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Discrimination of different red wine by Fourier-transform infrared and two-dimensional infrared correlation spectroscopy

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ABSTRACT

Fourier-transform infrared spectroscopy (FT-IR) and two-dimensional infrared (2D IR) correlation spectroscopy were applied to analyze main components of liquid red wine with different sugar contents and volatilization residues of dry red wine from different manufactures. The infrared spectra, second derivative spectra of dry red wine show the typical peaks of alcohol, while the spectra of sweet wine are composed of the peaks of both alcohol and sugar, and the contribution of sugar enhanced as the increase of sugar content. Using principal component analysis (PCA) method, dry and sweet wine can be readily classified. Analysis of the infrared spectra of the volatilization residues of dry red wine samples from five different manufactures indicates that dry red wine may be composed of glycerol, carboxylic acids or esters and carboxyl ate, at the same time, different dry red wine show different characteristic peaks in the second derivative spectra and 2D IR correlation spectra, which can be used to discriminate the different manufactures and evaluate the quality of wine samples. The results suggested that infrared spectroscopy is a direct and effective method for the analysis of principle components of different red wines and discrimination of different red wines.

1. Introduction

Wine is very popular in the world, which has relatively low alcohol content (13–16°), accepted and consumed by all ages. Wine not only has rich nutrition, but also gives people enjoyment. Wine is classified according to the content of sugar as dry ($\leqq$4.0 g L^{-1}), semi-dry (4.1–12.0 g L^{-1}), semi-sweet (12.1–45.0 g L^{-1}) and sweet ($\geqq$45.1 g L^{-1}) wine [1]. Wine is composed of water (80–90%), alcohol (~12%), sugar, carboxylic acid, tannin, polyphenol, amino acids, vitamin C, inorganic elements and many kinds of fragrance ingredients [2,3], among which alcohol and sugar are the two major constituents. Detecting the alcohol and sugar content of wine rapidly is of significant interest in evaluating the character and quality of wine samples. At present, the alcohol content of wine is tested by density bottle method and gas chromatography, while total and reducing sugar content are measured by HPLC, direct titration and indirect iodometry according to the national standards of People's Republic of China (GB 15038-2006) [4]. All the above methods include the pre-treatment process such as distillation, and the operation are complicated, time-consuming and laborious. Besides, as a new and potential technique, the electronic nose and electric tongue have been used to recognize typical aromas in white wine and predict sensorial descriptors of Italian red dry wines of different denominations of origin [5,6]. However, the high expenses make it hard to apply in the practical applications.

In recent years, the application of spectroscopic techniques in wine analysis has developed considerably. This technique could successfully analyze ethanol, polysaccharide, polymeric mannose, organic acids, polyphenol and other constituents in wine qualitatively and quantitatively [7–11], especially when assisted by computer-aided technology and chemometrics, such as principle component analysis (PCA), artificial neural network (ANN) and soft independent modeling of class analogy (SIMCA). Comparing to other techniques (besides wine tasters), the infrared spectroscopy is a fast, direct method, and the compositions of wine samples can be analyzed *in situ* and holistically with this technique. As we all know, the infrared spectroscopy has the disadvantage of low-resolution, but modern mathematical calculations can improve the resolution of the spectra greatly and supply more information.

The three-step infrared macro-fingerprint method, proposed by Prof. Sun [12], combines conventional IR spectra, the secondary derivative spectra, which can enhance the spectral resolution by amplifying tiny differences, with the two-dimensional infrared correlation spectroscopy. 2D IR spectroscopy, originally developed by Noda [13,14], was obtained by applying a periodic perturbation of low frequency, such as temperature, pressure and concentration, to a sample and then process the data by a mathematical

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Table 1
Labeled and tested alcohol and sugar content of wine samples.

No.	Labeled value of alcohol (vol.%)	Labeled value of sugar content (g/L)	Tested value of alcohol (vol.%)	Tested value of sugar content (g/L)
a	12	<4	12.53	4.00
b	11.50	40	10.03	41.04
c	14	70	13.56	82.00
d	11	⩾45.1	11.32	110.25
e	13.50	⩾45.1	13.89	160.38
f	12	<4	13.70	5.69
g	12	<4	11.69	5.51
h	12	<4	11.95	7.24
i	12	<4	11.93	5.79
j	12	<4	11.43	5.05

correlation analysis technique [15]. 2D IR correlation analysis can, not only enhance the resolution of IR spectra, but also provide much more detailed information about the variation of molecular structures and responses. In recent years, our research team has successfully applied 2D IR spectroscopy in the identification and classification of TCM and food, such as discrimination of herbal medicine materials from different origins [16], analysis of "Red Flower Oil" preparation from different manufacturers [17], sequential changes of main components in different kinds of milk powders [18], rapid identification of Chinese Sauce liquor from different fermentation positions [19].

Herein the three-step infrared macro-fingerprint method and principle components analysis (PCA) method are used to discriminate wines with different sugar content and differentiate dry red wine samples from different manufactures.

2. Experiment

2.1. Samples and preparations

Total of 120 samples of different kinds of wines were collected from the market, and ten specific samples were selected as Great Wall Dry Red Wine (a), Great Wall Semi-sweet Red Wine (b), Fengshou Red Wine (c), Changyu Red Wine (d), Dragonseal Red Wine (e), Great Wall Cabernet Dry Red Wine (f), Dynasty Cabernet Dry Red Wine (g), Dragonseal Cabernet Dry Red Wine (h), Harvest Cabernet Dry Red Wine (i), Changyu Cabernet Dry Red Wine (j). Transparent and viscous residues are obtained after 1 mL of each sample was dropped on a pan and volatilized under the infrared lamp for 8 h.

According to density bottle method and titration method in GB 15038-2006, the alcohol and sugar content of wine (a–j) were obtained as shown in Table 1.

2.2. Data collection and processing

The FT-IR spectra of liquid wines were recorded in the range of 4000–650 cm^{-1} on a Spectrum GX FT-IR spectrometer (PerkinElmer, UK), equipped with a DTGS (deuterated triglycine sulfate) detector and a horizontal attenuated total reflectance (HATR) accessory (PerkinElmer, UK). Each spectrum was an average of 32 scans at a resolution of 4 cm^{-1}. Secondary derivative IR spectra were obtained after ATR correction of the original IR spectra by using the software Spectrum v3.02 (PerkinElmer, UK).

The infrared spectra of 70 dry and 50 sweet wines were obtained using same equipment and software as above. The ATR correction and the baseline correction were carried out orderly by the software Spectrum v5.0 (PerkinElmer, UK). Every spectrum was normalized by subtracting the minimum absorbance in the range of 2000–1800 cm^{-1}. The PCA analysis of the IR spectra of 120 wine samples was carried out by MATLAB v7.0 (The Math Works, USA).

Each volatilization residue samples was coated on the KBr blocky crystal and then the crystal was ground and pressed into a tablet. The FT-IR spectra of the tablets were recorded as above except for the absence of the HATR accessory. Secondary derivative IR spectra were obtained after 13-point smoothing of the original IR spectra. 2D IR correlation spectra were obtained by treatment of the series of temperature-dependent dynamic spectra, which were recorded at different temperatures from 50 to 120 °C at an interval of 10 °C, with 2D IR correlation analysis software programmed by Department of Chemistry of Tsinghua University, Beijing, China.

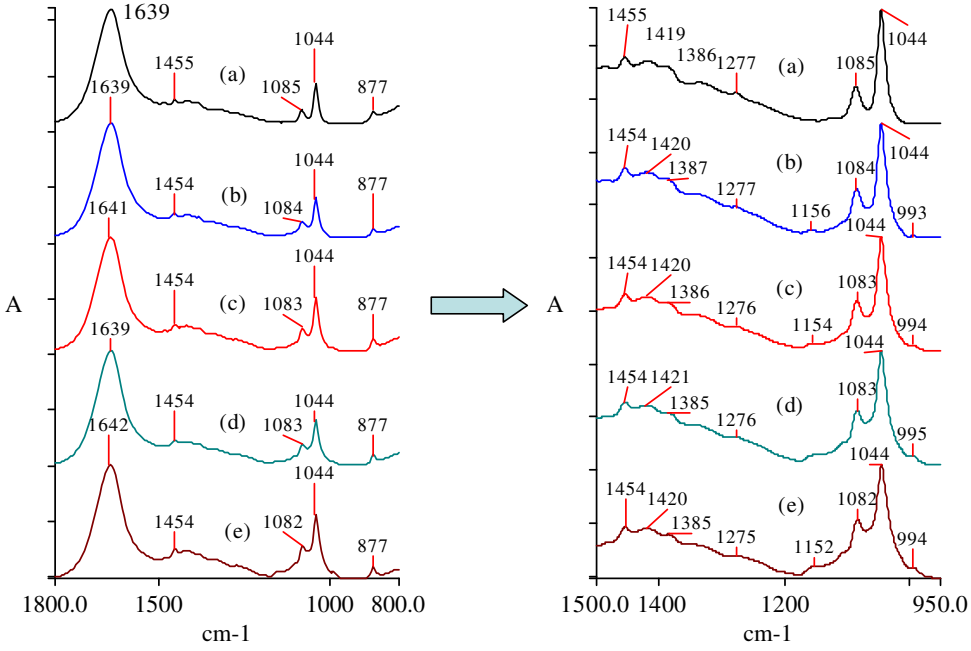

Fig. 1. FT-IR spectra of liquid wine samples (a–e).