Chemometrics and Intelligent Laboratory Systems 132 (2014) 1–7

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: www.elsevier.com/locate/chemolab

Exploration of liquid chromatographic-diode array data for Argentinean wines by extended multivariate curve resolution

Pablo L. Pisano [a], María F. Silva [b], Alejandro C. Olivieri [a,*]

[a] Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Instituto de Química Rosario (IQUIR-CONICET), Suipacha 531, Rosario S2002LRK, Argentina

[b] Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, Instituto de Biología Agrícola de Mendoza (IBAM-CONICET), Alte. Brown 500, Chacras de Coria, 5505 Mendoza, Argentina

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 22 December 2013
Accepted 26 December 2013
Available online 7 January 2014

Keywords:
Liquid chromatography
Multivariate curve resolution
Principal component analysis
Direct injection
Wine data exploration

ABSTRACT

Second-order data were measured using high-performance liquid-chromatography with diode array detection (HPLC-DAD) for a number of wine samples, which were directly injected in the HPLC-DAD system without sample pre-treatment. The data were arranged in data matrices whose modes were elution time and UV–visible absorption wavelength, and processed by extended multivariate curve resolution coupled to alternating least-squares (MCR–ALS). The individual data matrices were organized in a row-wise augmented data matrix sharing the time subspace, due to the high spectral similarity among several sample components. This required previous time alignment of the chromatograms using a suitable synchronization algorithm, in order to produce a bilinear augmented data matrix to be processed by MCR–ALS. The latter algorithm led to resolved component chromatograms and spectra, from which component scores could be estimated, which are proportional to the relative component concentrations in each studied sample. The matrix of sample scores was then submitted to principal component analysis, which was applied for data exploration according to grape *varietal* and geographical origin. The results showed that the present data generation and analysis are useful for the discrimination of all samples of the Malbec *varietal* from the remaining ones, but achieved partial success regarding geographical origin.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Wine is a complex matrix composed of water, ethanol and a variety of chemical compounds such as peptides, proteins, carbohydrates, thiols, and phenolic compounds [1]. The latter ones can be classified into flavonoids (flavanols, flavonols, dihydroflavonols, and anthocyanins) and non-flavonoids (phenolic acids, phenols, and stilbenes) [2]. Flavonoids share a common skeleton consisting of two phenolic rings (A and B) linked by a heterocyclic pyran ring (C), as shown in Fig. 1. Anthocyanins and flavanols are particularly abundant in grape and wine and are essential to wine quality. Indeed, anthocyanins are the red pigments of grapes and are responsible for the color of red wines, whereas flavanols contribute to taste (especially astringency and bitterness) [3]. Due to the presence of aromatic rings in their structure, most phenolic compounds present in wine absorb UV–visible radiation with an absorption maximum at 280 nm, with the exception of anthocyanins (520 nm), flavonols (360 nm) and phenolic acids (320 nm) [2].

Due to the complexity of wine data obtained by usual instrumental techniques, it is not possible to resolve or quantify all the chemical constituents present in wine. Therefore, the combination of these techniques with chemometric analysis can reveal latent patterns in the data, which may enable classification of the samples in terms of *varietal*, geographical origin, aging, adulteration, etc. [4]. Several instrumental techniques have been employed for wine classification, such as gas chromatography–mass spectrometry (GC–MS) [5–7], high-performance liquid chromatography with diode array detection (HPLC-DAD) [8,9] or liquid chromatography coupled to mass spectrometric detection (LC–MS) [10–12], proton nuclear magnetic resonance (^{1}H NMR) [13,14], near-infrared spectroscopy (NIR) [15,16], capillary electrophoresis (CE) [17,18] and elemental analysis [19,20]. To achieve sample discrimination, the obtained data have been processed by different chemometric algorithms such as principal component analysis (PCA), linear discriminant analysis (LDA), partial least-squares-discriminant analysis (PLS-DA), soft independent modelling of class analogy (SIMCA), and artificial neural networks (ANN) [4].

In the past few years, several reports employed HPLC-DAD coupled to chemometric tools in order to classify wines [21–26]. Nevertheless, to our knowledge, there are no reports of wine classification by direct injection HPLC-DAD without sample pre-treatment coupled to multivariate curve resolution–alternating least-squares (MCR–ALS) as data processing algorithm. In this work we employed the latter combination of techniques to attempt classification of wines by grape *varietal* and geographical origin of some Argentinean wines. The application of the MCR–ALS algorithm is usually made by joining the elution time–spectral data matrices adjacent to each other sharing the spectral subspace (i.e., by column-wise augmentation), creating the so-called augmented data matrix before MCR–ALS decomposition. However, for

* Corresponding author. Tel./fax: +54 341 4372704.
E-mail address: olivieri@iquir-conicet.gov.ar (A.C. Olivieri).

0169-7439/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemolab.2013.12.010

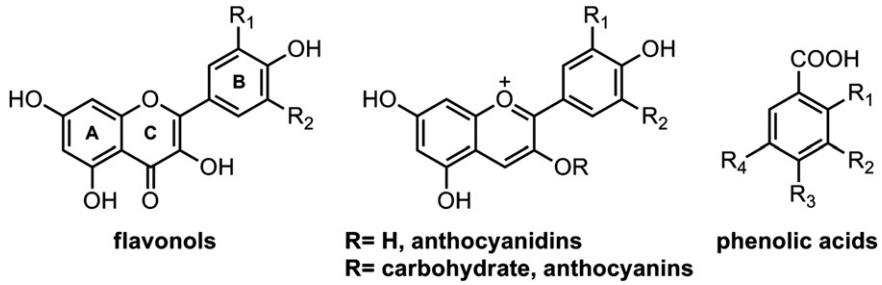

Fig. 1. Representative structures of the three main families of phenolic compounds found in wine.

reasons which will be clear below, we adopted the somewhat exceptional procedure of augmentation by sharing the time subspace (i.e., row-wise augmentation) [27,28]. This required previous alignment of the chromatographic–spectral data matrix in order to alleviate the time shifts between runs [29].

The purpose of the present work is to model direct injection LC-DAD data for wine samples with MCR–ALS, in order to extract information which may allow for wine discrimination according to *varietal* and geographical origin. The results of this data exploration indicate that the Malbec *varietal* can be adequately discriminated from the remaining ones, while only partial success is obtained regarding the geographical origin of samples.

2. Experimental section

2.1. Reagents and standards

HPLC grade acetonitrile were purchased from Panreac (Barcelona, Spain), formic acid from Cicarelli (Rosario, Argentina) was pro analysis grade and used directly. Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore Corp., Bedford, USA).

2.2. Wine samples

The 27 wine samples were obtained from red grapes of *V. vinífera* L. of eight varieties [Aspiran (A), Bonarda (B), Cabernet Sauvignon (C), Malbec (Ma), Merlot (Me), Sangiovese (Sa), Syrah (Sy) and Tempranillo (T)], harvested in 2012 from thirteen collaborating wineries of Mendoza and San Juan (Argentina), including an experimental winery from Facultad de Ciencias Agrarias (FCA), Universidad Nacional de Cuyo, Mendoza, Argentina. The thirteen wineries were: Galán (A, B, C, Ma, Me, T), CoViTu (B, C, Ma, Me, T), experimental winery FCA (C, Ma, Me), San Rafael (Ma, Sy), Agrelo (Ma, Me, Sa), San Juan (Cs, Ma -two samples-, Sy), Mayor Drummond (Cs), La Consulta (Sy), Plantago (Ma), and Albahaca (Ma). The wine samples from each winery were collected directly from fermentation tanks at the end of malolactic fermentation, transferred under nitrogen to completely filled amber glass bottles, and stored at 4 °C to ensure their preservation until their analysis in the laboratory.

2.3. HPLC-DAD

The optimization of HPLC method was based on the work developed by de Villiers et al. [8]. Prior to analysis, wine samples were filtered through a 0.45 μm pore size nylon membrane (Aura Industries Inc., New York, USA) without further treatment, and a volume of 20 μL of every sample was injected directly into the chromatographic system, consisting of a Hewlett-Packard 1100 series HPLC equipped with a degasser model G1322A, a quaternary pump model G1311A, and a photodiode array detector model G1315A (Agilent Technologies, Palo Alto, USA). Separation was performed on a reversed-phase column Lichrocart 250–4 Purospher STAR RP-18e column (Merck, Argentina) (250 mm × 4 mm, 5 μm particle size) with a Security Guard Gemini C18 guard cartridge (Phenomenex, USA) (4 mm × 3 mm) at 25 °C. Two mobile phases were employed for elution: A (water/formic acid, 99:1, v/v) and B (acetonitrile/formic acid, 99:1, v/v), and the gradient profile was as follows: 0% B (min 0); 3% B (min 1); 15% B (min 10); 30% B (min 25); 50% B (min 35); 95% B (min 40); and 0% B (min 45). The flow rate was 1.0 mL min^{-1}. Each sample was run by triplicate, and good repeatability was observed. No changes were detected in cromatographic parameters as retention time, and peak shapes and areas in a reference sample that was run at the beginning and at the end of the analysis. All the analyses were conducted with the same guard column cartridge, keeping the maximum working pressure in the range 165–170 bar, being 250 bar the maximum recommended working pressure for the column used in this study. Diode array detection proceeded from 200 to 600 nm with a bandwidth of 2 nm and a data acquisition of five points per second. The presence of formic acid in the elution solvents is needed to maintain the pH below 2.5, thus ensuring that anthocyanins are present as a single species (flavylium cation).

2.4. Software

All calculations were made using MATLAB software (version 7.0, The Mathworks Inc., USA). Chromatographic time alignment was performed using the COSHIFT algorithm [30] included in the software developed by Tomasi et al. [31]. MCR–ALS was implemented using the graphical interface provided by Tauler in his web page http://www.mcrals.info/ [32]. Principal component analysis was run using an in-house MATLAB code. All programs were run on an HP Pavilion dv5-2043la microcomputer with an Intel Pentium P6000, 1.86 GHz microprocessor and 6 GB of RAM. UV–visible data were exported from the HPLC-DAD system as.csv (comma separated values) using the HP ChemStationRev.A.05.02 software for subsequent data processing under MATLAB.

Preliminary LC-DAD data analysis showed absorption signals in the range 200 to 260 nm corresponding to the HPLC solvent that was subtracted from the original data before chemometric analysis. To carry out this study in acceptable computational times, it was necessary to reduce the data obtained in the HPLC-DAD runs. Therefore, each sample subject to analysis consisted of an array of 2400 × 170 data points (0–40 min taken in steps of 1 s and 262–600 nm taken in steps of 2 nm, respectively).

3. Theory

3.1. MCR–ALS

The first step in MCR–ALS is to roughly estimate the number of components, which can be simply performed by visual inspection of singular values or principal component analysis (PCA) plots for the experimental data matrix [32,33]. This initial number of components can be

Download English Version:

https://daneshyari.com/en/article/1179448

Download Persian Version:

https://daneshyari.com/article/1179448

Daneshyari.com