



## Analytical Methods

An approach to the simultaneous quantitative analysis of metabolites in table wines by  $^1\text{H}$  NMR self-constructed three-dimensional spectra

Bao Qiong Li, Min Li Xu, Xue Wang, Hong Lin Zhai\*, Jing Chen, Jin Jin Liu

College of Chemistry &amp; Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

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## ABSTRACT

Wine consists of several hundred components with different concentrations, including water, ethanol, glycerol, organic acids and sugars. Accurate quantification of target compounds in such complex samples is a difficult task based on conventional  $^1\text{H}$  NMR spectra due to some challenges. In this paper, the three-dimensional spectrum was constructed firstly by simply repeating  $^1\text{H}$  NMR spectrum itself so as to extract the features of target compounds by Tchebichef moment method. A proof-of-concept model system, the determination of five metabolites in wines was utilized to evaluate the performance of the proposed strategy. The results indicate that the proposed approach can provide accurate and reliable concentration predictions, probably the best results ever achieved using PLS and interval-PLS methods. Our novel strategy has not only good performance but also does not require laborious multi-step and subjective pretreatments. Therefore, it is expected that the proposed method could extend the application of conventional  $^1\text{H}$  NMR.

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## 1. Introduction

Like other types of metabolomic samples, wine consists of several hundred components with different concentrations (Mendes, Goncalves, & Camara, 2012). The major components are water, ethanol, glycerol, organic acids, sugars and various ions (Bailey & Rutan, 2013). Since it is one of the most welcomed beverages, it is critical to quality control the products. Because of the complex nature of wine, it is tedious and time-consuming for compound identification and quantitative analysis using some techniques.

Nuclear magnetic resonance (NMR) is a versatile spectroscopic technology that can be employed as a replacement for time-consuming methods in quality control of wines. Moreover, it has attracted considerable attention and has been widely used in many other scientific disciplines owing to its ability to analyze essentially all types of molecules at atomic resolution and provide rich qualitative and quantitative information rapidly. In the quantitative

analysis on the basis of  $^1\text{H}$  NMR spectra, a prerequisite for the application of conventional method for the accurate determination of absolute integrals is that a spectrum should be well phased and not suffer from baseline distortions (Muller-Maatsch, Caligiani, Tedeschi, Elst, & Sforza, 2014). Moreover, many traditional methods are still hampered by peak overlapping (Bingol & Bruschweiler, 2014), although the integral values of target peaks could be extracted by deconvolution operation (Schievano et al., 2015). Therefore, different pretreatments of the spectra are generally needed for the quantitative purpose. For quantitative analysis in some complex cases, conventional methods are not applicable due to the time-consuming pretreatments, especially when a great number of samples need to be analyzed.

Some chemometric methods (Izquierdo-Garcia et al., 2011; Lee et al., 2015; Schleif, Riemer, Borner, Schnapka-Hille, & Cross, 2011; Shao, Miao, Liu, Liu, & Cai, 2011) were provided for quantitative purpose with minimal handling of integrations. However, the extraction of quantitative information from the original signals is still difficult due to peak shifts, since some of these methods are usually sensitive to differences in peak position. Various alignment

\* Corresponding author.

E-mail address: [zhahl@163.com](mailto:zhahl@163.com) (H.L. Zhai).

methods have been proposed to address this problem, but different studies have taken different approaches to evaluate the performance of the alignment (Liebeke, Hao, Ebbels, & Bundy, 2013). Moreover, other pre-processing of spectral data such as binning and segmentation may reduce the spectral resolution (Smolinska, Blanchet, Buydens, & Wijmenga, 2012) and loss of useful spectral information (Chen, Zhao, Liu, Cai, & Liu, 2008). Therefore, there is reason to believe that the reliability and accuracy of quantitative analysis results can be affected by some pretreatments.

Image is an intuitive way of information presentation. Several image moments (such as Zernike moments, Wavelet moments and Tchebichef moments) have been successfully applied to the direct quantitative and qualitative analysis of three-dimensional (3D) spectra (Chen, Li, Cui, Yu, & Zhai, 2015; Chen, Li, Zhai, Lu, & Zhang, 2014; Li, Chen, Li, Wang, & Zhai, 2015; Li, Chen, Xu, Wang, & Zhai, 2016; Wang, Li, Zhai, Xiong, & Liu, 2016; Zhai, Shan, Li, & Yu, 2012; Zhai, Zhai, Li, & Tian, 2013). The idea behind these approaches is that the image of the 3D spectra is employed to reveal the information of the samples comprehensively, and the image moment methods with multiple advantages are used to eliminate the interferences in 3D spectra and capture important features for target analytes for further qualitative or quantitative analysis.

In this work, a novel strategy, Tchebichef moment (TM) method combined with Partial Least Squares (PLS) method (TM-PLS) was proposed for the quantitative analysis on the basis of the  $^1\text{H}$  NMR self-constructed 3D (SC-3D) spectrum, in which the SC-3D spectrum was constructed by the simply repeating  $^1\text{H}$  NMR spectrum itself. Unlike conventional quantitative analysis methods, the feature information of target compounds were directly and

effectively extracted by Tchebichef moment (TM) method from the  $^1\text{H}$  NMR SC-3D spectra without any pretreatment. Therefore, the proposed approach provides opportunity for simultaneous determination of five metabolites in table wines. The proposed strategy was then compared with the PLS and interval-PLS regression methods based on the same  $^1\text{H}$  NMR spectra to further validate the effect in quantitative analysis.

## 2. Data and methodology

### 2.1. Data set

The  $^1\text{H}$  NMR spectra of 40 table wines were derived from Ref. (Larsen, van den Berg, & Engelsens, 2006), in which the contents of the five metabolites (glycerol, ethanol, lactic acid, malic acid and methanol) were determined using infrared spectroscopy. The data were arranged as a two-dimensional matrix with the size of 40 (the number of table wines)  $\times$  8712 (chemical shift data points, covering the region from 0.5 to 6.0 ppm) that could be downloaded from the website (<http://www.models.life.ku.dk>). The  $^1\text{H}$  NMR spectra of the 40 table wines are shown in Fig. 1A, and the enlarged ones are illustrated in Fig. 1B. As can be seen, the peak shifts and interferences occur.

### 2.2. Analytical method

The proposed approach to the quantitative determination of the five metabolites in the table wines based on  $^1\text{H}$  NMR profiles consists of three main steps (illustrated in Fig. S1): (1) the construction

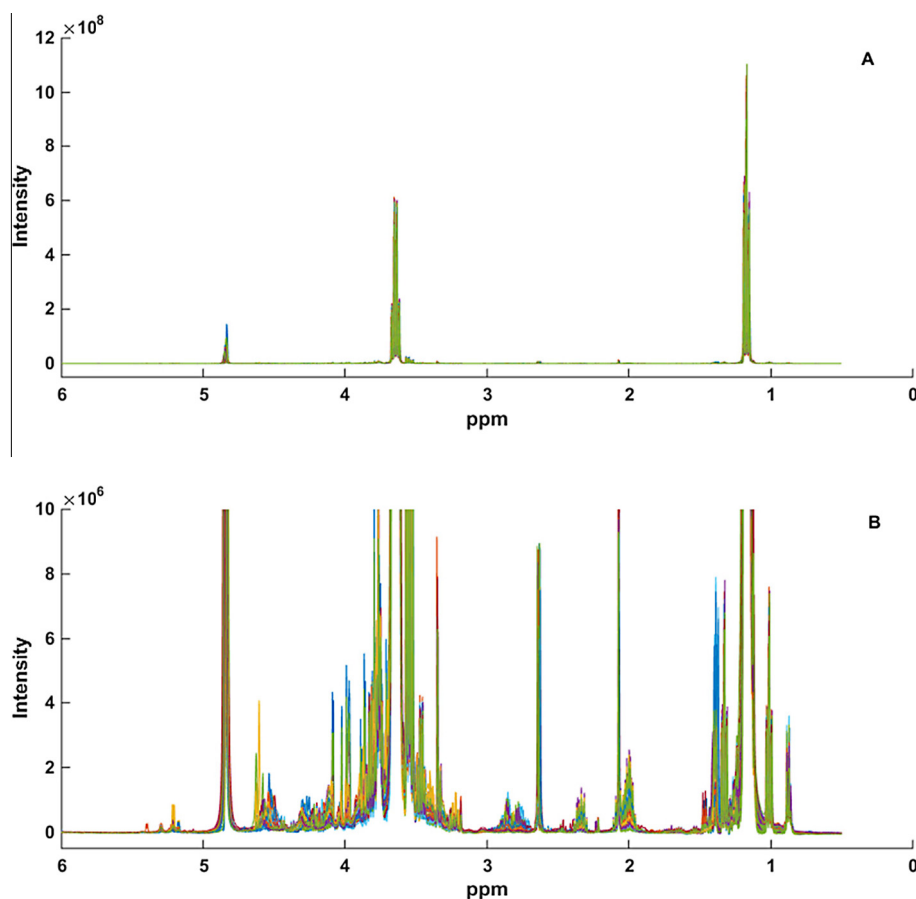


Fig. 1.  $^1\text{H}$  NMR spectra of 40 table wines: (A) raw spectra; (B) enlarged raw spectra to show the detail signals.

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