fenyang, Shanxi province), 42 Laobaigan (laobaiganxiang aroma type, made in Hengshui, Hebei province), 35 Langjiu (soy sauce aroma type, made in Gulin, Sichuan province), 6 Niulanshan (light aroma type, made in Shunyi, Beijing), 15 Yanghe Daqu (strong aroma type, made in Suqian, Jiangsu province), 7 Gubeichun (strong aroma type, made in Wucheng, Shandong province), 6 Jiannanchun (strong aroma type, made in Mianzhu, Sichuan province), and 8 Xifeng (fengxiang aroma type, made in Baoji, Shanxi province) liquor samples. The ethanol content of the liquor samples is in the range of 38–72%vol.

2.2. HS-SPME-MS

According to Fan and Qian's modified method (Fan & Qian, 2005), an automatic headspace sampling system (Multipurpose Sample MPS 2 with a SPME adapter, GERSTEL Inc., Mülheim, Germany) with a 50/30 μm DVB/CAR/PDMS fiber (2 cm, Sigma–Aldrich, Shanghai, China) was used for aroma extraction. Each liquor sample was diluted with deionized water to a final concentration of 10% vol ethanol, and the total 8 mL solution volume was put into a 20 mL autosampler vial. The diluted sample was saturated with sodium chloride (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). Then, the vial was tightly capped with a silicon septum. This sample was equilibrated at 40 °C in a thermostatic bath for 5 min and extracted for 15 min at the same temperature

under stirring. After extraction, the fiber was inserted into the injection port of GC (250 °C) to desorb the analytes during 5 min.

The SPME-MS was carried out using an Agilent GC6890 equipped with 5973 mass spectrometry detector (MSD). A general fused silica capillary without coating (1 m × 0.25 mm i.d., Agilent Technologies Inc., Shanghai, China) replaced a capillary analytical column. The injector temperature was 250 °C, and the splitless mode was used. The carrier gas was helium at a constant flow rate of 1 mL/min. The electron impact energy was 70 eV, and the ion source temperature was set at 230 °C. Without particular compounds separation by GC, an overall headspace spectrum was acquired. Mass spectra data were exported by NIST05a.L. (Agilent Technologies Inc., Shanghai, China).

2.3. Multivariate statistical and chemometric analysis

In the study, the analysis techniques such as PLS-DA, SLDA, and artificial neural network (ANN) were used to classify the liquor samples from different geographic origins. Firstly, the PLS-DA was used to pick out important ions and reduce data dimensionality, and then the SLDA further selected characteristic ions and visualized the classification result of liquor samples. At last an ANN model using the characteristic ions obtained as input and geographic origins as output was built, which was feasible to predict the geographic origin of unknown samples.

The chemometric analysis methods was performed using the following statistical software: PLS-DA—SIMCA-P (version 11.5, Umetrics, Malmö, Sweden), SLDA—IBM SPSS Statistics (version 20, IBM, Armonk, United States), ANN—MATLAB software (version 7.14, Mathworks, Natick, United States).

3. Results and discussion

The abundance of all mass-to-charge ratio (m/z) 55–191 ions was generated by the HS-SPME-MS technique; the differences between liquor samples were obtained based on the ion-fragments. All the liquor samples had similar m/z ions, but their abundance was different. As a result of the abundance of ions could be affected by experiment equipment and ethanol content, etc., the abundance of ions was replaced by relative intensity. Clearly, the m/z 88 ion with the highest abundance was a base peak, which was characteristic for ethyl esters (Jelen et al., 2010). So the relative intensity of ion m/z 88 was set as 100%. And then relative intensity of other ions was calculated by scaling. Taking Yanghe Daqu liquor for example, Fig. 1 shows the relative intensity mass spectrum of liquors in the range of m/z 55–191. Obviously the intensity of high mass-to-charge radio ions was relatively low, so they were redrawn in
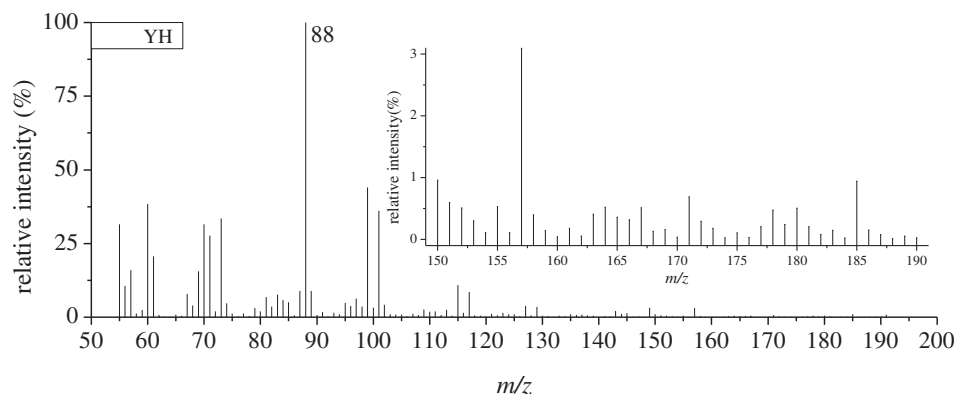

Fig. 1. The average mass spectrum of Yanghe Daqu liquor generated using the HS-SPME-MS technique in the range of m/z 55–191.