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Prediction of sugars and acids in Chinese rice wine by mid-infrared spectroscopy

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ABSTRACT

The use of Fourier transform mid-infrared spectroscopy (FT-MIR) for the rapid determination of sugars and acids in Chinese rice wine was presented in this study. Calibration models were developed by partial least squares regression (PLSR) for eleven parameters related to sugar content and acidity—namely, total sugar, non-sugar solid, glucose, maltose, isomaltotriose, isomaltose, panose, total acid, amino acid nitrogen, pH and lactic acid. In the calibration step, most of the parameters were accurately determined, obtaining regression coefficients of calibration (r_{cal}) ranging from 0.821 to 0.991. In validation, regression coefficients of validation (r_{val}) obtained for most parameters were higher than 0.85. Unsatisfactory predictions were obtained for isomaltotriose and isomaltose with r_{val} being 0.488 and 0.716, respectively. The residual predictive deviation (RPD) values were also higher than or close to 2.0 for all the parameters except for isomaltose and isomaltotriose. Overall, the results indicate that MIR spectroscopy can be applied to the quality determination of Chinese rice wine.

1. Introduction

Chinese rice wine, also named yellow wine, has been one of the most traditional alcoholic beverages in China for centuries. It is typically made from glutinous rice with wheat *Qu* and yeast. Glutinous rice contains higher starch and lower fat contents as compared to non-glutinous rice, and wheat *Qu* serves as an abundant carbon, nitrogen, and enzyme source for mold and yeast in fermentation (Chen & Xu, 2010). The brewing technology can be summarized as follows: glutinous rice is first cooked with steam, and mixed with *Qu* and yeast. Then the mixture is fermented for 20–25 days in jars. After fermentation, the rice wine mash is filtered and clarified with a wine-press. Afterwards, the finished rice wine is heated with steam and transferred to ceramic pottery for aging for at least one year. Because of the unique craft handed down from generations, rice wine often presents characteristics of bright brown color, subtle sweet aroma and low alcohol content (Que, Mao, Zhu, & Xie, 2006). Sugars in rice wine, mainly glucose, come from a hydrolysis reaction of carbohydrates in glutinous rice. Rice wine is divided into four kinds according to total sugar content: dry type (total sugar<15 g/L); semi-dry type (15.1 g/L<total sugar<40 g/L); semi-sweet type (40.1 g/L<total sugar<100 g/L); and sweet type (total sugar>100 g/L). Among them, semi-dry rice wine is the most popular. Sugars are not only important nutrient components of rice wine but also contribute to its taste and flavor. Rice wine is abundant in oligosaccharides, such as maltose, isomaltose, isomaltotriose and panose, which have been reported to be very valuable for human health (Niu et al., 2008). Acids, including lactic acid, acetic acid, tartaric acid, amino acids and many others, are important taste substances of rice wine, and constitute the unique aroma and flavor of rice wine together with other taste compounds. A certain amount of acids can play an important role in the reconciliation of rice wine flavor, and gradually form into aromatic esters during storage. However, excess acids in rice wine, especially lactic acid that may occasionally occur during fermentation and aging process, have a negative effect on rice wine's mouthfeel and result to rancidity finally (Feng, Sun, Ma, Sun, & Sun, 2010). Due to the increasingly recognized importance of sugars and acids and their relationship to wine quality, a rapid and accurate method to rapidly analyze these compounds is essentially required.

Generally, sugar and acid analyses are often carried out by wet chemistry and instrument analytical techniques, such as high-performance anion-exchange chromatography (HPAEC) (Guignard et al., 2005; Niessen et al., 1992) and high-performance liquid chromatography (HPLC) (Lopez & Gomez, 1996). Although these methods have a high accuracy, they are often time-consuming, labor intensive and require tedious and complex processing of wine samples. Hence, the development of rapid and cost-effective methods is required when large numbers of samples have to be screened.

Near-infrared (NIR) and mid-infrared (MIR) spectroscopy techniques have been gradually developed as alternatives to wet chemistry in the food industry and agriculture in recent years, mainly because they can be applied in a low-cost, rapid and non-destructive way (Shen et al., 2010). Recently, many studies have focused on the

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application of MIR technology, since it may offer a more accurate determination of constituents and properties than NIR method (Bauer et al., 2008). MIR technology is based on the measurement of the frequencies of chemical bonds in functional groups such as C–C, C–H, O–H, C=O and N–H, upon absorption of radiation in the mid-infrared region, which is usually defined as ranging from 400 to 4000 cm^{-1}, or in other terms, from 2500 to 25,000 nm (Smith, 1999). With the combination of multivariate analysis, such as principal component analysis (PCA) and partial least squares (PLS), the potential of MIR spectroscopy is greatly expanded (Cozzolino, Cynkar, Shah, & Smith, 2011b). Currently, various studies have applied MIR spectroscopy to the qualitative and quantitative analyses of wines and other beverages. Patz and co-workers determined a significant number of important parameters like alcohol, relative density, extract, sugar-free extract, refraction, conductivity, glycerol, total phenols, reducing sugar, fructose, glucose, sucrose, total acid, pH value, volatile acid, total SO_2, tartaric acid, malic acid, lactic acid and citric acid in German wines (Patz, Blieke, Ristow, & Dietrich, 2004). Quality indexes of juice, beer as well as spirit drinks were also determined by MIR spectroscopy (Lachenmeier, 2007; Lobo, Valles, Tascon, Madrera, & Garcia, 2006). Some interested compounds, such as tannins and anthocyanins, were also successfully quantified (Fernandez & Agosin, 2007; Soriano, Perez-Juan, Vicario, Gonzalez, & Perez-Coello, 2007). In addition, MIR spectroscopy has already been applied for the classification purpose to differentiate wines or vinegars according to origin, grape variety as well as manufacturing technique (Bevin, Dambergs, Fergusson, & Cozzolino, 2008; Guerrero, Mejias, Marin, Lovillo, & Barroso, 2010). On-line monitoring of sugars, alcohols, and organic acids during fermentation based on MIR spectra was also reported (Mazarevica, Diewok, Baena, Rosenberg, & Lendl, 2004; Nieuwoudt, Pretorius, Bauer, Nel, & Prior, 2006).

However, until now, few studies have been focused on the use of MIR spectroscopy for the quality determination of rice wine. Only a feasibility study was carried out to measure total sugar content in rice wine with a limited sample set of thirty (Shen, Ying, Sun, & Hu, 2009). The objective of this study was to investigate the possibility of MIR spectroscopy to determine eleven parameters in rice wine, namely total sugar, non-sugar solid, glucose, isomaltose, isomaltotriose, maltose, panose, total acid, amino acid nitrogen, pH and lactic acid.

2. Material and methods

2.1. Samples

A total of 90 samples were collected from three Shaoxing wine wineries ("*pagoda*", "*kuaijishan*" and "*guyuelongshan*"). Shaoxing rice wine is the most well-known rice wine in China, which is known by the generic name "Shaoxing", and labeled as the product of protected designation of origin (PDO) according to National Standard GB 17946–2008. Table 1 shows the distribution of the sample set in terms of winery, aging time as well as wine type. Every 30 samples were provided by each winery, respectively. 84 samples were labeled as semi-dry wine, and the other 6 samples were labeled as dry type wine. The samples were all from the vintage year of 2007 but were analyzed with different aging times. Each sample was selected from different batches of production, and was directly taken from ceramic pottery without any additive.

Table 1
Distribution of rice wine samples.

Origin	15 months		21 months		27 months	
	Semi-dry	Dry	Semi-dry	Dry	Semi-dry	Dry
Pagoda	9	1	9	1	9	1
Guyuelongshan	9	1	9	1	9	1
Kuaijishan	10	0	10	0	10	0
Total	28	2	28	2	28	2

2.2. Spectral measurement

Samples taken from freshly opened bottles were scanned in transmission mode at room temperature using an FT-IR spectrometer (Thermo Electron Corp., Madison, WI, USA), which was equipped with an interferometer, a Globar source and a deuterated triglycine sulphate (DTGS) detector with KBr beamsplitter. Measurement was carried out using a demountable liquid cell (Pike Technologies, Madison, WI, USA) equipped with two CaF_2 windows. Each window has a 32 mm diameter with 3 mm thickness. A polyethylene terephtalate spacer provides a 0.025 mm optical path-length. A total of 20.106 μL of the sample was used in each measurement. Special attention was taken in order to avoid air bubbles in the liquid cell during the scanning of sample spectra. The sample cuvette was cleaned with distilled water and wiped dry after each measurement to avoid cross-contamination. Each sample was scanned in triplicate. Background was collected using distilled water as the reference and was taken once in every five sample scans. Spectra were collected using OMNIC software (Thermo Electron Corp., Madison, WI, USA) and saved in absorbance format. Spectra were recorded in the range of 950–3300 cm^{-1}. The mirror velocity was 0.6236 $cm\,s^{-1}$ and the resolution was 4 cm^{-1}. The spectrum of each sample was the average of 32 successive scans.

2.3. Reference analysis

Reference analysis for total sugar, non-sugar solid, total acid, amino acid nitrogen and pH was carried out using official methods for rice wine according to Chinese National Standard GB 13662–2008. A detailed description of the official methods could be found in a previous work (Yu, Ying, Fu, & Lu, 2006). Lactic acid analysis was performed using a 1200 series high-performance liquid chromatography (HPLC) equipment (Agilent Technologies Inc, Santa Clara, CA, USA). The HPLC determination was accomplished by combining a C18 column (150 × 4 mm, i.d., 5 μm). Lactic acid was separated by KH_2PO_4 (0.01 mol/L) as mobile phase and detected using a UV detector (215 nm). Glucose, maltose, isomaltotriose, isomaltose and panose analyses were carried out using high-performance anion-exchange chromatograph couple with pulsed amperometric detection (HPAEC–PAD) (Dionex Corp., Sunnyvale, CA, USA). Chromatographic separation was performed by a Dionex CarboPac PA10 column (250 × 2 mm). Another column (50 × 2 mm) was used as guard column. Sugars were separated by stepwise gradient elution using Milli-Q distilled water, sodium hydroxide (250 mmol/L) and sodium acetate (1.0 mmol/L) as mobile phase. Analytical grade lactic acid, glucose, isomaltose, D−(+)-maltose monohydrate, D-panose, and isomaltotriose used in this study were all purchased from Sigma-Aldrich (Sigma, St. Louis, MO, USA). Because of laboratory capacity reason, only sixty samples were analyzed for glucose, maltose, isomaltotriose, isomaltose and panose in this study. A detailed description of the method was given elsewhere (Niu et al., 2008).

2.4. Multivariate analysis

Multivariate analysis was used to perform both descriptive and quantitative analyses of the data using a commercial software package, TQ analyst (version 6.2.1, Thermo Electron Corp., Madison, WI, USA). Spectra were exported from OMNIC software to TQ analyst for analysis. The descriptive analysis was carried out by PCA. PCA is used to reduce the dimensionality of the data in order to extract main information, and it is very useful to reveal grouping samples and to detect outliers. Before the development of calibration models, outlier detection is often applied. Outliers are considered as abnormal ones in