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Classification of monovarietal Argentinean white wines by their elemental profile

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ABSTRACT

The possibility of acquire a chemometric model to classify Argentinean white wines according to their provenance through elemental profile was assessed. A simple method for multielement determination in wines by inductively coupled plasma mass spectrometry along with chemometric pattern-recognition techniques is proposed. A total of 57 white wine samples of the main varieties from four winegrowing regions of Argentina: Mendoza, Rio Negro, San Juan, and Salta, were evaluated. The results of principal component analysis explained 95.95% of the variance data total. Linear discriminant analysis allowed correct discrimination according to the four geographical regions evaluated, using only five ultratrace elements (Ba, As, Pb, Mo, and Co). Discrimination rates higher than 96% for prediction and validation data sets were reached. The outcomes emphasize the skillfulness of ICPMS elemental determination in combination with chemometrics, for classification of white wine and show that could be a trustworthy technique to validate the geographical origin, authenticity and quality control of wines.

1. Introduction

Wine is an alcoholic beverage widely consumed throughout the world with a great social and economic importance (Grindlay, Mora, Gras, & de Loos-Vollebregt, 2011). The geographical origin of wine is a significant factor when determining its commercial value. According to statistics from the International Organization of Vine and Wine, Argentina has an important role in the global economy with respect to the production and export of wines (OIV, 2015). In this country, several regions have reputation producing wines of exceptional quality, being the most important provinces: Mendoza, San Juan, La Rioja, Salta, Córdoba, and Río Negro.

Daily consumption of wine in moderate quantities contributes significantly to the requirements of human organism for essential elements as Ca, Co, Cu, K, Fe, Mg, Mn, Mo, Ni, Se, Zn, and others. However, special attention must to be given to other elements which are found in wine such As, Cd, Cr, Hg, Pb, for their potential toxicity (Lara, Cerutti, Salonia, Olsina, & Martinez, 2005; Rodríguez-Solana, Salgado, Domínguez, & Cortés, 2014). The presence of these hazardous species is regulated by health-protection laws (CODEX, 2011; OIV, 2015; WHO, 2006).

The source of metals in wine could be due to both, endogenous as elements may naturally come from soil where grapes are grown, the grape variety and maturity, and the climatic conditions; and exogenous, associated with external impurities that reach wine during growth or at different winemaking procedures (Pohl, 2007; Sauvage, Frank, Stearne, & Millikan, 2002). Wine components analysis and its concentration is of great importance since it strongly determines its stability, and organoleptic or nutrition characteristics; being an excellent indicator of quality, and contributing to quality assurance and quality control (Pohl, 2007; Sauvage et al., 2002; Versari, Laurie, Ricci, Laghi, & Parpinello, 2014). Moreover, elemental information in finished wines appears to be an outstanding approach to identify the geographical origin (Almeida & Vasconcelos, 2003; Ashurst & Dennis, 1998; Coetzee, van Jaarsveld, & Vanhaecke, 2014; Saurina, 2010; Serapinas et al., 2008).

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Currently, inductively coupled plasma mass spectrometry (ICPMS) is one of the most used techniques for the determination of trace elements, due to its high sensitivity and multielement analysis (Coetzee et al., 2014; Grindlay et al., 2011; Martin de la Hinojosa, Tusseau, Mirat, Esteban Fernandez, & Hooghuis de Korver, 2011; Pyrzyńska, 2004). The quantification of trace elements in organic samples as well as sample preparation has always been a challenge in analytical chemistry. From an analytical point of view, wine is a relatively complex matrix consisting mainly of water, ethanol, sugars, organic acids and other inorganic and organic compounds (Grindlay et al., 2011; Pyrzyńska, 2004; Šperková & Suchánek, 2005). Thereby, direct analysis of wine by ICPMS could be difficult owing to this matrix that might affects plasma stability. Different pretreatment methods, such as water dilution, microwave digestion, etc., have been proposed to reduce or avoid possible interferences (Gonzálvez, Armenta, Pastor, & de la Guardia, 2008; Grindlay, Mora, Maestre, & Gras, 2008; Martin, Watling, & Lee, 2012; Rodrigues et al., 2011). Among them, a simple sample dilution has been proposed as the most advantageous, being time efficient, and reducing operation steps and contamination; also it could be established that the dilution contributes to reduce the ethanol concentration (between 1.2% and 1.37%), and also residual sugar and organic components (Coetzee et al., 2014; Grindlay et al., 2011; Thiel & Danzer, 1997).

In recent years, progresses have been done in wine authentication through fingerprinting techniques, in particular in terms of provenance determination (Coetzee et al., 2014; Pérez Trujillo, Conde, PérezPont, Câmara, & Marques, 2011; Sen & Tokatli, 2014; Serapinas et al., 2008; Thiel, Geisler, Blechschmidt, & Danzer, 2004). In these studies, chemometric pattern-recognition techniques have been applied, contributing in characterizing, classifying and authenticating samples (Arvanitoyannis, Katsota, Psarra, Soufleros, & Kallithraka, 1999; Bentlin, Pulgati, Dressler, & Pozebon, 2011; Garde-Cerdán et al., 2009; Saurina, 2010; Sen & Tokatli, 2014). Multielement data obtained by ICPMS for wine characterization is multivariate in nature. These data comprise a list or array of values, called of first-order data, that could be used to extract relevant information from unsupervised methods, such as principal component analysis (PCA) and cluster analysis (CA); as well as supervised chemometric techniques, as linear discriminant analysis (LDA), partial least square discriminant analysis (PLS-DA), K-means neighbours (KMN) soft independent modeling class analogy (SIMCA), and artificial neural networks (ANN) (Arvanitoyannis et al., 1999; Martin et al., 2012; Rodrigues et al., 2011; Serapinas et al., 2008; Šperková & Suchánek, 2005; Sun, Danzer, & Thiel, 1997; Thiel et al., 2004; Villagra, Santos, Vaz, Eberlin, & Felipe Laurie, 2012).

In Argentina, few studies on wine element composition together with chemometrics to distinguish varietal and/or geographical origin have been proposed (Di Paola-Naranjo et al., 2011; Fabani et al., 2010; Fabani, Toro, Vázquez, Díaz, & Wunderlin, 2009). To the best of our knowledge, only one of this works have performed elemental determination by ICPMS, but none have analyzed in detail the main varieties of monovarietal white wines produced and exported in Argentina (INV, 2004; OIV, 2015). Argentinean law establish as monovarietal those wine which contain more than 85% of the corresponding declared variety (INV, 2004).

The purpose of the current work was to develop and validate a chemometric model with the principal aim of find out relationships between element concentrations and geographical origin of Argentinean white wines, which would enable assessing their genuineness. Three white wine varieties of greatest exportation in Argentina, namely: Chardonnay, Torrontés, and Sauvignon blanc, from four different wine growing regions: Mendoza, Rio Negro, San Juan, y Salta, were evaluated throughout trace element determination by ICPMS. The effect of factors such as variety and vintage on the multielement composition of white wines was also investigated.

2. Material and methods

2.1. Instrumentation

All determinations were carried out with an inductively coupled plasma mass spectrometer, Perkin–Elmer SCIEX, ELAN DRC-e (Thornhill, Canada). The argon gas with a minimum purity of 99.996% was supplied by Air Liquide (Córdoba, Argentina). An HF-resistant and high performance perfluoracetate (PFA) nebulizer model PFA-ST, coupled to a baffled quartz-made cyclonic spray chamber, cooled with the PC^3 system from ESI (Omaha – NE, USA) was used.

Tygon black/black 0.76 mm i.d. and 40 cm length peristaltic pump tubing was used. The instrument conditions were: auto lens mode on, peak hopping measure mode, dwell time of 15 ms, 30 sweeps per reading, 1 reading per replicate and 3 replicates. Nickel sampler and skimmer cones were used. A performance check for sensitivity and oxide and doubly charged ion formation was carried out.

For comparison purpose, the samples were also digested in a microwave digestion system model START D from Milestone (Sorisole, Italy), and Milestone hermetically sealed 100-mL internal volume, 1-cm wall thickness polytetrafluoroethylene (PTFE) reactors.

2.2. Reagent

The used water was distilled and de-ionized, with a resistivity of 18.2 MΩ cm, produced by an Easy pure RF system from Barnstead (Dubuque, IA, USA). Concentrated nitric acid (65%v/v) from Sigma–Aldrich (Germany), hydrogen peroxide (40%v/v) from Carlo Erba (Italy), and high-purity ethanol from Merck (Germany), were used throughout. Multi-element standard solution 3 from Perkin Elmer Pure Plus Atomic Spectroscopy Standard, (Norwalk, USA), Hg mono-element standard solution from Perkin Elmer Pure Plus, $^{103}Rh^{+}$ mono-element standard solution from Perkin Elmer Pure Plus, Atomic Spectroscopy Standard, (Norwalk, USA), and a setup/mascal solution from Perkin Elmer Pure Plus, Atomic Spectroscopy Standard, (Norwalk, USA), were used.

2.3. Wine samples

A total of 57 monovarietal white wines samples were analyzed in this work. Argentinean laws establish as monovarietal wines those which contain more than 85% of the corresponding declared variety on their labels (INV, 2004). Samples of different monovarietal from four major wine production areas of Argentina were considered, consisted of: 33 samples from Mendoza (Torrontés, Chardonnay, Sauvignon blanc); 9 samples from Rio Negro (Torrontés, Sauvignon blanc); 9 samples from San Juan (Torrontés); and 6 samples from Salta (Chardonnay, Sauvignon blanc). The 57 wine samples were acquired from the local market (3 bottles per wine brand – of a total of 19 brands). In order to obtain a sufficient number of samples production areas, wines were selected from the 2009 to 2012 vintages. The alcoholic content ranged from 12% to 13.7% v.v^{-1} ethanol.

2.4. Sample preparation and analytical procedure

Prior to analysis, samples were transferred from bottles into air-tight 15 mL polypropylene tubes and stored in a refrigerator at